Crystal and Molecular Structure of *catena*-5,7,12,14-Tetramethyl-5-*aci*-nitromethyl-1,4,8,11-tetraazacyclotetradec-11-enenickel(II) Perchlorate Dihydrate†

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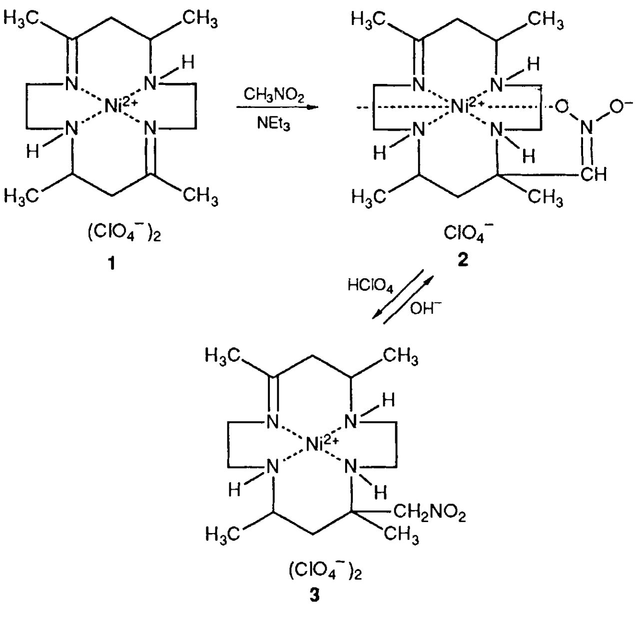
The crystal and molecular structure of *catena*-5,7,12,14-tetramethyl-5-*aci*-nitromethyl-1,4,8,11-tetraazacyclotetradec-11-enenickel(II) perchlorate dihydrate **2** has been determined on the basis of X-ray data. The crystals are orthorhombic, space group $Pna2_1$ ($Z = 4$) with cell dimensions a = 18.133(6), b = 10.285(3) and c = 12.212(4) Å. The structure was solved by direct methods, and the atomic parameters were refined anisotropically using 1920 independent reflections by a full-matrix least-squares procedure giving R = 0.047. An octahedral configuration of the nickel(II) co-ordination sphere was found to consist of the macrocyclic N_4 ring occupying the equatorial plane, and two apical *aci*-nitro groups (one belonging to a neighbouring ligand molecule). Thus, the bridging *aci*-nitromethyl results in a linear polymeric structure for the complex.

The synthesis and properties of metal-ion complexes of azamacrocyclic ligands with pendant arms able to interact with a metal ion in the central cavity has attracted considerable attention.[1,2] In our previous papers we have reported the synthesis of a series of such compounds including 5-nitromethyl derivatives of polyalkyl-1,4,8,11-tetraazacyclotetradecane and their nickel(II) complexes.[3,4]

Addition of a base to a nitromethane solution of *meso*-5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradeca-4,11-dienenickel(II) diperchlorate **1** (Scheme 1) leads to the formation of a sparingly soluble, purple, monoperchlorate salt **2**. The paramagnetic product **2** on protonation with perchloric acid gives a yellow, diamagnetic, diperchlorate **3** which was identified on the basis of ^{1}H and ^{13}C NMR evidence as 5,7,12,14-tetramethyl-5-nitromethyl-1,4,8,11-tetraazacyclotetradec-11-enenickel(II) diperchlorate.[4] The purple product **2** can be regenerated by addition of a base to a solution of the yellow diperchlorate **3**. The position of deprotonation of the ligand (C or N) of the complex **2** as well as the mode of co-ordination of the nitro group was difficult to establish on the basis of spectroscopic data. Therefore, we have undertaken the X-ray structural characterization of complex **2**.



Scheme 1

Experimental

Crystal-structure Determination.—A sample of the previously described[4] complex **2** was crystallized from diluted solution in aqueous ammonia. The excess of ammonia was first evaporated under vacuum at 10 °C, and then the remaining solution was placed in a desiccator, in the presence of concentrated sulphuric acid, and left in a refrigerator for *ca.* 1 week for crystallization.

A well shaped crystal (0.28 × 0.27 × 0.19 mm) was selected for X-ray measurements. The reflection intensities were collected on a Syntex-$P2_1$ single-crystal diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å) and the ω–2θ scan technique in the range up to $2\theta_{max}$ = 50°. The cell constants were obtained by a least-squares refinement from the setting angles of 20 reflections. A total of 2278 unique reflections were collected, of which 1920 had $I > 2\sigma_I$. Lorentz and polarization corrections were applied to the data. No absorption correction was applied at the measurement stage.

