$Co(NH_3)_5]^{2+}$ cation, two ClO_4^- anions and four H_2O's. In this cation, the Im anion bridges the Cu and Co atoms (Fig. 1). The Cu atom shows a distorted square-pyramidal coordination, surrounded by the approximately planar O(2), O(3) and N(1) from Ida and N(2) from Im, and a water on the axis. The Cu atom is 0·13 Å above the equatorial plane. The bond length Cu—O(15) 2·43 Å is longer than Cu—N(1), Cu—N(2), Cu—O(2) and Cu—O(3) in the equatorial plane. All the Cu—N and Cu—O bond distances accord with literature values (Hathaway & Billing, 1970). The Co atom is surrounded by six N atoms, five of which are from NH_3's and one from the Im group, forming a regular octahedral coordination. The bond distances and angles around the Co atom are in accord with similar values in the literature (Davis, Dewan & Lippard, 1981).

The coordinated Im and Ida groups show good planar conformation. The Im plane makes an angle of 22° with the square-pyramidal base plane [N(1), O(2), N(2), O(3)] and of 19·5° with the Ida-group plane. The Im plane almost divides the angles of N(4)—Co—N(5) and N(7)—Co—N(8) equally. The bond distances and the angles in the Im group are close to those in a free imidazole molecule (Sundberg & Martin, 1974). The bond distances N—C and C—C of the Ida group are similar to those in H_2Ida.HCl (Oskarsson, 1973).

The structure of the Im-bridged heterotrinuclear complex (II) consists of $[(NH_3)_5CoImCu(Ida)ImCo(NH_3)_5]^{4+}$, four ClO_4^- anions and four H_2O's. The Cu atom is coordinated by three N atoms and two O atoms, of which two N atoms are from two Im groups and the others from the Ida group, forming a square-pyramidal configuration as shown in Fig. 2. N(1), N(3), O(1) and N(15) form the equatorial plane and the Cu atom is located at the centre and 0·18 Å above this plane. The average bond distance of Cu—N_{Im} 1·963 Å is shorter than Cu—N_{Ida} 2·078 Å. The bond distance of the O(2) atom of Ida coordinated to Cu at the top of the square pyramid, 2·301 Å, is longer than that of Cu—O(1), 1·975 Å, which is in the equatorial plane. The Co configuration is the same as that in complex (I).

The non-H atoms in the Im group show a good planar conformation. The angle of each of the two Im planes with the equatorial plane of Cu is 81 and 29°, and the angle of the two Im planes is 84°. The bond distances in the Im groups are similar to those in the free imidazole molecule (Sundberg & Martin, 1974).

Compared with complex (I), the conformation of the coordinated Ida has changed. When the second $[(NH_3)_5CoIm]^{2+}$ group coordinates to the Cu^{II} atom of $[(Ida)CuImCo(NH_3)_5]^{2+}$, the plane of the Ida folds forming two planes. The angle between the two planes is 110·3°. One O atom of Ida coordinates with Cu in the equatorial plane while the other O atom is on the axis. The conformation of Ida may be changed by $[(NH_3)_5CoIm]^{2+}$ which has a larger steric effect than H_2O. The bond distances C—C and C—N of the Ida are the same in the two complexes.

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Acta Cryst. (1990). C**46**, 1429–1432

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

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Abstract. Bis{3,3′-(trimethylenedinitrilo)di[2-butanone oximato(1 −)]}nickel(II) perchlorate, $[Ni(C_{11}H_{19}N_4O_2)](ClO_4)$, $M_r = 397·5$, monoclinic, $P2_1/c$, $a = 7·162$ (3), $b = 16·805$ (7), $c = 13·703$ (5) Å, $\beta = 102·70$ (3)°, $V = 1609$ (1) Å^3, $Z = 4$, $D_x = 1·641$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, μ =

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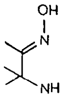
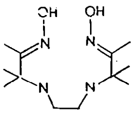
14·11 cm^{-1}, $F(000) = 824$, $T = 298$ K, $R = 0·0407$, $wR = 0·0393$, for 1639 independent reflections. An oxime proton is lost from the ligand in forming the complex and the remaining oxime proton forms a hydrogen bond of 2·421 (6) Å between the two oxime O atoms. The crystal consists of discrete square-planar $[Ni(C_{11}H_{19}N_4O_2)]^+$ cations and perchlorate anions. The four Ni—N distances span a narrow range, 1·869 (5)–1·892 (5) Å.

