ELSEVIER

www.elsevier.com/locate/ica
Inorganica Chimica Acta 324 (2001) 1–15

Inorganica Chimica Acta

Synthesis, characterization, redox properties, and representative X-ray structures of four- and five-coordinate copper(II) complexes with polydentate aminopyridine ligands

Elena V. Rybak-Akimova [a,*], Alexander Y. Nazarenko [b,*], Lisa Chen [a], Paul W. Krieger [a], Aida M. Herrera [a], Vladislav V. Tarasov [a], Paul D. Robinson [c]

[a] *Department of Chemistry, Tufts University, Medford, MA 02155, USA*
[b] *Department of Chemistry, State University of New York, College at Buffalo, Buffalo, NY 14222-1095, USA*
[c] *Department of Geology, Southern Illinois University, Carbondale, IL 62901, USA*

Received 20 December 2000; accepted 4 May 2001

Abstract

Four copper(II) complexes with the ligands bearing two or three alkylpyridine pendant arms attached to an ethylene diamine framework were isolated in pure form (four-coordinate species as perchlorates, and five-coordinate species as hexafluorophosphates). Three complexes and one tosylated ligand were characterized by X-ray diffraction. In the absence of additional mono- or bidentate ligands, linear tetradentate aminopyridines form distorted square-planar complexes with copper(II). This coordination mode is different from *cis*-configurations adopted by aminopyridine ligands in octahedral complexes. The degree of the tetrahedral distortion, caused by steric repulsion between pyridine rings, increases with an increase in the chelate ring sizes (555 vs. 656 sequence). Nearly planar arrangement of the two amine nitrogens and two pyridine nitrogens is retained in the five-coordinate copper(II) complex with a pentadentate ligand, in which the fifth pyridine donor occupies an axial position. EPR parameters of the four-coordinated aminopyridine complexes are very similar to those of the tetraamine species, and do not depend significantly on the degree of the tetrahedral distortion. Introducing of a fifth nitrogen donor in the long ethylpyridine pendant arm causes some weakening of the equatorial ligand field, as reflected in EPR parameters (an increase in $g_{//}$ and a decrease in $A_{//}$). The Cu(II)/Cu(I) redox potentials of the four-coordinate complexes increase with an increase in the chelate ring size, and with the alkylation of the amine nitrogen donors. A relatively weak coordination of the fifth pyridine nitrogen increases the redox potential of the Cu(II)/Cu(I) couple by 85–156 mV.

Keywords: Copper complexes; Aminopyridine ligands; X-ray structures; EPR; Electrochemistry; Electronic spectra

1. Introduction

Continued interest in studying structure–property relationships in copper(II) coordination chemistry originates from the need to understand and mimic functions of different families of copper proteins. In particular, significant attention was paid to the influence of the degree of tetrahedral distortion in four-coordinate copper complexes on their redox potentials and EPR spectral parameters [1–3]. These studies were aimed originally at explaining very unusual properties of blue copper (type I) proteins (their high redox potentials, intense absorption in the visible region, and small values of $A_{//}$ in the EPR spectra) [4]. The presence of sulfur donors in the copper coordination sphere (N_2S_2 donor set is typical of blue copper proteins) along with significant tetrahedral distortion of coordination polyhedra account for such unusual properties [1,2,5,6].

The spectral and redox properties of type II copper proteins, which are more similar to traditional polyaza copper(II) complexes, can also be tuned by modifying the number and type of nitrogen donors bound to the central metal ion, and by distortions from tetragonal

* Corresponding authors. Tel.: +1-617-627-3413; fax: +1-617-627-3443.
E-mail address: elena.rybak-akimova@tufts.edu (E.V. Rybak-Akimova).

0020-1693/01/$ - see front matter
PII: S0020-1693(01)00495-9

coordination geometries. Nitrogen donors dominate in the copper coordination sphere in type II proteins, forming four- or five-coordinate chromophores [7,8]. The fifth coordination site at the copper ion is believed to be involved in substrate binding. This site is vacant in four-coordinate species, and should easily be vacated in five-coordinate complexes, thus suggesting the coordination of a labile ligand in the fifth position.

An interest in pentadentate model ligands has emerged recently, and a growing number of five-coordinate copper(II) complexes with such ligands have been synthesized [9–13]. Five-coordinate copper(II) was also found in its complexes with bleomycin, an antibiotic and anti-cancer drug [14], and with bleomycin models [11,15–17]. A direct comparison between four- and five-coordinate complexes of similar structure is, however, scarce. In particular, the only example of acyclic diamine ligands with appended arms appears to be a series of benzimidazole containing compounds (two examples are shown in Fig. 1) [10,18], where the presence of a fifth donor decreases equatorial ligand field and increases the Cu(II)/Cu(I) redox potentials [10].

In this paper, we report the synthesis and characterization of a series of copper(II) complexes with tetra- and pentadentate aminopyridine ligands L1–L5 (Fig. 1). Substituted aminopyridine ligands are promising in the design of chiral stereo selective reagents and catalysts [19,20]. Additional interest in studying pentadentate ligands bearing pyridine arms stems from their applications, in the form of iron complexes, for peroxide activation at five-coordinate iron centers [21–31]. Thus, developing of simple synthetic approaches to such ligands and complexes is desirable, and isolating the ligands in the form of their copper(II) complexes is suggested as such a convenient approach.

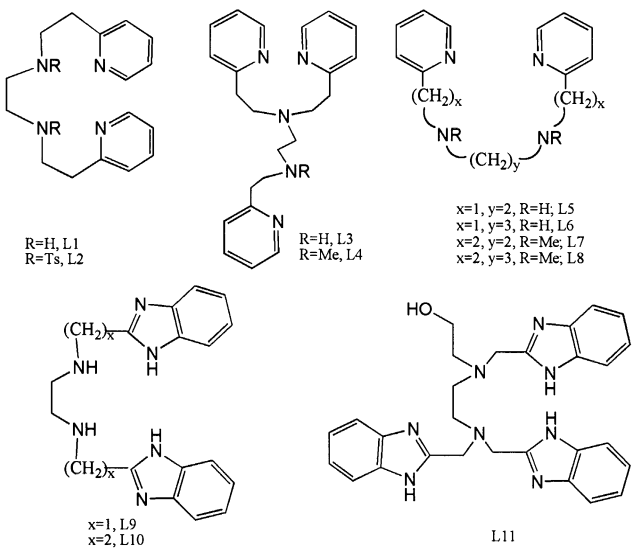

Fig. 1. Aminopyridine ligands and their analogs.

Although pyridine groups are often used in synthetic model complexes as adequate replacement of heterocyclic nitrogen donors (usually, imidazole of pyrimidine derivatives), limited data are available on the structure and properties of copper(II) complexes with linear tetradentate aminopyridine ligands [19,32–38]. Moreover, systematic studies on spectral and redox properties of four-coordinate aminopyridine copper(II) complexes [33,36] were not supported by structural information for the same compounds, which did not allow for the inclusion of the aminopyridine ligands in structure-property correlations [2].

The crystal structures for $[Cu(L1)](ClO_4)_2$ and $[Cu(L5)](ClO_4)_2$ reported here, along with their EPR, UV–Vis, and electrochemical characteristics, will supplement previously published data for related copper(II) complexes and will allow for direct comparison between structural features and properties for this class of complexes. For the most distorted complex in the series, $[Cu(L1)](ClO_4)_2$, the structure of the ligand tosylate (L2) has also been determined, in order to analyze possible changes in ligand metric parameters upon its complexation with copper(II). We also report five-coordinate analogs of $[Cu(L1)](ClO_4)_2$, the complexes $[Cu(L3)](PF_6)_2$ and $[Cu(L4)](PF_6)_2$, having three pyridine donor groups appended to an ethylenediamine framework. Long, flexible linkages between the amine donors and the pyridine rings were chosen in order to facilitate the dissociation of a fifth ligand in the complex. It is known that long pendant arms tend to form thermodynamically less stable complexes than their shorter analogs [6,39–44], which is important for modeling the metalloprotein functions.

The results reported herein help in analyzing the influence of the following factors on redox and spectral properties of copper(II) complexes with aminopyridine ligands: (1) the degree of tetrahedral distortion in four-coordinate complexes; (2) the presence of an additional pyridine-containing pendant arm in five-coordinate complexes as compared to their four-coordinate analogs; (3) the alkylation of amine donors.

2. Experimental

All reagents and solvents (reagent grade or better) were used as received. High purity dry dimethylsulfoxide and acetonitrile (Aldrich) were used for electrochemical experiments.

N,*N*′-ditosyl ethylene diamine was obtained by published procedure [45,46], recrystallized from methanol, and transformed into its disodium salt by interaction with sodium methoxide in dry ethanol [45].

The ligand L5 and its copper(II) complex $[Cu(L5)](ClO_4)_2$ were synthesized according to the procedures by Goodwin and Lions [47].

2.1. Synthesis of 2,6-bis(hydroxyethyl)pyridine ditosylate

Method A (modification of the synthesis of 1,2-di(*p*-toluenesulfonyloxy)ethane described by Searle and Geue [48]). 2-(2-Hydroxyethyl)pyridine (0.2. mol) (24.6. g, 22.6 ml) was dissolved in 100 ml of pyridine and cooled on an ice bath. Solid tosyl chloride (40 g, 0.21 mol) was added slowly, upon stirring, at such a rate that the temperature did not exceed 30 °C over a period of 3 h. The color of the solution turned yellow gradually, and a white precipitate started to form in about 2 h. After the addition of tosyl chloride was complete, 50 ml of pyridine were added to the reaction mixture, and the mixture was stirred overnight (during this time, the mixture slowly reached ambient temperature). The precipitate was filtered off (it consists primarily of a mixture of pyridine hydrochloride, 2,6-bis(hydroxyethyl)pyridine hydrochloride, and 2,6-bis(hydroxyethyl)pyridine ditosylate hydrochloride), and the filtrate was mixed with ice (ca. 1 kg) and refrigerated for 5 h. White solid product precipitated out and was filtered, washed with large amount of cold water, and dried in vacuum. Yield 17.1 g (31%). ^{1}H NMR ($CDCl_3$): 8.35 (d, 1H), 7.57 (d, 2H), 7.46 (t, 1H), 7.17 (d, 2H), 7.05 (m, 2H), 4.32 (t, 2H), 3.00 (t, 2H), 2.35 (s, 3H) ppm.

