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Structural Consequences of Deacylation of Nickel(II) Cyclidenes in Acidic and Basic Conditions *

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Abstract

Two nickel(II) complexes with deacylated unsaturated tetraaza macrocyclic cyclidene ligands were isolated and structurally characterized. Under acidic conditions, both acyl groups attached to the γ carbons in the precursor complex are cleaved off, yielding a symmetric dicationic complex (IIIc) which retains the usual saddle shaped conformation of the 16-membered cyclidene complexes. Under basic conditions, one acyl group remains attached to the cyclidene, while the other (deacylated) chelate ring becomes singly deprotonated. This asymmetric deacylation is observed for the first time in the family of cis-dimethyl cyclidenes. The presence of a deprotonated conjugated chelate ring in the 15-membered macrocycle (VIb) results in the overall planar shape of the molecule.

Introduction

Metal cyclidenes (Ia,b, Figure 1) constitute a well studied [1–3] class of highly unsaturated azamacrocyclic complexes [4]. Their ability to act as efficient dioxygen carriers [1, 2, 5–71 and cytochrome P450 models [8] is largely based on their lacunar shape (Ib, Figure 1). Two unsaturated six-membered chelate rings rise at an angle from the MN_4-plane forming a cavity, or void, around the metal ion. This type of spatial arrangements makes one of the two remaining coordination sites (located inside the cleft between the raised unsaturated chelate rings) accessible predominantly for inclusion of small ligands, i.e., O_2. A bridge between the R^1 or R^3 substituents (Figure I), which is often present in the cyclidene molecules, prevents the undesired oxidative dimerization of cyclidene-dioxygen complexes and further restricts the access of competitive large ligands into the cavity. Another remaining coordination site is easily accessible for monodentate ligand binding. Such coordination, when it occurs, increases electron density on the metal ion facilitating dioxygen binding.

The understanding of the factors determining spatial arrangements of cyclidene molecules is therefore important for the prediction of their reactivity and consequently attracted a great deal of attention in the literature. Over 50 crystal structures of the cyclidenes have been solved and thoroughly analyzed [1 and references therein]. These crystallographic studies as well as molecular dynamic calculations [9–11] revealed the influence of structural parameters on the overall shape of the molecule. Thus, the conformations of the saturated chelate rings X and Y in a combination with the rigid C=N bonds of the adjacent unsaturated chelate rings exert the most profound effect on the overall shape of the molecule [12].

Formation of fully deacylated cyclidenes (III and IV, Figure 1) is well documented in the literature [13–15]. Cationic complexes (111) are obtained upon refluxing Jäger complexes (II) in a methanolic solution of p-toluenesulfonic acid. These complexes are also known byproducts in the preparation of dimethoxycyclidenes (V) [141. Deprotonation of (III) and their transformations into neutral complexes (IV) occur upon addition of a strong base [13]. Reactions of 14-membered dimethoxycyclidene (Va) with aniline, *N*-alkyl substituted anilines or sodium methoxide lead to the formation of the asymmetric mono-deacylated complex (VIa) [16]; an analogous material (VId) derived from the 16-membered trans-complex (IId) has also been recently synthesized and characterized crystallographically [17]. To the best of our knowledge other deacylated cyclidenes were not structurally characterized.

As a part of our systematic study in nickel cyclidene chemistry, we report two new representatives of protonated and deprotonated deacylated cyclidenes. Mixed hexafluorophosphate tetrafluoroborate (IIIc) was crystallized as a byproduct in the preparation of (VII) hexafluorophosphate from (IIc), triethyloxonium tetrafluoroborate and ammonium hexafluorophosphate [14]. The second complex,