Introduction. Several metal complexes of α-amino oxime ligands (L_1–L_3) have been studied by X-ray and neutron diffraction to examine the effects of O···O distance and of crystallographic environment on the H atom position and the associated potential function (Ching & Schlemper, 1975; Sakhawat Hussain & Schlemper, 1979). However, very little attention has been devoted to the crystal structures of transition-metal complexes of α-imino oxime ligands. The crystal structure of the copper(II) complex of the deprotonated anion of 3,9-dimethyl-4,8-diaza-3,8-undecadiene-2,10-dione dioxime (L_4) has been reported by Bertrand, Smith & VanDerveer (1977). In order to examine the effect of the metal ion on the structure of the complex, we have prepared and studied the nickel(II) complex of the deprotonated anion of this ligand (L_4).



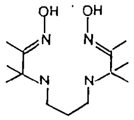
(AO)

L_1



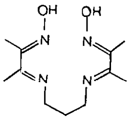
(EnAO)

L_2



(PnAO)

L_3



(DOH)$_2$Pn

L_4

Experimental. 2,3-Butanedione monoxime (115·4 mmol) was dissolved in ethanol (200 ml), and 1,3-butanediamine (49 mmol) in ethanol (100 ml) was added dropwise; the solution was refluxed for a further 2 h, then allowed to cool to room temperature. The solvent was removed under reduced pressure; the product L_4 was washed with cold acetonitrile and recrystallized from methanol as white product. A hot methanol solution of nickel perchlorate hexahydrate (10 mmol in 30 ml) was added to a hot methanol solution of L_4 (20 mmol in 20 ml); as the deep brown solution cooled, a brown product precipitated. The product was collected by filtration, washed with diethyl ether and dried in air.

A crystal of dimensions 0·27 × 0·27 × 0·15 mm was selected for X-ray analysis. The intensity data were collected using a MicroVAX II computer-controlled Nicolet *R3m/V* diffractometer and graphite-monochromated Mo $K\alpha$ radiation. Lattice constants were obtained from 18 reflections with $12·89 \leq 2\theta \leq 30·84°$. The space group was $P2_1/c$, the systematic absences: $0k0$, $k = 2n + 1$; $h0l$, $l = 2n + 1$. $\theta/2\theta$ scan data were collected at 298 K for two octants of the sphere ($0 \leq h < 8$, $0 \leq k \leq 20$, $-16 \leq l \leq 15$) out to the 2θ limit of 50° [$(\sin\theta)/\lambda = 0·6$ Å^{-1}]. Scan width 1·00° plus $K\alpha$ separation, scan speed 2·93–14·65° min^{-1}, and a scan-to-background ratio of 0·50. Three standard reflections were monitored every 50 reflections and showed no signs of crystal deterioration. The data were corrected for Lorentz and polarization effects. The crystal showed no significant absorption effect, thus no absorption correction was made. 3257 reflections were collected, 2850 unique, of which 1639 observed reflections with $I \geq 3·0\sigma(I)$ were used for solution and refinement of the structure. The structure was solved by direct methods using the *SHELXTL-Plus* program (Sheldrick, 1986). Full-matrix least-squares refinement based on F was used. Anomalous-dispersion corrections were applied to atoms with atomic numbers greater than 16. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974). The positions for all non-H atoms were deduced from an E map and were refined with anisotropic temperature factors. All H atoms except H(1*A*) included in the refinement were initially placed in positions (C—H = 0·96 Å, H—C—H = 109·4°) and then refined with fixed U (0·08 Å^2). H(1*A*) was deduced from a difference Fourier map and was refined with an isotropic temperature factor. For 212 variables and 1639 reflections the final agreement factors are $R = 0·0407$, $wR = 0·0393$, $w = 1·0/[\sigma^2(F) + 0·0004F^2]$. $\sigma^2(F)$ based on counting statistics, $(\Delta/\sigma)_{max} = 0·099$, GOF = 1·32, $(\Delta\rho)_{max} = 0·34$, $(\Delta\rho)_{min} = -0·44$ e Å^{-3}. All calculations were performed on a MicroVAX II computer using the *SHELXTL-Plus* programs.

