We thank the National Science Foundation for support of research (grant No. CHE 8417548) and the National Institutes of Health for an instrumentation grant (grant No. 1510 RRO 1486 01A1).

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Acta Cryst. (1987). C**43**, 1514–1516

[Bis(1-amino-13-methyl-3,6,9,12-tetraazapentadec-12-en-14-one oximato-*N,N',N'',N''',N'''',N'''''*)hydrogen(I)]dinickel(II) Triperchlorate

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(*Received* 20 *Feburary* 1987; *accepted* 31 *March* 1987)

Abstract. $[Ni_2(C_{12}H_{27}N_6O)_2H](ClO_4)_3$, $M_r = 959{\cdot}56$, monoclinic, $C2/c$, $a = 25{\cdot}404\ (8)$, $b = 10{\cdot}276\ (3)$, $c = 15{\cdot}760\ (5)$ Å, $\beta = 91{\cdot}60\ (3)°$, $V = 4113\ (2)$ Å^3, $Z = 4$, $D_m = 1{\cdot}55$, $D_x = 1{\cdot}549$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 11{\cdot}9$ cm^{-1}, $F(000) = 2008$, room temperature, $R = 0{\cdot}052$ for 3129 unique reflections. The structure consists of perchlorate anions and dinuclear complex cations. The two halves of the dimer are bridged by an O···H···O hydrogen bond between the oxime O atoms [O···O, 2·428 (6) Å]. The hydrogen bond is symmetrical as a result of crystallographic requirements. The Ni^{II} is bonded to the N-donor atoms of the hexadentate ligand in a distorted octahedral coordination environment.

Introduction. In the course of our studies on octahedral Ni^{II} and Ni^{IV} complexes of oxime ligands we discovered that the Ni—N(oxime) distance as well as the geometry of the oxime group are strongly dependent on whether or not the oxime proton is preserved on coordination (Korvenranta, Saarinen & Näsäkkälä, 1982). The present compound was examined by X-ray diffraction analysis after its stoichiometry was found to correspond to the composition $Ni_2L_2H(ClO_4)_3$ (HL is a neutral oxime). This suggests that only one of the two oxime groups in the complex is deprotonated, and it was of interest to determine the structural characteristics of the oxime function in such a hybrid structure. The hexadentate amine–imine–oxime ligand used here is especially attractive as it allows stabilization of a formally trivalent nickel complex $Ni^{III}L^{2+}$ (Chakravorty, 1985).

Experimental. The ligand HL was obtained by 1:1 condensation of 2,3-butanedione monoxime and tetraethylenepentamine. The complex was prepared by reacting the ligand with nickel(II) perchlorate in aqueous ethanol. Brown, block-like crystals grown from aqueous solution by slow cooling, crystal dimensions 0·2 × 0·3 × 0·3 mm; D_m by flotation in $HCCl_3/CCl_4$. Nicolet $P3$ four-circle diffractometer, graphite-monochromated Mo $K\alpha$; cell parameters from 20 reflections, $9 < 2\theta < 27°$; monoclinic Cc or $C2/c$ from systematic absences, $C2/c$ confirmed by refinement; ω-scan technique, scan rate 2·0–29·3° min^{-1}, two standards measured every 58 reflections, no significant variations;

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Table 1. *Final atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* ($\times 10^3$)

$$U_{eq} = \tfrac{1}{3}\textstyle\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j .$$

	x	y	z	U_{eq}(Å^2)
Ni	8727 (1)	2390 (1)	691 (1)	38
O(1)	7532 (1)	3210 (4)	615 (3)	59
N(1)	8040 (1)	3533 (4)	798 (2)	41
N(2)	8995 (2)	4050 (4)	1236 (3)	49
N(3)	9570 (2)	1987 (5)	729 (3)	62
N(4)	8893 (2)	2865 (4)	−585 (3)	49
N(5)	8433 (2)	706 (4)	126 (2)	44
N(6)	8574 (2)	1325 (5)	1813 (3)	59
C(1)	8111 (2)	4624 (5)	1185 (3)	50
C(2)	8668 (2)	4953 (5)	1388 (3)	49
C(3)	9560 (2)	4163 (7)	1402 (4)	72
C(4)	9785 (2)	2806 (8)	1433 (4)	77
C(5)	9793 (2)	2250 (7)	−117 (4)	72
C(6)	9461 (2)	3196 (7)	−625 (4)	68
C(7)	8724 (2)	1778 (6)	−1139 (3)	53
C(8)	8721 (2)	506 (5)	−658 (3)	53
C(9)	8449 (3)	−350 (5)	745 (4)	64
C(10)	8254 (3)	197 (6)	1571 (4)	68
C(11)	7672 (3)	5520 (7)	1412 (5)	95
C(12)	8809 (3)	6255 (6)	1732 (4)	80
H	7500	2500	0	115*
Cl(1)	8483 (1)	3677 (2)	3846 (1)	87
Cl(2)	10000	665 (2)	7500	51
O(2)	8206 (5)	2754 (10)	3434 (5)	256
O(3)	8652 (8)	3489 (14)	4587 (5)	337
O(4)	8893 (4)	3836 (17)	3332 (7)	271
O(5)	8220 (4)	4845 (8)	3796 (8)	206
O(6)	10000	2012 (10)	7500	178
O(7)	10181 (9)	48 (22)	6788 (14)	132
O(8)	9589 (7)	−25 (22)	7843 (14)	122
O(9)	10415 (5)	699 (12)	8077 (9)	112

