Co-ordination of 1,4,7,10-Tetraazacyclotridecane ([13]aneN_4) to Nickel(III). Crystal Structure of [Ni([13]aneN_4)Br_2]Br†

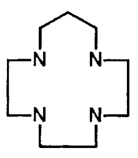
Hiroshi Miyamae,*,[a] **Kazuyo Yamauchi**[b] **and Masahiro Yamashita***,[b]
[a] *Department of Chemistry, Josai University, Keyakidai 1-1, Sakado-shi, Saitama 350-12, Japan*
[b] *College of General Education, Nagoya University, Furocho, Chikusa-ku, Nagoya 464-01, Japan*

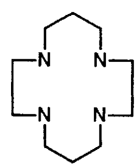
The crystal structure of [Ni([13]aneN_4)Br_2]Br ([13]aneN_4 = 1,4,7,10-tetraazacyclotridecane) has been determined by single-crystal X-ray diffraction: tetragonal, space group $P4_2$ with a = 7.8502(9), c = 12.464(2) Å and Z = 2. The Ni atom on the crystallographic two-fold axis is surrounded octahedrally by a square-planar array of four N atoms from the macrocycle with two bromide ions occupying the axial positions. The carbon atoms of the macrocycle are too disordered to be depicted because of the unexpected crystallographic symmetry. The tetragonal co-ordination geometry found in this complex is consistent with that proposed on the basis of the ESR spectrum in dimethyl sulphoxide. The correlation between the in-plane Ni–N and axial Ni–Br distances is discussed in terms of the size of the aperture in the cyclic ligand.

The chemistry of Ni^{III} has attracted much attention in several fields. This arises from its unusual oxidation state,[1] its presence as a trace bio-element,[2] its use in the study of the kinetics and mechanisms of the reactions of organic molecules or metal ions,[3] and the interesting solid-state properties displayed by some of its compounds.[4] However, not all compounds which appear to contain nickel(III) based on their empirical formula do in fact contain this ion, and may belong to one of the following groups: (*a*) discrete d^7 nickel(III) complexes, *e.g.* [Ni([14]aneN_4)Cl_2]ClO_4[5] ([14]aneN_4 = 1,4,8,11-tetraazacyclotetradecane); (*b*) nickel(II) complexes with cation radical ligands, *e.g.* [Ni(pdma)$_2$$Cl_2$]Cl[6] [pdma = *o*-phenylenebis(dimethylarsine)]; (*c*) halide-bridged one-dimensional Ni^{II}–Ni^{IV} mixed-valence complexes, *e.g.* Ni(en)$_2$Cl(ClO_4)$_2$[7] (en = ethylenediamine); (*d*) halide-bridged one-dimensional nickel(III) complexes, *e.g.* [Ni(chxn)$_2$$Br_3$][4] (chxn = 1,2-diaminocyclohexane), and (*e*) partially oxidized complexes, *e.g.* [Ni(Hdpg)$_2$I][8] (H_2dpg = diphenylglyoxime).

A number of electrochemical, optical, and magnetic investigations have been carried out on the complexes belonging to group (*a*), but there have been few crystal structure studies because of their instability and the difficulty in obtaining single crystals.[4,5,9,10] Among them, nickel(III) complexes with tetraazacycloalkanes are relatively stable in the solid state.[1]

For the three ligands shown the Ni–N bond lengths vary systematically with ring size, the ideal values of 1.92, 2.07 and 2.22 Å being obtained for [13]aneN_4, [14]aneN_4 and [15]aneN_4, respectively.[11] In the case of corresponding nickel(II) complexes, where the ideal Ni–N bond distances for high- and low-spin complexes are 2.10 and 1.90 Å respectively, studies have shown that [15]aneN_4 and [14]aneN_4 co-ordinate both high-spin octahedral Ni^{II}, *trans*-[Ni$N_4$$X_2$], and square-planar low-spin Ni^{II}, $[NiN_4]^{2+}$, where the macrocyclic ligands are planar. However, in the [13]aneN_4 case, only in the low-spin *nickel(II)* complex is the ligand planar, and in the octahedral high-spin complex the ligand is co-ordinated in a *cis*-folded manner, *cis*-[Ni$N_4$$X_2$]. This is attributed to the smaller hole size of the ligand compared with the ionic radius of high-spin Ni^{II}.[12] On the other hand, the co-ordination geometry about Ni^{III} with [14]aneN_4 and its methylated derivatives is commonly octahedral *trans*-$[Ni^{III}N_4X_2]^+$ with one unpaired electron in the d_{z^2} orbital.[10,13,14] In order to investigate the co-ordination of the [13]aneN_4 ligand to Ni^{III}, we have determined the crystal structure of [Ni([13]aneN_4)Br_2]Br and compared it with that of [Ni([14]aneN_4)Br_2]ClO_4 previously reported.[4]


