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Structure of {2,12-Dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-triene}(ethylenediamine)nickel(II) Diperchlorate

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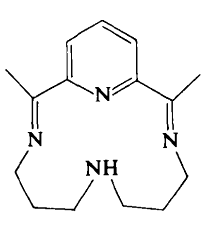
Abstract

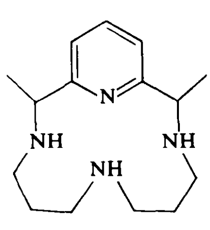
Crystals of the title compound are tetragonal, space group $I4_1/a$, $Z = 16$, with $a = 16{\cdot}857\,(9)$, $c = 36{\cdot}076\,(21)$ Å. 1439 independent reflections above background have been measured on a diffractometer and refined to $R = 0{\cdot}069$. The Ni atom in the discrete cations has a distorted octahedral environment being bonded to two N atoms of ethylenediamine [2·162 (13), 2·096 (14) Å] and four N atoms of the macrocycle [2·164 (12), 2·013 (11), 2·158 (12), 2·133 (12) Å]. The macrocycle, which is planar in other complexes, is folded to allow the ethylenediamine to coordinate to the metal in a bidentate fashion. These Ni—N(macrocycle) bond lengths are on average 0·07 Å longer than those observed in similar complexes where the macrocycle is planar. There are four independent perchlorate anions in the asymmetric unit, three of which are disordered.

Introduction

The condensation of 2,6-pyridinediyl diacetate with 3,3′-diaminodipropylamine in the presence of Ni^{II} salts produces the macrocyclic complex $[NiL^1]^{2+}$ which was first isolated as the perchlorate salt (Curry & Busch, 1964). Reduction of $[NiL^1]^{2+}$ under mild conditions gave $[NiL^2]^{2+}$ (Karn & Busch, 1969). Two forms of the complex were prepared, a red β form and a yellow α form. These have been characterized by single-crystal structure determinations as being respectively a *meso* isomer in which the methyl groups are on the same side of the ring (Drew & Hollis, 1980*a*) and a racemic form in which the methyl groups are on opposite sides of the ring (Dewar & Fleischer, 1969). In both structures, the macrocycle L^2 forms a planar girdle around the metal atom with the NiN_4 atoms planar within 0·11 Å. The structure of β-$[NiL^2(NO_2)_2]\cdot\frac{1}{2}H_2O$ has also been determined (Drew & Hollis, 1980*b*) and once more the macrocycle forms a planar girdle around the Ni atom. However, this time the metal is six-coordinate, being bonded to two nitrite ions (one through nitrogen and the other through oxygen) in axial positions.



L^1



L^2

Karn & Busch (1969) also prepared a series of complexes of general formula $[NiL^2X_2]$, with X a unidentate ligand such as Cl^-, Br^-, I^-, $HCOO^-$, N_3^-, OH_2, NH_3, and these presumably have octahedral structures equivalent to that observed in the dinitrite complex. Of particular interest was another complex, $[NiL^2(en)]^{2+}$, en = ethylenediamine, as in this complex the macrocycle L^2 must fold in order to allow the ethylenediamine ligand to coordinate to the Ni atom in the usual bidentate manner. Accordingly, we have prepared this complex, following the published method, and report here its crystal and molecular structure.

Experimental

Crystal data

$[Ni(C_2H_8N_2)(C_{15}H_{26}N_4)](ClO_4)_2$, $C_{17}H_{34}N_6Ni^{2+}.2ClO_4^-$, $M_r = 579{\cdot}9$, tetragonal, $a = 16{\cdot}857\,(9)$, $c = 36{\cdot}076\,(21)$ Å, $U = 10\,251{\cdot}3$ Å^3, $Z = 16$, $d_m = 1{\cdot}57\,(2)$, $d_c = 1{\cdot}50$ Mg m^{-3}, $F(000) = 5056$, $\lambda(\text{Mo } K\alpha) = 0{\cdot}7107$ Å, $\mu = 1{\cdot}00$ mm^{-1}. Space group $I4_1/a$ from the systematic absences hkl, $h + k + l = 2n + 1$, $hk0$, $h = 2n + 1$, $00l$, $l \neq 4n$.

A crystal of approximate size 0·5 × 0·4 × 0·6 mm was mounted with the c axis parallel to the instrument axis of a General Electric XRD5 diffractometer which was used to measure diffraction intensities, by a stationary-crystal–stationary-counter method using 10 s counts, and cell dimensions, by the least-squares

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† Deceased.

