Structure of Bis(5,6,11,12-Tetrahydro-2,8-dimethylphenhomazine)-nickel(II) Perchlorate *

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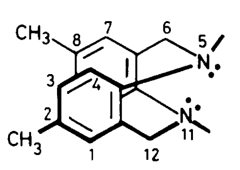
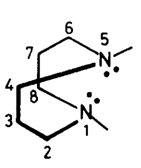
An *X*-ray diffraction study of the title compound, $[NiL_2][ClO_4]_2\cdot3CH_3NO_2$, was carried out to investigate the stereochemistry of the mesocyclic ligand complexed to nickel(II). The compound crystallizes in space group *Pbnb* with lattice constants a = 10.289(1), b = 18.471(3), c = 22.271(4) Å, and Z = 4. The intensity data were collected on a CAD-4 automated diffractometer and the structure was refined to a final R value of 0.068 for 1 339 unique reflections. The structure consists of discrete $[NiL_2]^{2+}$ cations, ClO_4^- anions, and CH_3NO_2 molecules of crystallization. The axial positions are shielded by the hydrogen atoms of the rings, thus preventing octahedral co-ordination. The average Ni–N distance is 1.912(7) Å and the chelate bite angle N(1)–Ni–N(2) is 86.6(2)°.

The geometries of complexes of saturated medium-ring systems (mesocycles) cover the range from octahedral,[1,2] square pyramidal,[3,4] to square planar [5] depending upon the steric requirements of the ligand and the anion present. The unique stereochemistry of chelated 1,5-diazacyclo-octane (daco) and 1,4-diazacycloheptane (dach) has been used to design quadridentate ligands and complexation [6] and structural studies [7] of these ligands have been carried out. In the title compound, the ligand 5,6,11,12-tetrahydro-2,8-dimethylphenhomazine (L) can be viewed as 1,5-diazacyclo-octane, but with carbon atom pairs 3,4 and 7,8 forming parts of the benzene rings and thus reducing the flexibility of daco to attain boat–boat, boat–chair, or chair–chair conformations. Although the out-of-plane positions in L_2 complexes are relatively open, only four-co-ordinated complexes could be prepared with L.[8,9] Because of this unusual behaviour the structure determination of a nickel(II) complex of L was undertaken and the results are reported here.



L



daco

Experimental

The compound was prepared as described previously [8] and orange single crystals were grown from a dilute solution of nitromethane. The intensity data were measured on a crystal having dimensions 0.3 × 0.2 × 0.1 mm mounted on a glass fibre in an arbitrary orientation. The lattice constants were obtained by least-squares refinement of the diffraction geometry for 25 centred reflections having $12 < \theta < 16°$ measured at an ambient temperature of 21 ± 2 °C.

Crystal Data.—$C_{35}H_{45}Cl_2N_7NiO_{14}$, M = 856, Orthorhombic, a = 10.289(1), b = 18.471(3), c = 22.271(4) Å, U = 4 233 Å^3, $F(000)$ = 1 784, D_m = 1.34, Z = 4, D_c = 1.344 g cm^{-3}, space group *Pbnb* [non-standard form of *Pccn* (no. 56)], Mo-K_α radiation, λ = 0.7107 Å, $\mu(\text{Mo-}K_\alpha)$ = 6.502 cm^{-1}.

Intensity data were collected on a CAD-4 diffractometer using graphite-monochromated Mo-K_α radiation and an ω—2θ scan mode. A total of 3 824 reflections with positive *hkl* and $1.5 < 2\theta < 55°$ were measured. Three standards were monitored after every 6 000 s of *X*-ray exposure time. The crystal orientation was controlled by checking the orientation of reference reflections after every 100 reflections. The raw intensities were corrected for Lorentz and polarization effects and F_o were further corrected for some decay of the data crystal with time. The absorption corrections were carried out using the PSI scan method and 1 339 unique reflections having $F_o^2 > 2.0\ \sigma(F_o^2)$ were used in the analysis.

