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Trigonal Distortion in a Nickel(II) Complex. Structure of [Ni([9]aneN$_3$)$_2$](NO$_3$)Cl·H$_2$O

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The thermodynamic and spectroscopic properties of transition metal complexes of the cyclic triamine 1,4,7-triazacyclononane, [9]aneN$_3$, are unusual. These complexes are several orders of magnitude more stable than corresponding complexes containing facially coordinated triamines [1, 2]. Further, it has recently been shown that the value of the ligand field parameter, Dq, for Ni([9]aneN$_3$)$_2^{2+}$ is extraordinarily large for a complex of an alkyl amine [2, 3].

The thermodynamic stability has been ascribed to the cyclic nature of the ligand and its associated large configurational entropy contribution [4, 5]. It has been postulated [2] that the spectroscopic behavior is due to a sizeable trigonal distortion (elongation of the C$_3$ axis of symmetry from octahedral geometry), but no direct evidence of this distortion has been presented. We report here an X-ray diffraction study of [Ni([9]aneN$_3$)$_2$](NO$_3$)Cl·H$_2$O which confirms the predicted trigonal distortion.

Experimental

Crystals were obtained by evaporation of a dimethylformamide solution containing the products of the reaction of [9]aneN$_3$·3HCl with Ni(NO$_3$)$_2$ and NaOH as previously described [2]. Cell dimensions and intensity data were measured with a Syntex P2$_1$ diffractometer using monochromated CuKα X-rays (λ = 1.54178 Å). The crystals of [Ni([9]aneN$_3$)$_2$]-(NO$_3$)Cl·H$_2$O, C$_{12}$H$_{32}$N$_7$O$_4$ClNi, are orthorhombic, space group Pna2$_1$ with a = 17.584 ± .006, b = 8.860 ± .003, c = 12.141 ± .003 Å, Z = 4 molecules/cell, d_m = 1.53, d_c = 1.51 g /cm^3. The structure was determined by Patterson and Fourier techniques and refined by least squares to a final value of $R = \Sigma \|F_o|-|F_c\| / |\Sigma|F_o| = 0.034$ for 1795 observed reflections. In the final cycles of least squares hydrogen atoms located in a ΔF map were 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.

TABLE I. Atomic Coordinates[a].

Atom	x	y	z
Ni	0.13079(3)	0.27367(7)	0.25
N(1)	0.1017(2)	0.2256(5)	0.0858(3)
N(2)	0.0129(2)	0.2530(4)	0.2724(3)
N(3)	0.1269(2)	0.0366(4)	0.2665(4)
N(4)	0.2505(2)	0.2851(4)	0.2336(4)
N(5)	0.1392(2)	0.5074(4)	0.2282(3)
N(6)	0.1560(2)	0.3305(5)	0.4149(3)
C(1)	0.0175(3)	0.2241(7)	0.0725(4)
C(2)	−0.0213(3)	0.3033(6)	0.1675(5)
C(3)	−0.0066(3)	0.0944(5)	0.3039(5)
C(4)	0.0618(3)	0.0083(6)	0.3401(5)
C(5)	0.1179(3)	−0.0318(6)	0.1559(5)
C(6)	0.1374(3)	0.0790(6)	0.0641(5)
C(7)	0.2639(3)	0.4122(6)	0.1590(5)
C(8)	0.2194(3)	0.5492(6)	0.1993(5)
C(9)	0.1136(3)	0.5725(6)	0.3337(5)
C(10)	0.1536(3)	0.4974(6)	0.4310(5)
C(11)	0.2317(3)	0.2647(6)	0.4363(5)
C(12)	0.2865(3)	0.3020(7)	0.3442(5)
N(7)	0.3139(3)	0.3654(5)	0.3052(4)
O(1)	0.3667(3)	0.7734(6)	0.3146(4)
O(2)	0.2641(3)	0.8743(6)	0.3779(4)
O(3)	0.3088(3)	0.9474(4)	0.2220(5)
O(4)	0.4308(2)	0.6863(5)	0.1061(4)
Cl	0.05917(7)	0.60945(15)	−0.00215(13)

[a] Estimated standard deviations are given in parentheses.

Results and Discussion

The crystal structure contains planar nitrate ions packed with a chloride ion and the nearly ocathedral Ni([9]aneN$_3$)$_2^{2+}$ ion. The water molecule is hydrogen bonded to NO$_3^-$ and Cl$^-$. Most ring N atoms are also hydrogen bonded. The Ni atom is coordinated by 6 nitrogen atoms, 3 from each ring in a trigonally distorted octahedron (Figure 1). The distortion is such as to cause the N–Ni–N angles where all N's come from one ring to average 82.6°, a considerable shift from the octahedral value of 90°. Similarly the N–Ni–N inter-ring angles average 97.5°. The N atoms of each ring form equilateral triangles which are parallel to each other and staggered about the approximate threefold axis shwon in Figure 2.