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refinement of some 15 high-angle data. The apparatus was equipped with a manual goniostat, scintillation counter and pulse-height discriminator. Several standard reflections monitored during the course of the experiment showed no significant change in intensity. 2390 independent reflections were measured for $2\theta < 40°$ of which 1441 with $I > 2\sigma(I)$ were used in the subsequent refinement. No absorption or extinction corrections were applied.

Structure determination

The positions of the Ni atoms were obtained from the Patterson map and those of the remaining atoms in the cation from Fourier maps. These were four independent Cl atoms in positions 16(*f*), 4(*a*), 8(*e*) and 4(*b*). Of these, only Cl(2) in 4(*a*) gave rise to an ordered perchlorate. For Cl(1), we refined two tetrahedra of O atoms with one shared atom, O(11), with population parameters 0·75 and 0·25. The electron density around Cl(3) was very complicated. Cl(3) is on a twofold axis and we included two tetrahedra both containing O(31) and O(31$^{\mathrm{III}}$) and two other atoms. Attempts to split O(31) into two in order to obtain two independent ideal tetrahedra were not successful, presumably because of complications introduced by the twofold axis. For Cl(4) two tetrahedra were invoked, each described by two O atoms given occupancy factors of 0·5. Details of these proposed tetrahedra are given in the Supplementary Publication.* This model may not represent

Table 1. *Atomic coordinates* ($\times 10^4$) *with estimated standard deviations in parentheses*

	x	y	z	U (Å^2 $\times 10^3$)*
Ni	2211 (1)	1138 (1)	−708 (0)	44 (2)
N(3)	1285 (7)	446 (8)	−969 (3)	52 (15)
C(4)	587 (9)	334 (10)	−726 (5)	71 (20)
C(5)	665 (11)	867 (9)	−377 (4)	71 (19)
N(6)	1399 (7)	1105 (7)	−299 (3)	42 (14)
C(7)	1540 (10)	1488 (9)	16 (5)	60 (19)
C(8)	2395 (10)	1676 (9)	82 (4)	53 (18)
N(9)	2801 (8)	1816 (7)	−282 (3)	54 (15)
C(10)	3681 (10)	1747 (11)	−260 (5)	62 (22)
C(11)	3941 (10)	895 (12)	−183 (5)	84 (23)
C(12)	3768 (9)	302 (11)	−492 (5)	76 (21)
N(13)	2894 (7)	133 (7)	−543 (3)	58 (14)
C(14)	2817 (10)	−571 (10)	−784 (5)	80 (21)
C(15)	1976 (11)	−830 (10)	−861 (5)	70 (21)
C(16)	1513 (10)	−329 (10)	−1126 (4)	58 (19)
C(17)	−211 (11)	438 (17)	−930 (6)	106 (28)
C(18)	37 (11)	1008 (10)	−150 (5)	85 (21)
C(19)	162 (12)	1415 (11)	177 (6)	110 (24)
C(20)	931 (13)	1675 (10)	264 (5)	95 (23)
C(21)	2548 (12)	2351 (11)	363 (5)	78 (24)
N(1)	1669 (8)	2207 (7)	−921 (4)	59 (16)
N(2)	2914 (8)	1303 (7)	−1181 (4)	56 (16)
C(1)	2172 (12)	2521 (9)	−1226 (5)	84 (21)
C(2)	2492 (11)	1848 (12)	−1441 (5)	89 (23)
Cl(1)	1695 (3)	87 (3)	2913 (1)	67 (5)
O(11)	1546 (10)	−635 (10)	2766 (5)	173 (6)
O(12)^a	2303 (12)	487 (12)	2712 (6)	136 (8)
O(13)^a	974 (11)	573 (12)	2840 (6)	145 (7)
O(14)^a	1819 (13)	147 (12)	3289 (5)	145 (7)
O(15)^b	2439 (20)	−120 (21)	3129 (10)	74 (11)
O(16)^b	1973 (22)	586 (18)	2621 (9)	52 (10)
O(17)^b	1194 (34)	369 (34)	3170 (16)	216 (21)
Cl(2)	5000	2500	3750	62 (4)
O(21)	608 (9)	2777 (9)	1018 (4)	148 (5)
Cl(3)	0	7500	1707 (2)	100 (8)
O(31)	601 (10)	7790 (10)	1911 (5)	164 (6)
O(32)^c	204 (20)	6883 (21)	1471 (10)	150 (11)
O(33)^b	0	7500	1308 (11)	106 (10)
O(34)^b	−579 (25)	8327 (25)	1687 (11)	72 (11)
Cl(4)	5000	7500	1250	73 (4)
O(41)^c	4998 (23)	6998 (20)	906 (10)	173 (12)
O(42)^c	5179 (17)	8322 (18)	1169 (9)	127 (9)

Population parameters: (*a*) 0·75, (*b*) 0·25, (*c*) 0·50.