Crystal data. $C_{15}H_{30}ClN_5NiO_6 \cdot 2H_2O$, M_r = 506.63, $F(000)$ = 1072, orthorhombic, space group $Pna2_1$ (no. 33), a = 18.133(6), b = 10.285(3), c = 12.212(4) Å, U = 2 278(1) Å^3, $Z = 4$, D_c = 1.48 Mg m^{-3}, μ(Mo-Kα) = 20.27 cm^{-1}.

Structure solution and refinement. The phase problem was solved by direct methods using the program SHELXS 86.[5] A total of 30 atoms were found in E maps. Initially, the positional parameters and individual isotropic thermal parameters of all non-hydrogen atoms were refined (with z coordinate of Ni fixed at zero) to give R = 0.103 (program SHELX 76[6]). At this stage an empirical, spherical, absorption correction (program DIFABS[7]) was performed. The minimum, maximum and

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Table 1 Non-hydrogen atomic fractional coordinates (× 10^4) of complex **2**[a]

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Ni	4782(1)	256(1)	0[b]	C(12)	3957(3)	2727(6)	−275(5)
N(1)	5585(2)	1690(5)	−171(5)	C(13)	4676(3)	3455(6)	−133(8)
C(2)	6210(3)	977(6)	−670(6)	C(14)	5355(3)	2895(6)	−735(6)
C(3)	6347(3)	−248(5)	−27(8)	C(15)	6294(4)	−2893(6)	919(7)
N(4)	5658(2)	−1003(4)	38(5)	C(16)	3577(4)	−3257(7)	1076(8)
C(5)	5618(3)	−1958(5)	953(5)	C(17)	3297(4)	3534(8)	−624(8)
C(6)	4908(3)	−2807(6)	816(6)	C(18)	5969(4)	3911(7)	−769(7)
C(7)	4156(3)	−2212(6)	1060(5)	C(19)	5654(3)	−1273(6)	2059(5)
N(8)	3973(3)	−1162(5)	240(4)	N(20)	5294(2)	−226(5)	2357(4)
C(9)	3303(3)	−434(6)	524(5)	O(21)	4858(2)	445(4)	1715(4)
C(10)	3234(3)	772(7)	−181(6)	O(22)	5370(2)	271(5)	3335(4)
N(11)	3924(2)	1515(5)	−115(5)				
Perchlorate group							
Cl	2760(1)	−2393(3)	−2544(2)	O(1A)[c]	2332(14)	−2565(20)	−1349(19)
O(1)	3273(5)	−2501(13)	−3288(9)	O(2A)	2213(17)	−2096(22)	−3228(21)
O(2)	3003(9)	−2590(13)	−1513(8)	O(3A)	3424(16)	−1663(21)	−2327(21)
O(3)	2144(6)	−3069(22)	−2734(4)	O(4A)	2768(17)	−3922(22)	−2899(22)
O(4)	2570(14)	−1002(23)	−2538(9)				
Crystallization water							
O(1W)	4341(3)	−2607(5)	2888(4)	O(2W)	4516(4)	4457(7)	−2337(7)

[a] In this and subsequent Tables the figures in parentheses are estimated standard deviations. [b] Fixed coordinate. [c] Disordered atoms with population 0.16 are designated A.

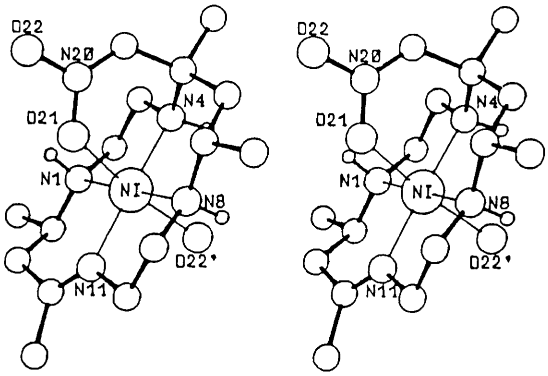

Fig. 1 A stereoview of the cation of complex **2** oriented at optimal viewing. For clarity, atom labelling is given for N and O atoms only. The omitted numbering in the macroring goes clockwise including nitrogen numbers. The co-ordinated O(22′) atom has the symmetry $1 - x, -y, -\frac{1}{2} + z$.