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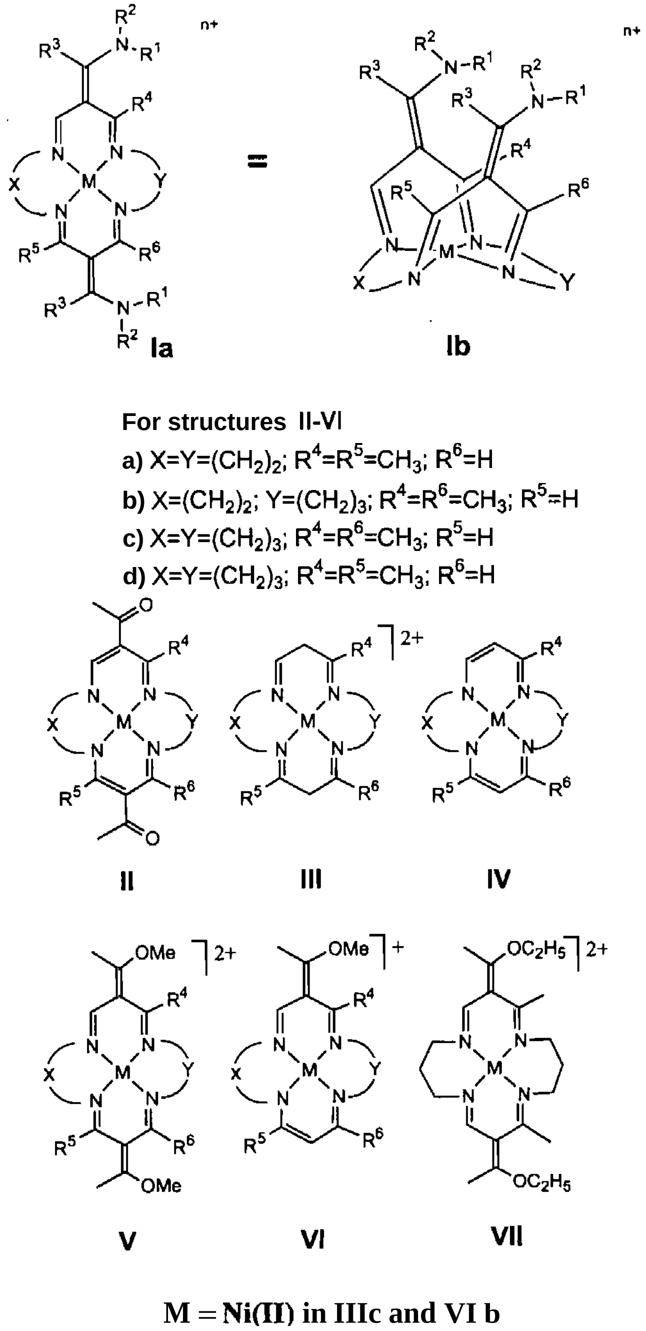

Ia

Ib

For structures II-VI

a) $X=Y=(CH_2)_2$; $R^4=R^5=CH_3$; $R^6=H$

b) $X=(CH_2)_2$; $Y=(CH_2)_3$; $R^4=R^6=CH_3$; $R^5=H$

c) $X=Y=(CH_2)_3$; $R^4=R^6=CH_3$; $R^5=H$

d) $X=Y=(CH_2)_3$; $R^4=R^5=CH_3$; $R^6=H$

II III IV

V VI VII

M = Ni(II) in IIIc and VI b

Figure 1. Jager and cyclidene macrocyclic metallocomplexes.

VIb, was obtained in the reaction of a 15-membered dimethoxy cyclidene (Vb) with di-t-butyl iminodiacetate.

The analyses of these two structures allow us to contrast structural consequences which deacylation exerts on the shape of cyclidene hosts in two different cases: (1) when deacylation is accompanied by deprotonation, or (2) deacylation is not accompanied by deprotonation of the macrocyclic ligand.

Experimental

Syntheses. Starting fifteen- and sixteen-membered dimethoxy cyclidenes and tert-butyl iminodiacetate were prepared according to the published procedures [14, 18].