Discussion. The molecular structure of $[Ni(C_{11}H_{19}N_4O_2)](ClO_4)$ and the atomic numbering schemes are shown in Fig. 1. Final positional and thermal parameters are listed in Table 1. Bond lengths and bond angles are listed in Table 2.* The crystals are built up of square-planar $[Ni(H_{-1}L_4)]^+$ cations and perchlorate anions. The four Ni—N distances span a narrow range, 1·869 (5)–1·892 (5) Å. There is a weak interaction between the Ni^{II} and an oxygen atom [O(6)] of the perchlorate group. The interatomic distance is 2·902 (5) Å between Ni^{II} and O(6). A stereoscopic view of the molecules in the unit cell is shown in Fig. 2. In the molecule, an oxime proton is lost from the ligand in forming the complex

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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 52790 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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

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

	x	*y*	*z*	U_{eq}
Ni	107 (1)	925	966 (1)	37 (1)
Cl	−2055 (2)	3043 (1)	229 (1)	52 (1)
N(1)	−1159 (6)	394 (3)	1830 (3)	41 (2)
N(2)	1996 (6)	1060 (3)	2158 (3)	43 (2)
N(3)	1347 (6)	1449 (3)	62 (3)	43 (2)
N(4)	−1782 (6)	757 (2)	−200 (3)	40 (2)
O(1)	−2874 (5)	54 (2)	1547 (3)	53 (2)
O(2)	−3432 (5)	375 (2)	−216 (3)	52 (1)
O(3)	−256 (8)	3247 (3)	66 (5)	119 (3)
O(4)	−2952 (7)	3721 (3)	531 (3)	90 (2)
O(5)	−3205 (8)	2743 (3)	−656 (3)	107 (2)
O(6)	−1822 (7)	2443 (3)	975 (3)	81 (2)
C(1)	−332 (7)	381 (3)	2770 (4)	40 (2)
C(2)	1570 (8)	764 (3)	2945 (4)	45 (2)
C(3)	3831 (8)	1456 (4)	2185 (5)	61 (2)
C(4)	3653 (9)	2099 (4)	1425 (5)	64 (3)
C(5)	3228 (8)	1829 (4)	354 (5)	60 (3)
C(6)	349 (9)	1480 (3)	−850 (4)	49 (2)
C(7)	−1518 (8)	1089 (3)	−1010 (4)	43 (2)
C(8)	−1203 (9)	18 (4)	3557 (4)	61 (2)
C(9)	2822 (9)	751 (4)	3974 (4)	65 (3)
C(10)	971 (10)	1864 (4)	−1706 (4)	74 (3)
C(11)	−2986 (9)	1087 (3)	−1969 (4)	59 (3)

Table 2. *Bond distances* (Å) *and angles* (°)

Ni—N(1)	1·869 (5)	Ni—N(2)	1·892 (4)
Ni—N(3)	1·892 (5)	Ni—N(4)	1·874 (4)
Cl—O(3)	1·398 (6)	Cl—O(4)	1·413 (5)
Cl—O(5)	1·402 (5)	Cl—O(6)	1·420 (5)
N(1)—O(1)	1·333 (6)	N(1)—C(1)	1·294 (6)
N(2)—C(2)	1·285 (7)	N(2)—C(3)	1·466 (7)
N(3)—C(5)	1·465 (7)	N(3)—C(6)	1·297 (7)
N(4)—O(2)	1·340 (6)	N(4)—C(7)	1·292 (7)
C(1)—C(2)	1·477 (7)	C(1)—C(8)	1·491 (8)
C(2)—C(9)	1·495 (7)	C(3)—C(4)	1·487 (9)
C(4)—C(5)	1·502 (9)	C(6)—C(7)	1·462 (8)
C(6)—C(10)	1·490 (9)	C(7)—C(11)	1·491 (7)
H(1*A*)—O(1)	1·15 (6)	H(1*A*)—O(2)	1·27 (6)
N(1)—Ni—N(2)	82·2 (2)	N(1)—Ni—N(3)	178·5 (2)
N(2)—Ni—N(3)	99·2 (2)	N(1)—Ni—N(4)	96·2 (2)
N(2)—Ni—N(4)	178·1 (2)	N(3)—Ni—N(4)	82·4 (2)
O(3)—Cl—O(4)	110·1 (3)	O(3)—Cl—O(5)	109·6 (4)
O(4)—Cl—O(5)	109·0 (3)	O(3)—Cl—O(6)	108·8 (3)
O(4)—Cl—O(6)	110·6 (3)	O(5)—Cl—O(6)	108·7 (3)
Ni—N(1)—O(1)	124·4 (3)	Ni—N(1)—C(1)	117·3 (4)
O(1)—N(1)—C(1)	118·2 (5)	Ni—N(2)—C(2)	115·0 (3)
Ni—N(2)—C(3)	122·9 (4)	C(2)—N(2)—C(3)	122·1 (4)
Ni—N(3)—C(5)	124·1 (4)	Ni—N(3)—C(6)	114·2 (4)
C(5)—N(3)—C(6)	121·6 (5)	Ni—N(4)—O(2)	123·7 (3)
Ni—N(4)—C(7)	116·9 (4)	O(2)—N(4)—C(7)	119·2 (4)
N(1)—C(1)—C(2)	111·0 (5)	N(1)—C(1)—C(8)	123·7 (5)
C(2)—C(1)—C(8)	125·3 (4)	N(2)—C(2)—C(1)	114·4 (4)
N(2)—C(2)—C(9)	126·4 (5)	C(1)—C(2)—C(9)	119·2 (5)
N(2)—C(3)—C(4)	111·9 (4)	C(3)—C(4)—C(5)	115·7 (5)
N(3)—C(5)—C(4)	112·0 (5)	N(3)—C(6)—C(7)	114·7 (5)
N(3)—C(6)—C(10)	125·4 (5)	C(7)—C(6)—C(10)	119·9 (5)
N(4)—C(7)—C(6)	111·5 (4)	N(4)—C(7)—C(11)	123·2 (5)
C(6)—C(7)—C(11)	125·2 (5)	O(1)—H(1*A*)—O(2)	173 (6)