Method B (a modification of the procedure proposed by Bradshaw et al. for the synthesis of pyridine-2,6-dimethanol ditosylate [49]). The reaction was run under N_2. Powdered KOH (20 g) was suspended in 175 ml of dry THF, and 22.6 ml (24.6 g, 0.20 mol) of 2-hydroxyethylpyridine were added. The mixture was cooled down to -5 °C in an ice-salt bath, and a solution of 43.5 g of tosyl chloride in 150 ml of dry THF was added dropwise, upon stirring, at such a rate that the temperature did not exceed 0 °C. During the addition, which took 5 h, white foamy precipitate was forming on the surface of the reaction mixture, while the bulk of the solution turned pink, and then purple. After the addition of tosyl chloride was complete, the reaction mixture was stirred for 5 h at 0 °C, and then left at room temperature overnight. The precipitate was filtered off and washed with THF. The combined THF solutions were rotary evaporated to dryness, leaving purple oil, which solidified in 2 h. It was redissolved in pyridine and poured on ice, leading to formation of pink precipitate. This precipitate was filtered, washed with cold water, and dried in vacuum. According to proton NMR, it consists primarily of the target product, with an admixture of vinyl-type byproducts. The material was dissolved in a minimum amount of ether, an undissolved brown material was separated out, and petroleum ether was slowly added to the clear ether solution, leading to crystallization of white solid, which was filtered, washed with petroleum ether and dried in vacuum. Yield 14.4 g (26%). The product was pure as judged by proton NMR, but did not give satisfactory elemental analysis and slowly decomposed upon storage, producing yellow oil within several weeks. The oil contains significant fraction of the material insoluble in ether, which appears to be primarily *p*-toluenesulfonate of 2-hydroxyethylpyridine (apparently, formed by hydrolysis). ^{1}H NMR of an insoluble product ($CDCl_3$): 8.79 (d, 1H), 8.27 (t, 1H), 7.78 (m, 6 H), 7.62 (d, 2H), 7.25 (d, 2H), 7.12 (d, 2H), 4.46 (t, 2H), 3.50 (t, 2H), 2.40 (s, 3H) ppm. Yellow oil can be purified by recrystallization from ether of a ether–chloroform mixture, producing the white target product (recrystallization yield ca. 20%). Analytically pure material was obtained from this product by recrystallizing it twice from ether–petroleum ether. *Anal.* Found (%): C, 60.98; H, 5.62; N, 4.88. Calc. for $C_{14}H_{15}NSO_3$ (%): C, 60.63; H, 5.45; N, 5.05%.

2.2. Synthesis of *N*,*N*′-ditosyl-bis(2-ethylpyridine)ethylenediamine (L2, **I**)

N,*N*′ - Ditosyl - bis(2 - ethylpyridine)ethylenediamine (L2, **I**) was synthesized by a modification of a Richman–Atkins procedure [50] (Fig. 2). Ethylene diamine ditosylate disodium salt (1.23 g) was suspended in 40 ml of dry DMP under nitrogen, and heated to 60 °C. Solid bis(hydroxyethyl)pyridine ditosylate (1.65 g) was added in several portions upon stirring. The components of the reaction mixture dissolved within several minutes, yielding brown solution. The temperature was increased gradually to 105 °C, and the reaction mixture was stirred at this temperature (under N_2) for 4 h. Most of the solvent was removed by rotary evaporation, the residue was mixed with a large excess of ice water, producing gummy solid. It was separated, dissolved in methylene chloride and dried with Na_2SO_4. The solvent was removed by rotary evaporation, and white solid residue was recrystallized twice from ethanol. Yield 0.35 g (20%). *Anal.* Found (%): C, 62.58; H, 6.17; N, 9.42. Calc. for $C_{30}H_{34}N_4S_2O_4$ (%): C, 62.26; H, 5.92; N, 9.68%. ^{1}H NMR ($CDCl_3$): 8.46 (d, 2H), 7.65 (d, 4H), 7.52 (t, 2H), 7.21 (d, 4H), 7.14 (d, 2H), 7.07 (m, 2H), 3.46 (t, 4H), 3.19 (s, 6H), 3.02 (t, 4H), 2.41 (s, 4H).

2.3. Synthesis of [Cu(L1)](ClO$_4$)$_2$ (**II**)

The complex [Cu(L1)](ClO_4)$_2$ (**II**) was synthesized according to the procedure described by Phillip et al. [32] and recrystallized twice from water (the peak $M=$ 438, corresponding to $[Cu(L3)]^{2+}$ complex, was present in the FAB mass spectrum of the complex prior to recrystallization). Alternatively, the condensation between vinyl pyridine and ethylene diamine was run under conditions suggested by Proft et al. [51], and the mixture of aminopyridyl products was fractionally dis-

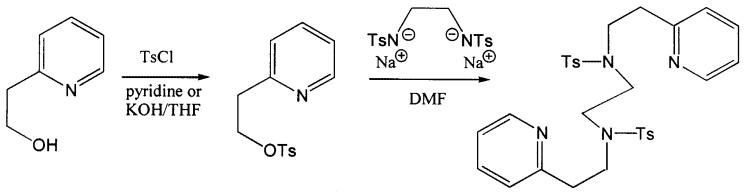

Fig. 2. Synthesis of the tosylated tetradentate ligand $(Etpy)_2Ts_2en$ (L2).

tilled in vacuum (1 torr). Five fractions were collected, with the boiling points of 80–140, 160–180, 190–200, 200–220 and 230–245 °C. According to proton NMR and GS-MS data, all of these fractions contained mixtures of products, the fractions 2 and 3 were enriched in monoand disubstituted products (Etpyen, $(Etpy)_2en$ and *iso*-$(Etpy)_2en$, Fig. 3), and the remaining high-boiling fractions contained di-, tri- (fraction 4) and tetra- (fraction 5) substituted ligands. In order to avoid possible admixtures of five-coordinate complex $[Cu(L3)]^{2+}$, the four-coordinate compound was synthesized from fraction 2 (b.p. 160–180 °C). Fraction 2 (a mixture of Etpyen, $(Etpy)_2en$ and *iso*-$(Etpy)_2en$) (1.4 g) was dissolved in 10 g of ethanol. $Cu(ClO_4)_2 \times 6H_2O$ (1.9 g) was dissolved in 10 ml of water, and this solution was heated to 60 °C. A solution of amines was added to this solution of the copper(II) perchlorate upon stirring, the reaction mixture was stirred at 60 °C for 30 min, and was cooled to ambient temperature and placed in a refrigerator. In 12 h, deep blue crystals were filtered, washed with small amounts of cold water, ethanol, and dried in vacuum. Yield 0.98 g (37%). Analytically pure sample was obtained after recrystallization from ethanol–water (1:1). *Anal.* Found (%): C, 36.38; H, 4.18; N, 10.46. Calc. for $C_{16}H_{22}N_4CuCl_2O_8$ (%): C, 36.07; H, 4.16; N, 10.52%. Mass spectrum (electrospray, methanol): 333 ($[Cu(L1)]^+$; isotopic pattern corresponds to the proposed formulation); 432 ($[Cu(L1)ClO_4]^+$; isotopic pattern corresponds to the proposed formulation).

2.4. Synthesis of $[Cu(L3)](PF_6)_2$

The compound was prepared using a variation of the procedure outlined by Phillip et al. [32]. Vinyl pyridine (26 g, 0.25 mol) and 7.5 g (0.125 mol) of ethylene diamine in ethanol (100 ml) and glacial acetic acid (3 g) were refluxed under nitrogen for 20 h. The resulting solution was mixed with 6.9 g of $CuCl_2 \times 2H_2O$ in 60 ml of water, and a small excess of NH_4PF_6 (14 g) was added. The resulting deep-blue solution was placed in a refrigerator for two days. The royal-blue microcrystalline product (5.8 g) was filtered, washed with small amounts of water, then with ethanol, and dried in vacuum. Additional amount of the product crystallized from the filtrate upon staying in a refrigerator for 10 days (4.2 g). Total yield 10 g (34%, based on copper chloride). *Anal.* Found (%): C, 37.54; H, 4.24; N, 9.37. Calc. for $C_{23}H_{29}N_5CuP_2F_{12}$ (%): C, 37.89; H, 4.01; N, 9.61. Mass-spectrum (FAB, NBA/acetonitrile): 438 ($[Cu(L3)]^+$, isotopic pattern corresponds to proposed formulation); 457 ($Cu(L3)F^+$), 583 ($Cu(L3)PF_6^+$).

The same compound was prepared, substituting an equivalent amount of $Cu(NO_3)_2 \times 2.5H_2O$ for $CuCl_2 \times 2H_2O$. The first crop of the product was isolated as blue powder (5.7 g), and the second crop formed large, dark blue shiny crystals (6.3 g). Total yield 41% (based on copper nitrate). IR, UV–Vis, and FAB mass-spectrum data are identical for the products prepared from the copper(II) chloride or from the copper(II) nitrate.

2.5. Synthesis of $[Cu(L4)](PF_6)_2$

This compound was prepared in the same fashion as $[Cu(L3)](PF_6)_2$, substituting *N*-methyl ethylene diamine for the ethylene diamine, and using 0.375 mol of vinyl pyridine instead of 0.25 mol. The solution after reflux was divided into two equal portions, and complexes with different copper salts. $CuCl_2 \times 2H_2O$ (3.450 g, 20.2 mmol) in 20 ml of water was added to one portion, and 4.708 g (20.2 mmol) of $Cu(NO_3)_2 \times 2.5H_2O$ in 20 ml of water was added to the other portion. A small excess of NH_4PF_6 (7 g, 43 mmol) was added to each portion, which then were cooled in a refrigerator, yielding blue solids with some white flecks (9.0 g, 60.6% from the chloride, and 9.5 g, 64% from the nitrate). The solid products were redissolved in a minimum amount of acetonitrile, white undissolved impurities were filtered off and the acetonitrile was removed by rotary evaporation. The solid residues were recrystallized from methanol, producing shiny dark-blue crystals (total yield of purification steps ca. 60%). *Anal.* Found (%): C, 38.47; H, 4.49; N, 9.56. Calc. for $C_{24}H_{31}N_5CuP_2F_{12}$ (%): C, 38.80; H, 4.21; N, 9.43. Mass-spectrum (FAB, NBA/acetonitrile): 452 ($[Cu(L4)]^+$); 471 ($[Cu(L4)F]^+$); isotopic patterns correspond to the proposed formulations.

2.6. Physical measurements

Cyclic voltammetry experiments were performed with a Model 273 potentiostat/galvanostat (EG and G PAR,

Princeton, NJ) interfaced to a DEC p420-SX microcomputer using the model 270 software (EG andG). Voltammetric experiments were performed in a three-electrode cell consisting of a Ag-wire reference electrode, a Pt-wire counter electrode, and a 3 mm glassy carbon (BAS) working electrode. Ferrocene was used as an internal standard, and tetrabutylammonium perchlorate (0.1 M) was used as a supporting electrolyte. Solutions were degassed prior to measurements by bubbling N_2 for 10 min, the measurements were also performed under nitrogen, in order to prevent any interaction of reduced copper species with dioxygen.

