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Analysis of Disorder by Force-Field Calculation: The Structure of 1,4,7,11-Tetraazacyclotetradecane (Isocyclam)–Nickel Perchlorate, $C_{10}H_{24}N_4$–$Ni(ClO_4)_2$

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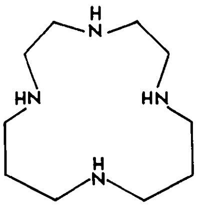
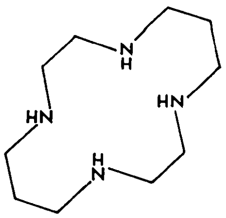
Abstract. $M_r = 457{\cdot}94$, $Pna2_1$, $a = 14{\cdot}215\,(6)$, $b = 12{\cdot}857\,(5)$, $c = 9{\cdot}907\,(4)$, $V = 1810{\cdot}6$ Å^3, $Z = 4$, $D_x = 1{\cdot}68$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 13{\cdot}3$ cm^{-1}, $F(000) = 952$, $T = 298$ K. The complex crystallizes from acetone with a disordered arrangement in space group $Pna2_1$. Inability to interpret fully the observed electron density in terms of two disordered individuals prompted the analysis of the complex by the methods of molecular mechanics. This produced chemically meaningful entities that were refined crystallographically as rigid bodies. The final structure is therefore at once optimized chemically, thermodynamically and crystallographically. The refinement of 39 crystallographic parameters with 1138 observations gave $R = 0{\cdot}13$.

Introduction. The 14-membered macrocyclic ligand 1,4,7,11-tetraazacyclotetradecane, isocyclam (I) (Sabatini & Fabbrizzi, 1979), forms complexes with metal salts with appreciably higher enthalpies of formation (Fabbrizzi, Micheloni & Paoletti, 1980) than the corresponding complexes of the more symmetrical 1,4,8,11 compound, cyclam (II). Similar effects were observed by Swisher, Dayhuff, Stuehr & Blinn (1980) with the suggestion that isocyclam was a tridentate rather than a tetradentate ligand in solution as well as in the solid state. This suggestion has never been tested crystallographically since suitable single crystals are not easily produced. The solitary crystal available for this study was of the $Ni(ClO_4)_2$ complex of isocyclam. When a disordered arrangement was found the special chemical interest of the material inspired this venture to resolve the disorder.



(I)



(II)

Experimental. Recrystallization from acetone yielded mainly polycrystalline material, together with one crystal, although of poor quality, still suitable for crystallographic analysis. Crystal needle-like but distinctly curved into a banana shape, mean diameter about 0·3 mm; to compensate for the odd crystal shape one hemisphere of data measured and merged into a unique orthorhombic set, data collection on a Philips PW1100 diffractometer with an incident-beam graphite-crystal monochromator for all reflections with $2 \leq \theta \leq 24°$, ω–2θ scans, scan width 1·1°, scan speed 0·037° s^{-1}, accurate cell constants obtained from a least-squares fit of the 2θ values of 25 reflections measured accurately on the diffractometer.

After correction of the intensity data for Lp only, an attempt was made to solve the structure by conventional heavy-atom procedures using the centrosymmetric space group *Pnma*. No progress was made and the non-centrosymmetric space group $Pna2_1$ had to be assumed. Recognizable features emerged readily and substantial fragments of the expected molecule could be discerned on electron-density maps. In fact, by careful assignment of peaks it was possible to interpret these in terms of a model of four coordination of Ni with (I). Not surprisingly, the perchlorate counterions were clearly disordered. Refinement of the trial structure did not converge and a complete shadow of the ligand (I) appeared coplanar with it on subsequent Fourier maps. Obviously the ligand was also disordered. On the assumption of statistical static disorder around the central Ni atom the eight half-weight N ligand atoms were fully resolved. Of the expected twenty C positions only seven could be recognized unambiguously. Eight more occurred as four doublet peaks, partially resolved into separate positions, but too closely spaced to allow independent refinement. The other five occurred in a region of utter confusion that resisted all attempts at disentanglement. This model was obtained at a level of refinement corresponding to $R = 0{\cdot}12$, and apart from the two separate coordination polyhedra of N atoms around a common Ni ion, both individuals representing disordered ligands were badly distorted geometrically. The measure of fit was clearly artificial and the atomic arrangement chemically virtually meaningless.