The co-ordinates of the Ni and Cl atoms were obtained from a three-dimensional Patterson synthesis and a Fourier map phased on these atoms revealed the location of most non-hydrogen atoms. Several cycles of anisotropic least-squares refinement followed by a difference-Fourier map revealed the positions of N(4), O(6), O(7), and C(18) of a CH_3NO_2 molecule of crystallization. Another three cycles of refinement followed by a difference map led to the positions of N(3) and C(17) at $\frac{1}{4}$, y, $\frac{1}{4}$ and the co-ordinates of O(5) of an additional half CH_3NO_2 molecule of crystallization. The occupancy factors for N(3) and C(17) refined close to 0.5 whereas that for O(5) was about 0.8. These occupancy factors were held constant for the atoms of the half nitromethane molecule. After several more cycles a difference map revealed the positions of most of the hydrogen atoms, which agreed well with the calculated positions. Since the nitromethane molecules were disordered hydrogen atoms from these molecules were not included nor were any efforts made to resolve the disorder. Three final cycles of anisotropic least-squares refinement of all non-hydrogen atoms with hydrogens held fixed in their refined positions led to the final residuals R = 0.068 and R' = 0.078 for 268 variables and 1 339 observations. The largest shift in any parameter during the final cycle of refinement was 0.05 times its estimated standard deviation. Atomic scattering factors were taken from ref. 10. The effects of anomalous dispersion were included in F_c by using the values of Cromer.[11]

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* Bis(5,6,11,12-tetrahydro-2,8-dimethyldibenzo[*b*,*f*][1,5]diazocine-N^5,N^{11})nickel(II) perchlorate.

Supplementary data available (No. SUP 23414, 11 pp.): H-atom co-ordinates, thermal parameters, least-squares planes, structure factors. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Table 1. Positional parameters for the non-hydrogen atoms *

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ni	0.7500	0.441 3(1)	0.2500	C(4)	0.877(1)	0.498 4(9)	0.153 7(7)
Cl	0.554 3(4)	0.189 4(2)	0.221 7(2)	C(5)	0.881(1)	0.429 0(7)	0.120 2(6)
O(1)	0.598(1)	0.249 9(5)	0.256 1(5)	C(6)	0.811(1)	0.368 3(8)	0.136 0(6)
O(2)	0.587(1)	0.124 1(5)	0.250 4(6)	C(7)	0.459(2)	0.463 5(8)	0.097 6(8)
O(3)	0.617(1)	0.191 1(8)	0.164 7(5)	C(8)	0.430(2)	0.528 0(9)	0.069 8(8)
O(4)	0.420(1)	0.193 1(8)	0.214 8(7)	C(9)	0.510(2)	0.586 2(9)	0.080 0(8)
O(5)	0.159(2)	0.447 2(9)	0.234 0(9)	C(10)	0.617(2)	0.580 0(8)	0.117 0(7)
O(6)	0.322(2)	0.300 8(9)	0.085 2(8)	C(11)	0.822(2)	0.304 4(8)	0.103 4(6)
O(7)	0.232(2)	0.203 1(10)	0.083 6(10)	C(12)	0.900(2)	0.302 8(9)	0.054 0(6)
N(1)	0.754(1)	0.512 4(6)	0.187 8(4)	C(13)	0.975(2)	0.361 5(8)	0.036 0(6)
N(2)	0.721(1)	0.371 7(6)	0.187 8(4)	C(14)	0.963(2)	0.423 7(8)	0.069 7(7)
N(3)	0.250	0.478 9(16)	0.2500	C(15)	0.310(2)	0.534 1(12)	0.029 4(9)
N(4)	0.245(2)	0.259 6(8)	0.107 3(8)	C(16)	1.061(2)	0.357 3(9)	−0.017 5(7)
C(1)	0.645(1)	0.514 9(7)	0.145 8(6)	C(17)	0.250	0.557 6(18)	0.2500
C(2)	0.567(1)	0.455 2(7)	0.136 9(7)	C(18)	0.170(3)	0.276 5(17)	0.160 3(9)
C(3)	0.585(1)	0.382 9(7)	0.166 1(6)				

* Estimated standard deviations are given in parentheses in this and in the subsequent table.