EPR spectra were recorded on a Bruker EMX spectrometer, NMR spectra on a 300 MHz Bruker AM300 spectrometer, UV–Vis spectra on a Hitachi U-200 UV–Vis spectrophotometer.

2.7. X-ray diffraction study

Single crystals of L2 (**I**) and $[Cu(L1)](ClO_4)_2$ (**II**) suitable for X-ray study were grown by recrystallization from ethanol, single crystals of $[Cu(L5)](ClO_4)_2$ (**III**) were obtained upon recrystallization from warm water, and single crystals of $[Cu(L3)](PF_6)_2 \times MeOH$ (**IV**) were grown by slow evaporation of its methanol solution.

Single-crystal intensity measurements were collected at room temperature with a Siemens four-circle diffractometer (**I**, **II**) or Rigaku AFCS diffractometer (**III**, **IV**), using Mo Kα radiation with graphite monochromator and $\omega/2\theta$-scans. Lattice parameters (Table 1) for **I**–**IV** were obtained using least-squares refinement of the angles of 24 reflections with $22 < 2\theta < 26°$. Empirical absorption correction was applied to all copper containing crystals. The structure was solved by direct methods using SHELXS-97 [52] and refined with all data by full-matrix least-squares on F^2 using SHELXL-97 [53]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were fixed in idealized positions with a riding model (**II**, **III**, **IV**) or refined isotropically (**I**).

3. Results and discussion

3.1. Synthesis

Ditosylate of a tetradentate ligand, L2, was obtained by a modification of Richman–Atkins [50] procedure (Fig. 2). Tosylation of an alcohol group in the β position to the pyridine ring proved to be more challenging than tosylation of aliphatic or benzylic alcohols, leading to low yield of the product. One complication is related to the presence of the basic center (pyridine ring) within the tosylated molecule, which competes with the standard solvent (pyridine [50]) for protons, producing a hardly separable mixture of hydrochloride and tosylate salts of the product. Another complication is related to competing elimination of a β-hydroxy group present in 2-hydroxyethylpyridine. Thus, using KOH as a base, which was suggested for tosylation of pyridine-containing alcohols [49], did not improve the yield and purity of the product, because the hard nucleophile OH^- facilitated elimination and related side-reactions. Apparently, elimination also competed with nucleophilic substitution at the next (condensation) step, again reducing the yield of the product. It can be concluded that the synthetic route outlined on Fig. 2 was satisfactory for the synthesis of a tosylated tetradentate ligand $(Etpy)_2Ts_2en$ (L2), but was impractical for the preparation of metal complexes with aminopyridine ligands bearing long ethylpyridine pendant arms.

Table 1
Structure data

Compound	**I**	**II**	**III**	**IV**
Formula	$C_{30}H_{34}N_4O_4S_2$	$C_{16}H_{20}C1_2CuN_4O_5$	$C_{14}H_{18}CuN_4Cl_2O_8$	$C_{24}H_{33}CuN_5OP_2F_{12}$
Formula weight	578.73	530.80	504.76	761.03
System	monoclinic	monoclinic	orthorhombic	monoclinic
Space group	$P2_1/c$	$C2/c$	$Pnma$	$P2_1/n$
a (Å)	11.4560(10)	14.5295(19)	14.408(3)	12.951(3)
b (Å)	7.9900(10)	9.7456(16)	26.497(5)	14.321(3)
c (Å)	15.804(2)	15.8829(13)	10.453(2)	17.611(4)
β (°)	97.900(10)	111.086(9)	90	105.29(3)
V	1432.9(3)	2098.4(5)	3990.6(14)	3150.7(12)
Z	2	4	8	4
Reflections measured	2523	1842	4684	5542
R	0.052	0.041	0.050	0.047
R_2	0.136	0.110	0.169	0.154
S	1.02	1.05	1.02	1.004
Max. residual electron density	0.19	0.52	0.95	0.49

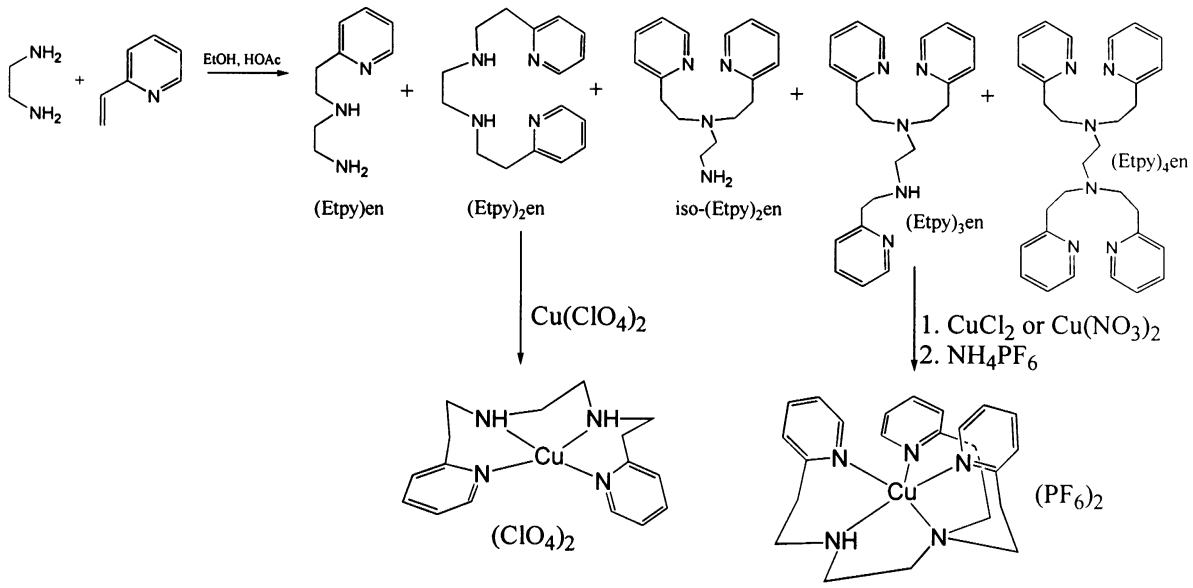

Fig. 3. Synthesis and isolation of the copper(II) complexes with tetra- and pentadentate aminopyridine ligands bearing ethylpyridine pendant arms.

The condensation of vinyl pyridine with ethylene diamine is known to produce a mixture of products (Fig. 3) containing desired tetra- and pentadentate ligands (Etpy)$_2$en (L1)and (Etpy)$_3$en (L3) [51]. This mixture can hardly be separated by vacuum distillation, because of partial decomposition of the products at elevated temperatures, and their relatively close boiling points (which is particularly true for two isomeric compounds (Etpy)$_2$en and *iso*-(Etpy)$_2$en (Fig. 3)). Phillip et al. suggested that only two components of the reaction mixture, (Etpy)$_2$en and (Etpy)$_3$en, are good ligands for the copper(II), and reported the isolation of the four-coordinate complex [Cu(L1)](ClO$_4$)$_2$ from the 2:1 condensation of vinylpyridine and ethylene diamine [32], and the five-coordinate complex [Cu(L3)](ClO$_4$)$_2$ from the analogous 3:1 condensation reaction [82]. In our hands, however, these procedures yielded contaminated products. Even though the complex [Cu(L1)](ClO$_4$)$_2$ is the major product isolated from the reaction mixture in the presence of perchlorate anions, it contains an admixture of the five-coordinate species [Cu((L3)]$^{2+}$ (as evidenced by mass spectrometry). In order to avoid this possible contamination, we prefer to prepare [Cu(L1)](ClO$_4$)$_2$ from the low-boiling fractions of aminopyridines, which do not contain polysubstituted products.

The perchlorate of the five-coordinate complex [Cu(L3)](ClO$_4$)$_2$ contained significant amounts of its four-coordinate counterpart, [Cu(L1)](ClO$_4$)$_2$, and was difficult to purify. We have demonstrated that an addition of copper(II) chloride or copper(II) nitrate to the vinylpyridine–ethylene diamine reaction mixture, followed by an addition of an excess of ammonium hexafluorophosphate, leads to slow crystallization of the complex [Cu(L3)](PF$_6$)$_2$. It is remarkable that the replacement of a non-coordinating counter ion is sufficient to isolate a different complex even from a 2:1 condensation: all the conditions in our preparation, except for the copper salt used, were identical to those used by Phillip et al. [32], and yet a five-coordinate complex [Cu(L3)]$^{2+}$ was obtained as a PF_6^- salt, while a four-coordinate complex [Cu(L1)]$^{2+}$ was isolated by Phillip [32] in the form of its perchlorate salt. Apparently, possible coordination of the chloride is insignificant, since both $CuCl_2$ and $Cu(NO_3)_2$ gave identical five-coordinate product in our preparations. The preferential isolation of one complex versus another is thus determined by different solubilities of ClO_4^- and PF_6 salts of [Cu(L1)]$^{2+}$ and [Cu(L3)]$^{2+}$. The identity and purity of the five-coordinate complex [Cu(L3)](PF$_6$)$_2$ was confirmed by elemental analysis, mass spectroscopy, and X-ray crystallography. The spectral and redox properties of [Cu(L3)]$^{2+}$ are also different from those of [Cu(L1)]$^{2+}$ (see below).

The five-coordinate complex [Cu(L4)](PF$_6$)$_2$ was also prepared in a manner similar to the synthesis and isolation of [Cu(L3)](PF$_6$)$_2$. As before, both copper(II) chloride and copper(II) nitrate can be used as starting copper salts, with the product precipitating slowly upon addition of NH_4PF_6.

3.2. Crystal structure of L2 (*I*)

The ethylenediamine fragment in this molecule has an open *trans* conformation, with two ethylpyridine groups also *trans* to each other (Fig. 4). This open conformation, with two pyridine nitrogens pointing to the opposite directions, is very different from the ligand

conformation in the copper complex discussed below. Bond lengths and angles in **I** are not unique (see Supplementary material).

3.3. Crystal structure of $[Cu(L1)](ClO_4)_2$ (II)

The coordination sphere of copper(II) in this complex has a tetrahedrally distorted square-planar geometry, with two additional perchlorate anions in the apical positions (Cu–O = 2.709 Å) (Fig. 5). The coordination chromophore in $[Cu(Etpy_2)en]^{2+}$ has typical Cu–N bond lengths [55] (Fig. 5), with Cu–N(amine) and Cu–N(py) being almost equal to each other. Angles at the Cu atom (ca. 95°, Fig. 5) are in between of those typical of a square planar geometry (90°) and a tetrahedral geometry (109.4°), being closer to the former one.