* $\bar{U}$ for atoms refined anisotropically, U for atoms refined isotropically.

Table 2. *Molecular dimensions*

Distances are in Å, angles in deg.

Ni—N(3)	2·164 (12)	Ni—N(13)	2·133 (12)
Ni—N(6)	2·013 (11)	Ni—N(1)	2·162 (13)
N—N(9)	2·158 (12)	Ni—N(2)	2·096 (14)
N(3)—Ni—N(6)	79·3 (4)	N(9)—Ni—N(1)	90·4 (5)
N(3)—Ni—N(9)	158·1 (4)	N(13)—Ni—N(1)	171·7 (5)
N(6)—Ni—N(9)	78·8 (5)	N(3)—Ni—N(2)	97·2 (5)
N(3)—Ni—N(13)	94·7 (5)	N(6)—Ni—N(2)	169·9 (5)
N(6)—Ni—N(13)	98·1 (5)	N(9)—Ni—N(2)	104·4 (5)
N(9)—Ni—N(13)	88·5 (4)	N(13)—Ni—N(2)	91·6 (5)
N(3)—Ni—N(1)	89·4 (5)	N(1)—Ni—N(2)	80·7 (5)
N(6)—Ni—N(1)	89·8 (5)		
N(3)—C(4)	1·479 (20)	C(10)—C(11)	1·527 (27)
N(3)—C(16)	1·475 (21)	C(11)—C(12)	1·525 (26)
C(4)—C(5)	1·552 (23)	C(12)—N(13)	1·512 (19)
C(4)—C(17)	1·543 (25)	N(13)—C(14)	1·477 (21)
C(5)—N(6)	1·331 (22)	C(14)—C(15)	1·509 (25)
C(5)—C(18)	1·359 (25)	C(15)—C(16)	1·495 (24)
N(6)—C(7)	1·328 (21)	C(18)—C(19)	1·381 (27)
C(7)—C(8)	1·495 (24)	C(19)—C(20)	1·404 (29)
C(7)—C(20)	1·398 (27)	N(1)—C(1)	1·486 (23)
C(8)—N(9)	1·500 (19)	N(2)—C(2)	1·493 (23)
C(8)—C(21)	1·546 (24)	C(1)—C(2)	1·476 (26)
N(9)—C(10)	1·490 (22)		
Ni—N(3)—C(4)	112·6 (9)	Ni—N(9)—C(10)	117·1 (10)
Ni—N(3)—C(16)	117·2 (9)	C(8)—N(9)—C(10)	113·3 (12)
C(4)—N(3)—C(16)	108·8 (12)	N(9)—C(10)—C(11)	111·6 (14)
N(3)—C(4)—C(5)	109·8 (13)	C(10)—C(11)—C(12)	115·4 (15)
N(3)—C(4)—C(17)	113·3 (15)	C(11)—C(12)—N(13)	113·5 (12)
C(5)—C(4)—C(17)	113·3 (15)	Ni—N(13)—C(12)	114·2 (10)
C(4)—C(5)—N(6)	115·1 (14)	Ni—N(13)—C(14)	115·2 (9)
C(4)—C(5)—C(18)	121·6 (15)	C(12)—N(13)—C(14)	108·0 (12)
N(6)—C(5)—C(18)	123·0 (14)	N(13)—C(14)—C(15)	115·0 (14)
Ni—N(6)—C(5)	119·0 (9)	C(14)—C(15)—C(16)	116·4 (15)
Ni—N(6)—C(7)	119·5 (10)	N(3)—C(16)—C(15)	113·0 (12)
C(5)—N(6)—C(7)	119·6 (13)	C(5)—C(18)—C(19)	118·9 (17)
N(6)—C(7)—C(8)	114·3 (14)	C(18)—C(19)—C(20)	119·1 (18)
N(6)—C(7)—C(20)	121·7 (16)	C(7)—C(20)—C(19)	117·7 (17)
C(8)—C(7)—C(20)	123·9 (16)	Ni—N(1)—C(1)	108·6 (10)
C(7)—C(8)—N(9)	109·5 (13)	Ni—N(2)—C(2)	108·9 (10)
C(7)—C(8)—C(21)	114·9 (14)	N(1)—C(1)—C(2)	108·9 (13)
N(9)—C(8)—C(21)	112·5 (13)	N(2)—C(2)—C(1)	108·5 (14)
Ni—N(9)—C(8)	109·3 (9)		

