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Copper(II) complexes of new unsymmetrical NSN thioether ligands

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Abstract

The reactions of 2-(mercaptoethyl)benzimidazole with 2-vinylpyridine and 2-picolyl chloride (in basic medium) yield the new unsymmetrical ligands 1-(2-benzimidazolyl)-5-(2′-pyridyl)-3-thiapentane (Biptp) and 1-(2-benzimidazolyl)-4-(2′-pyridyl)-3-thiabutane (Biptb), respectively. Copper(II) complexes of these ligands with differing anions were prepared. Crystal structures are reported for $[Cu(Biptp)](CF_3SO_3)_2{\cdot}2H_2O$ and $[Cu(Biptb)](CF_3SO_3)_2{\cdot}0.5(C_7H_8){\cdot}H_2O$, in which the Cu(II) ions exhibit distorted square-pyramidal geometries. Powder ESR spectra of the copper compounds are rhombic and the degree of rhombicity is related to the identity of the anions. Charge-transfer bands and intense absorption in the visible region are observed in the electronic spectra. Electrochemical studies indicate that one-electron reductions are involved, the reductions occurring at relatively high potentials.

Keywords: Crystal structures; Copper complexes; Electrochemistry; Voltammetry; ESR; UV–Vis

1. Introduction

Numerous research groups have become engaged in studying structure–function relationships for enzymes that have copper in their active sites [1–8]. The objective of such studies includes synthesizing ligands that contain the donor atoms that are present around the copper in the bio-systems, so that the copper complexes of these ligands resemble the overall structure of the active site. The complexes may be functional models [9], or may statically mimic the spectroscopic or other physical properties of the enzyme [10–12].

Among known linear multidentate ligands, a large fraction are symmetrical, in the sense that the termini are identical. Nevertheless, metal complexes with correspondingly unsymmetrical linear ligands are not uncommon. Most of these unsymmetrical ligands are Schiff bases obtained by the condensation of different types of amines with various ketones and aldehydes, and many of these in turn are tetradentate ligands [13,14], obtained by metal-templated syntheses [15] or by direct, unmediated condensation of amines and carbonyl groups [16]. Besides such neutral diimine ligands, metal complexes of anionic unsymmetrical ligands are also known [17].

Metal complexes with unsymmetrical tripodal amines which have both imidazolyl and pyridyl groups have been reported [18]. However, a linear neutral thioether ligand that has pyridyl as well as benzimidazolyl groups has not been previously synthesized. Herein, we present the synthesis of two linear unsymmetric tridentate thioether ligands which have a benzimidazolyl group at one end and a pyridyl group at the other end (Fig. 1). The two ligands are designed with different numbers of carbon atoms between the pyridyl groups and the thioether sulfur so as to discern any effect of chelate ring size on the properties of the copper complexes.

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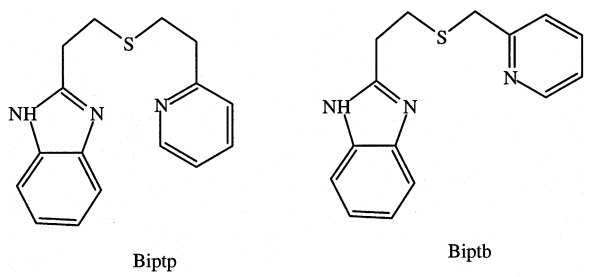

Fig. 1. The ligands Biptp and Biptb. In terms of their donor atom arrays and consequent chelate ring sizes, Biptb and Biptp may be described as giving rise to [NSN-5,6] and [NSN-6,6] chelates, respectively.

2. Experimental

2.1. Materials

All reagents for syntheses were used as received from Aldrich Chemical Co. Inc., or G.F. Smith Chemicals Inc. Literature procedures were followed for the preparation of 2-(mercaptomethyl)benzimidazole [19] and 2-(mercaptoethyl)benzimidazole [20]. For electrochemistry, tetraethylammonium perchlorate (TEAP) was recrystallized from water and dried in vacuo over P_2O_5, while acetonitrile was distilled off P_2O_5 under N_2. Tetrabutylammonium hexafluorophosphate was prepared by metathesis between aqueous Bu_4NBr and HPF_6 solutions, recrystallized from water and dried in vacuo over P_2O_5. All reactions involving thiols were carried out under a nitrogen atmosphere.