[2,12-Dimethyl-1,5,9,13-tetraazacyclohexadeca-1,4,9,12-tetraene] nickel(II) Hexafluorophospate **Tetra**fluoroborate (**[Ni(Me$_2$[16]tetraeneN$_4$)](PF$_6$)$_{1.25}$(BF$_4$)$_{0.75}$**, IIIc) To the solution of [Ni(Ac)$_2$Me$_2$[16]tetraenatoN$_4$] (IIc) (3.0 g, 7.7 mmol) in dry dichloromethane (50 mL) a 1 M solution of triethyloxonium tetrafluoroborate (23 mL) was added upon stirring. The mixture, which turned olive-green upon addition of ethylating agent, was stirred at room temperature for 24 hrs. Then, 3.3 mL of methanol was added. in order to destroy an excess of (Et$_3$O)$^+$BF$_4^-$, and stirring was continued for another 1 hour. The solvent was removed on a rotary evaporator, leaving dark brown-green viscous oil. The oil was dissolved in 6 mL of methanol, and a solution of 3.75 g of NH$_4$PF$_6$ in methanol was added to it, upon intensive stirring. A dark precipitate of (VII) hexafluophosphate began to form immediately. The solution was refrigerated for 6 hours, and microcrystalline precipitate was collected by filtration, yielding 7.1 g of yellow-green (VII) hexafluophosphate. The filtrate was refrigerated again, producing additional amounts of green solid product. This material was filtered, redissolved in *ca.* 100 mL of warm methanol and the resulting light green solution was refrigerated for two weeks. Transparent green crystals were gradually formed. Yield 0.2 g. Spectral characteristics of this material are identical to the bis-hexafluorophosphate salt of IIIc, [2,12-dimethyl-1,5,9,13-tetraazacyclohexadeca-1,4,9,12-tetraene] nickel(II) bis-hexafluorophosphate, synthesized independently according to the published procedure [19]: ^{1}H NMR (CD$_3$NO$_2$) – 1.87 (2H), 2.02 (2H), 2.26 (6H), 3.21 (4H), 3.79 (4H), 7.64 (2H) ppm (spectral lines are broad and extremely solvent-sensitive); UV–Vis (CH$_3$CN), $\lambda_{max}(\epsilon)$: 237 (sh, 7600), 289 (2120), 367 (295), 410 nm (sh, 150); IR (KBr) – 1680 (s), 1647, 1450, 1425, 1390, 1360 cm^{-1}. Spectral characteristics of doubly deprotonated IIIc are identical to those previously described for [2,12-dimethyl-1,5,9,13-tetraazacyclohexadeca-1,4,9,12-tetraenato] nickel(II). [13, 20]

[2,11-Dimethyl-3-(1-methoxyethylidene)-1,5,8,12-tetraazacyclopentadeca-1,4,9,11-tetraenato]nickel(II) Hexafluorophospate **[Ni[(MeOEthi)(H)Me$_2$[15]tetraeneN$_4$]]PF$_6$ (VIb)** To the solution of [Ni[(MeOEthi)$_2$Me$_2$[15]-tetraeneN$_4$]](PF$_6$)$_2$ (0.33 g; 0.47 mmol) in dry acetonitrile (10 mL) di-t-butyliminodiacetate (0.47 g, 1.9 mmol) in dry acetonitrile was added at once. The color of the reaction mixture rapidly turned red. Solvent was removed in *vacuo* and the residue was redissolved in dry methanol (25 mL) under reflux giving a dark-olive solution. The product crystallized in approximately two hours as brown rectangular plates. Longer crystallization time resulted in the precipitation of dark tarry byproducts. Yield 0.05 g (22%). NMR(CD$_3$CN): 8.00 (s, 1H), 6.54 (d, J = 7.0, 1H), 4.76 (d, J = 7.0, 1H), 4.00 (s, 3H), 3.86 (t, J = 7.5, 2H), 3.41 (t, J = 7.5, 2H), 3,14–3.18 (m, 4H), 2.36 (s, 3H), 2.26 (s, 3H), 1.99 (s, 3H), 1.92–1.97

(m, overlapped with residual solvent peak, 2H). UV–Vis (CH_3CN): λ_{max} 285,360,400 (sh), ca. 500 (broad sh) nm.