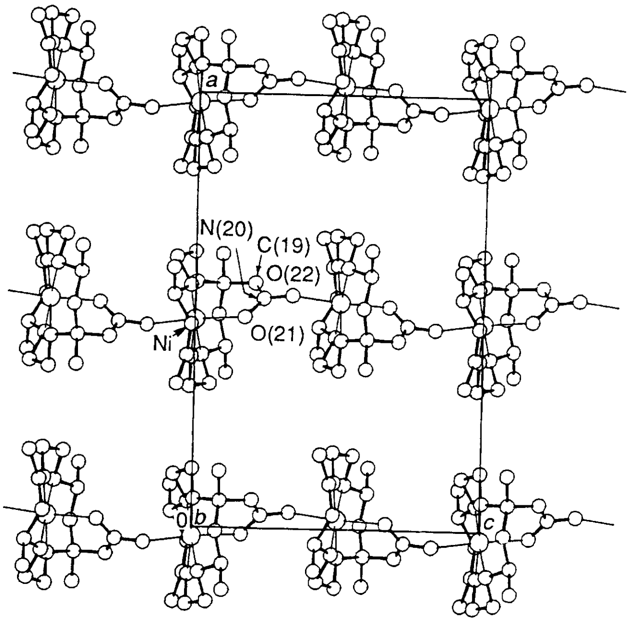

Fig. 2 Projection of the co-ordination chains of complex **2** down the *b* axis

average corrections were 0.797, 1.133 and 0.996, respectively. The positions of the C-attached hydrogen atoms were generated from assumed geometries and added to the set. Then, the refinement of non-H atomic positional and thermal anisotropic parameters was performed by the least-squares full-matrix procedure using SHELX 76. At the convegence level of R = 0.051 the positions of the amino and water hydrogen atoms were found from Fourier difference maps and added to the atomic set, and all hydrogen parameters were refined isotropically with a damping factor of 0.3. A thorough analysis of Fourier difference maps revealed a positional disorder of the perchlorate oxygen atoms, as though the perchlorate tetrahedron occupies simultaneously two positions related by 180° to each other. The new and old oxygen positions, isotropic thermal coefficients for newly added coordinates and the occupancy factor were then refined to give the occupancy ratio of 0.84:0.16. The final refinement step involved all positional and anisotropic thermal parameters (except those of H atoms). The final R was 0.0465, R' = 0.0495, where $w = 0.858/(\sigma_F^2 + 0.002F^2)$. The highest electron-density peak in the final difference map was 0.25 e Å^{-3}. The refined positional parameters for the non-H atoms of complex **2** are given in Table 1. Fig. 1 presents a stereoview of the ligand cation.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters, and remaining bond lengths and angles.

Results and Discussion

Nitromethane has very poor donor properties and only a few of its complexes with transition-metal ions have been synthesised and characterized.[8,9] *aci*-Nitromethane or *aci*-nitromethyl should have stronger donor properties, nevertheless to our knowledge no transition-metal complexes have been characterized. Here, we present the first structure of a polynuclear macrocyclic nickel(II) complex **2** in which the deprotonated pendant nitromethyl group serves as a bridging unit (μ-=NO_2^-)

Table 2 Interatomic distances (Å) and angles (°) in complex **2** (perchlorate anion omitted)