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* See deposition footnote.

the complete picture of the disorder, but we made innumerable attempts to explain the electron density around these Cl atoms and we consider our explanation to be as valid as any other.

For the cation, H atoms were introduced in tetrahedral or trigonal positions where appropriate. Their positional parameters were fixed but their thermal parameters were allowed to refine, which they did to convergence at reasonable values. Methyl H atoms were searched for by refining rigid groups; only those on C(21) were located and refined successfully. The final *R* value obtained by refining non-hydrogen atoms anisotropically was 0·069. Calculations were carried out on the CDC 7600 computer at the University of Manchester Computer Centre using *SHELX* 76 (Sheldrick, 1976). Scattering factors and dispersion corrections were taken from *International Tables for X-ray Crystallography* (1974). In the final cycle of refinement all shifts were less than 0·05σ. The difference Fourier map showed no significant peaks and the zero-weighted reflections gave no serious discrepancies. The final positions and molecular dimensions are given in Tables 1 and 2.*

Discussion

The structure of the cation is shown in Fig. 1. There are no contacts between the cation and the anions shorter than the sum of the van der Waals radii. The cation has no imposed symmetry. As expected, the Ni atom is bonded to the four N atoms of the macrocycle L^2 together with the two N atoms of the ethylenediamine ligand. The macrocycle L^2 is folded such that while Ni, N(3), N(6), N(9) are coplanar (maximum deviation of an atom from the plane <0·01 Å), the remaining donor atom N(13) is 2·11 Å from this plane. The Ni—N(3), N(6), N(9) bond lengths are 2·164 (12), 2·013 (11), 2·158 (12) Å, on average about 0·07 Å longer than those observed in the six-coordinate complex [NiL^2(NO$_2$)(ONO)] (Drew & Hollis, 1980*b*).

The folding of the macrocycle is described by the torsion angles, Table 3, which are compared with those found in the square-planar [NiL^2]$^{2+}$ complex; these latter are in fact very similar to those found in [NiL^2(NO$_2$)(ONO)]. First, it is clear that the part of the macrocycle from N(3) to N(9) through N(6) and including the pyridine ring is very similar to that observed in the planar structure. The first change in torsion angles between the two structures is apparent at C(16) as the C(16)—N(3)—C(4)—C(5) torsion angle is 141° rather than 164°. This is the only sign of strain in the whole folding operation, as around the N(3)—C(4) bond there are two H—N—C—C torsion angles of *ca* 24° and Ni—N(3)—C(4)—C(5) is 9·5°. From here unstrained angles of −79 (1), −72 (1) and 74 (1)° around the N(3)—C(16), C(16)—C(15) and C(15)—C(14) bonds, respectively, lead to N(13) in a position 2·11 Å above the NiN$_3$ plane. The geometry of this Ni, N(3), N(13), C(14), C(15), C(16) ring is a very flattened chair with C(15) only 0·17 Å from the NiN$_2$ plane. Torsion angles around the C(12)—N(13) and N(13)—C(14) bonds are comparable to those in [NiL^2]$^{2+}$ at *ca* 180°. The other six-membered ring containing Ni, N(13), N(9) is much less strained as C(11) is 0·74 Å from the NiN$_2$ plane. It is noticeable that the C(7)—C(8)—N(9)—C(10) torsion angle is −161 (1)°, much closer to 180° than the analogous angle about N(3)—C(4), again emphasizing that this side of the macrocycle is more strain-free.

