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The Crystal and Molecular Structure of Bis(1,4,7-triazacyclodecane) nickel(II) diperchlorate, $[Ni([10]aneN_3)_2](ClO_4)_2$

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This bis nickel(II) complexes of the cyclic triazaalkanes, 1,4,7-triazacyclononane, $[9]aneN_3$, and 1,4,7-triazacyclodecane, $[10]aneN_3$, have unusual electronic spectra. Both complexes have extremely large crystal field, Dq, and Racah, B, parameters for NiN_6 type chromophores when calculated on the basis of an octahedral model [1, 2]. We have recently shown that $Ni([9]aneN_3)_2^{2+}$ is trigonally distorted from octahedral symmetry [3] and it appears likely that this perturbation accounts for the anomalous values of Dq and B [4]. We now report the X-ray crystallographic structure of $[Ni([10]aneN_3)_2](ClO_4)_2$. This complex, like $Ni([9]aneN_3)_2^{2+}$, shows nearly trigonal distortion from octahedral symmetry.

Experimental

Crystals were obtained by evaporation of aqueous solutions containing $Ni(ClO_4)_2$ and $[10]aneN_3\cdot 3HCl$ which were neutralized with NaOH. Cell dimensions and intensity data were measured with a Syntex $P2_1$ diffractometer using monochromated MoKα X-rays (λ = 0.71069 Å). The crystals of $[Ni([10]aneN_3)_2](ClO_4)_2$, $C_{14}H_{34}N_6Cl_2O_8Ni$, are monoclinic, space group $P2_1/n$ with a = 9.496(5), b = 10.206(5), c = 11.467(6) Å, β = 91.42(10)°, Z = 2 molecules/cell, d_m = 1.80, d_c = 1.73 g/cm^3. The structure was determined by Patterson and Fourier techniques and refined by least-squares to a final value of $R = \Sigma||F_o|-|F_c||/|\Sigma|F_o|$ = 0.047 for 1542 observed reflections. In the final cycles of least squares, hydrogen atoms, located in a ΔF map, where included with isotropic temperature factors while all other atoms were refined anisotropically. The final values of the non-hydrogen atomic coordinates are listed in Table I. Table II gives the important interatomic distances and angles.

Results and Discussion

The crystal structure consists of nearly tetrahedral perchlorate ion packed with the Ni([10]ane-

TABLE I. Atomic Coordinates.[a]

Atom	x	y	z
Ni	0.00000	0.00000	0.00000
N(1)	0.0476(4)	0.1885(4)	−0.0669(3)
N(2)	0.2204(4)	−0.0196(5)	0.0060(3)
N(3)	0.0368(4)	0.0824(4)	0.1699(3)
C(1)	0.2028(5)	0.2102(5)	−0.0643(4)
C(2)	0.2808(5)	0.0803(5)	−0.0715(4)
C(3)	0.2681(5)	−0.0149(7)	0.1299(4)
C(4)	0.1898(5)	0.0891(6)	0.1966(4)
C(5)	−0.0349(6)	0.2077(5)	0.1950(5)
C(6)	0.0010(6)	0.3207(5)	0.1139(5)
C(7)	−0.0284(6)	0.3014(5)	−0.0149(5)
Cl	0.55624(14)	0.31797(15)	0.10641(11)
O(1)	0.5686(5)	0.3003(5)	−0.0153(3)
O(2)	0.4185(4)	0.3556(4)	0.1380(4)
O(3)	0.6542(4)	0.4129(4)	0.1504(3)
O(4)	0.5839(5)	0.1943(4)	0.1609(4)

[a] Estimated standard deviations are given in parentheses.

TABLE II. Some Important Bond Lengths and Bond Angles.[a]

Bond Lengths, Å			
Ni–N(1)	2.124	C(3)–C(4)	1.514
Ni–N(2)	2.102	C(4)–N(3)	1.479
Ni–N(3)	2.143	N(3)–C(5)	1.480
N(1)–C(1)	1.490	C(5)–C(6)	1.526
C(1)–C(2)	1.521	C(6)–C(7)	1.590
C(2)–N(2)	1.478	C(7)–N(1)	1.492
N(2)–C(3)	1.481		
Perchlorate			
Cl–O(1)	1.415	Cl–O(3)	1.427
Cl–O(2)	1.419	Cl–O(4)	1.430
Intraligand Angles at Ni, (°)			
N(1)–Ni–N(2)	83.0		
N(1)–Ni–N(3)	86.6		
N(2)–Ni–N(3)	82.4		
interligand Angles at Ni, (°)			
N(1)–Ni–N(2′)	97.1		
N(1)–Ni–N(3′)	93.4		
N(2)–Ni–N(3′)	97.6		
Adjacent Nitrogen Distance, Å			
Interligand		Interligand	
N(1)–N(2)	2.799	N(1)–N(2′)	3.167
N(1)–N(3)	2.797	N(1)–N(3′)	3.105
N(2)–N(3)	2.928	N(2)–N(3′)	3.194

[a] Uncertainties in bond lengths are approximately 0.004 Å for Ni–N bonds and 0.008 Å for all others. Uncertainties in bond angles are approximately 0.6°.