Macrocyclic cation							
N(1)–C(2)	1.481(7)	N(8)–C(9)	1.469(8)	C(5)–C(15)	1.559(9)	C(13)–C(14)	1.545(9)
N(1)–C(14)	1.478(8)	C(9)–C(10)	1.515(9)	C(5)–C(19)	1.525(9)	C(14)–C(18)	1.527(9)
C(2)–C(3)	1.505(9)	C(10)–N(11)	1.468(7)	C(6)–C(7)	1.524(8)	C(19)–N(10)	1.311(8)
C(3)–N(4)	1.473(7)	N(11)–C(12)	1.263(8)	C(7)–N(8)	1.510(8)	N(20)–O(21)	1.310(6)
N(4)–C(5)	1.489(8)	C(12)–C(13)	1.513(8)	C(7)–C(16)	1.503(9)	N(20)–O(22)	1.306(7)
C(5)–C(6)	1.565(8)	C(12)–C(17)	1.518(10)				
N(1)–C(2)–C(3)	109.0(6)	C(6)–C(7)–C(16)	109.9(5)	N(4)–C(5)–C(19)	111.0(4)	C(12)–C(13)–C(14)	116.6(6)
C(2)–N(1)–C(14)	116.1(5)	C(7)–N(8)–C(9)	112.9(5)	C(5)–C(6)–C(7)	119.4(5)	C(13)–C(12)–C(17)	116.2(6)
N(1)–C(14)–C(13)	108.4(5)	N(8)–C(7)–C(16)	111.5(5)	C(6)–C(5)–C(15)	107.5(4)	C(13)–C(14)–C(18)	109.8(5)
N(1)–C(14)–C(18)	112.4(5)	N(8)–C(9)–C(10)	110.6(5)	C(6)–C(5)–C(19)	112.8(5)	C(19)–N(20)–O(21)	124.6(5)
C(2)–C(3)–N(4)	109.2(5)	C(9)–C(10)–N(11)	108.9(5)	C(15)–C(5)–C(19)	106.0(5)	C(19)–N(20)–O(22)	121.5(5)
C(3)–N(4)–C(5)	115.4(5)	C(10)–N(11)–C(12)	123.1(5)	C(5)–C(19)–N(20)	127.2(5)	O(21)–N(20)–O(22)	113.9(5)
N(4)–C(5)–C(6)	109.1(5)	N(11)–C(12)–C(13)	120.8(5)	C(6)–C(7)–N(8)	110.7(5)		
N(4)–C(5)–C(15)	110.4(5)	N(11)–C(12)–C(17)	123.1(5)				
Co-ordination sphere							
Ni–N(1)	2.083(5)	Ni–N(11)	2.029(4)	Ni–N(8)	2.089(5)	Ni–O(22)[a]	2.122(5)
Ni–N(4)	2.050(4)	Ni–O(21)	2.108(5)				
N(1)–Ni–N(4)	84.7(2)	N(4)–Ni–O(22)[a]	87.8(2)	N(1)–Ni–O(22)[a]	100.1(2)	N(11)–Ni–O(21)	93.4(2)
N(1)–Ni–N(8)	177.6(2)	N(8)–Ni–N(11)	85.2(2)	N(4)–Ni–N(8)	95.7(2)	N(11)–Ni–O(22)[a]	89.8(2)
N(1)–Ni–N(11)	94.4(2)	N(8)–Ni–O(21)	88.3(2)	N(4)–Ni–N(11)	177.3(3)	O(21)–Ni–O(22)[a]	169.7(2)
N(1)–Ni–O(21)	89.3(2)	N(8)–Ni–O(22)[a]	82.2(2)	N(4)–Ni–O(21)	89.1(2)		
Other distances[b]							
Ni ··· Ni	6.179(3)	Ni ··· O(1W)	4.225(5)	Ni ··· Cl	5.524(3)	Ni ··· O(2W)	5.556(8)
O(1W) ··· O(2W)	2.827(9)						

[a] Key to symmetry operation: $1 - x, -y, -\frac{1}{2} + z$. [b] Closest distances from all possible symmetry operations.

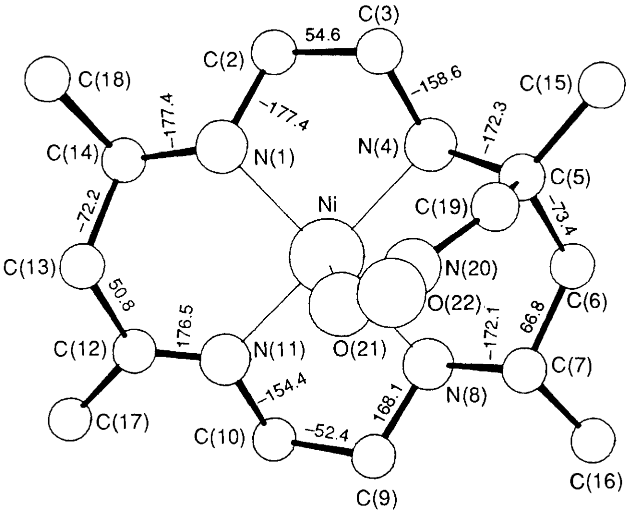

Fig. 3 Projection of the cation of complex **2** showing the endocyclic torsion angles (°) in the macroring with complete atom labels. The average standard deviation for the angles is 0.6°.

co-ordinating simultaneously two metal ions, thus forming infinite chains of the complex parallel to the *c* axis of the crystal. Fig. 2 shows the chains projected down the *b* axis. It is noteworthy that the opposite enantiomorphic molecules are separated into different chains.

