The Structure of Ni(cyclam)$I_2.H_2O$, $[Ni(C_{10}H_{24}N_4)I]I.H_2O$*

By L. Prasad[†]

Chemistry Division, National Research Council Canada, Ottawa, Ontario, Canada K1A 0R6

and A. McAuley

Chemistry Department, University of Victoria, Victoria, British Columbia, Canada V8W 2Y2

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Abstract. $M_r = 530{\cdot}9$, orthorhombic, *Pnma*, $a = 9{\cdot}406\ (1)$, $b = 12{\cdot}944\ (1)$, $c = 17{\cdot}018\ (1)$ Å, $V = 2071{\cdot}96$ Å^3, $F(000) = 1024$, $Z = 4$, $D_x = 1{\cdot}70$, $D_m = 1{\cdot}74$ Mg m^{-3}, $\lambda = 0{\cdot}70932$ Å, $\mu = 38{\cdot}8$ cm^{-1}. The final residual is $R_F = 0{\cdot}055$ for 1389 observed reflections at 296 K. The Ni atom is coordinated to the four N atoms of the cyclam ring in a square-planar arrangement. There is a long contact of 3·34 (1) Å between the Ni and a bridging iodide centre situated in an axial position. The second iodide (ionic) is located in the lattice, in a position not associated with the nickel cyclam.

Introduction. Although the complexes of Ni^{II} with tetraazamacrocyclic ligands have been the subject of considerable attention, there are relatively few data available on the structures of the complexes of the 'parent' ligand cyclam (1,4,8,11-tetraazacyclotetradecane). Some years ago, Tobe and co-workers (Bosnich, Tobe & Webb, 1965) described the preparation of the chloro, bromo and iodo complexes, together with that of the perchlorate species. The dichloro and dibromo complexes were shown to be paramagnetic, whereas the iodo anologue was diamagnetic. Recently, structural studies (Ito & Toriumi, 1981) have been carried out on the high-spin and low-spin nickel chloride complexes containing the *meso*-Me_6[14]aneN_4 ligand {[7*R*(*S*),14(*S*)*R*]-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane}. In the high-spin Ni(cyclam)Cl_2 complex (Bosnich, Mason, Pauling, Robertson & Tobe, 1965), the Ni—Cl bonds are long and no distortion of the cyclic ligand is observed. In the case of *N*-tetramethylated cyclam, however, although the free ligand shows a configuration of two methyl groups on either side of the N_4 plane (Prasad, 1982), a square-pyramidal [Ni(*N*-tetramethylcyclam)$N_3]^+$ cation has been observed with all four methyl groups on the same side of the molecule as the coordinated azide ion (Barefield & Wagner, 1973). In this case, the stereochemistry of the cation is considered to be kinetically controlled.

There has been recent interest (Haines & McAuley, 1981; Lovecchio, Gore & Busch, 1974; Zeigerson, Ginzburg, Schwartz, Luz & Meyerstein, 1979; Ferraudi & Patterson, 1977) in the oxidation of the Ni^{II} macrocycles to the Ni^{III} state. The products of oxidation are six-coordinate d^7 low-spin ions and in the case of the cyclam systems, there is ESR (Haines & McAuley, 1981; Desideri, Raynor & Poon, 1977) and X-ray crystal structure evidence (Ito, Sugimoto, Toriumi & Ito, 1981) for halide coordination to the Ni^{III} centre. Kinetic studies have been made on the rate of complex formation (Haines & McAuley, 1980) of Cl^- and Br^- to Ni^{III}, but in the case of the iodo complex, a redox reaction occurs with no evidence of a stable adduct.

In the present paper we describe the crystal structure of the *trans*-diiodo nickel(II) cyclam complex. This species is of interest in view of the finding of a diamagnetic complex (Bosnich, Tobe & Webb, 1965) and of the possibility of only a weak axial interaction of the halide ions with the metal centre.

Experimental. Crystals suitable for X-ray analysis were best prepared in an ethanol/water solvent mixture (1:3*v*/*v*), by reaction of Ni^{II}(cyclam) perchlorate with an excess (>15-fold) of sodium iodide. Slow evaporation resulted in long transparent brown needles. On isolation and leaving to dry in the air, the crystals became opaque and crumbled readily, indicating a possible loss of bound solvent. Analysis of the crystals, which were allowed to dry in air for 5–15 min (Canadian Microanalytical Services Ltd.), gave C 21·52 (21·8), H 5·30 (5·10), N 9·81 (10·2)% where the values in parentheses are those calculated for the complex Ni(cyclam)$I_2.2H_2O$. Density measurements were made by flotation using $CHBr_3/CCl_4$ solvent mixtures. The crystals dissolved. The structure analysis indicated the presence of one water molecule and a disordered C_2H_5OH/H_2O molecule. Studies reported here were carried out using freshly isolated crystals sealed in a tube with some saturated reactant solution.