[13]aneN_4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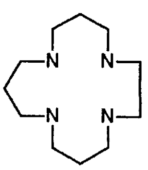
[15]aneN_4

Experimental

Synthesis.—An excess of $(NH_4)_2S_2O_8$ was added to a saturated aqueous solution of [Ni([13]aneN_4)][ClO_4]$_2$. The solution immediately turned dark green. An excess of hydrogen bromide was added to the solution. A red product precipitated immediately and was collected by filtration as quickly as possible to avoid decomposition. Yield: *ca* 60% (Found: C, 21.65; H, 4.20; N, 10.85. Calc. for $C_9H_{22}Br_2ClN_4NiO_4$: C, 21.45; H, 4.40; N, 11.10%). The compound was recrystallized from acetonitrile as dark red single crystals suitable for X-ray work which revealed this product to be [Ni^{III}([13]aneN_4)Br_2]Br (Found: C, 22.25; H, 4.60; N, 11.80. Calc. for $C_9H_{22}Br_3N_4Ni$: C, 22.30; H, 4.60; N, 11.55%). During the recrystallization a counter ClO_4^- ion was exchanged with a Br^- ion, which might originate from decomposed nickel(III) compounds.

Crystal Structure Determination of [Ni([13]aneN_4)Br_2]Br.—*Crystal data.* $C_9H_{22}Br_3N_4Ni$, M = 484.7, tetragonal, space group $P4_2$, a = 7.8502(9), c = 12.464(2) Å, U = 768.1(2) Å^3, D_c = 2.095 g cm^{-3}, Z = 2, F(000) = 474, μ(Mo-Kα) = 8.99 mm^{-1}, crystal dimensions *ca.* 0.2 × 0.2 × 0.2 mm.

Data collection and processing. 1323 Reflections with

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† Dibromo(1,4,7,10-tetraazacyclotridecane-κ$^4N^1,N^4,N^7,N^{10}$)nickel(III) bromide.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Table 1 Atomic positional parameters ($\times 10^4$) for [Ni([13]aneN_4)-Br_2]Br

Atom	*x*	*y*	*z*
Ni	5000	0	0
Br(2)	5000	−5000	−2494(7)
Br(1)	2321(2)	2083(2)	−12(5)
N(1)	4100(15)	−1385(15)	−1080(10)
N(2)	4009(18)	−1500(18)	1101(11)
C(1)	4421(18)	−261(21)	−2141(12)
C(2)	2394(21)	−2018(23)	−999(17)
C(4)	2319(20)	−2350(21)	635(14)
C(5)	3811(19)	−675(20)	2124(12)
C(3)	2365(36)	−3120(35)	183(38)