2.2. Preparation of compounds

2.2.1. 1-(Benzimidazol-2′-yl)-5-(2′-pyridyl)-3-thiapentane (Biptp)

After 4.65 g (26 mmol) of 2-mercaptoethylbenzimidazole and 2.7 g (26 mmol) of 2-vinylpyridine were refluxed in dry ethanol for 2 days, and treated with Norit-A decolorizing alkaline carbon, the solvent was removed at the rotary evaporator. The resulting colorless oil, on standing, solidified into white crystals which were recrystallized from toluene. (Yield 5.95 g, 80%). *Anal.* Calc. for $C_{16}H_{17}N_3S$: C, 67.8; H, 6.05; N, 14.8. Found: C, 67.9; H, 6.13; N, 14.9%. ^{1}H NMR ($CDCl_3$): 2.96–3.03 (m, 4H, $-CH_2-$), 3.08–3.14 (m, 2H, $-CH_2-$), 3.22 (t, $J = 6.93$ Hz, 2H, $-CH_2-$), 7.15–7.26 (m, 5H, aro), 7.63 (t d, $J = 1.85$ Hz, 7.66 Hz, 2H, aro), 8.58 (m 1H, aro), 9.32 (s, NH). FAB MS m/z 284 $[M + H]$ (100%).

2.2.2. 1-(Benzimidazol-2′-yl)-4-(2″-pyridyl)-3-thiabutane (Biptb)

To a suspension of 2.98 g (18.1 mmol) of 2-picolyl chloride hydrochloride in dry ethanol was added 0.4 g (18.1 mmol) of sodium. After the sodium dissolved, the NaCl was filtered off. To 3.23 g (18.1 mmol) of 2-mercaptoethylbenzimidazole in dry ethanol was added 0.4 g (18.1 mmol) of sodium, and after dissolution of the sodium, the 2-picolyl chloride solution was added dropwise, and the mixture was refluxed overnight. The resulting solution was filtered and treated with Norit-A decolorizing alkaline carbon. On removing the solvent under reduced pressure a pale brown oil was obtained, which on trituration with diethyl ether gave 3.15 g of white powder (yield 64%), subsequently purified by recrystallization from toluene. *Anal.* Calc. for $C_{15}H_{15}N_3S$: C, 66.9; H, 5.61; N, 15.6. Found: C 66.3; H, 5.40; N, 15.4%. ^{1}H NMR ($CDCl_3$): 3.00 (t, $J = 6.6$ Hz, 2H, $-CH_2-$); 3.27 (t, $J = 6.7$ Hz, 2H, $-CH_2-$); 3.92 (s, 2H, $-CH_2-$); 7.19–7.28 (m, 3H, aro); 7.35 (d, $J = 7.77$ Hz, 1H, aro); 7.42–7.45 (m, 1H, aro); 7.71 (t d, $J = 1.80$, 7.68 Hz, 2H, aro); 8.63 (m, 1H, aro); 8.67 (s, NH). FAB MS m/z 270 $[M + H]$ (100%).

2.2.3. [Cu(Biptp)]$(CF_3SO_3)_2 \cdot 2H_2O$ (1)

To 0.26 g (0.92 mmol) of the ligand in methanol, 0.92 mmol of $Cu(CF_3SO_3)_2 \cdot xH_2O$ was added as a (standardized) methanolic solution. On evaporation of the solvent, 0.4 g of blue microcrystals were obtained, which were filtered off and washed with cold methanol. Yield 67%. *Anal.* Calc. for $C_{18}H_{17}CuF_6N_3O_6S_32H_2O$: C, 31.7; H, 3.11; N, 6.17. Found: C, 31.6; H, 3.24; N, 6.14%. FAB MS m/z 495 $[M - CF_3SO_3]$ (53%), 346 $[M - 2CF_3SO_3]$ (100%).

Single crystals of **1** were obtained by diffusing toluene into a nitromethane solution of the complex.

All the following copper complexes were prepared by adopting procedures similar to the one used in the preparation of the complex **1**.

2.2.4. [Cu(Biptp)]$(BF_4)_2 \cdot 2.5H_2O$ (2)

Yield 97%. *Anal.* Calc. for $C_{16}H_{17}B_2CuF_8N_3S \cdot 2.5H_2O$: C, 34.0; H, 3.92; N, 7.43. Found: C, 33.8; H, 3.70; N, 7.32%. FAB MS m/z 431 $[M - 2BF_4]$ (100%).