Crystallographic data were collected with a four-circle Rigaku AFC5S diffractometer by using ω-scans. Lattice parameters for (IIIc) and (VIb) were obtained using least squares refinements of the angles of 24 reflections with 22" $< 2\theta <$ 28°. The structure was solved by direct methods using SHELXS-97 [21] and refined with all data by full-matrix least squares on F^2 using SHELXL-97 [22] (Table 1). All nonhydrogen atoms were refined anisotropically, and hydrogen atoms were fixed in idealized positions with a riding model. Restraints were applied to the hexafluorophosphate and tetrafluoroborate groups. Refinement of structure (VIb) showed substantial twinning with 8% of the complex being a mirror reflection of itself.

Results and discussion

The dicationic deacylated cyclidenes (III) can form spontaneously from (II) under acidic conditions. A small (stoichiometric or even sub-stoichiometric) amount of acid is sufficient to promote this type of deacylation, as is exemplified by the formation of (IIIc). This deacylation reaction is synthetically useful for introducing two identical substituents in the γ positions of the unsaturated chelate rings [13, 19,201. Another type of cyclidene deacylation occurs under basic conditions and yields the asymmetric products (VI). In this case, only one acyl group is cleaved off, and the deacylated chelate ring is deprotonated by the base. This reaction was previously considered to be highly unusual in the cyclidene family of macrocycles. It was reported [16] for the 14-membered complex which is known to have two methyl groups (Figure 1, VIa) in trans positions [1]. Very recently, the *trans* isomer (IId) of the 16-membered cyclidene was prepared [23], and the same asymmetric deacylation of the ligand was observed and used in the synthesis of a series of asymmetrically substituted cyclidenes [17]. Thus, the asymmetric deacylation under basic conditions was attributed to the *trans* geometry of the parent cyclidenes [17]. The results reported in this paper clearly demonstrate that singly deacylated, deprotonated cyclidenes can be readily synthesized from the usual cis isomers, such as (Vb). Thus, asymmetric deacylation accompanied by deprotonation is a common reaction in the cyclidene family of macrocyclic complexes.

The structures of two different deacylation products, (IIIc) and (VIb), are drastically different.

In the first substance (IIIc, Figure 2), which represents the protonated form of the deacylated complex, there are two crystallographically independent but otherwise very similar macrocyclic cations in the assymetric unit. In both independent complexes one of the saturated 6-membered rings has a chair conformation, while another one (adjacent to the methyl substituens) is a boat. This is in agreement with the previously noted preference of the six-membered chelate ring adjacent to a methyl in the R^4/R^6 position to adopt a boat conformation, in order to minimize the contact between the middle methylene group of the saturated ring and the methyl substituents [I]. The presence of two saturated rings in the sixteen-membered macrocycle (IIIc) in favorable boat and chair conformations along with four unsatuturated trigonal nitrogens results in the overall cleft-like shape of the molecule similar to other cis-dimethyl ($R^4 = R^6 =$ Me, $R^5 =$ H) unbridged sixteen-membered cyclidenes (Figure 2).

