

Neutron Diffraction Study of the Orthorhombic Form of [3,3'-Dimethyl-3,3'-(2-nitropropanediylidenediamino)bis(2-butanone oximato)-N,N',N'',N'''] Nickel(II)

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Abstract

A neutron diffraction study of the orthorhombic form of the neutral, monomeric complex $[\text{Ni}(\text{C}_{13}\text{H}_{21}\text{N}_5\text{O}_4)]$ is reported. The compound has eight molecules in the unit cell of symmetry $Pbca$ with $a = 13.764$ (2), $b = 19.978$ (4) and $c = 11.532$ (2) Å. The structure was solved by direct methods, and full-matrix least-squares refinement converged to a final $R(F) = 0.078$. The significant differences between this orthorhombic form and the previously reported, monoclinic form of the complex are in the $\text{O}\cdots\text{O}$ distance and in the twist of the plane of the nitro group with respect to the six-membered chelate ring. In contrast to the reduced precursor, the Ni–N(amine) distances in both forms of this oxidized complex are shorter than the Ni–N(oxime) distances because of the aromaticity of the six-membered chelate ring. The symmetry-unconstrained intramolecular hydrogen bond is symmetric with one of the shortest $\text{O}\cdots\text{O}$ distances [2.390 (8) Å] observed in the α -amine-oxime metal complexes.

Introduction

Crystallization by slow evaporation of a saturated acetonitrile solution of the title complex gave two forms of crystals. Preliminary X-ray precession photographs indicated that one modification was orthorhombic while the other was monoclinic. Approximate unit-cell dimensions for both forms were obtained from zero- and upper-level precession photographs, and systematic absences were established.

Dark-red hexagonal-shaped crystals of the orthorhombic form suitable for neutron-data collection were grown by very slow evaporation, at room temperature, of a dilute acetonitrile solution of the compound in the presence of a well formed seed crystal. A crystal of approximate dimensions $0.96 \times 2.5 \times 3.2$ mm in the general directions [100], [010]

and [111], was used for the collection of neutron intensity data. The data were measured at the University of Missouri Research Reactor with a monochromatic neutron beam of wavelength 1.058 Å [this wavelength was obtained by using a silicon crystal ($a = 5.4308$ Å)]. The crystal was mounted on a brass pin with the ϕ axis a few degrees from the c axis and optically centered inside the χ circle of a PDP 11/03 computer-controlled locally developed diffractometer interfaced to a PDP 11/40 computer. The cell parameters (Table 1) were determined in two separate refinements, one with a least-squares fit of the coordinates of 17 automatically centered neutron reflections and the other with a least-squares fit of the coordinates of 16 carefully centered reflections using a small crystal on a Picker X-ray diffractometer. All calculations were performed using the latter cell constants. The neutron intensities of all hkl and $h\bar{k}l$ reflections with $4^\circ < 2\theta < 92^\circ$ were measured using the $\theta/2\theta$ step-scan method. Scan widths of $\Delta(2\theta) = 2.22^\circ$ were used with 37 steps

Table 1. *Crystal data of orthorhombic* $[\text{Ni}\{\{\text{pnao} - 6\text{H}(\text{NO}_2)\}\}]$ *by neutron diffraction*

pnao = 3,3'-dimethyl-3,3'-(1,3-propanediylidenediamino)bis(2-butanone oxime); $[\text{Ni}(\text{pnao})]^{2+}$ = a Ni^{2+} complex ion of pnao without a hydrogen bond; $[\text{Ni}(\text{pnao}) - \text{H}]^+$ = a hydrogen-bonded complex ion formed by abstraction of a proton from an oxime group; $[\text{Ni}\{\{\text{pnao} - 6\text{H}(\text{NO}_2)\}\}]$ = neutral complex obtained by nitration of the oxidized form, $[\text{Ni}(\text{pnao}) - 5\text{H}]^+$, of the hydrogen-bonded complex $[\text{Ni}(\text{pnao}) - \text{H}]^+$. Excluding the H atom replaced by the NO_2 group in the title compound, the oxidized form has five less (*i.e.* -5H) whereas the title compound has six less (*i.e.* -6H) H atoms as compared to the parent $[\text{Ni}(\text{pnao})]^{2+}$ complex ion.