2.2.5. [Cu(Biptp)]$(ClO_4)_2 \cdot 2H_2O$ (3)

Yield 88%. *Anal.* Calc. for $C_{16}H_{17}CuCl_2N_3O_8S \cdot 2H_2O$: C, 33.0; H, 3.64; N, 7.22. Found: C, 32.9; H, 3.52; N, 7.23%. FAB MS m/z 445 $[M - ClO_4]$ (16%), 346 $[M - 2ClO_4]$ (100%).

Caution: although none of the compounds herein proved to be mechanically sensitive, due caution should be exercised when dealing with perchlorates, and they should be prepared only in small quantities.

2.2.6. [Cu(Biptb)]$(CF_3SO_3)_2 \cdot 0.5(C_7H_8) \cdot H_2O$ (4)

Yield 64%. Single crystals obtained by diffusing toluene into nitromethane solution of the complex. *Anal.* Calc. for $C_{17}H_{19}CuF_6N_3OS_3 \cdot 0.5C_7H_8 \cdot H_2O$: C, 35.4; H, 3.05; N, 6.05. Found: C, 35.4; H, 3.03; N, 5.99%. FAB MS m/z 480 $[M - CF_3SO_3]$ (55%), 332 $[M - 2CF_3SO_3]$ (100%).

2.2.7. [Cu(Biptb)]$(BF_4)_2 \cdot 2H_2O$ (5)

Yield 87%. *Anal.* Calc. for $C_{15}H_{15}B_2CuF_8N_3S \cdot 2H_2O$: C, 33.2; H, 3.53; N, 7.74. Found: C, 33.4; H, 3.38; N, 7.58%. FAB MS m/z 332 [$M - 2BF_4$] (100%).

2.2.8. [Cu(Biptb)]$(ClO_4)_2 \cdot 2H_2O$ (6)

Yield 69%. *Anal.* Calc. for $C_{15}H_{15}Cl_2CuN_3O_8S \cdot 2H_2O$: C, 31.7; H, 3.37; N, 7.40. Found: C, 31.5; H, 3.37; N, 7.31%. FAB MS m/z 431 [$M - ClO_4$] (32%), 332 [$M - 2ClO_4$] (100%).

2.3. Physical measurements

Infrared spectra were recorded on a Perkin–Elmer 1610 FT-IR instrument using KBr disks. EPR spectra were obtained with a Varian E-12 X-band spectrometer calibrated near $g = 2$ with diphenylpicrylhydrazyl radical. g-Values are ± 0.005 ($g_{\|}$) and ± 0.01 ($g_{\perp}$); isotropic g-values (± 0.005) are designated as g_o. The g_o and A_o were measured at ambient temperature and $g_{\|}$, $A_{\|}$ and $g_{\perp}$ at 77 K. The electronic spectra are either from a Perkin–Elmer 330 spectrophotometer, equipped with an integrating sphere for diffuse reflectance or from a Perkin–Elmer Lambda-2 UV–Vis spectrophotometer. Proton NMR spectra were recorded on a Bruker AC250 spectrometer using $CDCl_3$ solutions with TMS as internal standard. Electrochemical measurements were carried out at 25 °C in deoxygenated acetonitrile using a BAS 100A electrochemical analyzer. The three-electrode assembly comprised a Pt wire as working electrode, an Ag^+ (0.01 M $AgClO_4$, 0.1 M Et_4ClO_4, CH_3CN)/Ag reference electrode [21] and a Pt-mesh auxiliary electrode. The supporting electrolyte was 0.1 M Et_4NClO_4 or 0.1 M Bu_4NPF_6. Mass spectra were from a VG-ZABHF high resolution double focusing spectrometer. Elemental microanalyses were performed by Robertson Microlit Laboratories (Madison, NJ) or by the Microanalytical Laboratory of the University of Pennsylvania.