* U_{iso}.

4492 reflections measured for $2\theta < 54°$ ($h_{max} = 32$, $k_{max} = 13$, $l = -20$ to 20); corrected for Lp but not for absorption.

Structure solved by direct methods (*MULTAN*; Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), full-matrix least-squares refinement with *XRAY76* (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976); all H atoms found on difference map and refined isotropically; $\sum w(|F_o| - |F_c|)^2$, where $w = 1/(60{\cdot}0 + |F_o| + 0{\cdot}0047|F_o|^2)$; f' and f'' values from *International Tables for X-ray Crystallography* (1974); final R value 0·052 for 3129 reflections with $I > 2{\cdot}5\sigma(I)$, $wR = 0{\cdot}068$, $S = 0{\cdot}29$; maximum shift/e.s.d 0·97, $\Delta\rho < |0{\cdot}58|$ e Å^{-3}; atomic scattering factors were those included in the program.

Discussion. Final atomic parameters are given in Table 1.* Interatomic distances and the structure of the dimeric cation are shown in Fig. 1 and the arrangement of the ions in the unit cell is presented in Fig. 2.

The structure can be classified as a dimer consisting of $[Ni_2L_2H]^{3+}$ cations and perchlorate anions. The dinuclear complex moiety is centrosymmetric and describable in terms of two $[NiL]^+$ monomers, the oximato groups of which are interlinked through a crystallographically symmetrical O···H···O hydrogen bond, with the bridging H atom at the centre of symmetry (*cf.* Fig. 1). Thus the oxime proton is shared equally between two oximato O atoms. The 'intermolecular' hydrogen bond formed in this way is very short [O···O = 2·428 (6) Å], as are the intramolecular O···H···O hydrogen bonds frequently observed between the oximato groups in square-planar Ni^{II} complexes (Saarinen, Korvenranta, Orama & Raikas, 1984).

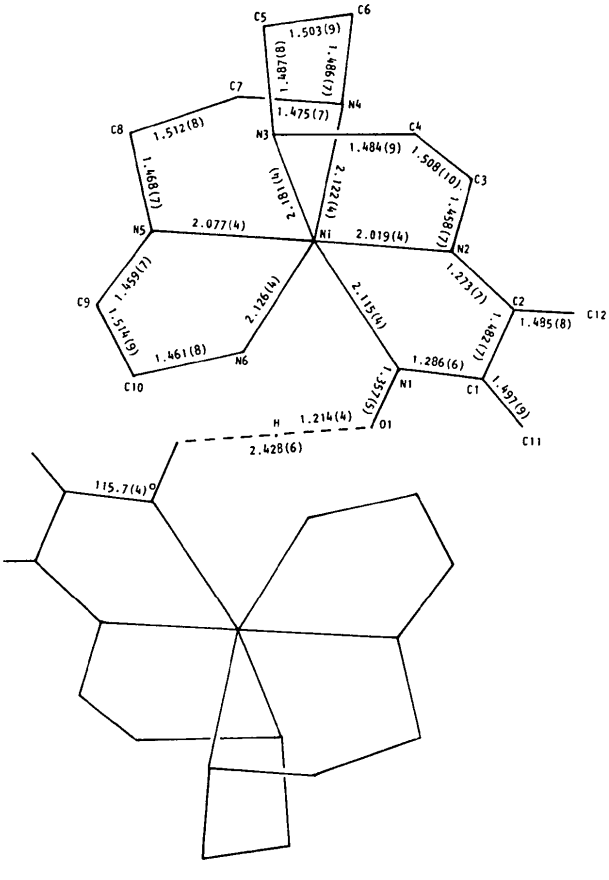

Fig. 1. Schematic representation of the complex ion $[Ni_2L_2H]^{3+}$ showing bond lengths (Å).