Crystal system:	orthorhombic		
Space group:	$Pbca$	Wavelength	1.058 Å 0.7107 Å
Formula:	$[\text{Ni}(\text{C}_{13}\text{H}_{21}\text{N}_5\text{O}_4)]^0$	a	13.784 (3) Å 13.764 (2) Å
		b	19.964 (4) 19.978 (4)
$M_r = 370.05$		c	11.534 (3) 11.532 (2)
$\rho(\text{obs.}) = 1.55 \text{ Mg m}^{-3}$	V		3174 Å^3 3171 Å^3
$\rho(\text{calc.}) = 1.549$			
$Z = 8$			
$F(000) = 1552$			

of 0.06° each. Three standard reflections measured after every 47 reflections revealed no significant systematic fluctuation. Inspection of the neutron intensity data confirmed systematic absences $h0l$ for $l = 2n + 1$, $hk0$ for $h = 2n + 1$ and $0kl$ for $k = 2n + 1$ observed in the precession photographs of the orthorhombic form. These absences are consistent with centrosymmetric space group $Pbca$. The 7462 measured reflections were corrected for background and Lorentz effects. The neutron absorption corrections were applied using an analytical procedure. The linear absorption coefficient ($\mu = 0.183 \text{ mm}^{-1}$) was calculated including an incoherent scattering cross section of $34 \times 10^{-28} \text{ m}^2$ for hydrogen. The resulting crystal transmission factors ranged from 0.67 to 0.85. The equivalent data were averaged yielding 2949 unique reflections of which the 1894 with $I > 2\sigma(I)$ were used in the least-squares refinement. The variances of F_o^2 were calculated from $\sigma^2(F_o^2) = \sigma_c^2(F_o^2) + (0.02F_o^2)^2$ where $\sigma_c^2(F_o^2)$ is determined from the counting statistics and 0.02 is an empirical 'ignorance factor'.

The structure was solved by the tangent formula as developed in *MULTAN* (Germain, Main & Woolfson, 1971). The statistical distribution of the observed normalized structure factor amplitudes ($|E|$'s) was in agreement with the theoretical values for the centrosymmetric case (Karle, Dragonette & Brenner, 1965). The positions of 21 nonhydrogen atoms were obtained from an E map based on the *MULTAN* solution. After

refinement of a scale factor (k) and positional and isotropic thermal parameters of these 21 atoms, a difference Fourier synthesis revealed the positions of the remaining two nonhydrogen atoms and those of all H atoms, with the latter appearing as negative nuclear scattering density. Several more cycles of full-matrix least-squares refinement with anisotropic thermal parameters for all 44 atoms converged to the final values of the discrepancy indices of 0.083 for $R(F_o^2) = \sum |F_o^2 - kF_c^2| / \sum F_o^2$, 0.099 for $R_w(F_o^2) = [\sum w(F_o^2 - kF_c^2)^2 / \sum wF_o^4]^{1/2}$, 0.078 for $R(F_o) = \sum |F_o| - |F_c| / \sum F_o$ and 1.985 for $[\sum w(F_o^2 - F_c^2) / (N_{\text{obs}} - N_{\text{param}})]^{1/2}$. The 397 parameters varied in the final refinement included a scale factor, 132 positional parameters and

Table 2. Atomic fractional coordinates for orthorhombic $[\text{Ni}\{\text{pnao} - 6\text{H}(\text{NO}_2)\}]$

Estimated standard deviations are given in parentheses.

	x	y	z	B_{eq} (\AA^2)
Ni	0.3409 (2)	0.3703 (1)	0.0036 (2)	2.48
N(1)	0.4295 (2)	0.3100 (1)	0.0707 (3)	3.25
N(2)	0.4325 (2)	0.4200 (1)	-0.0807 (2)	2.85
N(3)	0.2501 (2)	0.3212 (1)	0.0866 (2)	2.78
N(4)	0.2537 (2)	0.4312 (1)	-0.0594 (2)	2.60
N(5)	0.0078 (2)	0.3875 (2)	0.0290 (3)	3.80
C(1)	0.3965 (3)	0.2650 (2)	0.1416 (3)	2.95
C(2)	0.4034 (3)	0.4730 (2)	-0.1357 (3)	2.66
C(3)	0.2875 (3)	0.2645 (2)	0.1581 (3)	2.79
C(4)	0.2967 (3)	0.4876 (2)	-0.1273 (3)	2.58
C(5)	0.1602 (3)	0.4307 (2)	-0.0455 (3)	2.67
C(6)	0.1105 (3)	0.3827 (2)	0.0223 (4)	2.90
C(7)	0.1558 (3)	0.3706 (2)	0.0856 (3)	2.97
C(8)	0.4727 (4)	0.5172 (3)	-0.2009 (5)	3.82
C(9)	0.4618 (5)	0.2178 (3)	0.2048 (5)	4.30
C(10)	0.2802 (4)	0.5539 (2)	-0.0639 (4)	3.27
C(11)	0.2453 (5)	0.1980 (2)	0.1153 (5)	4.04
C(12)	0.2546 (4)	0.4903 (3)	-0.2499 (4)	4.07
C(13)	0.2642 (4)	0.2765 (3)	0.2866 (4)	3.99
O(1)	0.5259 (4)	0.3131 (3)	0.0516 (5)	4.45
O(2)	0.5277 (3)	0.4032 (3)	-0.0847 (5)	3.86
O(3)	-0.0373 (4)	0.3504 (3)	0.0941 (6)	6.22
O(4)	-0.0345 (4)	0.4287 (3)	-0.0329 (6)	5.49
H(OO)	0.5370 (6)	0.3570 (5)	-0.0185 (8)	4.87
1H(5)	0.1161 (6)	0.4704 (4)	-0.0837 (8)	4.64
1H(7)	0.1036 (7)	0.2988 (5)	0.1363 (9)	5.28
1H(8)	0.4445 (11)	0.5632 (7)	-0.2165 (14)	10.19
2H(8)	0.5351 (11)	0.5255 (7)	-0.1532 (12)	8.39
3H(8)	0.4932 (12)	0.4956 (8)	-0.2782 (11)	9.83
1H(9)	0.4241 (10)	0.1697 (6)	0.2133 (14)	9.32
2H(9)	0.3263 (13)	0.2133 (8)	0.1655 (14)	9.35
3H(9)	0.4760 (13)	0.2340 (7)	0.2859 (12)	9.92
1H(10)	0.3180 (8)	0.5952 (4)	-0.1072 (9)	5.45
2H(10)	0.3125 (9)	0.5516 (5)	0.0211 (9)	5.76
3H(10)	0.2055 (9)	0.5654 (5)	-0.0585 (10)	5.76
1H(11)	0.2777 (10)	0.1568 (5)	0.1627 (11)	7.92
2H(11)	0.2604 (12)	0.1908 (5)	0.0260 (10)	7.98
3H(11)	0.1691 (11)	0.1955 (6)	0.1286 (13)	7.88
1H(12)	0.2870 (10)	0.5293 (6)	-0.3005 (9)	6.93
2H(12)	0.2656 (15)	0.4462 (6)	-0.2956 (10)	11.09
3H(12)	0.1779 (9)	0.5023 (9)	-0.2492 (11)	9.44
1H(13)	0.1870 (9)	0.2800 (6)	0.3015 (9)	6.38
2H(13)	0.2959 (10)	0.3214 (6)	0.3173 (9)	6.61
3H(13)	0.2934 (11)	0.2361 (6)	0.3378 (8)	7.55