Refinement of the structure into a chemically meaningful arrangement was accomplished by using the methods of molecular mechanics to obtain a trial structure that could be refined as a rigid body. It was assumed that each of the individuals in the disordered

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arrangement represented a configuration with minimal steric strain. The first objective was to refine separately each of the two approximate structures obtained crystallographically with a suitable force field into the thermodynamically most probable structure. The resulting configurations can then again be refined crystallographically as separate rigid bodies with a common centroid. Since the interaction between H atoms is of decisive importance in force-field analyses it was necessary to calculate approximate positions for all hydrogen atoms before molecular refinement could commence. The force-field refinement was accomplished by means of the minimization program described by McDougall, Hancock & Boeyens (1978). The potential constants, force constants and strain-free bond parameters for the low-spin nickel complex as used in this analysis are collated in Table 1. All torsional interactions were described by the function $U_t = V/2(1 + \cos 3\varphi)$ for torsion angles $\varphi < 60°$, and $V = 5{\cdot}7 \times 10^{-21}$ J molecule^{-1}.

To prevent translation and rotation of the molecule during force-field refinement the number of atomic coordinates was reduced to $3n-6$ by keeping the first atom fixed, fixing y and z of the second atom and the z coordinate of the third atom; the second atom was chosen so as to ensure that $[\Delta y^2(1,2) + \Delta z^2(1,2)]^{1/2} < d°(1,2)$, the strain-free distance between the first two atoms, since only x_2 can be varied to reduce this separation if necessary. Another effect of limiting the degrees of freedom is that the orientation of a refining molecule changes with respect to the fixed parameters. To relate a molecular structure obtained by force-field refinement to the observed electron density therefore requires reorientation within the unit cell.

Table 1. *Non-bonded potential constants and force constants*

(*a*) Non-bonded potential constants for the Buckingham function: $U(r) = a \exp(-br) - c/r^6$

Interaction	$10^{18}a$(J molecule^{-1})	b(Å^{-1})	$10^{18}c$(J Å^6 molecule^{-1})
N–N	1295·0	4·55	1·39
C–N	1472·0	4·44	1·695
C–C	1640·0	4·32	2·07
N–H	195·0	4·32	0·69
C–H	218·0	4·2	0·84
H–H	45·8	4·08	0·341

(*b*) Force constants (k) for bond-length and bond-angle deformation with strain-free values (p^0) of the parameters

Parameter	$10^{-3}k$(Nm^{-1})	p^0(Å or rad)
Ni–N	0·68	1·9
N–C	6·0	1·48
C–C	5·0	1·54
N–H	6·16	0·99
C–H	5·0	1·08
Ni–N–C	0·2	1·911
Ni–N–H	0·1	1·911
N–Ni–N	0·3	1·571
N–C–C	0·9	1·911
N–C–H	0·65	1·911
C–N–C	0·9	1·911
C–N–H	0·56	1·911
C–C–C	1·0	1·911
C–C–H	0·65	1·911
H–C–H	0·52	1·911

Both of the distorted individuals obtained from the disordered crystallographic arrangement refined to identical configurations in separate force-field refinements.

In order to rotate the refined molecules into crystallographically meaningful orientations, least-squares planes were calculated through each refined molecule as well as the distorted starting arrangements first obtained crystallographically. Rotation through 180° around the bisector between the plane normals of refined and starting structures returns the refined molecule to the mean plane through the observed electron density. Comparison of refined and starting structures on molecular axes then enables a further rotation of the refined structure about the common plane normal to achieve optimum coincidence of refined and starting atomic coordinates. This procedure was followed for both individuals to yield a trial structure for rigid-body refinement. To ensure meaningful refinement of the perchlorate counter ions, each of these disordered arrangements was approximated by two ideal ClO_4 tetrahedra with bond lengths of 1·48 Å. This completed the trial structure.

