Cu(2)—O(1)— is folded with a dihedral angle $\varphi_{CD} =$ 111·2° defined between the best plane C [deviations (Å) in parentheses], Cu(1) (0·04), O(2) (−0·07), C(3) (0·03), Cu(2) (−0·03), O(3) (0·03) and the plane D, Cu(1), O(1), Cu(2).

Two structural effects are associated with the methanolic oxygen atoms O(6), O(6'). (i) The hydrogen bridge O(5)···H(O6)—O(6), O(5)—O(6) = 2·650 (7) Å, O(5)—H(O6)—O(6) = 175 (2)°, stabilizes the folded structure. (ii) The *trans* angle O(2)—Cu(1)—N(1) = 164·7 (2)° is influenced by the Cu(1)—O(6) = 2·830 (5) Å distance as the O(6) position may be described as the apical position in a square-planar pyramidal Cu(1) coordination. This correlation is observed within the series of related trinuclear compounds (Gehring, 1990). A smaller Cu(1)—O(6) distance leads to a more distorted Cu(1) basal plane A with smaller angles O(2)—Cu(1)—N(1) while the other *trans* angle O(1)—Cu(1)—O(4) remains nearly unchanged at 176 ± 1°.

Distances and angles within the ligands agree with those found in related compounds. The molecular structure of the 3-methyl derivative shows no significant differences to the unsubstituted analogues mentioned in the *Introduction*.

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Structure of a Nickel(II) Complex of the Deprotonated Anion of 3,10-Dimethyl-4,9-diaza-3,9-dodecadiene-2,11-dione Dioxime

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Abstract. μ-[3,10-Dimethyl-4,9-diaza-3,9-dodecadiene-2,11-dione dioximato(1−)-μ-O,N,N',N'',N''']nickel(II) perchlorate, $[Ni(C_{12}H_{21}N_4O_2)]^+.ClO_4^-$, $M_r = 411.5$, triclinic, $P\bar{1}$, $a = 6.533$ (2), $b = 10.840$ (3), $c = 12.979$ Å, $\alpha = 103.57$ (3), $\beta = 95.76$ (3), $\gamma = 103.16$ (2)°, $V = 858.5$ (5) Å^3, $Z = 2$, $D_x = 1.592$ Mg m^{-3}, $\lambda(Mo\ K\alpha) = 0.71073$ Å, $\mu = 1.33$ mm^{-1}, $F(000) = 428$, $R = 0.0440$, $wR = 0.0494$ for 2417 independent reflections at 296 K. An oxime proton is lost from the ligand in forming the complex and the remaining oxime proton forms an intramolecular hydrogen bond between the two oxime oxygens. The Ni^{II} atom is in a distorted square planar coordination. The average values for the important bond distances are Ni—N(oxime) = 1.871, Ni—N(imine) = 1.907, O···O = 2.443 Å for the intramolecular hydrogen bond.

Introduction. It is well established that deprotonated tetradentate diimine dioximes and diamine dioximes coordinate with transition metal ions to form complexes having strong intramolecular hydrogen bonds between *cis* oxime groups (Wang, Chung, Cheng & Wang, 1990; Fair & Schlemper, 1978; Gavel & Schlemper, 1979; Liss & Schlemper, 1975). The O···O distance can be varied either by changing the ligand or by changing the size of the metal ion. The X-ray crystal structures of the complexes of deprotonated

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diamine dioximes have been studied extensively (Pal, Murmann, Schlemper, Fair & Hussain, 1986); however, only a few structures of the complexes of deprotonated diimine dioximes have been reported (Bertrand, Smith & VanDerveer, 1977). In the present study the nickel(II) complex of the deprotonated 3,10-dimethyl-4,9-diaza-3,9-dodecadiene-2,11-dione dioxime, [(DOH)$_2$Bn—H], was chosen for comparison with the copper(II) complex of this ligand (Wang, Wang, Wang & Chung, 1990) and with a recently reported nickel(II) complex of deprotonated 3,9-dimethyl-4,8-diaza-3,8-undecadiene-2,10-dione dioxime, [(DOH)$_2$Pn—H] (Wang, Chung, Cheng & Wang, 1990).

