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Structure of a Nickel(II) Complex of the Deprotonated Anion of 3,6,6,9-Tetramethyl-4,8-diaza-3,8-undecadiene-2,10-dione Dioxime

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(*Received* 7 *May* 1992; *accepted* 23 *September* 1992)

Abstract. [3,3′-(2,2-Dimethyl-1,3-propanediyldinitrilo)di(2-butanone oximato)(1 −)-*N*,*N*′,*N*″,*N*‴] nickel perchlorate, [$Ni(C_{13}H_{23}N_4O_2)$](ClO_4), M_r = 425.5, monoclinic, $P2_1/c$, $a = 7.161$ (3), $b = 18.945$ (3), $c = 13.949$ (4) Å, $\beta = 103.47$ (1)°, $V = 1840.2$ (9) Å^3, $Z = 4$, $D_x = 1.536$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.7093 Å, $\mu = 1.24$ mm^{-1}, $F(000) = 887.81$, $T = 298$ (4) K, $R = 0.039$, $wR = 0.040$, for 2729 significant reflections. The coordination about Ni^{II} is slightly distorted square planar. The Ni^{II} ion is a little (0.056 Å) out of the square coordination plane, towards the perchlorate ion. There are intramolecular and intermolecular hydrogen bonds between O atoms.

Introduction. Transition-metal complexes of deprotonated diaza-dioximes present considerable interest in the formation of strong intramolecular hydrogen bonds between *cis* oxime groups (Wang, Chung, Cheng & Wang, 1990; Fair & Schlemper, 1978; Gavel & Schlemper, 1979; Liss & Schlemper, 1975). We have recently reported the structure of a Ni^{II} complex with the deprotonated anion of 3,9-dimethyl-4,8-diaza-3,8-undecadiene-2,10-dione dioxime (Wang, Chung, Cheng & Wang, 1990).

Experimental. 2,3-Butanedione monoxime (115.4 mmol) was dissolved in ethanol (200 ml), to which 2,2-dimethyl-1,3-propanediamine (49 mmol) in ethanol (100 ml) was added dropwise; the solution was refluxed for 5 h, then allowed to cool to room temperature. The solvent was removed under reduced pressure, and the white product was washed with cold acetonitrile and recrystallized from benzene. A hot methanol solution of nickel(II) perchlorate hexahydrate (10 mmol in 30 ml) was added to a hot methanol solution of the ligand 3,6,6,9-tetramethyl-4,8-diaza-3,8-undecadiene-2,10-dione dioxime (10 mmol in 20 ml). The orange solution was cooled and precipitated into orange products which were collected by filtration, washed with diethyl ether, dried in air and then recrystallized from methanol. The crystal used for the X-ray study had dimensions 0.38 × 0.63 × 0.69 mm. The intensity data were collected on a Nonius CAD-4 diffractometer using the θ–2θ scan mode. Cell dimensions were obtained from 25 reflections with 2θ angles in the range 11–32°. The *hkl* ranges were $-8 \leq h \leq 8$, $0 \leq k \leq 22$, $0 \leq l \leq 16$. Maximum $\sin\theta/\lambda = 0.594$ Å^{-1}. Three normalized standard reflections ($\bar{2}\bar{5}\bar{3}$, $\bar{2}71$ and $\bar{2}80$) fluctuated within 1%. 3509 valid reflections were measured, of which 3234 were unique with 2729 significant [$I \geq 2.5\sigma(I)$]. An empirical absorption correction was applied based on azimuthal rotation from three reflections (364, 333 and 586) (North, Philips & Mathews, 1968); the maximum and minimum transmission factors were 0.759 and 0.758, respectively. Patterson synthesis, difference Fourier synthesis and least-squares fit were used to locate the Ni atom and other atoms. The function minimized in the full-matrix least-squares fit was $\sum(|F_o| - |F_c|)^2$, with unit weights. 262 parameters were refined with anisotropic temperature factors for non-H atoms and isotropic for H atoms, the H-atom positions

0108-2701/93/040666-03$06.00

Table 1. *Atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

B_{eq} is the mean of the principal axes of the thermal ellipsoid.