2.4. Structure analyses

Suitable crystals mounted on a glass fiber with epoxy cement and attached to a goniometer head were transfered to a Rigaku AFC5S (**1**) or Siemens P4S (**4**) diffractometer which employed graphite-monochromated Mo Kα radiation (0.7103 Å). Intensities were collected using the ω–2θ scan mode. Absorption corrections were applied to the data set of each crystal using the ψ-scan technique. The structures were solved by direct methods (**1**) or by combination of Patterson and direct methods (**4**) with successive Fourier syntheses [22]. Full-matrix least-squares refinement on F^2 was performed using SHELXL-97 [24] with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were fixed in idealized positions with a riding model. For **1** a total of 3865 reflections were collected ($0 = h = 13$, $-14 = k = 15$, $-8 = l = 8$) in the range of 1.94–22.50° with 3665 being unique ($R_{int} = 0.0235$). For **4**, a suitable crystal mounted on a glass fiber with epoxy cement and attached to a goniometer head was transferred to a Siemens P4S diffractometer which employed graphite–monochromated Mo Kα radiation ($\lambda =$ 0.7103 Å). Absorption correction was performed by the integration method [23]. The structure was solved by a combination of Patterson and direct methods and refined by full-matrix least-squares on F^2. For [Cu(Biptp)$(H_2O)_2$]$(CF_3SO_3)_2$, a total of 6470 reflections were collected ($-12 = h = 0$, $-12 = k = 11$, $-21 = l = -21$) in the range of 2.34–27.50° with 6131 being unique ($R_{int} = 0.0308$). The empirically derived transmission coefficient ranged from 0.8013 to 0.6987. For clarity of presentation, thermal ellipsoids are shown at the 20% level, and H-atoms are shown as spheres of arbitrary size.

3. Results and discussion

The ligand Biptp was prepared by the addition of thiol across the vinyl group in one step. Biptb was synthesized by nucleophilic displacement of the halide by the thiolate. Copper(II) complexes of these two ligands with differing anions were prepared without any difficulties. The constitutions of the ligands and complexes were verified by elemental analysis as well as by mass and NMR (for the ligands) spectroscopy.

The copper complexes are soluble in methanol, ethanol, acetone, DMF, nitromethane and acetonitrile.

3.1. Description of the structures

The ORTEP diagrams of the complexes **1** and **4** are shown in Figs. 2 and 3, respectively, while the crystallographic data are given in Table 1. In both complexes the coordination spheres consist of an N_2SO_2 donor set. While the nitrogen and sulfur donors are from the ligands, the source of the oxygen donor atoms varies between the two complexes. In the [NSN-6,6] chelate [Cu(Biptp)$(H_2O)_2$]$(CF_3SO_3)_2$ the two oxygen donor atoms are from coordinated water molecules, while on the other hand in the [NSN-5,6] system [Cu(Biptb)$(CF_3SO_3)(H_2O)$](CF_3SO_3) one of the oxygen donors is from a molecule of water while the second oxygen donor atom is from a triflate (trifluoromethanesulfonate) anion. In the crystals of **1**, the complex cations and triflate anions are connected via a network of hydrogen bonds; each semi-coordinated triflate counterion is H-bonded to the water ligands of two adjacent complex cations.

Tridentate ligands with a thioether sulfur donor on complexation with Cu(II) ion often result in pentacoor-

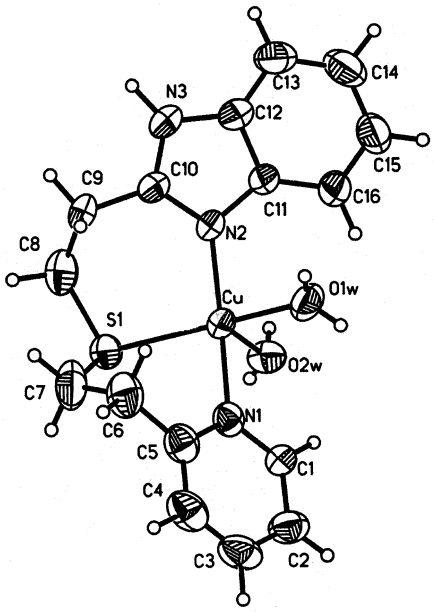

Fig. 2. Structure of the $[Cu(Biptp)(H_2O)_2]^{2+}$ ion, showing the atom-numbering scheme.