Experimental. The ligand, 3,10-dimethyl-4,9-diaza-3,9-dodecadiene-2,11-dione dioxime, was prepared as described in the literature (Wang, Chung, Cheng & Wang, 1990). A hot methanol solution (20 ml) of nickel perchlorate (10 mmol) was added to a hot methanol solution (20 ml) of the ligand (20 mmol), 3,10-dimethyl-4,9-daza-3,9-dodecadiene-2,11-dione dioxime; as the brown solution cooled, an orange product precipitated. The product was collected by filtration, and recrystallized from water; it was dried in air.

An orange crystal of approximate dimensions 0·38 × 0·20 × 0·18 mm was mounted on a Nicolet *R3m*/*V* diffractometer equipped with a graphite monochromator. Unit-cell constants were determined from a least-squares fit to the automatically centered settings for 24 reflections with $11·88 \le 2\theta \le 29·54°$. $\theta/2\theta$ scan data were collected at room temperature (297 K) for four octants of the sphere $(0 \le h \le 7, -12 \le k \le 12, -15 \le l \le 15)$ out to the 2θ limit of 50°. A variable scan speed of $2·93–14·65°$ min^{-1} was used. Three standard reflections were monitored every 50 reflections and showed no signs of crystal deterioration. The data were corrected for Lorentz and polarization effects. 3438 reflections were collected, 3037 unique, of which 2417 observed reflections with $I > 3\sigma(I)$ were used for refinement of the structure.

The structure was solved by direct methods using *SHELXTL-Plus* (Sheldrick, 1986). Most of the non-H atoms were found on *E* maps. The other atoms were located on difference maps. Full-matrix least-squares refinement based on *F* with anomalous-dispersion corrections was used. Neutral-atom scattering form factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). All the non-H atoms were refined anisotropically. The weights had the form $w = [\sigma^2(F) + gF^2]^{-1}$ with $g = 0·0019$. The H atoms of the methyl groups were placed in idealized positions (C—H = 0·96 Å, H—C—H = 109·4°) with fixed U (0·08 Å^2). The other H atoms were obtained from difference maps

Table 1. *Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients (Å$^2 \times 10^3$)*

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Ni(1)	727 (1)	307 (1)	1815 (1)	31 (1)
O(1)	3872 (6)	1862 (3)	968 (3)	47 (1)
O(2)	2834 (5)	−482 (3)	48 (3)	48 (1)
N(1)	2861 (5)	1776 (3)	1797 (3)	35 (1)
N(2)	749 (6)	1353 (3)	3204 (3)	38 (1)
N(3)	−1607 (5)	−1194 (3)	1705 (3)	38 (1)
N(4)	1269 (6)	−829 (3)	606 (3)	36 (1)
C(1)	3293 (7)	2787 (4)	2618 (3)	40 (1)
C(2)	2058 (7)	2500 (4)	3465 (3)	41 (2)
C(3)	−410 (9)	833 (5)	3998 (4)	49 (2)
C(4)	−2731 (10)	811 (6)	3826 (5)	62 (2)
C(5)	−3871 (9)	100 (6)	2675 (5)	56 (2)
C(6)	−3507 (8)	−1243 (5)	2248 (5)	51 (2)
C(7)	−1487 (7)	−2235 (4)	1027 (4)	40 (2)
C(8)	268 (7)	−2046 (4)	392 (3)	39 (1)
C(9)	4916 (10)	4030 (5)	2703 (5)	64 (2)
C(10)	2467 (11)	3497 (5)	4525 (4)	65 (2)
C(11)	−3000 (9)	−3559 (5)	801 (5)	58 (2)
C(12)	775 (9)	−3107 (5)	−420 (4)	56 (2)
Cl(1)	1519 (2)	6693 (2)	3103 (1)	69 (1)
O(3)	1910 (8)	6430 (5)	2046 (3)	90 (2)
O(4)	3233 (13)	6810 (7)	3839 (5)	150 (4)
O(5)	174 (18)	5520 (15)	3172 (9)	299 (9)
O(6)	469 (25)	7544 (13)	3343 (5)	306 (10)