and the remaining oxime proton forms a hydrogen bond between the two oxime O atoms. All non-H atoms except C(4) define a very good plane, and C(4) is displaced from this plane by 0·671 (14) Å. The maximum deviation of any N atom is 0·076 (14) Å indicating no significant deviation from planarity. The $\mathrm{Ni^{II}}$ atom is displaced from this plane by 0·018 (14) Å toward the perchlorate anion.

Several related nickel(II) and copper(II) complexes have been reported (Schlemper, 1968; Schlemper, Hamilton & LaPlaca, 1971; Schlemper & Fair, 1977; Ching & Schlemper, 1975; Fair & Schlemper, 1978; Bertrand, Smith & VanDerveer, 1977). The Ni—N and O···O distances for the complex studied in this work are similar to those found in the *α*-amino oxime complexes of nickel(II). However, the N(imine)–Ni–N(imine) angle is larger than the N(amine)–Ni–N(amine) angle; the N(oxime)–Ni–N(imine) angles are smaller than the N(oxime)–Ni–N(amine) angles. Of greater interest are the locations of the H atoms in these short intramolecular hydrogen bonds. As reported previously (Schlemper, 1968; Schlemper, LaPlaca & Hamilton; 1971; Murmann & Schlemper, 1973), the H atom in the complex with O···O distances of 2·42–2·43 Å is apparently nearly centered between the O atoms. A similar result was found in this work.

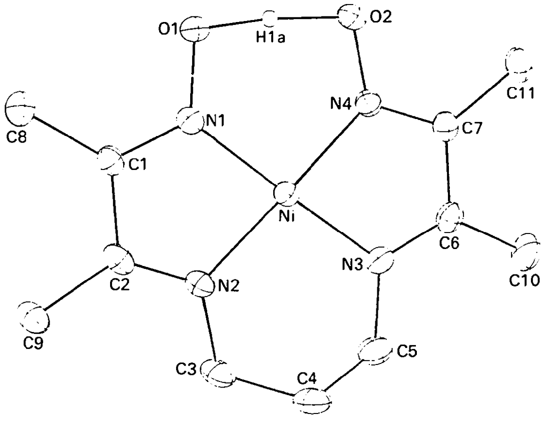

Fig. 1. Perspective view of the monomeric unit showing the hydrogen bonding between the two oxime oxygens.

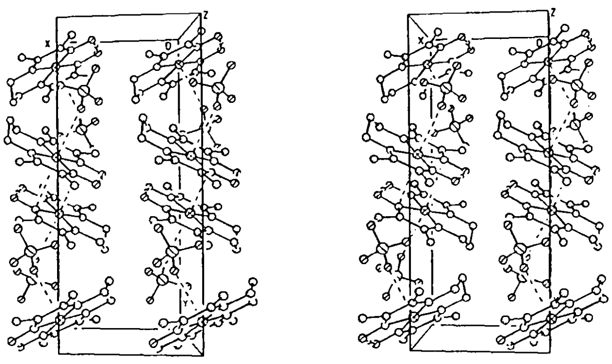

Fig. 2. Stereoscopic view of the molecules in the unit cell.