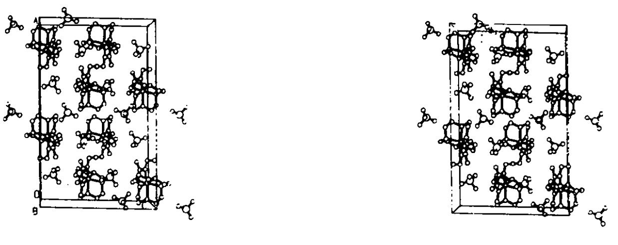

Fig. 2. Stereoscopic view of the molecular packing of $[Ni_2L_2H](ClO_4)_3$ in the unit cell, with H atoms omitted for clarity.

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* Lists of structure factors, bond angles, H-atom parameters and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43930 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The coordination about Ni is distorted octahedral, with bonds being formed to the oxime, imine and amine N atoms of the hexadentate ligand. The average Ni—N(amine) and Ni—N(imine) distances (2·127 and 2·019 Å, respectively) are normal and agree well with the corresponding bond lengths in comparable Ni^{II} complexes.

In an earlier paper we concluded that in octahedral Ni^{II} complexes deprotonation of the coordinated oxime group is accompanied by a shortening of about 0·1 Å in the Ni—N(oxime) bond length, from *ca* 2·10 to 2·01 Å (Korvenranta, Saarinen & Näsäkkälä, 1982). The Ni—N(oxime) distance found here (2·126 Å) is consistent with the bond length in typical undissociated structures.

The N—O and C—N(oxime) bond lengths and the C—N—O bond angle in the complex are 1·357 (5), 1·286 (6) Å, and 115·7 (4)°, respectively. Even though the C—N—O angle is relatively large, all these values are in satisfactory agreement with the ranges 1·38 ±0·03, 1·29±0·02 Å, and 112±2° reported for the undissociated oxime group and deviate considerably from the corresponding range 1·26±0·01, 1·36 ±0·02 Å, and 121±2° found for several octahedral oximato structures (Korvenranta, Saarinen & Näsäkkälä, 1982). In sum, an H atom symmetrically disposed in the O···O bond between two oximato O atoms seems to be sufficient to fix the geometry of the NOH function, and in its essential features the present complex generally resembles those of other octahedral Ni^{II} complexes formed without loss of the oxime proton.

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Acta Cryst. (1987). C**43**, 1516–1518

The Structure of the Mixed-Ligand Compound {*N*,*N*-Bis[(3,5-dimethyl-1-pyrazolyl)methyl]aniline}(3,5-dimethylpyrazole)nitratozinc(II) Nitrate

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(*Received* 9 *February* 1987; *accepted* 25 *March* 1987)

Abstract. $[Zn(C_5H_8N_2)(C_{18}H_{23}N_5)(NO_3)]NO_3$, M_r = 594·93, triclinic, $P\bar{1}$, a = 12·932 (3), b = 15·402 (15), c = 15·451 (2) Å, α = 90·91 (4), β = 108·61 (2), γ = 107·03 (4)°, V = 2768·3 Å^3, Z = 4, D_x = 1·43 g cm^{-3}, λ(Mo $K\bar{\alpha}$) = 0·71073 Å, μ = 9·58 cm^{-1}, $F(000)$ = 1241, T = 293 K, final R = 0·037 for 3154 significant reflections. The asymmetric unit consists of two different formula units of almost identical dimensions. In each of these molecules Zn is tetrahedrally surrounded by two azole N atoms of the ligand *N*,*N*-bis[(3,5-dimethyl-1-pyrazolyl)methyl]aniline (pabd), by an azole N atom of 3,5-dimethylpyrazole and an O atom of one of the nitrate anions. Distances from Zn to the donor atoms are in the narrow range of 1·98 to 2·06 Å. The 3,5-dimethylpyrazole ligand is hydrogen bonded, through the H atom on the other azole N atom, to the second nitrate ion, with an N···O distance of 2·72 Å. The aniline N atom of pabd does not participate in the coordination. Bond angles around this N atom are close to 120°, indicating a delocalized lone pair of electrons.

Introduction. The synthesis and characterization of several transition-metal compounds of *N*,*N*-bis[(3,5-dimethyl-1-pyrazolyl)methyl]aniline (pabd) have been described recently (Blonk, Driessen & Reedijk, 1985). Mostly well defined coordination compounds are formed. With some metal salts, however, products have been isolated which contain fragments of pabd. Cluster

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0108-2701/87/081516-03$01.50