The relatively short C(19)–N(20) bond [1.311(8) Å] and the planarity of a pendant arm [C(5), C(19), N(20), O(21) and O(22)] indicate that the CH_2 of the CH_2NO_2 side chain has been deprotonated.

Selected bond lengths and valence angles are listed in Table 2.

Co-ordination Sphere.—The four nitrogen atoms of the macrocycle and the nickel(II) ion are in a planar arrangement. The Ni–N distances are in the range typical for octahedral co-ordination.[10] The axial positions are occupied by oxygen atoms [O(21) and O(22′)] of pendant *aci*-nitromethyl groups. The axial O(21)–Ni and O(22′)–Ni distances may be regarded as short for a μ-$=NO_2^-$ bridging group, when compared with the average Ni–O bond distance for co-ordinated NO_2^- or NO_3^-.[11] The oxygen atoms are slightly displaced from the apices of a regular octahedron, their bonds with Ni^{II} forming angles with the normal to the least-squares plane of $Ni(N_4)$ of 2.3(1) and 8.9(1)° for Ni–O(21) and Ni–O(22′), respectively.

Ligand Stereochemistry.—The X-ray structure analysis defines the stereochemistry of complex **2** as shown in the stereodiagram (Fig. 1). The macrocyclic ring adopts the *trans*-III type structure, which on the basis of endocyclic torsion angles sequence analysis[12] (Fig. 3), is classified as the 3434 conformation. The co-ordination of the *aci*-nitromethyl group to Ni^{II} is sterically convenient. It does not induce any deformation of the N(4)–Ni–N(8)–C(7)–C(6)–C(5) chelate ring in comparison with that ring in 5,12-dimethyl-1,4,8,11-tetraazacyclotetradecanenickel(II) diperchlorate.[13]

Here we define the conformation of chelate rings on the basis of puckering parameters[14] calculated with a RING program.[15] The saturated six-membered chelate ring [N(4)–Ni–N(8)–C(7)–C(6)–C(5)] adopts a chair conformation (${}^1C_4$). The unsaturated six-membered ring [N(1)–Ni–N(11)=C(12)–C(13)–C(14)] has a half-chair conformation (${}^5H_6$). The N(1)–Ni–N(4)–C(3)–C(2) and N(8)–Ni–N(11)–C(10)–C(9) five-membered rings exist in an envelope (E_5) and a twist (${}^5T_4$) conformation respectively. The co-ordinated pendant arm forms another unsaturated six-membered ring [N(4)–Ni–O(21)–N(20)=C(19)–C(5)] which has a skew-boat (${}^6S_1$) conformation. The relative configurations of the chiral centres in complex **2** were found to be 1*SR*,4*SR*,5*RS*,7*SR*,8*RS*,14*RS* consistent with the structure of the ligand postulated for its diamagnetic complex **1**.[4]

Hydrogen Bonding.—Many hydrogen donor groups and a relatively large number of potential acceptor atoms present in compound **2** create numerous possibilities of hydrogen bridging. The most probable are shown in Table 3. As donors

Table 3 Hydrogen-bonding scheme in complex **2**

Hydrogen bond D–H ··· A	Acceptor symmetry	D ··· A/Å	D–H/Å	H ··· A/Å	D–H ··· A/°
N(1)–H(1) ··· O(21)	x, y, z	2.947	0.94	2.58	104
N(4)–H(4) ··· O(1W)	x, y, z	3.101	0.95	2.16	177
N(8)–H(8) ··· O(22)	$1 - x, -y, -\frac{1}{2} + z$	2.770	0.94	2.35	106
O(1W)–H(2W1) ··· O(21)	$1 - x, -y, -\frac{1}{2} + z$	2.806	0.93	1.90	164
O(2W)–H(1W2) ··· O(1W)	$1 - x, -y, \frac{1}{2} + z$	2.827	0.95	1.89	169

they involve all amino groups in the ligand ring and both water molecules. The acceptors are the oxygen atoms only: one water oxygen and, of particular interest, both *aci*-nitro oxygens [O(21) and O(22)]. The two hydrogen bonds involving the *aci*-nitro groups are rather weak and form two four-atom chelate rings placed approximately centrosymmetrically with respect to Ni, thus showing the intramolecular nature. Two more potential hydrogen bonds of the O–H ··· O type possibly exist. They exhibit donor–acceptor distances longer than 3.0 Å and involve water molecules of crystallization and perchlorate oxygens (one of them of lower occupancy). They are, however, less probable. Other considered hydrogen bridges link the co-ordination chains of the cations into a spatial lattice of most complicated structure.

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