Final rigid-body refinement commenced at $R = 0{\cdot}18$. In the first step the three central atoms were fixed in space and the separate individuals centred at each fixed atom were refined as rigid bodies in separate least-squares cycles. The was necessary to optimize the relative orientation of individuals constituting one disordered arrangement around each of the central atoms. In the final step these disordered arrangements were refined as rigid bodies, free to translate within the unit cell. This ensured optimal positioning without distorting the relationship between individuals. During this process anisotropic thermal vibration was assumed for the central atoms only. All other atoms were assigned site occupancy factors of 0·5 and common isotropic temperature factors within each disordered unit. The final fit as defined by the agreement index $R = 0{\cdot}13$ can certainly be improved by relaxing the constraints in refinement procedure. However, the structure at the present state of refinement has several carbon atoms in almost exact overlap. Any unrestricted refinement of atomic coordinates must therefore lead to molecular distortions. Unit weights were used throughout.

The refinement described here consists of the adjustment of only 39 parameters using 1138 observations and constitutes an overdetermination of almost 30 to 1. The final structure is also the thermodynamically most probable and hence crystallographically correct in a trial-and-error sense. All crystallographic computations were carried out with *SHELX* (Sheldrick, 1978).

Discussion. The final atomic coordinates are in Table 2* and the atomic numbering scheme is shown in Fig 1.

The Ni–isocyclam complex ion has a molecular mirror plane through N(1)–Ni–N(3). The asymmetric unit contains, apart from perchlorate groups, two ligands, statistically disordered around the common Ni atom, and related by a local twofold axis in the plane containing C(5), Ni and C(10). This is illustrated schematically in Fig. 2.

The molecular geometry is summarized in Fig 1. A molecular mirror plane contains N(1), H[N(1)], Ni, N(3) and H[N(3)]. Bond angles and endocyclic torsion angles between non-hydrogen atoms are shown in the right half of the drawing. Bond lengths and exocyclic torsion angles are shown on the left. A stereoscopic drawing is shown in Fig. 3. The conformations of the six- and five-membered rings were calculated in terms of

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38454 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Atomic coordinates and anisotropic thermal parameters*

(*a*) Fractional atomic coordinates. Asterisks are used to distinguish between individuals related by rotational disorder around the same (ordered) central atom