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

Ni(1)—N(1)	1·869 (3)	Ni(1)—N(2)	1·887 (3)
Ni(1)—N(3)	1·927 (3)	Ni(1)—N(4)	1·873 (4)
O(1)—N(1)	1·328 (5)	O(2)—N(4)	1·346 (5)
N(1)—C(1)	1·291 (5)	N(2)—C(2)	1·285 (5)
N(2)—C(3)	1·479 (7)	N(3)—C(6)	1·485 (7)
N(3)—C(7)	1·282 (6)	N(4)—C(8)	1·283 (5)
C(1)—C(2)	1·476 (7)	C(1)—C(9)	1·486 (7)
C(2)—C(10)	1·494 (6)	C(3)—C(4)	1·504 (9)
C(4)—C(5)	1·535 (7)	C(5)—C(6)	1·512 (8)
C(7)—C(8)	1·483 (7)	C(7)—C(11)	1·490 (6)
C(8)—C(12)	1·489 (7)	Cl(1)—O(3)	1·397 (5)
Cl(1)—O(4)	1·358 (8)	Cl(1)—O(5)	1·399 (14)
Cl(1)—O(6)	1·271 (16)*	O(1)—H(1)	0·699 (49)†
N(1)—Ni(1)—N(2)	81·9 (2)	N(1)—Ni(1)—N(3)	174·5 (2)
N(2)—Ni(1)—N(3)	101·4 (2)	N(1)—Ni(1)—N(4)	96·0 (2)
N(2)—Ni(1)—N(4)	166·0 (2)	N(3)—Ni(1)—N(4)	81·8 (2)
Ni(1)—N(1)—O(1)	123·8 (2)	Ni(1)—N(1)—C(1)	117·7 (3)
O(1)—N(1)—C(1)	118·4 (3)	Ni(1)—N(2)—C(2)	115·3 (3)
Ni(1)—N(2)—C(3)	122·6 (3)	C(2)—N(2)—C(3)	121·5 (4)
Ni(1)—N(3)—C(6)	127·9 (3)	Ni(1)—N(3)—C(7)	113·2 (3)
C(6)—N(3)—C(7)	118·8 (4)	Ni(1)—N(4)—O(2)	123·9 (2)
Ni(1)—N(4)—C(8)	117·1 (3)	O(2)—N(4)—C(8)	118·3 (4)
N(1)—C(1)—C(2)	110·7 (4)	N(1)—C(1)—C(9)	123·5 (5)
C(2)—C(1)—C(9)	125·6 (4)	N(2)—C(2)—C(1)	114·2 (4)
N(2)—C(2)—C(10)	126·4 (5)	C(1)—C(2)—C(10)	119·4 (4)
N(2)—C(3)—C(4)	112·5 (5)	C(3)—C(4)—C(5)	113·4 (5)
C(4)—C(5)—C(6)	114·2 (5)	C(3)—C(6)—C(5)	112·8 (4)
N(3)—C(7)—C(8)	115·1 (4)	N(3)—C(7)—C(11)	125·6 (5)
C(8)—C(7)—C(11)	119·2 (4)	N(4)—C(8)—C(7)	111·0 (4)
N(4)—C(8)—C(12)	123·7 (4)	C(7)—C(8)—C(12)	125·3 (4)
O(3)—Cl(1)—O(4)	113·6 (4)	O(3)—Cl(1)—O(5)	104·6 (5)
O(4)—Cl(1)—O(5)	100·8 (6)	O(3)—Cl(1)—O(6)	114·9 (5)
O(4)—Cl(1)—O(6)	115·9 (5)	O(5)—Cl(1)—O(6)	104·7 (8)
H(1)—O(2)—N(4)	95 (5)	H(1)—O(1)—N(1)	98 (5)
O(1)—H(1)—O(2)	155 (5)		

* Libration correction gave 1·399 Å for Cl(1)—O(6).

† This value is calculated from a refined H(1) position. H(1) was originally located from a difference map on which the electron density peaked at 1·306 Å from O(1).