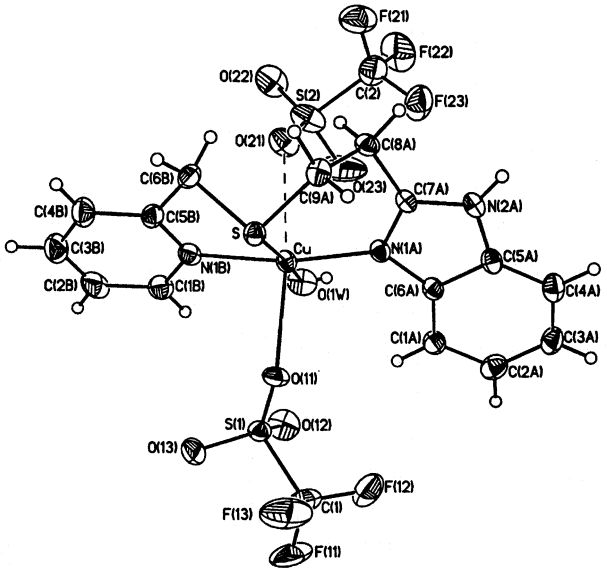

Fig. 3. ORTEP projection with atom-labelling scheme for $[Cu(Biptb)(H_2O)](CF_3SO_3)_2$.

dinate complexes due either to coordination of solvent molecules or of counteranions [24,25]. Higher coordination number may also be achieved by introducing a second chelating agent like Acac and Bipy [24,26]. Under these circumstances it is noticed that the enolate group with its stronger ligand field pushes sulfur to the axial position, but the thioether sulfur binds in the basal plane in the presence of the solvent methanol [24] or anions like perchlorate [25] or triflate (this work). In the present compounds, all three of the sulfur and nitrogen donors are bound to the basal plane. Pentacoordinate copper(II) complexes adopt either trigonal bipyramidal or square pyramidal geometries. However, perfect square pyramidal or trigonal bipyramidal complexes are seldom encountered, and the distortion from either of these geometries is expressed by the τ-value [27]. The low τ-values of 0.16 and 0.11 for the complexes $[Cu(Biptp)(H_2O)_2](CF_3SO_3)_2$ and $[Cu(Biptb)(H_2O)(CF_3SO_3)]-(CF_3SO_3)$, respectively, indicate that the geometries around copper should be considered as slightly distorted square pyramidal rather than as distorted trigonal bipyramidal.

On comparing the two complexes, one observes that the change in chelate ring size has the expected effect on the bond lengths. The Cu–S bond distance in the [NSN–5,6] chelate $[Cu(Biptb)(H_2O)(CF_3SO_3)]^+$ is shorter by 0.02 Å compared to [NSN-6,6] molecule $[Cu(Biptp)(H_2O)_2]^{2+}$. The increased strain due to the five-membered chelate ring in $[Cu(Biptb)(H_2O)(CF_3SO_3)]^+$ is reflected by the lengthening of the Cu–N(py) bond by 0.02 Å compared to the Cu–N(py) bond length in $[Cu(Biptp)(H_2O)_2]^{2+}$ ion. However, the Cu–N(benzimidazyl) bond distances in the two compounds do not differ significantly (only 0.006 Å). The greatest difference in bond lengths between the two compounds among similar donor atoms bound in the basal plane is noticed when the bond lengths of the coordinated water molecules are compared. The Cu–O(W) bond in $[Cu(Biptb)(H_2O)(CF_3SO_3)]^+$ ion is shorter by 0.044 Å than Cu–O(1W) in the $[Cu(Biptp)(H_2O)_2]^{2+}$ ion. Among all the bonds to the

Table 1
Crystallographic data

	$[Cu(Biptp)](CF_3SO_3)_2\cdot 2H_2O$	$[Cu(Biptb)(CF_3SO_3)(H_2O)](CF_3SO_3)\cdot 0.5(C_7H_8)$
Empirical formula	$C_{18}H_{21}CuF_6N_3O_8S_3$	$C_{20.5}H_{25}CuF_6N_3O_7S_3$
f_w	681.10	699.15
Crystal system	triclinic	triclinic
Crystal size (mm)	$0.11\times0.30\times0.36$	$0.17\times0.68\times0.24$
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	12.667 (3)	9.420 (2)
b (Å)	14.362 (3)	9.569 (2)
c (Å)	8.086 (2)	16.653 (3)
α (°)	99.17 (2)	85.07 (1)
β (°)	96.84 (2)	82.97 (1)
γ (°)	74.74 (2)	65.62 (1)
V (Å^3)	1396.5 (6)	1356.0 (4)
Z	2	2
D_{calc} (g cm^{-3})	1.620	1.712
$F(000)$	690	712
μ (mm^{-1})	1.092	1.124
λ (Mo Kα) (Å)	0.71069	0.71073
T (K)	293 (2)	293(2)
R_1 [a]; wR_2 [b]	0.0513; 0.1295	0.0682; 0.1726