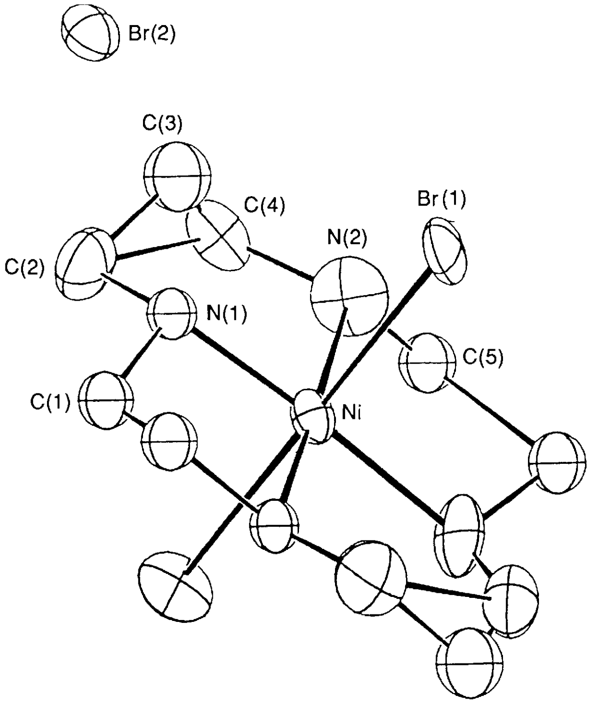

Fig. 1 Structure of [Ni([13]aneN_4)Br_2]Br with atom numbering drawn by ORTEP.[17] Thermal ellipsoids are at the 50% probability level

Table 2 Bond distances (Å) and angles (°) within the cation *

Ni–Br(1)	2.664(1)	N(2)–C(5)	1.439(20)
Ni–N(1)	1.869(12)	C(1)–C(1^I)	0.998(20)
Ni–N(2)	1.969(14)	C(2)–C(4)	2.054(27)
N(1)–C(1)	1.609(19)	C(2)–C(3)	1.708(47)
N(1)–C(2)	1.432(20)	C(4)–C(3)	0.828(41)
N(2)–C(4)	1.594(21)	C(5)–C(5^I)	2.146(22)
Br(1)–Ni–N(1)	93.14(37)	N(1)–Ni–N(2)	90.27(54)
Br(1)–Ni–N(2)	93.39(42)	N(1)–Ni–N(1^I)	87.85(51)
Br(1)–Ni–Br(1^I)	179.34(20)	N(1)–Ni–N(2^I)	178.09(54)
Br(1)–Ni–N(1^I)	86.39(37)	N(2)–Ni–N(2^I)	91.61(56)
Br(1)–Ni–N(2^I)	87.07(42)		
Ni–N(1)–C(1)	102.3(8)	N(1)–C(2)–C(4)	98.1(12)
Ni–N(1)–C(2)	120.3(11)	N(1)–C(2)–C(3)	104.4(15)
C(1)–N(1)–C(2)	113.2(12)	N(2)–C(4)–C(2)	106.5(11)
Ni–N(2)–C(4)	109.0(9)	N(2)–C(4)–C(3)	121.2(25)
Ni–N(2)–C(5)	113.0(10)	N(2)–C(5)–C(5^I)	97.4(10)
C(4)–N(2)–C(5)	114.9(12)	C(2)–C(3)–C(4)	102.6(29)
N(1)–C(1)–C(1^I)	111.6(15)		

* Symmetry operation: I $1 - x, -y, z$.

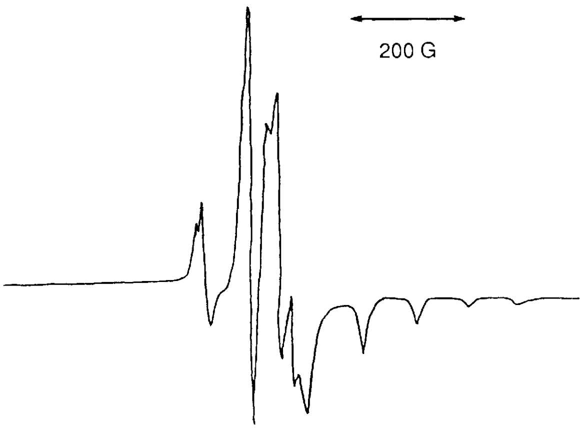

Fig. 2 The ESR spectrum of [Ni([13]aneN_4)Br_2]ClO_4 in dmso solution, contains some concentrated hydrobromic acid. The conditions are the same as those used for [Ni([14]aneN_4)Br_2]ClO_4[13]; G = 10^{-4} T

$2\theta < 60°$ (*h* 0–11, *k* 0–11, *l* 0–17) were collected by 2θ–θ scan technique on a Rigaku AFC-5 four-circle diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å). During data collection three standard reflections were monitored every 100 measurements, and fluctuations were found to be within 1%. The unit-cell dimensions were refined from a least-squares fit of 18 independent 2θ values ($27 < 2\theta < 34°$).