Table 3. *Selected structural data for nickel(II) and copper(II) diimine dioxime complexes*

	[Ni{(DOH)$_2$Pn-H}](ClO$_4$)	[Cu{(DOH)$_2$Pn-H}](ClO$_4$)	[Ni{(DOH)$_2$Bn-H}](ClO$_4$)	[Cu{(DOH)$_2$Bn-H}]$_2$(ClO$_4$)$_2$
M—N(imine) (Å)	1·892 (4)	1·947 (5)	1·887 (3)	1·978 (4)
	1·892 (5)	1·961 (5)	1·927 (3)	1·977 (4)
M—N(oxime) (Å)	1·874 (4)	1·937 (5)	1·869 (3)	1·957 (4)
	1·869 (5)	1·847 (5)	1·873 (4)	1·992 (5)
		2·511 (5)		
O···O (Å)	2·421 (6)	2·505 (5)	2·443	2·608
O—H (Å)	1·15 (6)	—	1·133	0·74 (6)
O···H (Å)	1·27 (6)		1·306	
N(imine)—M—N(imine) (°)	99·2 (2)	100·2 (2)	101·5 (1)	102·8 (2)
N(imine)—M—N(oxime) (°)	82·4 (2)	80·6 (2)	81·9 (1)	79·7 (2)
	82·2 (2)	81·6 (2)	81·6 (1)	80·5 (2)
trans-N—M—N (°)	178·5 (2)	—	166·0 (2)	150·2 (2)
	178·1 (2)		174·5 (1)	173·0 (2)
Coordination geometry	Distorted square planar	Distorted square pyramidal	Distorted square planar	Distorted square pyramidal
Reference	Wang, Chung, Cheng & Wang (1990)	Bertrand, Smith & VanDerveer (1977)	This work	Wang, Wang, Wang & Chung (1990)

and refined with isotropic U's. For 253 variables and 2417 reflections the final agreement factors are $R = 0.0440$, $wR = 0.0494$. Max., min. $\Delta\rho$ 0·62, -0.43 e Å^{-3}; $(\Delta/\sigma)_{max} = 0.040$. All calculations were performed with the Nicolet *SHELXTL-Plus* system on a MicroVAX II.

Discussion. The atomic coordinates and temperature factors are listed in Table 1.* The bond distances and angles are listed in Table 2. A perspective view of the molecule with the numbering scheme is shown in Fig. 1. A stereoview of the unit cell is shown in Fig. 2.

The present complex is a stable four-coordinate species; the Ni^{II} and four donor N atoms are coplanar within 0·151 Å. The distances and angles in the present compound along with those for some related compounds are given in Table 3. It is interesting that all the reported crystal structures of the nickel(II) complexes of deprotonated diimine dioximes are four-coordinate distorted square planar species, while all the reported crystal structures of the copper(II) complexes of these ligands are five-coordinate distorted square pyramidal species. The Ni—N bond lengths in this complex are very similar to those in [Ni(DOH)$_2$Pn—H]$^+$ (Pn = —CH$_2$CH$_2$CH$_2$—) but shorter than those in [(Cu{(DOH)$_2$Bn—H})$_2$]$^{2+}$, consistent with the larger size of copper(II) as shown in Table 3. The M—N (oxime) bond distances in all these complexes are significantly shorter than the M—N (imine) bond distances. The N—M—N angles in all of these complexes are distorted from the ideal
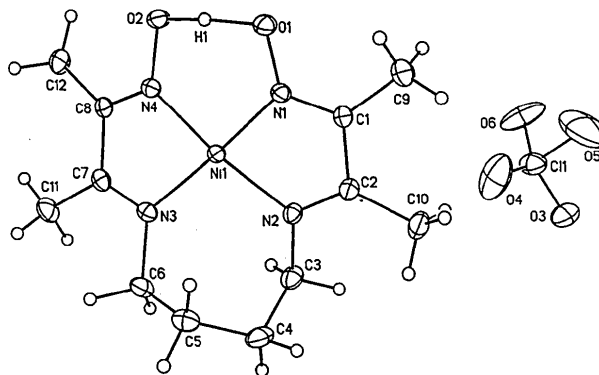

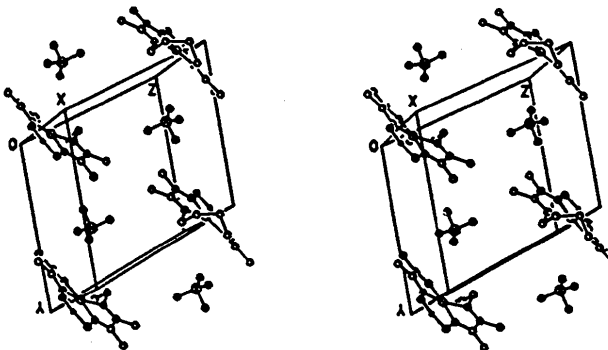Fig. 1. Perspective view with the atom-numbering scheme.