	x	y	z		x	y	z
Ni	0·1239	0·2067	0·0000				
N(1)	0·0934	0·3571	0·0277	N(1)*	0·0664	0·2694	0·1654
N(2)	0·1627	0·2278	−0·1909	N(2)*	0·1390	0·0676	0·0852
N(3)	0·1642	0·0614	−0·0268	N(3)*	0·1716	0·1397	−0·1652
N(4)	0·1616	0·1856	0·1915	N(4)*	0·0519	0·2983	−0·1244
C(1)	0·0407	0·4058	−0·0860	C(1)*	0·1144	0·2401	0·2939
C(2)	0·0976	0·4068	0·2187	C(2)*	0·1093	0·1222	0·3227
C(3)	0·1045	0·2962	−0·2781	C(3)*	0·1743	0·0620	0·2261
C(4)	0·1718	0·1241	−0·2558	C(4)*	0·2007	0·0035	−0·0031
C(5)	0·2192	0·0516	−0·1533	C(5)*	0·1713	0·0249	−0·1496
C(6)	0·2183	0·0245	0·0917	C(6)*	0·1155	0·1727	−0·2839
C(7)	0·1703	0·0719	0·2160	C(7)*	0·0932	0·2883	−0·2618
C(8)	0·1025	0·2323	0·2993	C(8)*	0·0427	0·4104	−0·0904
C(9)	0·0960	0·3512	0·2826	C(9)*	−0·0049	0·4248	0·0480
C(10)	0·0400	0·3794	0·1543	C(10)*	0·0595	0·3852	0·1623
H[N(1)]	0·1562	0·3901	0·0343	H[N(1)]*	0·0019	0·2398	0·1658
H[N(2)]	0·2263	0·2590	−0·1801	N[N(2)]*	0·0740	0·0398	0·0813
H[N(3)]	0·1038	0·0231	−0·0343	H[N(3)]*	0·2371	0·1660	−0·1722
H[N(4)]	0·2250	0·2175	0·1933	H[N(4)]*	−0·0112	0·2653	−0·1234
H^1[C(1)]	0·0249	0·4860	−0·0614	H^1[C(1)]*	0·0806	0·2794	0·3775
H^2[C(1)]	−0·0248	0·3651	−0·1014	H^2[C(1)]*	0·1870	0·2645	0·2905
H^1[C(2)]	0·1674	0·4381	−0·2016	H^1[C(2)]*	0·0376	0·0950	0·3134
H^2[C(2)]	0·0621	0·4560	−0·2908	H^2[C(2)]*	0·1324	0·1084	0·4252
H^1[C(3)]	0·0346	0·2639	−0·2883	H^1[C(3)]*	0·2446	0·0936	0·2318
H^2[C(3)]	0·1359	0·3011	−0·3773	H^2[C(3)]*	0·1766	−0·0185	0·2582
H^1[C(4)]	0·2135	0·1288	−0·3471	H^1[C(4)]*	0·1934	−0·0783	0·0197
H^2[C(4)]	0·1028	0·0936	−0·2800	H^2[C(4)]*	0·2735	0·0265	0·0101
H^1[C(5)]	0·2194	−0·0279	−0·1891	H^1[C(5)]*	0·2198	−0·0113	−0·2198
H^2[C(5)]	0·2908	0·0775	−0·1379	H^2[C(5)]*	0·1014	−0·0059	−0·1653
H^1[C(6)]	0·2901	0·0524	0·0873	H^1[C(6)]*	0·0501	0·1300	−0·2886
H^2[C(6)]	0·2183	−0·0596	0·0970	H^2[C(6)]*	0·1545	0·1613	−0·3766
H^1[C(7)]	0·1012	0·0376	0·2271	H^1[C(7)]*	0·1578	0·3324	−0·2681
H^2[C(7)]	0·2113	0·0565	0·3056	H^2[C(7)]*	0·0447	0·3155	−0·3379
H^1[C(8)]	0·1333	0·2154	0·3968	H^1[C(8)]*	0·0004	0·4486	−0·1664
H^2[C(8)]	0·0325	0·1993	0·2965	H^2[C(8)]*	0·1113	0·4466	−0·0889
H^1[C(9)]	0·0600	0·3830	0·3693	H^1[C(9)]*	−0·0178	0·5069	0·0633
H^2[C(9)]	0·1658	0·3849	0·2784	H^2[C(9)]*	−0·0717	0·3845	0·0505
H^1[C(10)]	−0·0257	0·3369	0·1532	H^1[C(10)]*	0·1290	0·4183	0·1508
H^2[C(10)]	0·0242	0·4616	0·1595	H^2[C(10)]*	0·0303	0·4127	0·2565
Cl(1)	−0·1379	0·1396	0·0024	Cl(2)	0·3670	0·2153	0·4828
O(1)	−0·2278	0·0943	−0·0451	O(5)	0·2759	0·2700	0·4680
O(2)	−0·1319	0·2495	−0·0416	O(6)	0·3942	0·1690	0·3517
O(3)	−0·1340	0·1345	0·1516	O(7)	0·4400	0·2902	0·5262
O(4)	−0·0583	0·0802	−0·0554	O(8)	0·3578	0·1321	0·5851
O(1)*	−0·2045	0·0512	0·0103	O(5)*	0·4233	0·3107	0·4618
O(2)*	−0·1689	0·2231	0·0951	O(6)*	0·2748	0·2433	0·5421
O(3)*	−0·1357	0·1799	−0·1376	O(7)*	0·4177	0·1446	0·5755
O(4)*	−0·0429	0·1039	0·0415	O(8)*	0·3521	0·1627	0·3516

(*b*) Anisotropic thermal vibration parameters (Å^2 × 10^3) of ordered atoms and common isotropic parameters for the disordered atoms, with standard deviations in parentheses. The U_{ij} are coefficients in the expression

$$T = \exp\left[-2\pi^2 \textstyle\sum_i \sum_j h_i h_j a_i^* a_j^* U_{ij}\right].$$

Atom or group	U_{11} or $U_{\rm iso}$	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ni	71 (1)	81 (1)	75 (1)	−5 (3)	−1 (3)	0 (1)
Ligand	126					
Cl(1)	70	124 (4)	117 (4)	−43 (7)	−16 (6)	−24 (3)
Ion 1	136 (5)					
Cl(2)	83 (4)	172 (7)	301 (12)	0 (18)	1 (12)	5 (5)
Ion 2	198 (7)					

their parameters of puckering (Cremer & Pople, 1975; Boeyens, 1978). They have the conformations $^1C_4$ and $^4T_3$ respectively.