Despite these variations in the torsion angles described above, the overall conformation of the macrocycle approximates to C_s symmetry, as indeed it does in [NiL^2]$^{2+}$. This is shown clearly by the torsion

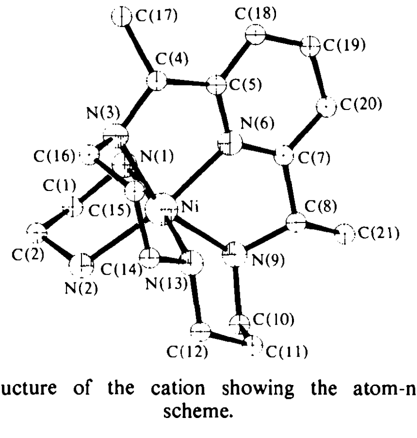

Fig. 1. Structure of the cation showing the atom-numbering scheme.

Table 3. *Torsion angles* (°)

	Title compound	[NiL^2]$^{2+}$
C(7)—C(8)—N(9)—C(10)	−161 (1)	−153
C(21)—C(8)—N(9)—C(10)	70 (1)	79
C(8)—N(9)—C(10)—C(11)	68 (1)	−174
N(9)—C(10)—C(11)—C(12)	66 (1)	−65
C(10)—C(11)—C(12)—N(13)	−69 (1)	68
C(11)—C(12)—N(13)—C(14)	−167 (1)	172
C(12)—N(13)—C(14)—C(15)	179 (1)	−179
N(13)—C(14)—C(15)—C(16)	74 (1)	−73
C(14)—C(15)—C(16)—N(3)	−72 (1)	70
C(15)—C(16)—N(3)—C(4)	−79 (1)	177
C(16)—N(3)—C(4)—C(17)	−91 (1)	−72
C(16)—N(3)—C(4)—C(5)	141 (1)	164
N(3)—C(4)—C(5)—N(6)	−21 (1)	−26
N(9)—C(8)—C(7)—N(6)	32 (1)	18
N(1)—C(1)—C(2)—N(2)	−55 (1)	–

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* Lists of structure factors, anisotropic thermal parameters, H atom positions and thermal parameters, dimensions of the perchlorate ions and details of the least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35489 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

angles in Table 3. The variations from C_s symmetry are also illustrated by planes 1 and 5.* From plane 5, the pyridine ring plane, we note that N(3) is 0·22 and N(9) 0·62 Å above the plane. The two methyl groups C(17) and C(21) are also on this (positive) side of the plane. N(13) is −1·42 (1) Å from the plane, however, indicating that the macrocycle folds such that N(13) approaches the two H atoms on C(4) and C(8) and avoids the two methyl groups. Karn & Busch (1969) were not able to prepare racemic $[NiL^2(en)]^{2+}$, the α form in which one of the methyl groups would have to be the same side as N(13), and from models they concluded that the racemic form of the macrocycle could not fold without one of the methyl groups becoming too close to other atoms in the macrocycle. While models can be misleading, support for this view comes from the present structure where close contacts exist between H(4) and H(8) and several atoms [*e.g.* H(4)···C(15) 2·66, H(8)···C(11) 2·65 Å] and clearly if (as in the racemic form) H(4) or H(8) were replaced by a methyl group the distances would be too short. Thus, it seems likely that Karn & Busch (1969) are correct in their view.

The Ni atom is 0·52 Å from the pyridine ring plane although it is coplanar with N(3), N(6) and N(9) (see plane 1).* Indeed, the angle between the pyridine ring and the NiN_3 plane is 16·1° and it can be presumed that this angle is distorted from 0° by the steric effects of the fold in the macrocycle. Thus, the fold leads to a larger 'hole' and subsequently to longer Ni—N bond lengths than in $[NiL^2(NO_2)(ONO)]$ where the macrocycle is planar. An additional (but not independent) reason for the lengthening (about 0·07 Å in all four bonds) could involve the en ligand. For, if the Ni atom were more strongly bonded to the macrocycle, then contacts between the en ligand and the macrocycle L^2 would be decreased. As it is, there are several H···H contacts between the two ligands of *ca* 2·2 Å. The Ni—N(en) bond lengths are Ni—N(1) 2·162 (13), Ni—N(2) 2·096 (14) Å; N(1) is *trans* to N(13) and it may be that the Ni—N(1) bond length is thus more susceptible to repulsions from the macrocycle atoms than is Ni—N(2).

There are no strong contacts between the cations and anions. The shortest distance from a non-hydrogen atom in the cation to a perchlorate oxygen is 3·02 Å from N(1) to $O(13^{V})$. There are several contacts of this length which may indicate weak hydrogen bonds of the type N—H···O, but clearly, in view of the disorder among the perchlorate anions, these interactions must be very weak.

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* See deposition footnote.

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