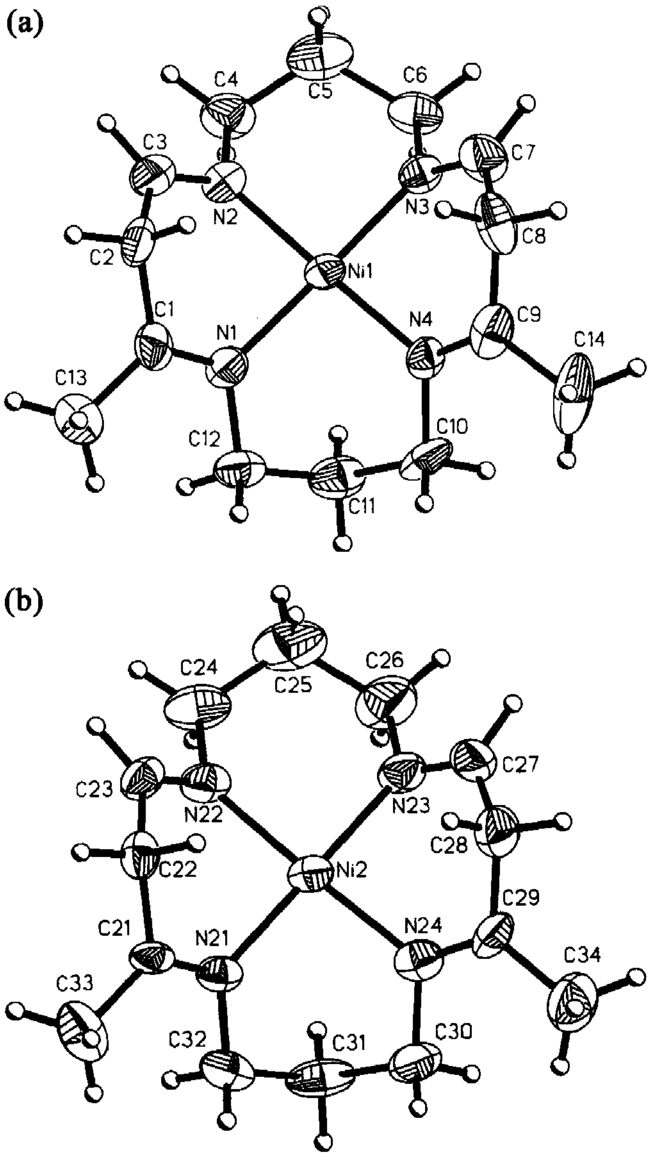

Figure 2. Crystal structures of the two crystallographically independent cations of IIIc.

No signs of conjugation are observed in unsaturated rings. All four nitrogen atoms are connected by double bonds to the appropriate carbon atoms, with C=N bond lengths ranging from 1.23 to 1.29 Å. Carbon-carbon bonds in the saturated rings are single bonds ranging from 1.46 to 1.54 Å (Table 2).

The angles α and β and the distance d_1 (see Figure 3) are traditionally [1, 12] used to measure the extent to which the macrocycle takes up a saddle conformation. For the two crystallographically independent molecules of (IIIc) the angles α are equal to 95° and 93°, and the angles β are 22" and 20° respectively. For the previously studied unbridged cis-dimethyl ($R^4 = R^6 =$ Me, $R^5 =$ H, Figure 1) cyclidenes

Table 1. Crystal data and structure refinement parameters

Compound	IIIc	VIb
Crystal system. space group	Monoclinic, C2/c (No. 15)	Orthorhombic, $P2_12_12$ (No. 18)
Unit cell dimensions:		
a	29.172(6)	21.08(2)
b	16.471(3)	9.006(2)
c	18.820(4)	11.015(3)
β	93.34(3)	90
V	9027(3)	2091(2)
Z	8	4
Reflections collected/unique	836014111	2398/2361
Refinement method	Full-matrix least-squares on F^2	
Goodness-of-fit on F^2	1.024	1.058
Final R^1 (wR2) indices [$I > 2\sigma(I)$]	0.077(0.19)	0.054(0.13)
R^1 (wR2) indices (all data)	0.14(0.23)	0.11(0.16)

Table 2. Selected bond lengths (Å) and angles (°)