	x	y	z	B_{eq}
Ni	0.02611 (6)	0.06629 (3)	0.10420 (3)	3.01 (2)
Cl	0.7608 (3)	0.32505 (5)	0.0029 (1)	7.0 (1)
O(1)	−0.2733 (3)	−0.0178 (1)	0.1467 (2)	4.2 (1)
O(2)	−0.3387 (3)	0.0326 (1)	−0.0173 (2)	4.1 (1)
O(3)	0.7807 (9)	0.3809 (3)	−0.0540 (3)	12.2 (3)
O(4)	0.723 (2)	0.3536 (4)	0.0887 (6)	12.4 (6)
O(5)	0.651 (2)	0.2740 (5)	−0.0491 (5)	14.7 (7)
O(6)	0.883 (2)	0.2745 (6)	0.0243 (10)	18.5 (9)
O(4*s*)	0.852 (2)	0.3241 (8)	0.1021 (10)	6.4 (3)
O(5*s*)	0.544 (3)	0.3148 (1)	−0.0266 (13)	9.2 (4)
O(6*s*)	0.968 (4)	0.3321 (2)	−0.0264 (20)	16.1 (8)
N(1)	−0.1008 (4)	0.0113 (2)	0.1810 (2)	3.3 (1)
N(2)	0.2196 (4)	0.0665 (2)	0.2216 (2)	3.6 (1)
N(3)	0.1433 (4)	0.1270 (2)	0.0284 (2)	3.5 (1)
N(4)	−0.1747 (4)	0.0688 (2)	−0.0084 (2)	3.3 (1)
C(1)	−0.0208 (5)	0.0057 (2)	0.2733 (3)	3.7 (2)
C(2)	0.1718 (6)	0.0383 (2)	0.2959 (3)	3.9 (2)
C(3)	0.4131 (5)	0.0957 (2)	0.2275 (3)	4.5 (2)
C(4)	0.4134 (5)	0.1634 (2)	0.1696 (3)	4.0 (2)
C(5)	0.3444 (6)	0.1521 (2)	0.0594 (3)	4.4 (2)
C(6)	0.0373 (6)	0.1431 (2)	−0.0559 (3)	3.8 (2)
C(7)	−0.1553 (5)	0.1102 (2)	−0.0789 (3)	3.6 (2)
C(8)	−0.1122 (6)	−0.0305 (3)	0.3449 (3)	5.1 (2)
C(9)	0.2932 (7)	0.0333 (3)	0.3979 (3)	6.7 (3)
C(10)	0.2955 (7)	0.2207 (3)	0.2051 (4)	5.8 (2)
C(11)	0.6236 (6)	0.1872 (3)	0.1883 (4)	5.5 (2)
C(12)	0.0955 (7)	0.1889 (3)	−0.1311 (3)	5.6 (2)
C(13)	−0.3080 (6)	0.1221 (2)	−0.1693 (3)	4.9 (2)

Table 2. *Selected bond lengths* (Å) *and bond angles* (°)

Ni—N(1)	1.873 (3)	N(4)—C(7)	1.291 (5)
Ni—N(2)	1.882 (3)	C(1)—C(2)	1.477 (5)
Ni—N(3)	1.887 (3)	C(1)—C(8)	1.486 (7)
Ni—N(4)	1.866 (3)	C(2)—C(9)	1.491 (6)
O(1)—N(1)	1.336 (4)	C(3)—C(4)	1.516 (6)
O(2)—N(4)	1.341 (4)	C(4)—C(5)	1.516 (6)
N(1)—C(1)	1.286 (5)	C(4)—C(10)	1.528 (6)
N(2)—C(2)	1.282 (5)	C(4)—C(11)	1.536 (6)
N(2)—C(3)	1.476 (5)	C(6)—C(7)	1.478 (6)
N(3)—C(5)	1.482 (5)	C(6)—C(12)	1.497 (7)
N(3)—C(6)	1.278 (5)	C(7)—C(13)	1.483 (5)
N(1)—Ni—N(2)	82.0 (2)	N(1)—C(1)—C(2)	110.8 (3)
N(1)—Ni—N(3)	176.0 (1)	N(1)—C(1)—C(8)	123.3 (3)
N(1)—Ni—N(4)	96.6 (1)	C(2)—C(1)—C(8)	125.9 (3)
N(2)—Ni—N(3)	98.8 (1)	N(2)—C(2)—C(1)	114.4 (3)
N(2)—Ni—N(4)	176.8 (1)	N(2)—C(2)—C(9)	126.4 (4)
N(3)—Ni—N(4)	82.5 (1)	C(1)—C(2)—C(9)	119.0 (3)
N(1)—O(1)—HO	106.6 (2)	N(2)—C(3)—C(4)	113.9 (3)
N(4)—O(2)—HO	104.3 (2)	C(3)—C(4)—C(5)	112.3 (3)
Ni—N(1)—O(1)	123.8 (2)	C(3)—C(4)—C(10)	111.0 (3)
Ni—N(1)—C(1)	117.2 (3)	C(3)—C(4)—C(11)	106.3 (3)
O(1)—N(1)—C(1)	118.9 (3)	C(5)—C(4)—C(10)	110.8 (4)
Ni—N(2)—C(2)	114.9 (3)	C(5)—C(4)—C(11)	106.8 (3)
Ni—N(2)—C(3)	122.7 (2)	C(10)—C(4)—C(11)	109.3 (3)
C(2)—N(2)—C(3)	122.3 (3)	N(3)—C(5)—C(4)	114.0 (3)
Ni—N(3)—C(5)	124.1 (3)	N(3)—C(6)—C(7)	115.0 (3)
Ni—N(3)—C(6)	114.5 (3)	N(3)—C(6)—C(12)	125.5 (4)
C(5)—N(3)—C(6)	121.4 (3)	C(7)—C(6)—C(12)	119.4 (4)
Ni—N(4)—O(2)	123.5 (2)	N(4)—C(7)—C(6)	110.6 (3)
Ni—N(4)—C(7)	117.2 (3)	N(4)—C(7)—C(13)	123.5 (4)
O(2)—N(4)—C(7)	119.2 (3)	C(6)—C(7)—C(13)	125.9 (3)