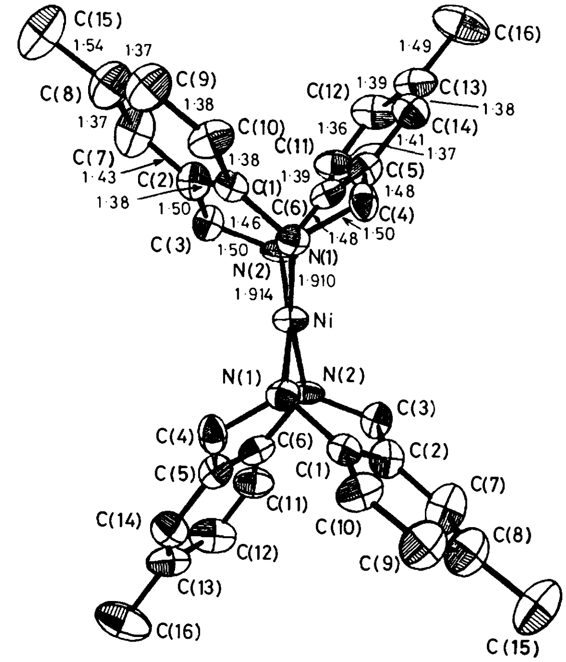

Figure. ORTEP plot of the $[NiL_2]^{2+}$ cation showing bonding distances and atom labelling. The standard deviations in the distances are Ni–N 0.007, N–C 0.01, and C–C 0.01—0.02 Å

Table 2. Bond distances (Å) and angles (°) in $[NiL_2][ClO_4]_2 \cdot 3CH_3NO_2$

N(1)–Ni–N(2)	86.6(2)	C(8)–C(9)–C(10)	120.7(9)
N(1)–Ni–N(1) *	93.1(4)	C(9)–C(10)–C(1)	121(1)
N(2)–Ni–N(2) *	95.5(4)	C(6)–C(11)–C(12)	119(1)
C(1)–N(1)–Ni	117.9(6)	C(11)–C(12)–C(13)	123(1)
C(4)–N(1)–Ni	105.6(6)	C(12)–C(13)–C(14)	116(1)
C(3)–N(2)–Ni	106.5(6)	C(13)–C(14)–C(5)	123(1)
C(6)–N(2)–Ni	119.7(6)	C(14)–C(5)–C(6)	117.3(9)
C(1)–N(1)–C(4)	109.3(6)	C(15)–C(8)–C(9)	121(1)
C(3)–N(2)–C(6)	109.9(7)	C(15)–C(8)–C(7)	120(1)
C(2)–C(3)–N(2)	111.9(8)	C(16)–C(13)–C(12)	121(1)
C(5)–C(4)–N(1)	94.2(6)	C(16)–C(13)–C(14)	122(1)
C(1)–C(2)–C(3)	125.7(9)	O(1)–Cl–O(2)	110.8(5)
C(6)–C(5)–C(4)	124.3(9)	O(2)–Cl–O(3)	108.4(5)
C(2)–C(1)–C(10)	120.4(9)	O(3)–Cl–O(4)	110.5(6)
C(5)–C(6)–C(11)	121.2(9)	O(4)–Cl–O(1)	109.4(6)
C(1)–C(2)–C(7)	117.1(9)	O(1)–Cl–O(3)	108.5(5)
C(2)–C(7)–C(8)	122.5(9)	O(1)–Cl–O(4)	109.4(6)
C(7)–C(8)–C(9)	118.5(9)	O(2)–Cl–O(4)	109.3(6)
N(1) ··· N(2)	2.622(8)	Cl–O(1)	1.427(7)
N(1) ··· N(1) *	2.77(1)	Cl–O(2)	1.404(6)
Ni ··· O(2)	3.771(6)	Cl–O(3)	1.426(7)
O(1) ··· HN(2)	2.359(7)	Cl–O(4)	1.396(8)
O(3) ··· HN(2)	2.988(9)		

* Co-ordinates are related to those in Table 1 by the transformation $\frac{1}{2} - x, y, \frac{1}{2} - z$.