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* NRC Contribution No. 21286 [systematic name for title compound: *catena*-*μ*-iodo-(1,4,8,11-tetraazacyclotetradecane)-nickel(II) iodide monohydrate].

[†] Present address: Department of Chemistry, University of Toronto, 80 St George Street, Toronto, Ontario, Canada M5S 1A1.

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0·4 × 0·3 × 0·3 mm crystal; Picker diffractometer, graphite-monochromatized Mo $K\alpha$, $2\theta_{\max} = 50°$; $\theta/2\theta$ scan with line-profile analysis (Grant & Gabe, 1978); 2947 reflections; 1911 unique (agreement between equivalent reflections 0·01), 1389 with $I \geq 2{\cdot}5\sigma(I)$, Lp correction, correction for measured direct-beam polarization (Le Page, Gabe & Calvert, 1979), no absorption corrections; least-squares refinement of cell parameters with 62 reflections ($2\theta > 40°$). From systematic absences space group is *Pnma* or $Pn2_1a$; structure refined in *Pnma*.

The Ni and two I atoms were located by application of *MULTAN* (Germain, Main & Woolfson, 1971); Ni at a centre of symmetry ($\frac{1}{2},\frac{1}{2},\frac{1}{2}$) and the two I atoms on a mirror plane ($y = 0{\cdot}25$). All the other atoms were located in a heavy-atom-phased Fourier map. One water molecule O atom was also on a mirror plane. Anisotropic refinement on $|F|$ to an R value of 0·06 by block-diagonal least squares with counting-statistics weights. The positions of the 10 unique methylene H atoms in the cyclam ring were calculated and included in structure factor calculations but not refined. A difference map calculated at this point had three peaks with heights of approximately 2 e Å^{-3} which indicated that the second water molecule present was disordered. The distances between the peaks were consistent with the random occupancy of such sites by solvent molecule C_2H_5OH. Efforts to refine the occupancy factors and/or the positions of these three peaks failed. Therefore, an occupancy factor of 0·5 was given to these three peaks and was not refined. The H atoms bonded to the N atoms and the water molecule H atoms were not located. The final difference map showed only small peaks of the order of 0·5 e Å^{-3} in the vicinity of the Ni and I atoms and several peaks smeared out near the disordered H_2O and/or C_2H_5OH molecule. The final residual is $R_F = 0{\cdot}055$ and $R_{wF} = 0{\cdot}094$ for 1389 observed reflections and $R_F = 0{\cdot}077$ and $R_{wF} = 0{\cdot}094$ for all 1911 reflections. The scattering curves for neutral atoms were from *International Tables for X-ray Crystallography* (1974). The atomic positional and equivalent isotropic temperature factors are listed in Table 1.* All calculations were performed using the NRC PDP8-E system of programs (Larson & Gabe, 1978).

Discussion. The atom numbering, bond lengths and angles for the Ni(cyclam) are shown in Fig. 1. The structure is of interest in that, unlike the preparation from hot 1-butanol (Bosnich, Tobe & Webb, 1965), where an anhydrous material was formed, in the EtOH/H_2O mixture one molecule of H_2O is retained along with some residual solvent. The geometry around the Ni is pseudo-octahedral. One of the I atoms [I(1)] appears to be bonded to the Ni atom [Ni—I(1) = 3·34 (1) Å] forming a bridge to an adjacent Ni atom (Fig. 2). The structural aspects are not unlike those of a bridged azide complex ion $[Ni_2(N\text{-methylcyclam})_2N_3]^+$ observed by Wagner, Mocella, D'Aniello, Wang & Barefield (1974).

Table 1. *Atomic coordinates and B_{eq} values*

E.s.d.'s refer to the last digit printed.

$$B_{eq} = \tfrac{8}{3}\pi^2(U_{11} + U_{22} + U_{33}).$$

	x	y	z	B_{eq}(Å^2)
I(1)	0·48157 (16)	$\frac{1}{4}$	0·54789 (7)	4·49 (7)
I(2)	0·09223 (16)	$\frac{1}{4}$	0·37437 (9)	6·03 (8)
Ni	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	2·72 (10)
N(1)	0·3279 (9)	0·4746 (7)	0·4402 (5)	3·2 (5)
N(2)	0·3751 (10)	0·5463 (7)	0·5851 (5)	2·9 (5)
C(1)	0·3255 (13)	0·5026 (10)	0·3546 (6)	4·3 (7)
C(2)	0·4394 (15)	0·4493 (10)	0·3109 (6)	4·5 (7)
C(3)	0·4125 (15)	0·5154 (10)	0·6662 (6)	4·1 (7)
C(4)	0·2293 (14)	0·5111 (9)	0·5666 (6)	4·1 (6)
C(5)	0·2074 (13)	0·5271 (10)	0·4812 (6)	4·2 (7)
O(1)	0·7226 (14)	0·25000	0·3340 (7)	5·9 (8)