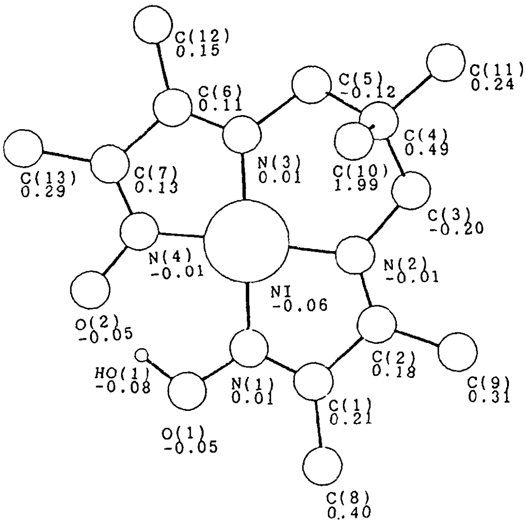

Fig. 1. Perspective view of the atom-numbering scheme of the molecule excluding the majority of H atoms and the perchlorate group. The displacements from the best plane formed by the four N atoms coordinated to the Ni^{II} atom are indicated.

being fixed. $R(F) = 0.039$, $wR = 0.040$, $S = 1.56$, $(\Delta/\sigma)_{\max} = 0.21$, $(\Delta\rho)_{\max} = 0.530$, $(\Delta\rho)_{\min} = -0.480$ e Å^{-3}. Secondary-extinction coefficient = 0.39 (2) × 10^{-2} (length in cm). Atomic scattering factors were obtained from *International Tables for X-ray Crystallography* (1974, Vol. IV). *NRCVAX* programs (Gabe, Le Page, White & Lee, 1987) for the VAX compiler were used to solve the structure.

Discussion. Atomic coordinates and temperature factors for non-H atoms are listed in Table 1.* Bond lengths and bond angles between non-H atoms are listed in Table 2. The structure of the complex with the numbering scheme and the displacements above and below the best plane formed by the four N atoms are shown in Fig. 1. The perchlorate group is disordered in the lattice and far from the Ni^{II} ion at a distance of 2.84 Å. Thus, this ion is not within the bonding distance of the Ni^{II}. The occupancies of the disordered perchlorate atoms O(4*s*), O(5*s*) and O(6*s*) are 0.3 and those of O(4), O(5) and O(6) are 0.7. The Ni^{II} ion bonds only with the four N atoms of the deprotonated ligand; the geometry about the Ni^{II} ion is very slightly distorted square planar. The displacement of the Ni^{II} ion from the best plane formed by the four N atoms is 0.056 Å towards the perchlorate ion (Fig. 1). The four Ni—N distances span a rather narrow range, 1.867 (3)–1.886 (3) Å, which are normal for this type of Ni^{II} complex. There are intramolecular and intermolecular hydrogen bonds between O(1) and O(2) with O···O distances of 2.422 and 2.953 Å, respectively. Compared with the reported structure of the Ni^{II} complex with the deprotonated anion of 3,9-dimethyl-4,8-diaza-3,8-undecadiene-2,10-dione dioxime, the structure of the

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55693 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS1016]

title complex has larger cell dimensions, higher distortion of the central best plane and smaller *trans* N—Ni—N bond angles. These differences arise mainly from the steric effect of the two C-methyl groups.