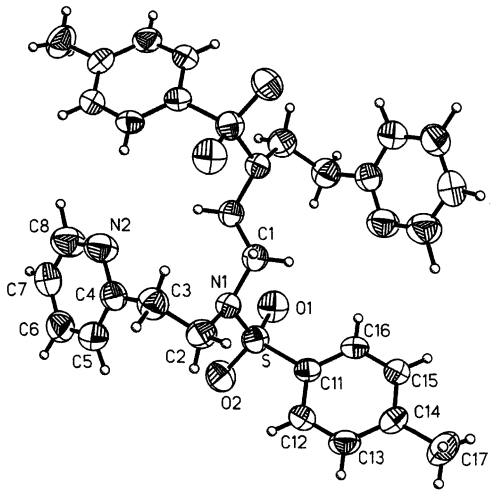

Fig. 4. Molecular structure of **I**.

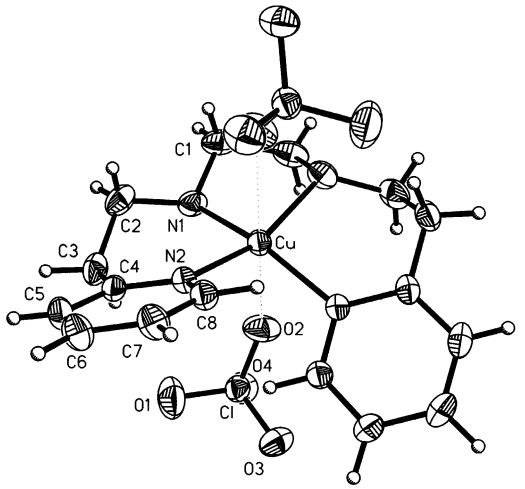

Fig. 5. Structure of **II**. Selected bond lengths (Å) and angles (°): Cu–N(1) 2.015(3), Cu–N(2) 2.016(3); N(1a)–Cu–N(1) 83.42(19), N(1a)–Cu–N(2) 156.97(12), N(1)–Cu–N(2) 94.82(13), N(2)–Cu–N(2a) 95.46(16).

Significant deviation of L1 from planarity is caused by steric interaction between 6- and 6′-hydrogen atoms in the terminal pyridine rings. The degree of tetrahedral distortion in square planar complexes is usually defined by parameters β or ω. [2] Parameter β is defined as a half of the value of the mean *trans* ligand–metal–ligand angle θ and equals 90° for a purely square-planar geometry (D_{4h}), and 54.7° for a tetrahedral one (T_d). Another parameter, ω, is a dihedral angle between two planes, each of which contains the central metal ion and two *cis*-ligands. For the square-planar geometry, $\omega = 0$, and for the tetrahedral geometry, $\omega = 90°$ [2] These two parameters are related by the following equation:

$$\cos\omega = \pm\frac{1 - 3\cos^2\beta}{1 + \cos^2\beta} \quad (1)$$

For the complex $[Cu(L1)]^{2+}$, $\beta = 78.49°$ (a half of an angle N(1)–Cu–N(2)a, Fig. 5), and $\omega = 32.14°$ (an angle between the planes Cu–N1–N1a and Cu–N2–N2a). These values indicate a moderate degree of tetrahedral distortion in this complex, which is somewhat higher than, for example, in the copper(II) complex with L6 ($\beta = 84.5$ [54]), but smaller than in a four-coordinate Cu(II) complex with a tetradentate ligand bearing terminal benzimidazole rings ($\beta = 77.65$ [18]).

Cu occupies a special position on the C2 axes, that is why its deviation from the mean plane formed by four donor nitrogens is exactly zero. N1 and N2 are at +0.41 and −0.36 Å from this plane, respectively. Plane Cu–N2–N2a is at 14° from the mean plane and Cu–N1–N1a is at −18° from the mean plane. In addition to the distortions of the copper(II) coordination sphere, pyridine rings are twisted, thus further reducing van der Waals repulsion between the hydrogen atoms.

The bond lengths and angles within the L1 ligand are practically identical in the compounds $[Cu(L1)](ClO_4)_2$ and L2 (Supplementary material). Thus, the distorted ligand geometry in the copper complex is accomplished by torsional deformations rather than by deviations in bond lengths and angles from their equilibrium values.

3.4. Crystal structure of $[Cu(L5)](ClO_4)_2$ (III)

The aminopyridine ligand in this complex occupies an equatorial plane, and oxygen atoms of the perchlorate anions are in the axial positions (Cu–O12 is 2.61 Å), which makes the Cu(II) coordination number 4 + 2 (Fig. 6). Two complex cations are linked together into a dimer unit via weak copper–perchlorate coordination as well as via system of hydrogen bonds (Fig. 7). The CuN_4 donor set is almost planar, with ±0.04 Å deviations from the mean plane for N atoms, and only 0.02 Å Cu(II) displacement of the mean plane. Cu–N bond distances are typical, and they are remarkably similar

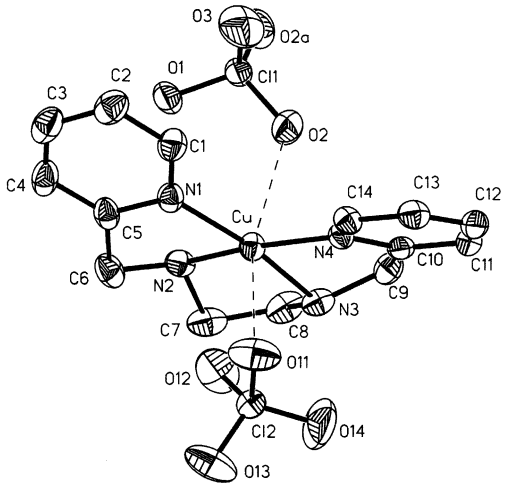

Fig. 6. Structure of **III**. All H atoms are omitted. Selected bond lengths (Å) and angles (°): Cu–N(2) 1.980(3), Cu–N(4) 1.992(3), Cu–N(3) 1.992(4), Cu–N(1) 1.992(4); N(2)–Cu–N(3) 85.42(15), N(2)–Cu–N(1) 82.52(15), N(4)–Cu–N(1) 110.35(14), N(2)–Cu–N(4) 166.52(15)) N(4)–Cu–N(3) 81.79(14), N(3)–Cu–N(1) 167.85(15).

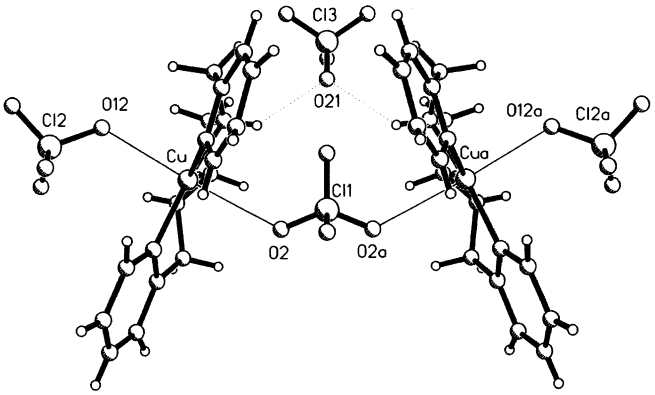

Fig. 7. View of the dimer made of two complex cations of **III**.

for pyridine and amine nitrogen donors, ranging from 1.980 to 1.992 Å. *trans* N–Cu–N bond angles indicate only a slight tetrahedral distortion of the coordination sphere: $\beta = 83.26$ (N2–Cu–N4) or 83.925° (N1–Cu–N3); $\omega = 18.12$ or 18.98°, respectively. These formal indexes of tetrahedral distortion, however, do not adequately describe the structure of CuN_4 chromophore in $[Cu(L5)](ClO_4)_2$, because the deviations from tetragonal geometry are not precisely tetrahedral in this case. Indeed, the bond angles between copper atom and *cis* nitrogen donors are, with one exception (N4–Cu–N1 = 110.35°), smaller than 90° (Fig. 6), which is characteristic of tetragonal pyramidal type structures.

3.5. Crystal structure of $[Cu(L3)](PF_6)_2 \cdot MeOH$ (IV)

In this compound, all five nitrogen atoms are coordinated to the copper(II) ion, in a distorted square-pyramidal fashion (Fig. 8), with two amine nitrogen atoms (N1 and N2) and two pyridine nitrogen atoms (N4 and N5) in the basal plane, and another pyridine nitrogen atom (N3) in the apical position. Deviations of N1, N2, N4, and N5 atoms from the mean plane are + 0.06 Å, while Cu atom out-of-plane displacement (ρ) is 0.33 Å. Cu–N3 is almost normal to the N_4 mean plane (deviation of 4°).

Several approaches have been proposed, in order to quantitatively describe the structural deviation of the copper(II) five-coordinate complexes from ideal square pyramidal (SP) or trigonal bipyramidal (TBP) geometries, in an assumption that the intermediate structures lie on the classical Berry pathway [7,56–58]. Applications of these methods to SP, TBP, and intermediate copper complexes have been reported recently [9,59]. One of the simplest methods utilizes the difference in basal angles θ and ω formed by the *trans*-ligands and the central metal ion [56]. These angles are 180° in an ideal square pyramid, but they are usually smaller and fall in the range of 160–170° due to displacement of the metal ion from the basal plane [7]. The degree of trigonal distortion $\tau = [(\theta - \varphi)/60] \times 100\%$, with $\tau = 0$ in an ideal SP complexes, and $\tau = 100$ for an ideal TBP geometry. For the complex $[Cu(L3)]^{2+}$, angle N(1)–Cu–N(4) = $\theta = 163.92°$, angle N(S)–Cu–N(2) = $\varphi = 157.74°$ and $\tau = 10.3$, indicating only slight distortion from an ideal square-pyramidal geometry. In accordance with this conclusion, the in-plane bond angles around the Cu(II) ion are close to 90° (Fig. 8). The angles formed by the apical pyridine

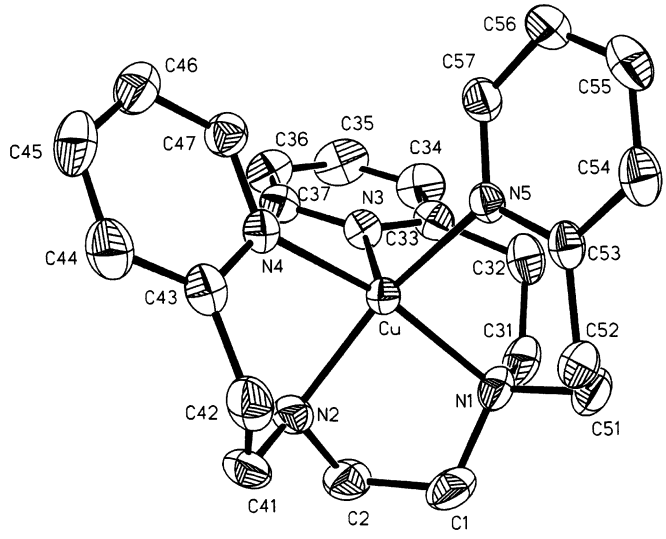

Fig. 8. View of the complex cation in the crystal of **IV**. All H atoms are omitted. Selected bond lengths (Å) and angles (°): Cu–N(5) 2.021(4), Cu–N(2) 2.031(4), Cu–N(4) 2.049(4), Cu–N(1) 2.096(4), Cu–N(3) 2.196(4); N(5)–Cu–N(2) 157.74(16), N(5)–Cu–N(4) 91.12(15), N(2)–Cu–N(4) 86.24(17), N(5)–Cu–N(1) 91.49(16), N(2)–Cu–N(1) 85.35(17), N(4)–Cu–N(1) 163.92(17), N(5)–Cu–N(3) 103.75(15), N(2)–Cu–N(3) 98.46(16), N(4)–Cu–N(3) 100.39(15), N(1)–Cu–N(3) 94.39(16).

nitrogen (N3), the copper ion, and equatorial nitrogens are somewhat higher than 90°, as expected for the Cu(II) ion displaced from the basal plane toward the apical pyridine nitrogen.