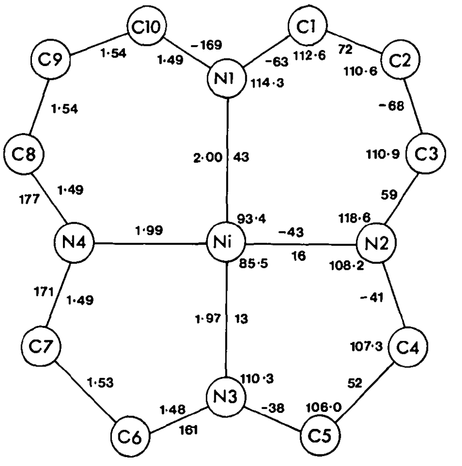

Fig. 1. Schematic drawing showing endocyclic torsion angles and bond angles (°) on the right of the mirror plane through N(1)–Ni–N(3) and exocyclic torsion angles (°) and bond lengths (Å), on the left. The angles N(2)–Ni–N(4) = 148·3° and N(1)–Ni–N(3) = 175·7°.

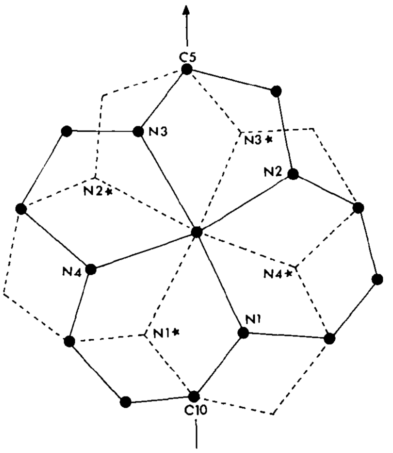

Fig. 2. Projection of the disordered ligand on the mean plane.

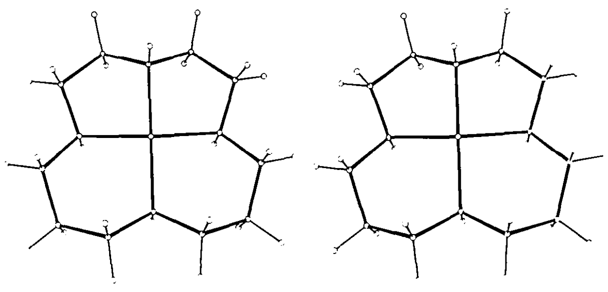

Fig. 3. Stereoscopic drawing of the Ni–isocyclam complex ion.

Table 3. *Close contacts between perchlorate groups and hydrogen atoms of the ligand*

Asterisks are used to distinguish between different individuals in a disordered unit. Atoms distinguished by a prime are at equivalent position $\frac{1}{2}+x, \frac{1}{2}-y, z$.

Contact	Distance (Å)
O′(1)–H[N(1)]	1·84
O(4)*–H[N(2)]*	1·90
O(2)–H[N(4)]*	1·91
O′(2)*–H[N(4)]	1·95
O′(1)*–H[N(1)]	2·13
O′(1)–H[N(2)]	2·40

The steric strain in the Ni–isocyclam complex ion as calculated during the force-field analysis amounts to 51·9 kJ mol^{-1} with contributions of 7·5, 18·4 15·9 and 10·1 kJ mol^{-1} from bond deformations, non-bonded interactions, angle deformations and torsional interactions, respectively. This aspect will be discussed more fully elsewhere.

Comparison of the two independent perchlorate ions reveals a significant difference in their vibrational behaviour. The perchlorate O atoms associated with Cl(2) have thermal vibration parameters that are substantially higher than those of the Cl(1) perchlorate groups. Only the O atoms of the latter groups approach the N–H groupings sufficiently closely to represent hydrogen bonding. These close contacts are summarized in Table 3. The cations and anions distinguished by asterisks do not necessarily occur together in the same unit cell. In any case, the more rigid behaviour of the Cl(1) perchlorate groups is quite clearly due to hydrogen bonding with the disordered ligand.

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