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$.
[b] $wR_2 = \{\Sigma w[(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

Table 2
Selected bond distances (Å) and bond angles (°) for [Cu(Biptp)-$(H_2O)_2$]$(CF_3SO_3)_2$

Bond distances			
Cu–N(2)	1.962(5)	Cu–O(2W)	2.181(7)
Cu–N(1)	1.994(6)	Cu–S(1)	2.369(2)
Cu–O(1W)	2.024(5)		
Bond angles			
N(2)–Cu–N(1)	171.6(2)	O(1W)–Cu–O(2W)	101.4(2)
N(2)–Cu–O(1W)	90.8(2)	N(2)–Cu–S(1)	93.7(2)
N(1)–Cu–O(1W)	86.2(2)	N(1)–Cu–S(1)	86.9(2)
N(2)–Cu–O(2W)	97.6(2)	O(1W)–Cu–S(1)	162.3(2)
N(1)–Cu–O(2W)	90.7(2)	O(2W)–Cu–S(1)	95.0(2)

Table 3
Selected bond distances (Å) and bond angles (°) for [Cu(Biptb)-$(H_2O)(CF_3SO_3)$]$(CF_3SO_3)(0.5C_7H_8)$

Bond distances			
Cu–N(1A)	1.956(8)	Cu–O(1W)	1.980(11)
Cu–N(1B)	2.015(9)	Cu–S	2.350(3)
Cu–O(11)	2.367(7)		
Bond angles			
N(1A)–Cu–O(1W)	93.9(6)	N(1A)–Cu–N(1B)	168.6(4)
O(1W)–Cu–N(1B)	93.4(7)	N(1A)–Cu–S	91.2(2)
O(1W)–Cu–S	174.9(6)	N(1B)–Cu–S	81.6(3)
N(1A)–Cu–O(11)	98.8(3)	O(1W)–Cu–O(11)	87.8(5)
N(1B)–Cu–O(11)	90.2(3)	S–Cu–O(11)	92.0(2)

copper(II) ion in the two complexes, the Cu–N-(BenzIm) bond length is the shortest in each complex (Tables 2 and 3).

In the [NSN-5,6] Biptd-chelate **4**, one of the triflate ions is coordinated to copper (2.367 Å) while the other triflate ion is semi-coordinated [28] with the Cu–O distance being 2.676 Å. Evidence for the coordination of triflate ion is also available in the IR spectrum. The asymmetric S–O stretch in the vicinity of 1250 cm^{-1} in **4** is split by 25 cm^{-1} [29], while uncoordinated triflate ions show no such a splitting [30]. The methylene hydrogen atom is hydrogen-bonded to the semi-coordinated triflate ion at 2.537 Å [31].

Because of static Jahn–Teller distortion, the bond to the axially coordinated water [Cu–O(2W)] is 0.157 Å longer than to the water coordinated in the basal plane of the $[Cu(Biptb)(H_2O)(CF_3SO_3)]^+$ ion. The crystal lattice of this complex is stabilized by stacking of a molecule of toluene for every two molecules of the complex.

3.2. Electronic absorption spectra

The UV-region of the electronic spectrum is dominated by the $\pi \rightarrow \pi^*$ transitions of the ligand [32], both free and in the coordinated form. The intensity of the $S \rightarrow Cu$ charge-transfer band relates to the number of sulfur donor atoms in the basal plane. Copper complexes with three [33] or two [34] sulfur donor atoms show higher absorptions than complexes studied in this work, which have only one sulfur atom in the ligand framework.

For these compounds, the absorptions in the charge-transfer region are not influenced by the nature of the solvent, but the d–d transitions exhibit solvent dependence (Table 4). Weakly coordinating *O*-donor methanol does not shift the position of the peaks noticeably, while the spectra recorded in *N*-donor acetonitrile show a 50 nm blue shift with respect to the solid-state spectra.