The in-plane Cu–N distances (Fig. 8) are within the range for copper–amine and copper–pyridine donors. [55] At the secondary amine N2, the distances Cu–N(am) (Cu–N2) and Cu–N(py) (Cu–N4) are almost equal to each other. At the tertiary nitrogen bearing two ethylpyridine arms, the in-plane distances Cu–N(am) (Cu–N1) and CuN(py) (Cu–N5) are distinctly different from each other, with Cu–N(py) bond (2.021 Å) being significantly shorter than Cu–N(am) bond (2.096 Å). This unusual ratio of bond lengths probably arises in order to provide a square-pyramidal coordination mode of the two pyridine arms attached to the tertiary amine nitrogen. An apical Cu–N3 bond (2.196 Å) is substantially elongated in comparison with in-plane Cu-nitrogen bonds. The bond length deviations from octahedral geometry are described by the tetragonality T^5, defined as the ratio of an average in-plane Cu–L distance to the length of an apical Cu–L bond [7,58]. For the $[Cu(L3)]^{2+}$ complex, an average Cu–N (in-plane) = 2.049 Å, an apical bond Cu–N3 = 2.196 Å and $T^5 = 0.933$, within the usual range of 0.90–0.96 found for five-coordinate copper(II) complexes [7]. The τ and T^5 values for the $[Cu(L3)]^{2+}$ fall inside the usual (although scattered) linear correlation between these two parameters [7,59]. Another relationship established for five-coordinate copper(II) complexes, an inverse correlation between the Cu(II) out-of-plane displacement ρ and the axial bond length Cu–L(ax) [7], does not quantitatively hold for $[Cu(Etpy)_3en]^{2+}$. A shorter Cu–N3 bond of 2.12 Å is expected, based on the data summarized by Hathaway in Fig. 22a [7], and using the experimental value of 0.33 Å for the copper(II) displacement from the basal plane. This elongation of an axial Cu–N(py) bond suggests a relatively weak coordination of an axial pyridine nitrogen in the long ethylpyridyl pendant arm.

3.6. Coordination of aminopyridine ligands to copper(II): structural aspects

The distorted planar coordination mode of polydentate aminopyridine ligands observed in the copper(II) complexes (**II**–**IV**) is somewhat unusual. The van der Waals repulsion between 6,6′-hydrogen atoms in pyridine rings prevents a symmetrical in-plane coordination of tetradentate ligands having terminal heterocyclic groups. This can be alleviated by partial or complete movement of the terminal pyridine rings away from the equatorial plane, giving rise to several different structural motifs. In octahedral complexes, the tetradentate ligands adopt either *cis*-α configuration (with both pyridine nitrogens in the axial positions, and both amine nitrogens in the equatorial plane), or *cis*-β configuration (with two amine nitrogens and one pyridine nitrogen in the basal plane, and the remaining pyridine nitrogen donor in the axial position) [19,38,60–71]. Metal ions with strong preference for square-planar coordination geometry, such as Pd(II), enforce a somewhat distorted square-planar coordination mode of aminopyridine ligands [54,72]. The copper(II) ion, with its highly variable coordination geometries [7], may form different types of complexes with aminopyridine ligands and their analogs. While the four-coordinate structure, with a distorted square-planar geometry, has been predicted by molecular mechanics calculations for the $[Cu(L5)]^{2+}$ complex [73], the previously conducted crystallographic studies identified non-planar arrangement of the ligand L5 in two copper complexes [35,38]. In the presence of additional Cl^- or $C_2O_4^{2-}$ ligands, L5 and its analogs adopted *cis*-β or *cis*-α geometry [19,35,38]. In all these cases, the complexes contained three five-membered chelate rings (555), a structural feature expected to facilitate out-of-plane ligand coordination [74]. It was unclear, however, what structure would the tetradentate ligand adopt in its copper(II) complex in the absence of additional monodentate ligands. The direct structural data obtained in our work prove that $[Cu(L5)]^{2+}$ forms a tetragonal complex, with an in-plane coordination of a tetradentate 555 polychelate ligand (in agreement with early spectorscopic studies by McKenzie and Gibson [33]). A distorted in-plane coordination of the ligand L6 (565 sequence of chelate rings) has been reported previously for the four-coordinate Cu(II) complex [54], and is now found for the $[Cu(L1)]^{2+}$ complex, having 656 chelate rings. Thus, the chelate ring sequence is not as important as the Cu(II) coordination number in determining the binding mode of the aminopyridine ligands.

The degree of tetrahedral distortion in four-coordinate copper(II) complexes with aminopyridine ligands depends on the chelate ring sequence. Previous molecular mechanics calculations indicated that the steric clash between *ortho*-hydrogens on two pyridine rings is somewhat less severe (the distance between 6- and 6′-hydrogen atoms is greater) for the ligand L5 (555) than is expected for the L1 (656) [73]. As a result, the copper(II) coordination sphere in **III** remains almost undistorted, as can be seen in Fig. 6. The twist of two pyridine rings appears to be sufficient in order to reduce van der Waals repulsion between these hydrogens. The complex **II** is significantly more distorted (Fig. 5).

3.7. Electronic spectra

Visible spectra of the four-coordinate complex $[Cu(L1)]^{2+}$ measured in three different solvents contain a single broad, relatively intense d–d absorption band

Table 2
Electronic spectra of the solutions of four- and five-coordinate copper(II) complexes with aminopyridine ligands

Complex	Solvent	λ_{max} (nm) (ε, M^{-1} dm^3)	Reference
$[Cu(L1)](ClO_4)_2$	CH_3CN	579 (180)	this work
	DMSO	604 (190)	this work
	methanol	597(170)	this work
	CH_3NO_2	584 (220)	[32]
$[Cu(L3)](PF_6)_2$	CH_3CN	598 (220); ~850 shoulder (~30)	this work
	DMSO	607 (230); ~860 shoulder (~30)	this work
	methanol	598 (220); ~850 shoulder (~30)	this work
$[Cu(L4)](PF_6)_2$	CH_3CN	604 (250); ~850 shoulder (~20)	this work
	DMSO	613 (210); ~860 shoulder (~30)	this work
	methanol	610 (220); ~850 shoulder (~25)	this work
$[Cu(L5)](ClO_4)_2$	H_2O	603 (152)	[36]
	CH_3CN	599(182)	[36]
	methanol	599(182)	[36]
$[Cu(L6)](ClO_4)_2$	H_2O	603 (143)	[36]
	CH_3CN	596(145)	[36]
	methanol	599(153)	[36]
$[Cu(L7)](ClO_4)_2$	H_2O	589 (245)	[36]
	CH_3CN	628 (277)	[36]
	methanol	599 (277)	[36]
$[Cu(L8)]ClO_4)_2$	H_2O	659 (274)	[36]
$[Cu(L8)]ClO_4)_2$	CH_3CN	653 (285)	[36]
	methanol	645 (340)	[36]
$[Cu(L9)]$ $(ClO_4)_2$	methanol	617 (72)	[18]
$[Cu(L10)](ClO_4)_2$	CH_3CN	617 (160)	[18]
	methanol	629(120)	[18]
$[Cu(L11)](ClO_4)_2$	methanol	690 (103); 1075 (40)	[10]

at about 600 nm (Table 2). The energy of these transitions is somewhat lower than that in typical square-planar copper(II) complexes (500–588 nm) [7]. This can be attributed to tetrahedral distortion of the CuN_4 chromophore, as determined by X-ray crystallography. Alternatively, the relatively weak ligand field of pyridine nitrogens in 656 chelate-ring system may also cause a red shift in the absorption maxima, as compared to all-amine CuN_4 chromophores described by Hathaway [7,58]. Comparison with the data reported by Urbach and coworkers [36] (Table 2) indicate that the nature of the donor atoms, rather than the chelate ring size sequence, plays the major role in the position of absorption bands in the visible spectra of copper(II) complexes with tetradentate aminopyridine ligands. Complexes with benzimidazole residues in place of pyridine groups also have lower-energy bands in the visible region [18]. The degree of tetragonal distortion of CuN_4 chromophore is somewhat smaller in $[Cu(L6)]^{2+}$ [54] than in $[Cu(L1)]^{2+}$, while their visible spectra, especially in methanol solutions, do not differ substantially (Table 2).

The λ_{max} in visible spectra of $[Cu(L1)]^{2+}$ are solvent-sensitive, indicating solvation of the copper(II) center. This is typical of four-coordinate copper(II) coordination compounds [18,36]. The shape of the absorption spectrum is, however, distinctly different from five-coordinate complexes discussed below.

Both five-coordinate complexes, $[Cu(L3)]^{2+}$ and $[Cu(L4)]^{2+}$, display two-band visible spectra in all solvents studied (Table 2), with the intensity of the higher-energy band (ε of about 220) being significantly higher than the intensity of the lower-energy shoulder (ε of about 30). This pattern is characteristic for distorted square-pyramidal copper(II) complexes (the opposite ratio of intensities is typical of trigonal-bipyramidal complexes) [7,75]. Similar spectra were reported previously for a number of five-coordinate copper(II) complexes with TP geometry [7,9–12,75]. The absorption band at approximately 600 nm is more narrow and intense, and is positioned at somewhat lower energies (up to 20 nm lower) in the spectra of five-coordinate complexes as compared to their four-coordinate counterparts (Table 2). This shift, however, is less pronounced than the one in analogous four- and five-coordinate complexes with terminal benzyimidazole groups [10,18] (Table 2). The *N*-methylated derivative L4 has a weaker ligand field than the non-methylated ligand L3, an effect similar to that observed for four-coordinate compounds [36]. Spectra of five-coordinate copper complexes (Table 2) are not as sensitive to the nature of the solvent as those of four-coordinate compound $[Cu(Etpy)_2en]^{2+}$, since the fifth coordination site is now occupied by a nitrogen donor from an axially bound pyridine arm and is inaccessible to solvent molecules. Difference in spectral shapes of five- versus four-coordinate complexes suggests that axial pendant arm remains coordinated to the copper(II) ion in acetonitrile, methanol, and dimethylsulfoxide solutions.