766 Unique reflections with $|F| > 3\sigma(|F|)$ were used for structure determination. Intensities were corrected for Lorentz and polarization effects and absorption (minimum and maximum A^* = 1.776 and 2.068), but not for extinction.

Structure analysis and refinement. The structure was solved by using the heavy-atom method to locate the $NiBr_2$ skeleton. Successive Fourier difference maps gave the coordinates of the remaining non-H atoms. They were refined assuming anisotropic thermal parameters, except for C(3). The parameters were refined by the block-diagonal least-squares method using the UNICS-III program system,[15] minimizing $\Sigma w(|F_o|^2 - |F_c|^2)/\Sigma w|F_o|^2$, where $w = 1/(\sigma|F_o|^2 + 0.02|F_o|^2)$.

The H atoms were not included in the refinement because of the disorder of the macrocycle. Complex neutral atom scattering factors were obtained from ref. 16. The final conventional *R* converged at 0.062 and *R'* at 0.052 with *S* = 1.9201. The final atomic parameters with estimated standard deviations are listed in Table 1.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal paramaters and remaining bond lengths and angles.

ESR Spectroscopy.—The ESR spectrum was recorded on a Varian X-band spectrometer at liquid-nitrogen temperature.

Results and Discussion

Fig. 1 shows a perspective view of the complex with the atom numbering. Relevant bond lengths and angles are listed in Table 2.

The Ni^{III} atom is required to be on the crystallographic two-fold axis and surrounded pseudo-octahedrally by four secondary nitrogens of the macrocyclic ligand and two bromo atoms in *trans* positions. However, the carbon atoms of the macrocyclic ligand are too disordered to be depicted. Hence, the five- and six-membered chelate rings cannot be distinguished from each other, resulting in the bond lengths and angles of the macrocyclic ligand being abnormal. Such disorder is very similar to that previously observed in complexes containing the [15]aneN_4 ligand.[18]

The tetragonal co-ordination geometry found in the complex is consistent with that proposed on the basis of the ESR spectrum in dimethyl sulphoxide (dmso) shown in Fig. 2, which is very similar to that of [Ni([14]aneN_4)Br_2]ClO_4.[13] From both results it can be concluded that the [13]aneN_4 ligand coordinates to the octahedral Ni^{III} in a planar fashion, both in the solid state and in dmso solution, due to the smaller ionic radius of Ni^{III} compared with that of Ni^{II}.

The average Ni–Br [Ni–N] bond lengths of $[Ni([13]aneN_4)Br_2]Br$ and $[Ni([14]aneN_4)Br_2]ClO_4$[4] are 2.664(1) [1.919(13)] and 2.616(1) [1.971(7)] Å. The Ni–N bond lengths in the former are *ca.* 0.05 Å shorter than in the latter due to the smaller hole size of the $[13]aneN_4$ ligand. On the other hand, the Ni–Br bond distance in the former is *ca.* 0.05 Å longer than that in the latter. Previously Ito *et al.*[19] investigated the metal-ion characteristics viewed from a correlation between the axial and in-plane co-ordination bond distances in tetragonal six-co-ordinate complexes of the *trans*-MN_4X_2 type, where M = Zn^{2+} (d^{10}), Ni^{2+}(d^8), or Co^{3+}(d^6). Both experimentally and theoretically, it has been found that the axial M–X distance decreases as the in-plane M–N distance increases. The degree of the negative correlation is strongly metal-ion dependent and varies in the order $Zn^{2+} > Ni^{2+} > Co^{3+}$, which is correlated with the electron occupancy of the $d_{x^2-y^2}$ and d_{z^2} orbitals. Therefore, there is little negative correlation for the cobalt(III) complexes. On the other hand, so far there have been few experimental investigations on d^7 systems such as Ni^{3+} and Co^{2+} because of the difficulty of synthesising complexes of the type *trans*-MN_4X_2. Our crystal-structure results show a similar negative correlation in *trans*-$[Ni^{III}N_4Br_2]^+$. This is due to the electronic structure of Ni^{III} which has one unpaired electron in the d_{z^2} orbital, as evidenced by the ESR spectrum.

We are now trying to get a single crystal of a nickel(III) complex with the $[15]aneN_4$ ligand in order to discuss the correlation between axial and in-plane bond lengths in more detail.

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