TABLE III. Electronic Spectra of Nickel(II) Complexes.[a]

Complex	ν_3 (O_h, $^3A_{2g} \rightarrow {}^3T_{1g}(P)$)	ν_2 (O_h, $^3A_{2g} \rightarrow {}^3T_{1g}$)	ν_1 (O_h, $^3A_{2g} \rightarrow {}^3T_{2g}$)	sh (O_h, $^3A_{2g} \rightarrow {}^1E_g$)
Ni([9]aneN_3)$^{2+}$	30,800	19,800	12,500	11,500[b]
Ni([10]aneN_3)$^{2+}$	30,600	19,500	12,500	11,500[b]
Ni(haec)$^{2+}$	29,400	19,000	11,400	12,200

[a] Spectra recorded in aqueous solution at 25 °C. Energy in cm^{-1}. [b] This shoulder is usually ascribed to the spin-forbidden (^1E) transition but analysis of the Ni([9]aneN_3)$_2^{2+}$ spectrum indicates that it may be due to one of the components of the spin allowed ($^3T_{2g}$) transition when this state is split in trigonal symmetry.

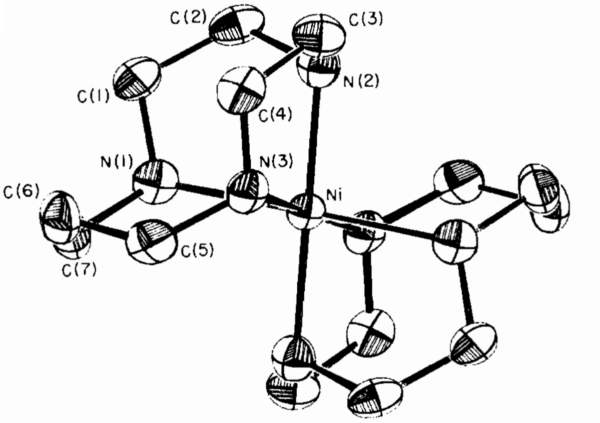

Fig. 1. Structure of the Ni([10]aneN_3)$_2^{2+}$ ion.

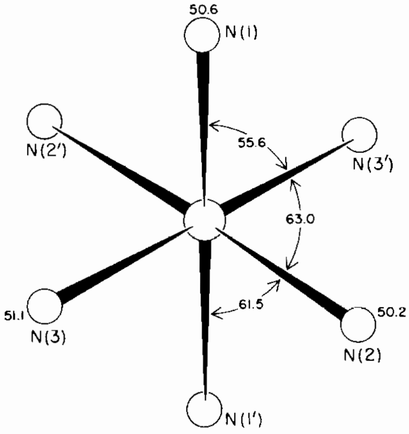

Fig. 2. Projection of the NiN_6 core onto the plane nearly perpendicular to the C_3 axis (all nitrogens attached to one ligand define plane), the trigonal twist angles are indicated between N–Ni–N angles and the polar angles are shown adjacent to the N atoms.

$N_3)_2^{2+}$ ion. The Ni atom is coordinated by 6 nitrogen atoms, 3 from each ligand ring in a distorted octahedral arrangement (Figs. 1 and 2). This distortion, which is predominantly trigonal, arises from the nitrogen atoms of each ligand being folded back along a pseudo-C_3 axis which bisects the center of the 10-membered ligand rings and passes through the nickel (Fig. 2). Two of the N–Ni–N intraligand angles are similar to those found in Ni([9]aneN_3)$_2^{2+}$ (82.6°) [3] while the third is approximately 3° larger resulting from the relief of strain in the 6-membered chelate ring. Although trigonal distortion predominates this larger bond angle further lowers the symmetry of the NiN_6 group to C_{2h}.

Similar to Ni([9]aneN_3)$_2^{2+}$ the degree of trigonal twists is small with the trigonal twist angles, ϕ, (the angle describing the twist of the faces perpendicular to the three-fold axis) deviating only a few degrees from the octahedral value of 60° (Fig. 2). The polar angles, θ, (the angle between a Ni–N bond and the C_3 axis) also shown in Fig. 2 indicates the degree of trigonal distortion of the NiN_6 chromophore (54.75° for the undistorted octahedron *versus* 50.6 ± 0.5 °C for this compound). There exists the possibility of two geometrical isomers for the Ni([10]aneN_3)$_2^{2+}$ ion [1] and in this case the trimethylene bridges are *trans* to one another.

The electronic spectra of Ni([x]aneN_3)$_2^{2+}$ (x = 9, 10) are quite similar and we believe this is due to the trigonal stereochemistry of the NiN_6 chromophore. The Ni complex of the 20-membered ring dimer of [10]aneN_3, 1,4,7,11,14,17-hexaazaeicosane (haec) forms a similar series of 5- and 6-membered chelate rings with almost identical Ni–N bond lengths [5]. However, the distortion in Ni(haec)$^{2+}$ is not trigonal and the anomalous electronic spectrum is not observed (Table III).

Acknowledgement

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