The main conclusions from analysis of the electronic spectra can be summarizes as follows: (1) both four- and five-coordinate complexes with aminopyridine ligands studied in this work retain in solutions their solid-state coordination geometry determined by X-ray crystallography (distorted square-planar and distorted square-pyramidal, respectively); (2) the axial coordination of an ethylpyridine pendant arm leads to minor changes in in-plane ligand field; (3) alkylation of secondary amine donors reduces the strength of the ligand field in aminopyridine copper(II) complexes.

3.8. Electron paramagnetic resonance spectra

Anisotropic spectra of the complexes $[Cu(L1)](ClO_4)_2$, $[Cu(L3)](PF_6)_2$ and $[Cu(L4)](PF_6)_2$, measured in frozen acetonitrile solutions, are axial, with $g_{//} > g_{\perp}$

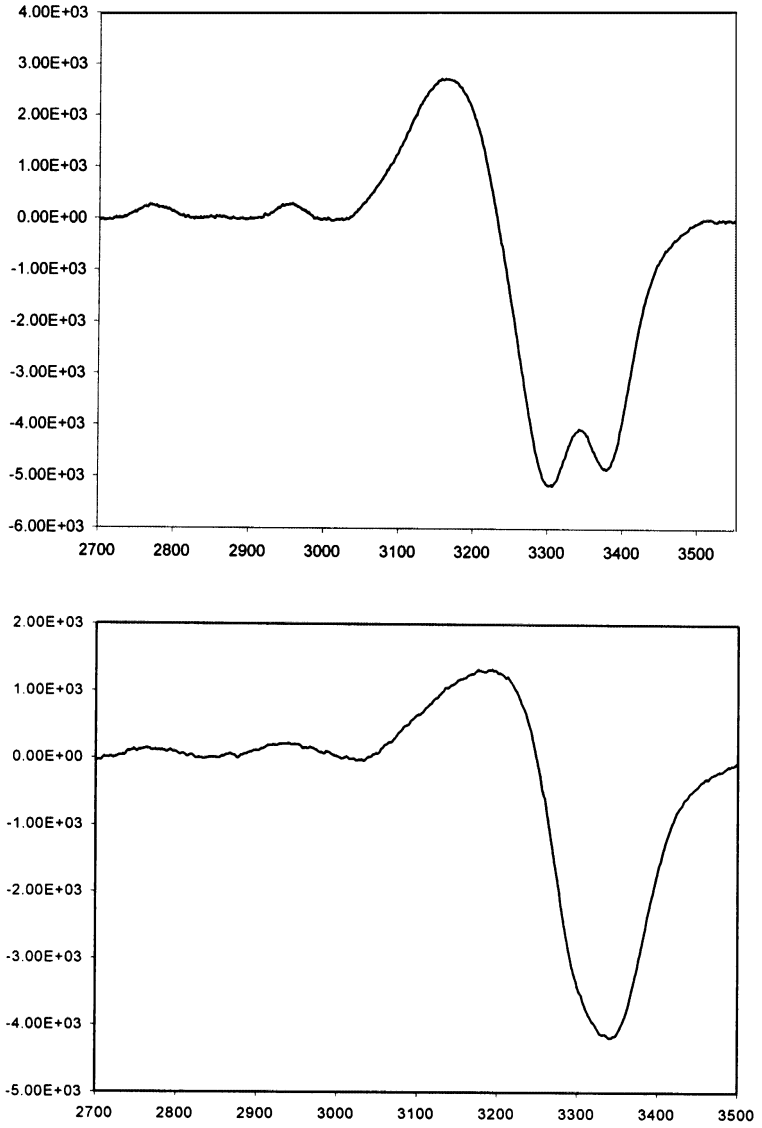

Fig. 9. EPR spectra of a four-coordinate complex $[Cu(L1)](ClO_4)_2$ (top) and a five-coordinate complex $[Cu(L3)](PF_6)_2$ (bottom) measured in CH_3CN frozen glass (77 K).

Table 3
Anisotropic EPR spectral data for the copper(II) complexes (CH_3CN, 77 K)

Compound	$g_{//}$	$g_{\perp}$	10^4 $A_{//}$ (cm^{-1})	$g_{//}/A_{//}$ (cm^{-1})	Reference
$[Cu(L1)](ClO_4)_2$	2.206	2.074	193	114	this work
$[Cu(L3)](PF_6)_2$	2.220	2.062	174	128	this work
$[Cu(L4)](PF_6)_2$	2.223	2.072	171	130	this work
$[Cu(L5)](ClO_4)_2$	2.205	2.075; 2.085 [a]	193	114	[36] [b]
$[Cu(L6)](ClO_4)_2$	2.215	2.053;2.053 [a]	196	112	[36] [b]
$[Cu(L7)](ClO_4)_2$	2.212	2.068; 2.083 [a]	184	114	[36] [b]
$[Cu(L8)](ClO_4)_2$	2.225	2.100;2.100 [a]	158	141	[36] [b]
$[Cu(L9)](ClO_4)_2$	2.217	2.098	164	135	[36] [d]
$[Cu(L10)](NO_3)_2$	2.202	2.050 [c]	190	116	[18] [d]
$[Cu(L11)](ClO_4)_2$	2.270	2.076 [c]	159	143	[10] [d]

[a] g_x and g_y were reported.
[b] Spectra obtained in 9:1 methanol/ethanol glasses
[c] Calculated as $g_{\perp} = 1/2(3g_0 - g_{//})$.
[d] Spectra obtained in 4:1 methanol/acetone glasses.

(Fig. 9), indicating a $d_{x^2-y^2}$ ground state [7]. Spectral parameters (Table 3) fall in the range typical of square-based coordination polyhedra [7]. These results, in accord with the electronic spectral data, suggest that both four- and five-coordinate complexes retain their solid-state structure (distorted square-planar, or distorted square-pyramidal, respectively) in acetonitrile solutions.

Numerous correlations between the degree of tetrahedral distortion and the EPR parameters have been suggested for the four-coordinate copper(II) complexes [2,7,76,77], including the linear correlation between $g_{//}$ and $A_{//}$ [2], the linear dependency between $g_{//}$ and dihedral angle function $\Omega = (3 + \cos\omega)^2/(1 + \cos\omega)^2$ [2], and another linear correlation between $g_{//}$ and a structural parameter $1/\sin^4\beta$ [78,79]. The correlation parameters (slopes and intercepts) depend on the exact donor set in the complexes, with the majority of previously available data obtained for either tetramine (N_4(am)), or tetra-imidazol-type (N_4(im)) copper coordination environments [2]. The complexes listed in Table 3 offer the experimental data (both structural and EPR) for N_2(am)N_2(py) donor set. The $g_{//}$ and $A_{//}$ parameters for all these N_2(am)N_2(py) complexes fall on the straight lines obtained for N_4(am) complexes [2,76].

EPR parameters also reflect the degree of tetrahedral distortion of square-planar copper(II) complexes. The $g_{//}/A_{//}$ can be used as a rough estimate of coordination geometry, with the values of 110–120 being typical of planar complexes, while the range of 130–150 is characteristic of slight to moderate distortion, and 180–250 indicate considerable distortion [2]. In the case of $[Cu(L1)]^{2+}$, the X-ray structural data show a distorted structure, with $\omega = 32°$, and somewhat higher than 114 value for the $g_{//}/A_{//}$ parameter may have been expected. Both $g_{//}$ and $A_{//}$ depend on ω, and the slopes of these non-linear relationships increase markedly as ω increases [2,77]. As a result, only small changes in EPR spectral parameters can be observed for the moderately distorted complexes. Relative insensitivity of the EPR parameters to small distortions of the tetragonal coordination polyhedron does not allow for spectroscopic distinguishing between the geometry of $[CuL1]^{2+}$ and analogous N_2py_2 complexes $[CuL5]^{2+}$ ($\beta = 83.90$) and $[CuL6]^{2+}$ ($\beta = 84.50$ [54]) which are less distorted than $[CuL1]^{2+}$.

For the five-coordinate complexes $[Cu(L3)]^{2+}$ and $[Cu(L4)]^{2+}$, EPR parameters are almost identical (Table 3) and fall within the usual range for CuN_5 chromophores [7,9–13]. An increase in $g_{//}$ and decrease in $A_{//}$ as compared to the four-coordinate $[Cu(L1)]^{2+}$ represent, as expected [7], an increasing axial interaction. The difference between the structurally related complexes bearing two or three ethylpyridine pendant arms is, however, small. Significantly more pronounced changes in EPR parameters were observed in a series of four- and five-coordinate copper complexes with benzimidazolyl groups appended to the diamine frameworks [10,18] ($g_{//} = 2.27$, $A_{//} = 159$ for $[Cu(L11)]^{2+}$ [10], and $g_{//}$ in the range of 2.20–2.21, $A_{//}$ ranging from 164 to 190 for analogous four-coordinate complexes [18]). It appears that the axial pyridine nitrogen appended on a long linker forms a weak bond with the central copper(II) ion. This conclusion is in agreement with a long apical Cu–N(py) bond in $[Cu(L3)]^{2+}$ found by X-ray crystallography. Another structural parameter which influences EPR spectra of tetragonal-pyramidal copper complexes, the copper out-of-plane displacement ρ, is not unique in our case (0.33 Å). For example, $\rho = 0.36$ Å for tripodal tetramine ligand with an appended pyridine arm [9], where $g_{//} = 2.20$, $A_{//} = 155$ and $\rho = 0.41$ Å for a dipeptide ligand containing three pyridine rings, giving rise to $g_{//} = 2.20$, $A_{//} = 154$ [11]. As expected, the equatorial ligand field weakens, and $A_{//}$ decreases as the copper(II) ion moves out of the basal plane.

