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Refinement of the Structure of the Nickel Perchlorate Complex of 1,4-Diazacyclooctane, [Ni(Daco)$_2$](ClO$_4$)$_2$·2H$_2$O by Empirical Force-Field Methods

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Reinterpretation of the published X-ray diffraction data of Ni(Daco)$_2$(ClO$_4$)$_2$·2H$_2$O revealed molecular disorder not noticed before. Refinement of the disorder model converged to R = *0.10, assuming isotropic vibration for all atoms except Ni and Cl. The molecular mirror plane observed in the original analysis is shown to represent disorder symmetry. The observed molecular structure now corresponds to the model expected on chemical grounds.*

Introduction

As part of a program for the application of Empirical Force Field (EFF) calculations to coordination compounds [1–3], primarily complexes of polyamines, the literature has been searched for complexes with unusual conformational features. One particularly striking structure was that reported by Royer, Schievelbein, Kalyanaraman and Bertrand [4] for [Ni(Daco)$_2$][ClO$_4$]$_2$·2H$_2$O. (Daco = 1,5-diazacyclooctane). Complexes of Daco had been prepared by Musker and Hussain [5], who had, on the basis of models, suggested that both eight-membered rings had the chair-boat form. In contrast to this, Royer *et al.* [4] found "a planar eight-membered ring folded along the 1,5-axis (the N,N-axis)". The coordinates from this structure determination were used as trial coordinates in the EFF program used previously [1–3], and found that the above planar arrangement, with all hydrogens in the eclipsed position could not be maintained once refinement commenced. Instead the program produced as the lowest energy form the chair-boat form suggested by Musker and Hussain [5]. In a more recent structure analysis [6] of the complex with tetraphenylborate as anion, the expected conformation as predicted [5] was found, which further strengthened the suspicion that the reported [4] structure for the perchlorate salt was in error.

Two recent studies [7, 8] have characterised crystallographic disorder which introduces enhanced symmetry, readily interpretable as molecular symmetry. The 'high-symmetry' arrangement in each case represented a chemically impossible situation of the type described above for [Ni(Daco)$_2$]-[ClO$_4$]$_2$·2H$_2$O. This suggested that the methods developed in those investigations [7, 8] to resolve disorder could be used to refine a possible disordered arrangement of the present structure.

Structure Refinement

The method of molecular trial and error [7, 8] consists of using a molecular structure, optimized by the EFF method, as a rigid-body trial structure in a crystallographic least-squares refinement. In those instances [8] where the pseudo-molecular symmetry coincides with a crystallographic symmetry element, the corresponding symmetry operator is used to generate the second individual of the disordered pair from the refining coordinates of the first individual. Each atom is considered to have a site occupancy factor of one half.

In other cases [7] where the pseudo molecular symmetry is of local, non-crystallographic nature, it it necessary to refine two independent half-occupancy rigid bodies. Their final disposition reflects the presence of the local symmetry elements; either a mirror plane of a two-fold axis.

The trial-structure rigid body used in the present analysis was derived from the observed structure of the cation in the nickel tetraphenylborate complex [6], after optimisation using the EFF [1–3, 7, 8]. The resulting molecule and its mirror image were then positioned in the unit cell with half site occupancy to coincide optimally with the observed electron density as measured by the data obtained by Royer *et al.* [4]. The two individuals in the resulting disordered pair share the common nickel atom at the origin. A trial model for the perchlorate group was obtained by fitting the best regular tetrahedron to the atomic coordinates of Royer *et al.* [4].

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TABLE I. Crystal Data (From ref. 1).

Space group	$P\bar{1}$
a/Å	8.586(6)
b/Å	9.324(2)
c/Å	16.863(4)
α/deg	156.34(2)
β/deg	86.80(2)
γ/deg	92.86(2)
Vol/Å^3	540.95
Z	1
μ(Mo-K$_\alpha$)/cm^{-1}	11.25
No. of reflections	525
D_{calc}/gcm^{-3}	1.60
D_{meas}/gcm^{-3}	1.60(2)
Scan	$\omega - 2\theta$
Scan rate/° s^{-1}	0.167
Range/°	$0 \leqslant \Theta \leqslant 25$

Rigid-body refinement of the two cationic individuals pivoted at the special nickel position, was carried out in separare least-squares cycles, together with refinement of the perchlorate tetrahedron. The difference Fourier calculated after one pass showed up another tetrahedral arrangement centered at the position of the chlorine atom. Further refinement of the perchlorate group was hence carried out in terms of two rigid tetrahedral molecules with a common centroid and half occupancy of the oxygen atoms, in strict analogy with the cation. The refinement was based exclusively on the cell and diffraction data of Royer *et al.* as summarized in Table I. The program SHELX [9] was used for all crystallographic computing.