3.3. Electrochemistry

The redox potentials of the complexes are given in Table 5. The diffusivity values [35] are appropriate to

Table 4
Electronic absorption spectroscopic data

Compound	Medium	λ_{max}, nm (ε, $M^{-1}cm^{-1}$)
Biptp	MeOH	280 (7000), 275 (8100), 269 (9300), 250 (7700), 208 (27600)
Biptb	MeOH	280 (7800), 275 (10200), 270 (10800), 250 (7700), 208 (33600)
$[Cu(Biptpn)](ClO_4)_2 \cdot 2H_2O$	Solid	650
	CH_3OH	650 (225), 341 (1800), 270 (13400)
	CH_3CN	605 (330), 349 (2070), 270 (12500)
$[Cu(Biptpn)](BF_4)_2 \cdot 2.5H_2O$	Solid	650
	CH_3OH	651 (200), 335 (1540), 270 (12100)
	CH_3CN	606 (340), 350 (2200), 270 (14500)
$[Cu(Biptpn)](CF_3SO_3)_2 \cdot 2H_2O$	Solid	650
	CH_3OH	650 (230), 342 (1900), 270 (13450)
	CH_3CN	607 (330), 348 (2100), 270 (14800)
$[Cu(Biptbu)](ClO_4)_2 \cdot 2H_2O$	Solid	645
	CH_3OH	646 (160), 342 (1700), 270 (12600)
	CH_3CN	604 (310), 347 (2000), 270 (13400)
$[Cu(Biptbu)](BF_4)_2 \cdot 2H_2O$	Solid	650
	CH_3OH	646 (160), 340 (2200), 270 (11500)
	CH_3CN	604 (290), 346 (1900), 270(12600)
$[Cu(Biptbu)](CF_3SO_3)_2 \cdot 0.5(C_7H_8).H_2O$	Solid	660
	CH_3OH	646 (180), 341 (1800), 270 (12800)
	CH_3CN	604 (310), 348 (2000), 270 (12800)

Table 5
Redox properties of the complexes[a]

Compound	$E_{1/2}$ (mV) [observed] [b]	$E_{1/2}$ (mV) [vs. SHE]	$10^8 D\eta$ (g cm s^{-2})
$[Cu(Biptp)](ClO_4)_2 \cdot 2H_2O$ [c]	+281	+821	2.3
$[Cu(Biptp)](BF_4)_2 \cdot 2.5H_2O$ [c]	+284	+824	2.3
$[Cu(Biptp)](CF_3SO_3)_2 \cdot 2H_2O$ [c]	+280	+820	1.6
$[Cu(Biptb)](CF_3SO_3)_2 \cdot 0.5(C_7H_8) \cdot H_2O$ [c]	+223	+763	1.1
$[Cu(Biptb)](CF_3SO_3)_2 \cdot 0.5(C_7H_8) \cdot H_2O$ [d]	+237	+777	1.0
$[Cu(Biptb)]ClO_4)_2 \cdot 2H_2O$ [c]	+220	+760	2.1
$[Cu(Biptb)](BF_4)_2 \cdot 2H_2O$ [c]	+221	+761	1.1

[a] As described in Section 2.
[b] Scan rate 100 mV s^{-1}.
[c] Supporting electrolyte TEAP.
[d] Supporting electrolyte Bu_4NPF_6.

Table 6
Electron spin resonance data[a]

Compound	Medium [b]	g_o [c]	$-10^4 A_o$ [c] (cm^{-1})	$g_{\|\|}$	$-10^4 A_{\|\|}$ (cm^{-1})	$g_\perp$ [d]	$-10^4 A_\perp$ [e] (cm^{-1})	$(g_{\|\|}-2)/\|A_{\|\|}\|$	R [f]
$[Cu(Biptb)](CF_3SO_3)_2 \cdot 0.5(C_7H_8) \cdot H_2O$	acetone/toluene	2.111	44.2	2.232	150	2.05	−8.8	15.5	
	Powder	$g_1 = 2.03$	$g_2 = 2.07$	$g_3 = 2.25$					0.176
$[Cu(Biptb)](BF_4)_2 \cdot 2H_2O$	acetone/toluene	2.125	50.0	2.279	195	2.05	−22.5	14.3	
	Powder	$g_1 = 2.03$	$g_2 = 2.11$	$g_3 = 2.20$					0.474
$[Cu(Biptb)](ClO_4)_2 \cdot 2H_2O$	acetone/toluene	2.132	50.0	2.275	192	2.06	−21.0	14.3	
	Powder	$g_1 = 2.05$	$g_2 = 2.10$	$g_3 = 2.16$					0.455
$[Cu(Biptp)](CF_3SO_3)_2 \cdot 2H_2O$	acetone/toluene	2.157	35.0	2.270	160	2.10	−15.5	16.8	
	Powder	$g_1 = 2.03$	$g_2 = 2.09$	$g_3 = 2.24$					0.257
$[Cu(Biptp)](BF_4)_2 \cdot 2.5H_2O$	acetone/toluene	2.137	38.3	2.234	135	2.09	−10.0	17.3	
	Powder	$g_1 = 2.06$	$g_2 = 2.13$	$g_3 = 2.15$					0.778
$[Cu(Biptp)](ClO_4)_2 \cdot 2H_2O$	acetone/toluene	2.155	38.3	2.269	165	2.10	−32.5	16.3	
	Powder	$g_1 = 2.04$	$g_2 = 2.14$	$g_3 = 2.15$					0.852