The authors thank the National Science Council, for support in the form of both a research grant NSC81-0208-M007-110 and the use of the Nonius CAD-4 diffractometer. They are also indebted to Ms Shu-Fang Tung for collecting the diffraction data.

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Acta Cryst. (1993). **C49**, 668–671

Structure of Dipiperidinium *catena*-Poly[nickel-tri-μ-chloro(1−)] Chloride

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(*Received* 24 *October* 1991; *accepted* 17 *August* 1992)

Abstract. $2C_5H_{12}N^+.NiCl_3^-.Cl^-$, $M_r = 372.84$, monoclinic, $P2_1/n$, $a = 10.131$ (1), $b = 6.1431$ (8), $c = 26.081$ (5) Å, $\beta = 98.01$ (1)°, $V = 1607.3$ (4) Å^3, $Z = 4$, $D_x = 1.54$ g cm^{-3}, λ(Cu $K\alpha$) = 1.5418 Å (graphite monochromator), $\mu = 78.8$ cm^{-1}, $F(000) = 776$, $T = 295$ K. Refinement of 186 least-squares parameters, $R = 0.0382$ for 1752 unique observed $[|F| > 3\sigma(|F|)]$ reflections. The compound is more properly formulated (piperidinium chloride).[piperidinium trichloronickelate(II)] and consists of anionic $(NiCl_3)_n^{n-}$ chains separated by the piperidinium cations and by an isolated lattice chloride anion. This new A_2NiX_4 structure type is constructed by *ABAB* stacking of hexagonal close packed (h.c.p.) A_2X_4 layers.

Introduction. The range of structural variation within the A_2NiX_4 family (A = monopositive cation, X = halide) is small. Nickel(II) assumes octahedral coordination with the small fluoride ion, as found in the familiar K_2NiF_4 (layer perovskite) structure (Muller & Roy, 1974) or in the Li_2NiF_4 (inverse spinel) structure (Rüdorff & Kandler, 1962). Tetrahedral coordination, on the other hand, should be stabilized by larger halide ions. This is indeed the case for a series of quaternary ammonium salts in which isolated tetrahedral NiX_4^{2-} ions (X = Cl, Br, I) are separated by large quaternary ammonium cations such as $(CH_3)_4N^+$ or $(CH_3)_3(C_6H_5)N^+$ (Gill & Nyholm, 1959; Stucky, Folkers & Kistenmacher, 1967). Structural behavior between these stereochemical extremes is found for several thermochromic $(R_xNH_{4-x})_2NiCl_4$ compounds (R = alky, $1 < x < 3$) in which low-temperature phases are yellow, the characteristic color of octahedral $NiCl_6^{4-}$ salts, but high-temperature phases are blue, the characteristic color of tetrahedral $NiCl_4^{2-}$ salts (Bloomquist & Willett, 1982). Spectroscopic, EPR and powder X-ray diffraction data verify this assignment of local Ni^{II} geometries in the two phases but the lack of reported single-crystal structure determinations leaves questions about their extended geometries unresolved, particularly concerning the bridging arrangements between octahedral Ni^{II} complexes in the polymeric low-temperature phase (Ferraro & Sherren, 1978).

In the course of our recent study (Bond & Willett, 1992; Bond, 1990) of the structural and magnetic properties of a series of ANiCl$_3$ hexagonal perovskites (A = organoammonium ion), we synthesized a yellow crystalline solid containing the piperidinium cation. Since the color of the compound indicates the presence of octahedral Ni^{II} we expected the crystal structure determination to reveal a distorted CsNiCl$_3$-type structure, *i.e.* parallel chains of face-sharing $NiCl_6^{4-}$ octahedra separated by the monopositive piperidinium cations. To our surprise we found an A_2NiCl_4 compound whose structure type, although similar in form to a distorted CsNiCl$_3$-type structure, is new to the A_2NiX_4 family.

Experimental. Yellow needle-like crystals obtained by slow evaporation of 6M HCl solution (maintained

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