Fig. 2. Stereoscopic drawing of the crystal packing in the unit cell.

square planar values, depending on the sizes of the chelate rings and the size of the metal ion. The N(imine)—M—N(imine) angle in this complex is slightly larger than that in [Ni(DOH)$_2$Pn—H]$^+$, but slightly smaller than that in [(Cu{(DOH)$_2$Bn—H})$_2$]$^{2+}$. Conversely the N(imine)—M—N(oxime)

* 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 53975 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

angles in this complex are slightly smaller than those in [Ni(DOH)₂Pn—H]⁺, but slightly larger than those in [(Cu{(DOH)₂Bn—H})₂]²⁺ (Table 3).

It is now well established that the O···O distance in the complex of diazadioxime varies as a function of (1) the size of the metal ion, (2) the constraint imposed by the methylene carbons bridging the amine N atoms, and (3) changing from an sp^3 amine nitrogen to an sp^2 imine nitrogen (Liss & Schlemper, 1975; Pal, Murmann, Schlemper, Fair & Hussain, 1986). As shown in Table 3, the O···O distance in the present complex is about 0·18 Å shorter than that in [Cu(DOH)₂Bn—H]⁺, consistent with the smaller size of nickel(II). The O···O distance in the present complex is similar to that in [Ni(DOH)₂Pn—H]⁺. These results indicate the bridge in (DOH)₂Bn—H is essentially the same as the propylene bridge in (DOH)₂Pn—H. Similar results were also found in the copper(II) complexes (Liss & Schlemper, 1975; Pal, Murmann, Schlemper, Fair & Hussain, 1986).

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Bis(pentafluorophenyl)(N,N,N',N'-tetramethylethylenediamine)platinum(II)

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Abstract. [Pt(C₆F₅)₂(tmen)], C₁₈H₁₆F₁₀N₂Pt, M_r = 645·5, monoclinic, C2/c, a = 19·526 (6), b = 8·554 (1), c = 13·282 (2) Å, β = 113·43 (2)°, V = 2036 (3) Å³, Z = 4, D_x = 2·106 g cm⁻³, λ(Mo Kα) = 0·7107 Å, μ = 70·21 cm⁻¹, F(000) = 1224, T = 293 (1) K, R = 0·040 for 1906 observed reflections. The Pt atom in the title compound, which lies on a crystallographic twofold axis, exists in a distorted square planar geometry comprised of a chelating tetramethylethylenediamine (tmen) ligand [Pt—N 2·141 (5) Å] and two pentafluorophenyl groups [Pt—C 2·006 (6) Å] which make an angle of 87·1° with the square plane.

Introduction. In synthetic studies of polyfluorophenyl complexes of platinum, the title compound [Pt(C₆F₅)₂(tmen)] was prepared (Deacon & Nelson-Reed, 1987). Subsequently, crystals of this compound have been obtained and the structure investigated in order to provide detailed information on the Pt coordination geometry and thereby provide additional data on the relative *trans* influence of the pentafluorophenyl ligand.

Experimental. [Pt(C₆F₅)₂(tmen)] was prepared as in the literature (Deacon & Nelson-Reed, 1987) and crystals were obtained by the slow evaporation of an ether/petroleum ether solution of the compound; m.p. 573–575 K (dec.). Enraf–Nonius CAD-4F diffractometer controlled by a PDP8/A computer, graphite-monochromated Mo Kα radiation; ω:2θ scan technique. Cell parameters by least squares on 25 reflections (11 ≤ θ ≤ 20°) (de Boer & Duisenberg, 1984) on a crystal 0·14 × 0·28 × 0·56 mm. Analytical absorption correction applied; max. and min. transmission factors 0·345 and 0·067 (SHELX76; Sheldrick, 1976). 2738 reflections (1·5 ≤ θ ≤ 26·0°)