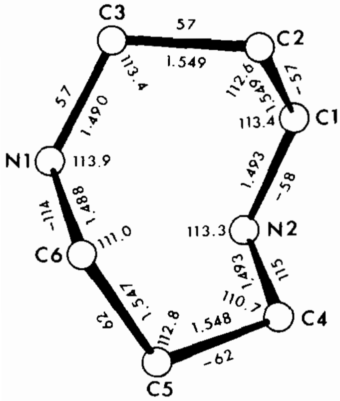

Fig. 1. Schematic diagram to define the atomic numbering and molecular geometry. The endocyclic torsion angles (degrees) are shown on the outside and bond lengths (Å) on the inside of the bonds. Bond angles (degrees) are shown at each atom.

TABLE II. Fractional Atomic Coordinates ($\times 10^4$) and Isotrpic Thermal Vibration Parameters (u $\times$ 10^3) with e.s.d. where Applicable in Parentheses. The e.s.d. of the rigid-body rotational parameters (rad $\times$ 10^3) are tabulated below pivot atoms. Only the Cl atom has unit site occupancy; all other s.o.f. = 0.5.

Atom	x/a	y/b	z/c	u
Ni	5000	5000	5000	a
σ(Rot)	11	25	28	
N1	4754	6482	6860	47(21)
N2	7262	4998	5093	33(16)
C1	7831	8669	7123	44(19)
C2	7259	10080	8668	76(27)
C3	5458	10070	8787	53(22)
C4	7727	2282	4309	41(18)
C5	6275	778	4018	65(24)
C6	5353	3679	5972	56(24)
N1*	4993	5854	6575	42(20)
N2*	7237	3977	4487	43(18)
C1*	7532	760	3352	41(18)
C2*	7123	1337	4541	51(21)
C3*	5407	2527	5316	93(36)
C4*	8115	7197	6361	52(21)
C5*	6980	10148	8176	78(29)
C6*	5990	8970	8328	63(24)
Cl	8553(10)	5049(28)	8498(16)	a
σ(Rot)	29	87	73	
O1	8520	7052	10218	193(44)
O2	8702	7325	8999	97(30)
O3	9808	2657	7279	87(19)
O4	7158	3102	7489	82(18)
O1*	8509	1547	6410	242(54)
O2*	9031	7414	9115	308(101
O3*	7071	5919	9265	187(38)
O4*	9609	5026	9099	260(58)
O5	8491(26)	4936(67)	13367(38)	61(9)

a. Anisotropic thermal vibration paramaters u_{ij} (Å^2 $\times$ 10^3) for the pivot atoms

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ni	18(3)	29(4)	25(4)	24(4)	2(3)	2(3)
Cl	67(9)	76(9)	78(10)	75(9)	0(7)	−1(7)

The refinement converged rapidly. To emphasize the disordered nature of the structure, anisotropic thermal vibration parameters were assigned to the central nickel and chlorine atoms only, since anisotropic refinement can mask disorder quite effectively, as in the Royer structure [4].

The final refined atomic and thermal parameters are in Table II, tabulated according to the numbering scheme of Royer *et al.* [4], shown in Fig. 1. Asterisks are used to identify atoms of the second individual of the disordered pair, related by the local mirror plane through the nickel atom, normal to the coordination plane and between the eight-membered rings.

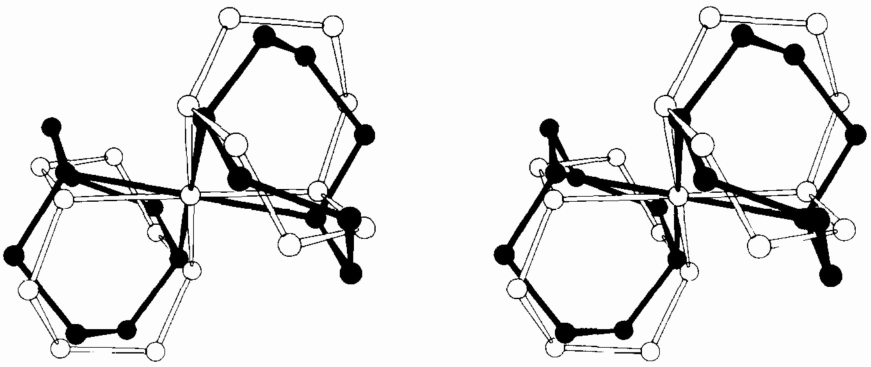

Fig. 2. Stereoscopic view of the disordered cation.