Although the trigonal distortion is large the trigonal twist distortion is relatively small. The trigonal twist angles, ϕ, (the angle describing the twist of the faces perpendicular to the threefold axis) deviate by 3.8 ± 0.8° from the octahedral value of 60° (Figure 2). The polar angles, θ, (the angle between a Ni–N bond and the C$_3$ axis) also shown in Figure 2 reflects the trigonal distortion (54.75° for the regular octahedron *versus* 49.6 ± 0.3° for this compound). The

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

Bond Lengths, Å			
Ligand 1			
Ni–N(1)	2.102	N(2)–C(3)	1.496
Ni–N(2)	2.098	C(3)–C(4)	1.491
Ni–N(3)	2.111	C(4)–N(3)	1.473
N(1)–C(1)	1.489	N(3)–C(5)	1.482
C(1)–C(2)	1.513	C(5)–C(6)	1.524
C(2)–N(2)	1.477	C(5)–C(6)	1.467
Ligand 2			
Ni–N(4)	2.116	N(5)–C(9)	1.475
Ni–N(5)	2.093	C(9)–C(10)	1.527
Ni–N(6)	2.111	C(10)–N(6)	1.493
N(4)–C(7)	1.464	N(6)–C(11)	1.477
C(7)–C(8)	1.524	C(11)–C(12)	1.513
C(8)–N(5)	1.501	C(12)–N(4)	1.492
Bond Lengths, Å			
Nitrate			
N(7)–O(1)	1.241		
N(7)–O(2)	1.246		
N(7)–O(3)	1.247		
Bond Angles, Deg.			
Ligand 1		Ligand 2	
N(1)–Ni–N(2)	82.2	N(4)–Ni–N(5)	82.6
N(2)–Ni–N(3)	82.5	N(5)–Ni–N(6)	82.5
N(3)–Ni–N(1)	83.1	N(6)–Ni–N(4)	82.5
Interligand Angles at Ni, Deg.			
N(1)–Ni–N(4)	99.4		
N(1)–Ni–N(5)	95.6		
N(2)–Ni–N(5)	99.9		
N(2)–Ni–N(6)	96.0		
N(3)–Ni–N(4)	95.1		
N(3)–Ni–N(6)	98.9		
N(1)–Ni–N(6)	177.2		
N(2)–Ni–N(4)	176.0		
N(3)–Ni–N(5)	177.2		
Bond Angles, Deg.			
Nitrate			
O(1)–N–O(2)	120.1		
O(2)–N–O(3)	119.1		
O(3)–N–O(1)	120.8		
Adjacent Nitrogen Distance, Å			
Ligand 1		Ligand 2	
N(1)–N(2)	2.762	N(4)–N(5)	2.778
N(2)–N(3)	2.774	N(5)–N(6)	2.772
N(3)–N(1)	2.796	N(6)–N(4)	2.787
Interligand			
N(1)–N(4)	3.217	N(2)–N(6)	3.129
N(1)–N(5)	3.108	N(3)–N(4)	3.120
N(2)–N(5)	3.209	N(3)–N(6)	3.207

[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°

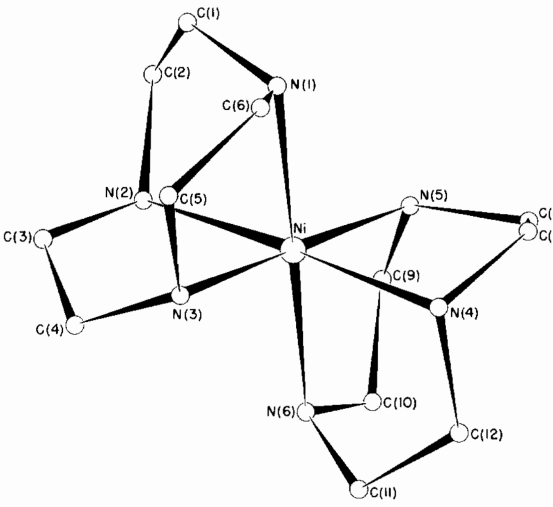

Figure 1. Structure of the $Ni([9]aneN_3)_2^{2+}$ ion.

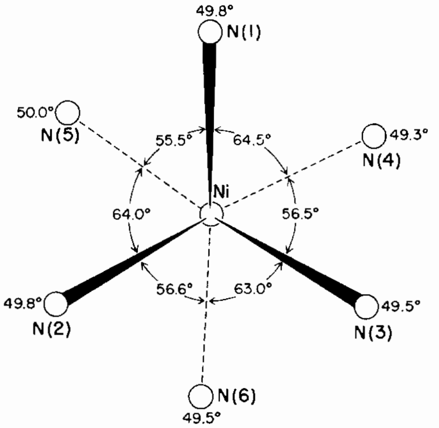

Figure 2. Projection of the NiN_6 core onto the plane perpendicular to the C_3 axis. The trigonal twist angles are indicated between N–Ni–N angles and the polar angles are shown adjacent to the N atoms.

symmetry of the NiN_6 core of this complex is D_3, but distortion from D_{3d} is slight.

All Ni–N bond distances are equivalent within experimental error and are normal for structures of this type [6]. The conformations of the two [9]ane-N_3 ligands are almost identical.

Because $[Ni([9]aneN_3)_2](NO_3)Cl \cdot H_2O$ contains NO_3^- which interferes {absorbs at 303 nm ($\epsilon \sim 7$)} with the near ultraviolet portion of the d–d absorption spectrum the complex $[Ni([9]aneN_3)_2](ClO_4)_2$ is a superior compound for spectral studies. With the exception of the NO_3^- absorbance the room temperature solid state (nujol mull) and solution (H_2O, DMF) spectra of both compounds are identical. Thus it may be assumed that the NiN_6 microsymmetry is nearly identical in both compounds. We therefore have a trigonally distorted complex of nickel(II) which provides an unrestricted (with regard to charge transfer) spectrum of the entire d–d absorption region. As a result of this distortion the excited T states (O_h symmetry) split into A and E components. The absorption bands of the complex are resolvable into several components. A spectral interpretation band upon these structural findings and the resolved peak positions will be forthcoming.

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