Compound IIIc				Compound VIb	
Ni(1)–N(1)	1.887(11)	Ni(2)-N(21)	1.885(11)	Ni–N(1)	1.908(6)
Ni(1)–N(2)	1.873(10)	Ni(2)-N(22)	1.879(12)	Ni–N(2)	1.867(7)
Ni(1)–N(3)	1.880(11)	Ni(2)-N(23)	1.870(13)	Ni–N(3)	1.837(7)
Ni(1)–N(4)	1.887(10)	Ni(2)-N(24)	1.896(12)	Ni–N(4)	1.862(7)
N(1)–C(1)	1.267(16)	N(21)–C(21)	1.291(15)	N(1)–C(1)	1.286(9)
N(1)–C(12)	1.487(16)	N(21)–C(32)	1.461(16)	N(1)–C(11)	1.467(11)
N(2)–C(3)	1.258(16)	N(22)–C(23)	1.280(16)	N(2)–C(3)	1.271(10)
N(2)–C(4)	1.487(14)	N(22)–C(24)	1.492(17)	N(2)–C(4)	1.479(10)
N(3)–C(7)	1.232(16)	N(23)–C(27)	1.260(19)	N(3)–C(6)	1.306(12)
N(3)–C(6)	1.467(16)	N(23)–C(26)	1.455(19)	N(3)–C(5)	1.466(12)
N(4)–C(9)	1.256(18)	N(24)–C(29)	1.295(16)	N(4)–C(8)	1.338(10)
N(4)–C(10)	1.460(17)	N(24)–C(30)	1.486(16)	N(4)–C(9)	1.489(11)
N(2)–Ni(1)–N(3)	89.7(5)			N(3)–Ni–N(4)	93.1(3)
N(2)–Ni(1)–N(4)	175.1(5)			N(3)–Ni–N(2)	85.9(3)
N(3)–Ni(1)–N(4)	90.1(5)			N(4)–Ni–N(2)	172.7(3)
2 – N i l)–N(1)	89.9(5)			N(3)–Ni–N(1)	168.7(4)
N(3)–Ni(1)–N(1)	177.3(5)			N(4)–Ni–N(1)	92.6(3)
N(23)–Ni(2)–N(22)	89.7(5)			N(2)–Ni–N(1)	89.7(3)
N(23)–Ni(2)–N(21)	176.7(6)				
N(22)–Ni(2)–N(21)	90.5(5)				
N(23)–Ni(2)–N(24)	89.6(5)				
N(22)–Ni(2)–N(24)	173.2(5)				
N(21)–Ni(2)–N(24)	89.9(5)				

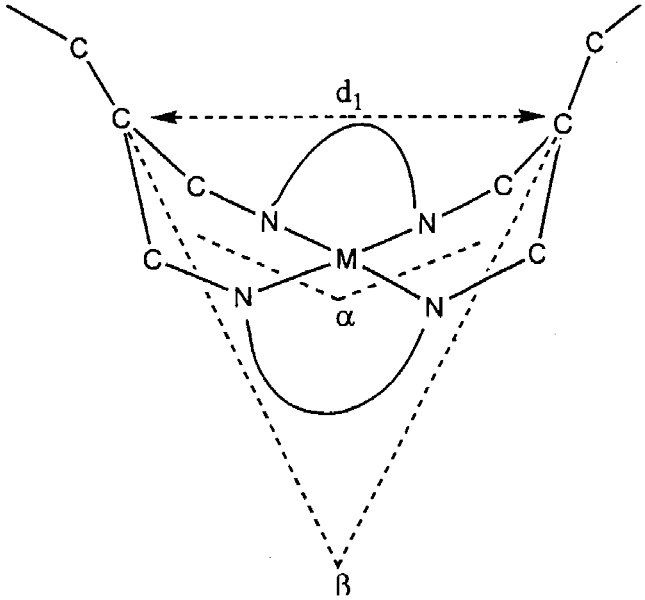

Figure 3. Geometric parameters defining the molecular shape of cyclidene macrocyclea.

the angle α ranges from 94" to 110°, the angle β ranges from 48° to 77" [1]. The distances d_1 for (IIIc) (C(2)–C(8), 4.83 Å, and C(22)–C(28), 4.80 Å; for atom numbering see Figure 2) are smaller than those observed for other unbridged cyclidenes (5.18–6.55 Å). The smaller (tetrahedral) angle at the fully saturated C(2), C(8), C(22), and C(28) y-carbon atoms in (IIIc), compared to fully or partially unsaturated y-carbon atoms in other cyclidenes, clearly contributes to its greater deviation from the {N(1)N(2)C(1)C(3)}plane (or analogous planes N(3)N(4)C(7)C(9), N(21)N(22)C(21)C(23), N(23)N(24)C(29)C(27)) and consequently shorter distance dl.