At the termination of unit weight refinement, residual electron density nowhere exceeded the 0.8 e Å^{-3} observed in the vicinity of the perchlorate groups. The observed temperature factors of the atoms in the Daco rings are all within a reasonable range, in striking contrast to the values obtained before [4]. The difference is particularly obvious in the case of the central of the three carbon atoms (C2, C5) forming the trimethylene bridge between the nitrogen donor atoms of the rings. This is exactly where the disorder model predicts the largest separation between corresponding atoms of the two individuals. The disordered arrangement is shown stereoscopically in Fig. 2. The molecular geometry of the coordinating Daco ring is shown in Fig. 1. This is the molecular structure as optimized by the EFF using potential constants defined before [1]. It should be noted that the ideal Ni–N bond length used here is the 1.89 Å appropriate to low-spin Ni(II). The crystallographic refinement consisted of optimizing the orientation of a pair of Daco rings and their centrosymmetrically related counterparts, with respect to the unit cell axes. The featureless difference Fourier calculated subsequently confirmed that this arrangement also satisfies the crystallographic data.

This geometry deviates drastically from that found before [4], especially with respect to conformation, here described by the endocyclic torsion angles. The values calculated for the average apparent molecule are ±83° and ±3°, corresponding to the flat NC_3N fragments.

The disordered pair of tetrahedral perchlorate groups with d(Cl–O) = 1.40 Å, also provides an improved description of the anions. The resolution of the disorder is not as good in the case of the perchlorate groups as for the cations, as indicated by the uniformly higher thermal vibration parameters and some unresolved electron density. The water molecules in the structure act as bridges between neighbouring cations through a set of O–H··N hydrogen bonds, as evidenced by the following O–N distances:

d(O–N1) = 2.91, d(O–N1*) = 3.06, d(O–N2) = 2.99, d(O–N2*) = 2.88 Å.

Discussion

The Daco structure [4] provided an important test of the EFF approach, and it is noteworthy that it was the EFF predicted structure which proved to be more reliable than the experimentally determined crystal structure. Of further interest is the ability of the EFF method to reproduce the coordination geometry around the metal ion. What is crucial here is that in most cases the 'ideal' or strain-free M–N bond length is considerably shorter than that actually observed [10]. The importance of this lies in the unusual behaviour of complexes, such as those of N-donor macrocycles, where the ligand field strengths and thermodynamic stability can be observed [10] and it is of prime importance whether the EFF calculations can reproduce the observed bond lengths in the Daco complex using the ideal Ni–N bond length of 1.89 Å for low-spin Ni(II).

The EFF generated coordination geometry around the Ni(II) can now be compared with the Royer structure [4], which should still provide a reasonable indication of bond lengths and angles, if one corrects for the fact that the two disordered individuals are inclined with respect to each other by about 11°, sharing a common nickel atom. This predicts that an averaged structure lying between the two individuals would have slightly shorter Ni–N lengths and a larger N–Ni–N angle in the chelate ring than predicted by EFF calculation. Thus, the EFF predicted Ni–N length of 1.955 Å, which gives a Ni–N length of 1.947 Å in the averaged structure, can be compared with that of 1.95 Å found previously [4]. It should be noted that this has been generated from the ideal Ni–N length of 1.89 Å by Van der Waals non-bonded repulsions between the hydrogens on the alkyl bridges of the Daco rings. The Daco complex is unusual in that, even though the coordination number of the metal ion is only four, the bulk of the ligands makes this a sterically crowded complex. The N–Ni–N angle in the chelate ring was predicted by the EFF calculations to be 88.6°, which in the averaged structure lying midway between the two disordered individuals should give an angle of 89.1°, compared to the observed angle [4] of 90.5(9)°. This confirms the excellent ability of the EFF program to reproduce coordination geometry around metal ions, which is of particular importance in that the stretching of M–N bonds indicated by the EFF program has considerable effect on the chemical properties of the complexes of small metal ions such as Co(III) and low-spin Ni(II) [10].

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