[a] Values determined as described in Section 2.
[b] Neat powder spectra recorded at 77 K.
[c] From fluid spectrum at 298 K.
[d] $g_\perp$ from simulation [24].
[e] $A_\perp = (3A_o - A_{\|})/2$.
[f] $R = (g_2 - g_1)/(g_3 - g_1)$ [25].

one-electron processes: the reduction of Cu(II) to Cu(I). The relatively positive potentials shown by the Cu(II) complexes are consistent with the presence of thioether donors. The magnitude of the positive potential depends on the number of sulfur atoms; for example Cu(II) complexes with two or three sulfur donors exhibit higher positive potentials than the complexes with one sulfur atom [36]. The presence of only one sulfur atom in the ligands of this work justifies the moderately high potential observed for the Cu(II)/Cu(I) couple. Axially coordinated sulfur atoms have been suggested to have little influence on the redox properties of copper complexes [37]. Along these lines, if the sulfur atoms were coordinated axially or the coordinated sulfur atoms replaced by solvent molecules, then the reduction potential would be lower than the observed.

The reason for the high potentials commonly found in the copper(II) with thioether donors has been attributed for some time due to the stabilization of the Cu(I) by sulfur donors relative to the stabilization of the Cu(II). Rorabacher et al. [38] have advanced that the major part of these free energy differences is associated with the affinity between the donors and Cu(II), so that the higher potentials observed for copper complexes with certain thioether donors are mainly due to reduced Cu(II)–thioether affinity.

The size of the chelate ring is another factor which affects the electrochemistry of the copper complexes. Contiguous smaller chelate rings normally lower redox potentials for the Cu(II)/Cu(I) couple [39]. On compar-

ing the $E_{1/2}$ value for the [NSN-6,6] complex [Cu(Biptp)]$(ClO_4)_2 \cdot 2H_2O$ with that for the [NSN-5,6] [Cu(Biptb)]$(ClO_4)_2 \cdot 2H_2O$, one observes that increasing the chelate ring size from five to six members has increased the potential by 60 mV.

3.4. EPR spectroscopy

The $g_{\|}$ values obtained for Cu(II) complexes are significantly influenced by the donor atoms and the geometry. Hard donors and distortion from planarity increase $g_{\|}$ while soft donors and planar geometry decrease $g_{\|}$ [40]. From the crystal structures of **1** and **4** we find that there is only slight distortion of the basal plane geometry in each of them, the twist angles being 17.0 and 18.5°, respectively. This aspect, plus the presence of basal sulfur donors results in rather low $g_{\|}$-values, in the range of 2.23–2.28 (Table 6).

The spectra for the neat powders of the complexes are rhombic, the additional $-CH_2-$ unit in Biptp leading to increased rhombicity, as judged by the rhombicity parameter R [41]. The magnitude of the rhombicity is related to the identity of the anion as well, the BF_4^- and ClO_4^- salts of the complexes being more rhombic than the $CF_3SO_3^-$ salts [33].

For the [NSN-5,6] chelate $[Cu(Biptp)]^{2+}$, five N-superhyperfine lines ($|A_N| = 18 \pm 1 \times 10^{-4}$ cm^{-1}) appear in the cryogenic solution spectrum. These are consistent with the presence of the two sp^2-hybridised nitrogen atoms in the coordination sphere [42]; such superhyperfine structure is not apparent in the spectra of $[Cu(Biptb)]^{2+}$.

4. Supplementary material

Tabulations of atomic coordinates, anisotropic thermal parameters, F_{obs} and F_{calc} and views of unit cell contents are available from the authors upon request.

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