3.9. Electrochemistry

The redox behavior of the Cu(II)/Cu(I) couple in aminopyridyl complexes was investigated by cyclic voltammetry in acetonitrile and DMSO solutions (Table 4). One quasi-reversible reduction wave was observed in all cases except for $[Cu(L5)](ClO_4)_2$ in acetonitrile, where reduction was rather irreversible under our conditions, as can be judged from i_{pc}/i_{pa} ratio. Further reduction of all investigated complexes caused irreversible deposition of Cu metal on the electrode surface. No reversible metal oxidation waves were registered at the potentials up to $+0.8$ V (vs. NHE), solvent or ligand oxidation interfered with the measurements at higher potentials. The $E_{1/2}$ values are solvent-dependent, being more negative in DMSO than in acetonitrile (by 183 and 161 mV for the four-coordinate complexes $[Cu(L5)]^{2+}$ and $[Cu(L1)]^{2+}$, and by 90 and 43 mV for the five-coordinate ones, $[Cu(L3)]^{2+}$ and $[Cu(L4)]^{2+}$, respectively). This difference can be attributed, at least partially, to different solvation of the Cu(II) compounds in DMSO and CH_3CN, as can be seen from the changes in their d–d spectra upon changing the solvent (Table 2). Another significant factor is solvation of the Cu(I) oxidation state, which is known to be stabilized in acetonitrile solutions [79].

The electrochemical data for the four-coordinate $[Cu(L1)]^{2+}$ compare well with those obtained previously for a series of copper(II) complexes with tetradentate aminopyridine ligands [36] and improve the understanding of structure–redox-potential relationships. One of the trends observed by Urbach et al. [36] is the monotonic increase in the redox potentials as the chelate ring sizes are increased in a series 555 (L5) < 565 (L6) < 656 (L7) < 666 (L8) (Table 4). While the

Table 4
Electrochemical data for the copper complexes with aminopyridine ligands (cyclic voltammetry, scan rate 50 mV s^{-1}, 25 °C)

Complex	Solvent	$E_{1/2}$ (V)	ΔE_p (mV)	i_{pc}/i_{pa}	Reference
$[Cu(L1)](ClO_4)_2$	CH_3CN	−0.534 [a]	94	1.10	This work
	DMSO	−0.695 [a]	126	1.11	This work
$[Cu(L3)](PF_6)_2$	CH_3CN	−0.449 [a]	208	1.17	This work
	DMSO	−0.539 [a]	214	1.16	This work
$[Cu(L4)](PF_6)_2$	CH_3CN	−0.380 [a]	84	1.07	This work
	DMSO	−0.423 [a]	98	1.10	This work
$[Cu(L5)](ClO_4)_2$	CH_3CN	−0.549 [a]	142	4.40	This work
	DMSO	−0.732 [a]	112	1.21	This work
	CH_3CN	−0.169 [b]	70	0.88	[36]
	H_2O	−0.196 [c]	138	0.96	[36]
$[Cu(L6)](ClO_4)_2$	CH_3CN	−0.148 [b]	72	0.60	[36]
	H_2O	−0.106 [c]	78	0.81	[36]
$[Cu(L7)](ClO_4)_2$	CH_3CN	+0.083 [b]	196	1.09	[36]
	H_2O	+0.099 [c]	115	1.07	[36]
	H_2O	+0.144 [c]	80		[37]
$[Cu(L8)](ClO_4)_2$	CH_3CN	+0.310 [b]	94	1.15	[36]
	H_2O	+0.275	74	1.02	[36]

[a] Measured vs. Fc^+/Fc internal standard; to convert to NHE, add 0.400 mV ([36] and references therein).
[b] Measured vs. SCE with internal ferrocene standard and referenced to the NHE by adding 0.400 V [36].
[c] Measured vs. SCE, converted to NHE scale by adding 0.244 V [36].

first two ligands in this series have secondary amine donors, the other two are *N*-methylated, tertiary amine derivatives. The ligand L1 is a non-methylated analog of L7, with 656 chelate ring sequence. While $E_{1/2}$ for $[Cu(L1)]^{2+}$ (−134 mV vs. NHE) is somewhat higher that that for $[Cu(L5)]^{2+}$ and $[Cu(L6)]^{2+}$ (−169 and −148 mV, respectively [36]), as expected based on its chelate ring size, this potential is significantly lower than that for a *N*-methylated analog $[Cu(L7)]^{2+}$ (+83 mV [36]). Clearly, methylation of two secondary amino groups increases the redox potential of the copper complex $[Cu(L1)]^{2+}$ by more than 200 mV. The opposite effect of *N*-methylation on the redox potentials (a decrease in $E_{1/2}$) may be expected, based on the inductive effect of methyl groups which should stabilize higher oxidation states of the metal ion. The observed increase in $E_{1/2}$ may be attributed to a reduced stability of the copper(II) complexes with tertiary amines. [80] Rorabacher and coworkers have shown that an increase in Cu(II)/Cu(I) redox potentials is often related to the relative destabilization of the Cu(II) complexes, rather than to stabilization of the Cu(I) species [6,81]. It can be concluded that a remarkable range of almost 500 mV, observed by Urbach et al. for their series of aminopyridyl ligands [36], is caused by two parallel effects, namely, the changes in the chelate ring sizes, and the methylation of amine nitrogen donors.

Relative stabilization of the Cu(I) oxidation state in the complexes with larger chelate rings is usually qualitatively explained by greater flexibility of longer aliphatic chains which allows to better adjust to the tetrahedral geometry preferred by Cu(I) complexes [36]. Quantitative correlations between $E_{1/2}$ and the degree of tetrahedral distortion of Cu(II) complexes appear to be reasonable [79], but do not provide reliable results [2,79]. For a given set of donor atoms, the potentials indeed somewhat increase as ω increases (Table 4), although changes in redox potentials are relatively small.

The redox potential of the Cu(II)/Cu(I) couple in the five-coordinate complex $[Cu(L3)]^{2+}$ is substantially higher than that of its four-coordinate counterpart $[Cu(L1)]^{2+}$ (by 85 mV in acetonitrile, and by 156 mV in DMSO), indicating relative destabilization of the Cu(II) and/or stabilization of the Cu(I) oxidation states upon axial coordination of the fifth ligand. Similar, although smaller effect of the 'forced axial coordination' to a planar CuN_4 chromophore has been reported for benzimidazole analogs of the ligands L1 and L3: the potential increased by 21 mV upon appending of an extra benzimidazole-containing arm to a tetradentate $N_2(am)N_2(BzIm)$ ligand [10]. Interestingly, the difference in EPR and visible spectra between four- and five-coordinate complexes, which primarily reflects the changes in in-plane Cu(II) coordination, is greater in benzimidazole series [10,18] than in pyridine series explored here. It appears that acceptor properties of an axially coordinated pyridine ring play a major role in relative stabilization of Cu(I) in $[Cu(L3)]^{2+}$.

N-Methylation of a secondary amino group in a pentadentate ligand L3 leads to an increase in $E_{1/2}$ of the copper complex. This trend parallels the one observed for the four-coordinate complexes, although the quantitative effect is substantially smaller for the five-coordinate species (compare L3 and L4, Table 4), since only one secondary amine donor becomes a tertiary amine donor.

4. Conclusions

A convenient method of isolation for four- and five-coordinate copper(II) complexes with 'long-armed' aminopyridine ligands L1, L3, and L4 has been developed. In the absence of additional monodentate ligands, all four nitrogen donors in tetradentate aminopyridine ligands L1 and L5 occupy equatorial positions, forming distorted tetragonal copper(II) complexes. The main reason for the observed deviations from planarity is van der Waals repulsion between *ortho*-hydrogens from two different pyridine rings. The degree of tetrahedral distortion of the 'long-armed' complex $[Cu(L1)]^{2+}$ ($\omega = 32.14°$) is significantly greater than that in its 'short-armed' analogs $[Cu(L5)]^{2+}$ and $[Cu(L6)]^{2+}$. Nevertheless, UV–Vis and EPR spectral parameters are insensitive to these differences in tetrahedral distortion. The redox potentials for the Cu(II)/Cu(I) couple reflect the expected trend of stabilizing Cu(I) species in tetrahedral coordination environment. Introducing of a fifth nitrogen donor in the 'long' ethylpyridine pendant arm leads to a distorted tetragonal pyramidal copper(II) complex with an elongated apical bond and a Cu(II) ion displaced from the equatorial plane by 0.33 Å. These structural features cause some (although relatively small) weakening of the equatorial ligand field, as reflected in EPR parameters. A relatively weak coordination of the fifth pyridine nitrogen increases the redox potential of the Cu(II)/Cu(I) couple by 85–156 mV, depending on the solvent. Methylation of the secondary amine nitrogen donors in both tetra- and pentadentate ligands reduces an equatorial ligand field in the copper(II) complexes, and destabilizes Cu(II) with respect to Cu(I) (increases the Cu(II)/Cu(I) redox potential).

5. Supplementary material

Tables giving full details for the crystal data are available on request from the author.

Acknowledgements

This work was supported by Tufts University. EPR facility at Tufts was supported by the NSF (CHE9723772). The authors thank Professor S.P. Kounaves for an access to electrochemical instrumentation.