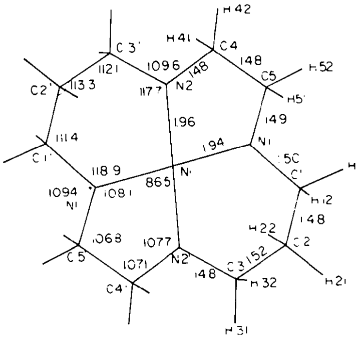

Fig. 1. Atom numbering, bond lengths and angles for the Ni(cyclam) (e.s.d.'s on bond lengths: Ni—N = 0·01 Å, C—C and C—N = 0·02 Å; on bond angles: N—Ni—N = 0·4°, others 1·0°).

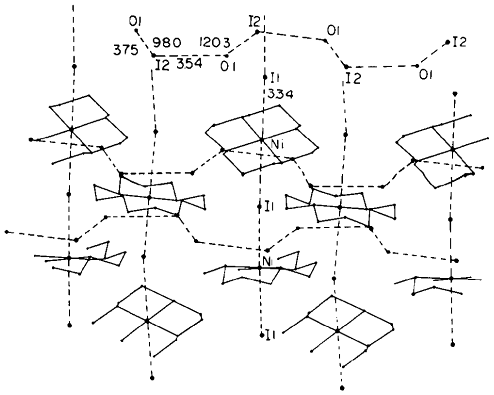

Fig. 2. The bridging iodides and I—O links (e.s.d.'s 0·01 Å and 1·0°).

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* The hydrogen-atom parameters, anisotropic thermal parameters and structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38526 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The ring structure is similar to type (*c*) *trans* III in the classification of Bosnich, Poon & Tobe (1965). A similar ring configuration is found in the *trans*-dichloronickel(III) ion (Ito, Sugimoto, Toriumi & Ito, 1981). The bond lengths and angles of the cyclam macrocycle are similar to those in Ni$^{\rm II}$(cyclam)Cl$_2$ (Bosnich, Mason, Pauling, Robertson & Tobe, 1965). The six-membered chelate ring has a chair configuration with C(2) 0·71 (1) Å above and Ni 0·77 (1) Å below the plane of N(1), C(1), C(3) and N(2)′. In the five-membered chelate ring C(4) is 0·36 (2) Å below and C(5) is 0·34 (2) Å above the plane of Ni, N(1) and N(2).

The other iodide [I(2)] is present in the lattice in an ionic form and is quite distinct from that associated with the metal. There is a possibility of hydrogen bonding between I(2) and the water molecule oxygen O [I(2)—O($x-1,y,z$) = 3·54 (1) Å and I(2)—O($x-\frac{1}{2},y,z$) = 3·75 (1) Å], forming a zigzag chain parallel to the plane of the Ni(cyclam) (Fig. 2).

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Etude Stéréochimique du Tricarbonyl[5a–9a-η-(méthyl-4 tétrahydro-3a,4,5,9b 1*H*-benz[*e*]indazolecarboxylate-3a de méthyle)]chrome(III), [Cr($C_{14}H_{16}N_2O_2$)(CO)$_3$]

Par René Mercier et Jacques Douglade

Laboratoire d'Electrochimie des Solides–ERA 810, *Université de Franche-Comté,* 25030 – *Besançon CEDEX, France*

et Joël Vebrel

Laboratoire de Chimie Appliquée, Université de Franche-Comté, 25030 – *Besançon CEDEX, France*

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Abstract. $M_r = 380{\cdot}3$, monoclinic, $P2_1/c$, $a = 18{\cdot}142$ (5), $b = 10{\cdot}973$ (4), $c = 8{\cdot}450$ (2) Å, $\beta = 98{\cdot}38$ (2)°, $Z = 4$, $V = 1664$ Å^3, $D_m = 1{\cdot}49$ (3), $D_x = 1{\cdot}52$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0{\cdot}75$ mm^{-1}, $T = 293$ K, $F(000) = 784$. Final $R_w = 0{\cdot}028$ for 1495 independent reflections. The formation of this molecule by cycloaddition of the CH_2N_2 dipole on the dipolarophilic ligand involves a twisting of the hexagonal ring so that the methyl group changes from an axial to an equatorial configuration. The decomplexation of this molecule gives rise to a novel diastereoisomeric pyrazoline.

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