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Acta Cryst. (1990). C**46**, 1432–1434

π-Arene Complexes. 5. Structure of Tricarbonyl(η^6-hexamethylbenzene)-manganese(I) Pentacarbonyliodochromate(0)

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Abstract. $[\mathrm{Mn(C_{12}H_{18})(CO)_3}][\mathrm{CrI(CO)_5}]$, $M_r = 620{\cdot}6$, monoclinic, $P2_1/c$, $a = 8{\cdot}957\,(3)$, $b = 19{\cdot}017\,(3)$, $c = 14{\cdot}328\,(3)$ Å, $\beta = 106{\cdot}96\,(2)°$, $V = 2334\,(1)$ Å^3, $Z = 4$, $D_x = 1{\cdot}77$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 2{\cdot}23$ mm^{-1}, $F(000) = 1216$, $T = 298$ K. Final $R = 0{\cdot}049$, $wR = 0{\cdot}031$ for 2316 observed reflections with $F > 4\sigma(F_o)$ and 301 variable parameters. The structure consists of an $[\mathrm{Mn}(\eta^6\text{-}\mathrm{C_6Me_6})(\mathrm{CO})_3]^+$ cation linked to a $[\mathrm{Cr(CO)_5I}]^-$ anion in the asymmetric unit. The cation displays the well known 'piano stool' conformation found in half-sandwich complexes with the three carbonyl ligands in a staggered orientation relative to the C atoms of the substituted benzene ring. The central Cr atom of the anion is octahedrally coordinated and the iodo ligand is directed towards the arene ligand of the cation.

Introduction. The use of cationic arene complexes of manganese as starting materials for synthetic purposes is currently of interest (Bernhardt, Wilmoth, Weers, LaBrush, Eyman & Huffman, 1986; Ittel, Whitney, Chung, Williard & Sweigart, 1988). As part of our continuing interest in the activation/deactivation of the arene ring towards nucleophiles for such compounds, and the possible correlation with structural features, the crystal structure of the manganese complex with hexamethylbenzene as arene ligand (compound 1) was determined. The parent complex ion, $[\mathrm{Mn}(\eta^6\text{-}\mathrm{C_6Me_6})(\mathrm{CO})_3]^+$, is furthermore an important reference compound for the structural studies of complexes of the type $[\mathrm{Mn}(\eta^6\text{-}\mathrm{C_6Me_6})(\mathrm{CO})_2L]^+$ and $[\mathrm{Mn}(\eta^6\text{-}\mathrm{C_6Me_6})(\mathrm{CO})_2X]$ (L = neutral and X = anionic ligands). Initial problems encountered in growing suitable diffraction-quality single crystals were solved by using $[\mathrm{Cr(CO)_5I}]^-$ as a counter ion.

Experimental. The title compound was formed by the standard $\mathrm{AlCl_3}$ reaction to yield the $[\mathrm{Mn}(\eta^6\text{-}\mathrm{C_6Me_6})(\mathrm{CO})_3]^+$ cation (Winkhaus, Pratt & Wilkinson, 1961), followed by the addition of a THF (tetrahydrofuran) solution of $\mathrm{Cr(CO)_6}$ and excess NaI which was irradiated with a medium-pressure mercury arc. The colour of the solution changed to orange and the solvent was removed *in vacuo*. Recrystallization of this compound from a $\mathrm{CH_2Cl_2}$–hexane solution yielded diffraction-quality single crystals: crystal size 0·23 × 0·21 × 0·19 mm; Enraf–Nonius CAD-4 diffractometer, graphite-monochromatized Mo $K\alpha$ radiation; unit cell from 25 reflections ($7 < \theta < 16°$); 4231 reflections for $3 < \theta < 25°$ in the range ($0 < h < 10$, $0 < k < 22$ and $-17 < l < 17$) using ω scans where ω changed as $(0{\cdot}57 + 0{\cdot}34\tan\theta)°$ with a variable but maximum speed that corresponded to 3·30° min^{-1}. Three standard reflections varied less than 3%, measured every hour; Lorenz–polarization and empirical absorption corrections based on ψ scans of nine reflections were applied (North, Phillips & Mathews, 1968): transmission factors 0·935–1·00, av. 0·976. 2316 unique reflections were observed $[I > 2\sigma(I)]$. Structure solved using *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) and refined using *SHELX*76 (Sheldrick, 1976), H atoms

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