The cation (VIb) of the mono-deacylated, singly deprotonated cyclidene has both 5- and 6-membered saturated chelate rings in skew conformations (Figure 4, ORTEP). They thrust the two unsaturated chelate rings onto opposite sides of the MN_4 plane in much the same way as it was observed for compound (IIb) [12]. As one may expect, similar conformations of the saturated chelate rings in (VIb) and (IIb) result in a very similar overall shape for both molecules. In both (VIb) and (IIb) a relatively rigid trimethylene bridge, locked in an unfavorable skew conformation, slightly twists the MN_4 fragment with a torsional angle N(1)N(2)N(3)N(4) of 12° and 9.5" respectively.

In contrast to (IIb) (which has two equivalent unsaturated rings), in compound (VIb) a significant difference is observed between the raising angles of the two unsatur-

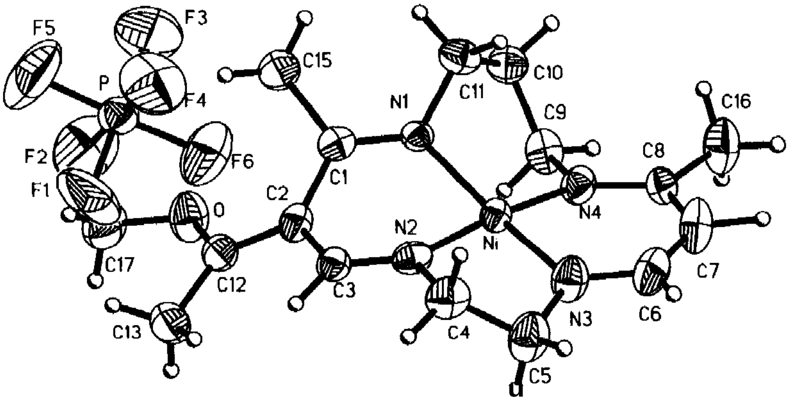

Figure 4. Crystal structure of VIb.

ated chelate rings. The angle between the deacylated (and deprotonated) chelate ring (represented by the mean {Ni-N(3)-N(4)-C(6)-C(7)-C(8)} plane, Figure 4) and the mean MN_4 plane is only 15°, while another, substituted chelate ring {Ni-N(1)-N(2)-C(1)-C(2)-C(3)} makes a 21° angle with the MN_4 plane. The reason for such a difference lies in the effective delocalization of the electron density within the deacylated deprotonated ring and the pseudoaromaticity of the Ni-N(3)-C(6)-C(7)-C(8)-N(4) fragment. This is indicated by the fact that the carbon-nitrogen and carbon-carbon bond lengths (ranging from 1.31 to 1.39 Å) are substantially more uniform compared to the corresponding bonds in the other unsaturated ring (1.27 and 1.29 Å for a double bond, 1.45 and 1.49 for a single bond) and even more so compared to completely unconjugated structures in (IIIc) (Table 2). The tendency of the pseudoaromatic ring to retain a planar conformation is in conflict with the forces originating from the conformations of the saturated chelate rings. The resulting balance between these forces gives a small raising angle and an almost flat Ni-N(3)-C(6)-C(7)-C(8)-N(4) fragment. The nickel atom deviates from the mean {Ni-N(3)-C(6)-C(7)-C(8)-N(4)} plane by only 0.13 Å, while the deviation of the Ni atom from the mean {Ni-N(1)-C(1)-C(2)-C(3)-N(2)} plane is twice as large.

Conclusions

The results above show that formation of a conjugated pseudoaromatic fragment in the deprotonated species of the deacylated cyclidenes substantially influences cyclidene geometry. making the unsaturated chelate ring more planar. Inversely, protonation of the deacylated chelate ring generates a saturated sp^3 carbon atom in the middle of the unsaturated chelate ring, which sticks out from the plane of the ring and makes the cyclidene molecule even more bowed. Consequently, singly deprotonated, mono-deacylated cyclidenes do not have the potential to encapsulate guests, while doubly deacylated, dicationic cyclidenes form a well shaped cavity suitable for encapsulating small guests.