The final positional parameters of non-hydrogen atoms are given in Table 1.

Results and Discussion

Selected distances and angles are given in the Figure and Table 2. The structure consists of discrete square-planar $[NiL_2]^{2+}$ cations, ClO_4^- anions, and the CH_3NO_2 molecules of crystallization. A nickel atom co-ordinated to one L, one ClO_4^- anion, and 1.5 nitromethane molecules form the crystallographic asymmetric unit. The Ni atom is at $\frac{3}{4}$ y, $\frac{1}{4}$ and N(3) and C(17) of CH_3NO_2 are at special position $\frac{1}{4}$, y, $\frac{1}{4}$. The conformation of the eight-membered ring in $[NiL_2]^{2+}$ is best described as almost planar, folded along the N–N axis with the two folds making an angle of 93° with each other. All carbon atoms of each chelate ring [except C(3) and C(4)], the carbons of the phenyl group, and a nitrogen atom are coplanar, with the other nitrogen about 0.5 Å out of the plane. A slight skewing of C(3) and C(4) causes the hydrogen atoms on these carbons to move towards the axial positions, preventing five- and/or six-co-ordination.

The conformation of the eight-membered ring in $[NiL_2]^{2+}$ resembles that observed in $[Ni(daco)_2]^{2+}$, but differs from the boat–chair conformation predicted [1,12] for $[Ni(daco)_2]^{2+}$ on the basis of spectral data and that observed in the case of [Ni(dacoda)] (dacoda = 1,5-diazacyclo-octane-*NN′*-diacetate) from the crystal-structure determination.[7] The Ni–N bond distances of 1.910(7) and 1.914(7) Å lie at the lower end of the range reported for the corresponding distance in related structures.[3,5,7] The chelate bite angle of 86.6(2)° for L is larger than the angle observed [3] in $[Cu(dach)_2]^{2+}$ but smaller than the angle [89.5(9)°] observed [5] in $[Ni(daco)_2]^{2+}$. This difference can be explained on the basis of the reduced flexibility of L and dach compared to daco. All chemically equivalent C–C and C–N distances are within one standard deviation of each other.

The perchlorate ions lie roughly along the axial positions with a Ni · · · O(2) non-bonding distance of 3.771(6) Å. All atoms of the nitromethane molecules are more than 4.2 Å away from the nickel atom and are not involved in any non-bonded interaction with ClO_4^- or with $[NiL_2]^{2+}$.

The Cl–O distances in the ClO_4^- anion are normal and the anion has nearly perfect tetrahedral geometry, probably because of weak hydrogen bonds formed between amine nitrogens and O(1) and O(3). A completely free ClO_4^- anion deviates appreciably from tetrahedral geometry.[5]

The structure of the compound is consistent with its diamagnetic behaviour, a sharp band at 440 nm, and its electrolytic behaviour. Because of the similarity of its solid-state spectra with $[Ni(daco)_2]^{2+}$, the present compound can be considered as another example of a nickel(II) complex having *d*-orbital energy-level order: $d_{x^2-y^2} > d_{xy} > d_{xz} > d_{yz} > d_{z^2}$.

Acknowledgements

Financial support in the form of travel grant from the University to present this paper at the ACA Washington Meeting (April 1982) is gratefully acknowledged.

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Received 22nd March 1982; *Paper* 2/490