References

[1] G.S. Patterson, R.H. Holm, Bioinorg. Chem. 4 (1975) 257.
[2] A.W. Addison, Spectroscopic and redox trends from model copper complexes, in: K.D. Karlin, J. Zubieta (Eds.), Copper Coordination Chemistry: Biochemical and Inorganic Perspectives, Adenine Press, New York, 1983.
[3] A.W. Addison, Inorg. Chim. Acta 162 (1989) 217.
[4] A. Messerschmidt, Blue copper oxidases, in: G. Sykes (Ed.), Advances in Inorganic Chemistry, vol. 40, Academic Press, San Diego, 1994, pp. 121–185.
[5] E.R. Docal, T.E. Jones, W.F. Sokol, R.J. Engerer, D.B. Rorabacher, L.A. Ochrymowycz, J. Am. Chem. Soc. 98 (1976) 4322.
[6] E.A. Ambundo, M.-V. Deydier, A.J. Grall, N. Aguera-Vega, L.T. Dressel, T.H. Cooper, M.J. Heeg, L.A. Ochrymowycz, D.B. Rorabacher, Inorg. Chem. 38 (1999) 4233.
[7] B.J. Hathaway, Copper, in: Comprehensive Coordination Chemistry, vol. 5, Pergamon Press, Oxford, 1987, pp. 533–774.
[8] W. Kaim, J. Rall, Angew. Chem., Int. Ed. Engl. 35 (1996) 43.
[9] G.A. McLachlan, G.D. Fallon, R.L. Martin, L. Spiccia, Inorg. Chem. 34 (1995) 254 and references cited therein.
[10] M. Murali, M. Palaniandavar, T. Pandiyan, Inorg. Chim. Acta 224 (1994) 19.
[11] F.A. Chavez, M.M. Olmstead, P.K. Mascharak, Inorg. Chem. 35 (1996) 1410.
[12] F.A. Chavez, M.M. Olmstead, P.K. Mascharak, Inorg. Chim. Acta 269 (1998) 269.
[13] S.J. Brudenell, L. Spiccia, A.M. Bond, P. Comba, D.C.R. Hockless, Inorg. Chem. 37 (1998) 3705 and references cited therein.
[14] Y. Sugiura, T. Takita, H. Umezawa, Bleomycin antibiotics: metal complexes and their biological action, in: H. Siegel (Ed.), Metal Ions in Biological Systems, vol. 19, Marcel Dekker, New York, 1985, pp. 81–108.
[15] Y. Iitaka, H. Nakamura, T. Nakatani, Y. Murata, A. Fujii, T. Takita, H. Umezawa, J. Antibiot. 31 (1978) 1070.
[16] S.J. Brown, S.E. Hudson, D.W. Stephan, P.K. Mascharak, Inorg. Chem. 28 (1989) 468.
[17] S.J. Brown, D.W. Stephan, P.K. Mascharak, J. Am. Chem. Soc. 110 (1988) 1996.
[18] T. Pandiyan, M. Palaniandavar, M. Lakshminarayanan, H. Manohar, J. Chem. Soc., Dalton Trans. (1992) 3377.
[19] C. Ng, M. Sabat, C.L. Fraser, Inorg. Chem. 38 (1999) 5545.
[20] J.R. Aldrich-Write, R.S. Vagg, P.A. Williams, Coord. Chem. Rev. 166 (1997) 361.
[21] L. Huang, J.C. Quada Jr, J.W. Lown, Curr. Med. Chem. 2 (1995) 543.
[22] Y. Ishikawa, Y. Morishita, T. Yamamoto, H. Kurosaki, M. Goto, H. Matsuo, M. Sugiyama, Chem. Lett. (1998) 39.
[23] M. Lubben, A. Meetsma, E.C. Wilkinson, B. Feringa, L. Que Jr, Angew. Chem., Int. Ed Engl. 34 (1995) 1512.
[24] G. Roelfes, M. Lubben, S.W. Leppard, E.P. Schudde, R.M. Hermant, R. Hage, E.C. Wilkinson, L. Que Jr, B.L. Feringa, J. Mol. Catal. A: Chem. 117 (1997) 223.
[25] G. Roelfes, M. Lubben, K. Chen, R.Y.N. Ho, A. Meetsma, S. Genseberger, R.M. Hermant, R. Hage, S.K. Mandal, V.G. Young, Y. Zang, H. Kooijman, A.L. Spek, L. Que Jr, B.L. Feringa, Inorg. Chem. 38 (1999) 1929.
[26] R.Y.N. Ho, G. Roelfes, R. Hermant, R. Hage, B.L. Feringa, L. Que, Jr., Chem. Commun. (1999) 2161.
[27] K.B. Jensen, C.J. McKenzie, L.P. Nielsen, J.Z. Pedersen, H.M. Svendsen, Chem. Commun. (1999) 1313.
[28] X. Zhang, D. Zhang, D.H. Busch, R. van Eldik, J Chem. Soc., Dalton Trans. (1999) 2751.
[29] I. Bernal, I.M. Jensen, K.B. Jensen, C.J. McKenzie, H. Toftlund, J.P. Tuchagues, J. Chem. Soc., Dalton Trans. (1995) 3667.
[30] P. Mialane, A. Nivorojkine, G. Pratviel, L. Azema, M. Slany, F. Godde, A. Simaan, F. Banse, T. Kargar-Grisel, G. Bouchoux, J. Sainton, O. Homer, J. Guilhem, L. Tchertanova, B. Meunier, J.J. Girerd, Inorg. Chem. 38 (1999) 1085.
[31] A.J. Simaan, F. Bance, P. Mialane, A. Boussac, S. Un, T. Kargar-Grisel, G. Bouchoux, J.-J. Girerd, Eur. J. Inorg. Chem. (1999) 993.

[32] A.T. Phillip, A.T. Casey, C.R. Thompson, Aust. J. Chem. 23 (1970) 491.
[33] JG. Gibson, E.D. McKenzie, J. Chem. Soc. A (1971) 1666.
[34] N.A. Bailey, E.D. McKenzie, J. Chem. Soc., Dalton Trans. (1972) 1566.
[35] N.A. Bailey, E.D. McKenzie, J.W. Worthington, J. Chem. Soc., Dalton Trans. (1973) 1227.
[36] D.E. Nickles, M.J. Powers, F.L. Urbach, Inorg. Chem. 22 (1983) 3210.
[37] K.M. Davies, B. Guliani, Inorg. Chim. Acta 127 (1987) 223.
[38] J. Glerup, P.A. Goodson, D.J. Hodgson, K. Michelsen, Inorg. Chem. 34 (1995) 6255.
[39] A. Schiegg, T.A. Kaden, Helv. Chim. Acta 73 (1990) 716.
[40] P.S. Pallavacini, A. Perotti, A. Poggi, B. Seghi, L. Fabbrizzi, J. Am. Chem. Soc. 109 (1987) 5139.
[41] N.W. Alcock, R.G. Kingston, P. Moore, C. Pierpoint, J. Chem. Soc., Dalton Trans. (1984) 1937.
[42] N.W. Alcock, K.P. Balakrishnan, P. Moore, H.A.A. Omar, J, Chem. Soc., Dalton Trans. (1987) 545.
[43] S.J. Grant, P. Moore, H.A.A. Omar, N.W. Alcock, J. Chem. Soc., Dalton Trans. (1994) 485.
[44] E.V. Rybak-Akimova, A.Y. Nazarenko, S.S. Silchenko, Inorg. Chem. 38 (1999) 2974.
[45] G.R. Newcome, S. Pappalardo, V.K. Gupta, F.R. Fronczek, J. Org. Chem. 48 (1983) 4848.
[46] A. Bencini, L. Fabbrizzi, A. Poggi, Inorg. Chem. 20 (1981) 2544.
[47] H.A. Goodwin, F. Lions, J. Am. Chem. Soc. 82 (1960) 5013.
[48] G.H. Searle, R.J. Geue, Aust. J. Chem. 37 (1984) 959.
[49] J.S. Bradshaw, P. Huszthy, C.W. McDaniel, C.Y. Zhu, N.K. Dalley, R.M. Izatt, J. Org. Chem. 55 (1990) 3129.
[50] J.E. Richman, T.J. Atkins, J Am. Chem. Soc. 96 (1974) 2268.
[51] E. Proft, S. Lojack, Rev. Chim. Acad. Rep. Papulaire Roumanie 7 (1962) 405.
[52] G.M. Sheldrick, SHELXS-97, Computer Program for Crystal Structure Determination, University of Göttingen, 1997.
[53] G.M. Sheldrick, SHELXL-97, Computer Program for Crystal Structure Refinement, University of Göttingen, 1997.
[54] E.D. McKenzie, E.S. Stephens, Inorg. Chim. Acta 42 (1980) 1.
[55] M. Melnik, M. Kabesova, M. Dunaj Jurko, C.E. Holloway, J. Coord. Chem. 41 (1997) 35.
[56] A.W. Addison, T.N. Rao, J. Reedijk, J. van Rijn, G.C. Verschoor, J. Chem. Soc., Dalton Trans. (1984) 1349.
[57] E.L. Muettertieth, L.J. Guggenberger, J. Am. Chem. Soc. 96 (1974) 1748.
[58] B.J. Hathaway, Struct. Bond. 14 (1973) 49.
[59] T. Murakami, T. Takei, Y. Ishikawa, S. Kita, Polyhedron 15 (1996) 4391.
[60] P.A. Goodson, A.R. Oki, J. Glerup, D.J. Hodgson, J. Am. Chem. Soc. 112 (1990) 6248.
[61] D.J. Hodgson, K. Michelsen, E. Pedersen, D.K. Towle, Inorg. Chem. 30 (1991) 815.
[62] H.R. Fisher, D.J. Hodgson, K. Michelsen, E. Pedersen, Inorg. Chim. Acta 88 (1984) 143.
[63] M.A. Heinrichs, D.J. Hodgson, K. Michelsen, E. Pedersen, Inorg. Chem. 23 (1984) 3174.
[64] P.A. Goodson, J. Glerup, D.J. Hodgson, K. Michelsen, U. Rychlewska, Inorg. Chem. 33 (1994) 359.
[65] P.A. Goodson, J. Glerup, D.J. Hodgson, K. Michelsen, E. Pedersen, Inorg. Chem. 29 (1990) 503.
[66] P.A. Goodson, J. Glerup, D.J. Hodgson, K. Michelsen, H. Weihe, Inorg. Chem. 30 (1991) 4909.
[67] N. Arulsamy, J. Glerup, A. Hazell, D.J. Hodgson, C.J. McKenzie, H. Toftlund, Inorg. Chem. 33 (1994) 3023.
[68] J. Glerup, P.A. Goodson, A. Hazell, R. Hazell, D.J. Hodgson, C.J. McKenzie, K. Michelsen, U. Rychlewska, H. Toftlund, Inorg. Chem. 33 (1994) 4105.
[69] N. Arulsamy, D.J. Hodgson, J. Glerup, Inorg. Chim. Acta 209 (1993) 61.
[70] N. Arulsamy, P.A. Goodson, D.J. Hodgson, J. Glerup, K. Michelsen, Inorg. Chim. Acta 216 (1994) 21.
[71] N.W. Alcock, E.V. Rybak-Akimova, D.H. Busch, Acta Crystallogr., Sect. C 53 (1997) 1385.
[72] G.R. Newcome, Y.A. Frere, F.R. Fronczek, V.K. Gupta, Inorg. Chem. 24 (1985) 1001.
[73] I. Cukrowski, E. Cukrowska, R.D. Hancock, G. Anderegg, Anal. Chim. Acta 312 (1995) 307.
[74] B. Bosnich, J.M. Harrowfield, H. Boucher, Inorg. Chem. 14 (1975) 815.
[75] A.B.P. Lever, Inorganic Electronic Spectroscopy, Elsevier, Amsterdam, 1984.
[76] J. Peisach, W.E. Blumberg, Arch. Biochem. Biophys. 165 (1974) 691.
[77] E.I. Solomon, J.W. Hare, D.M. Dooley, J.H. Dawson, P.J. Stephens, H.B. Gray, J. Am. Chem. Soc. 102 (1980) 168.
[78] C.M. Groeneveld, R. Aasa, B. Rejinhammar, G.W. Canters, J. Inorg. Biochem. 31 (1987) 143.
[79] V.V. Pavlishchuk, Theor. Exp. Chem. 31 (1995) 1.
[80] A.E. Martell, R.D. Hancock, Metal Complexes in Aqueous Solutions, Plenum Press, New York, 1996.
[81] M.M. Bernardo, M.J. Heeg, R.R. Schroeder, L.A. Ochrymowycz, D.B. Rorabacher, Inorg. Chem. 31 (1992) 191.
[82] A.T. Phillip, W. Mazurek, A.T. Casey, Aust. J. Chem. 24 (1971) 501.