References

1. D.H. Busch and N.W. Alcock: *Chem. Rev.* 94,585 (1994).
2. D.H. Busch and N.A. Stephenson: ***The Transition Metal Cyclidenes: A Broad Family of Complexes Well Suited to Inclusion Chemistry.*** In J.L. Atwood, J.E.D. Davies and D. MacNicol (eds.), *Inclusion* **Compounds,** Vol. 5, Oxford: Oxford University Press (1991), pp. 276–310.
3. D.H. Busch: ***Pure** Appl. Chem.* **52,** 2477 (1980).
4. J.S. Bradshaw, K.E. Krakowiak and R.M. Izatt: *Aza-crown macrocycles*, Wiley (1993), 885 pp.
5. D.H. Busch, P.J. Jackson, M. Kojima. P. Chmielewski, N. Matsumoto, J.C. Stevens. W. Wu, D. Nosco, N. Herron. N. Ye, P.R. Warbunon, M. Masarwa, N.A. Stephenson, G. Christoph and N.W. Alcock: ***Inorg.** Chem.* **33,** 910 (1994).
6. A.G. Kolchinski. B. Korybut-Daskiewisz, E.V. Rybak-Akimova, D.H. Busch, N.W. Alcock and H.J. Clase: ***J.** Am. Chem. Soc.* **119,** 4160 (1997).
7. P.S.K. Chia, M. Masarwa, P.R. Warburton, W. Wu, M. Kojima, D. Nosco, N.W. Alcock and D.H. Busch: *Inorg. Chem.* **32,** 2736 (1993).
8. T.J. Meade, K.J. Takeuchi and D.H. Busch: ***J. Am.** Chem. Soc.* **109,** 725 (1987).
9. E.V. Kybak-Akimova, K. Kuczera, G.S. Jas, Y. Deng and D.H. Busch: *Inorg.* ***Chem.*** 38, 3423 (1999).
10. E.V. Rybak-Akimova and K. Kuczera: ***Inorg.** Chem.* 39, 2462 (11000).
11. W.-K. Lin, N.W. Alcock and D.H. Busch: ***J. Am. Chem.** Soc.* **113,** 7603 (1991).
12. N.W. Alcock, W.-K. Lin, A. Jircitano. J.D. Mokren. P.W.R. Corticld, G. Johnson, G. Novotnak, C. Cairns and D.H. Busch: ***Inorg. Chem.*** 26,440 (1987).
13. B. Korybut-Daskiewicz, M. Kojirna, J.H. Cameron, N. Herron, M.Y. Chavan, A.J. Jircitano, B.K. Coltrain, G.L. Necr, N.W. Alcock and D.H. Busch: *Inorg.* ***Chem.* 23,** 903 (1984).
14. C.J. Cairns and D.H. Busch: *Inorg. Synth.* **27,** 261 (1990).
15. D.P. Riley and D.H. Busch: *Inorg. Synth.* 18, 37 (1978).
16. C.P. Horwitz, R. Navarro and G.C. Dailey: *Inorg.* ***Chem.* 29,** 4262 (1990).
17. J.H. Cameron and D.P. Nicol: *Chemistry of the Z-shaped Isomer of a Jäger [16]-Macrocyclic Complex*, 34th international Conference on Coordination Chemistry, Edinburgh (2000). p. I151.
18. H. Takalo. P. Pasanen and J. Kankarc: *Acta Chem. Scand.* B42. 373 (1988).
19. J.H. Cameron, M. Kojima, B. Koryhut-Daszkiewicz, B.K. Coltrain, T.J. Meade. N.W. Alcock and D.H. Busch: ***Inorg.** Chem.* **26,** 427 (1987).
20. J.A. Streeky. D.G. Pillsbury and D.H. Busch: ***Inorg. Chem.* 19,** 3148 (1980).
21. G.M. Sheldrick: ***SHELXS-97** Program for Structure Solution*, University of Goettingen (1997).
22. G.M. Sheldrick: *SHELXL-97 Program for Structure Refinement*, University of Goerringen (1997).
23. J.H. Cameron, D.P. Nicol and G.M. Rosair: *J. Chem. Soc.* ***Chem.*** *Commun.* 1595 (1998).