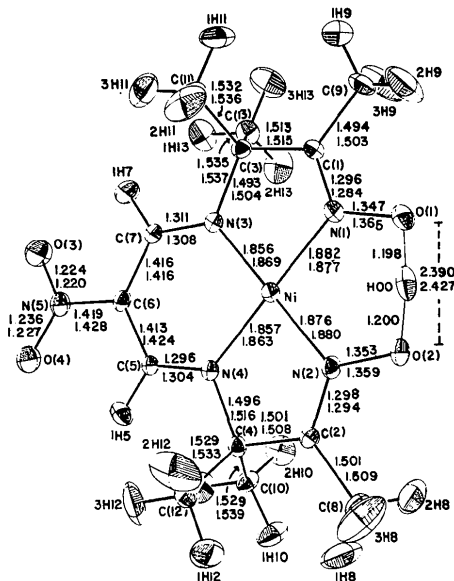


Fig. 1. A comparison of the bond distances (\AA) in the orthorhombic and monoclinic forms of $[\text{Ni}\{\text{pnao} - 6\text{H}(\text{NO}_2)\}]$. The values in the lower line are from the low-temperature X-ray diffraction study of the monoclinic form. The standard deviations in the neutron results of the orthorhombic form are Ni-N 0.003-0.004, N-C 0.004-0.005, C-C 0.005-0.006, N-O 0.005-0.006, O-O 0.008 and O-H 0.01 \AA .

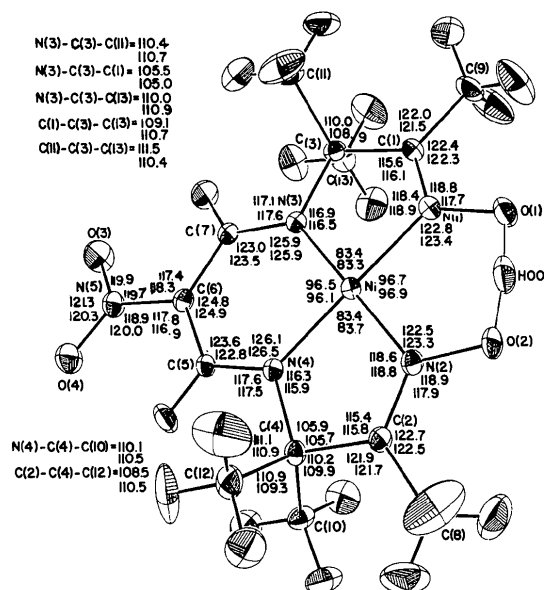


Fig. 2. A comparison of the bond angles ($^{\circ}$) of the two forms of $[\text{Ni}(\text{pnao}) \cdot 6\text{H}(\text{NO}_2)]$. The standard deviations in the neutron results are N-Ni-N 0.1–0.2, Ni-N-C 0.3, N-C-C 0.3–0.4, C-C-C 0.4–0.5, O-N-Ni 0.3–0.4, O-N-C 0.4 and O-N-O 0.5 $^{\circ}$.

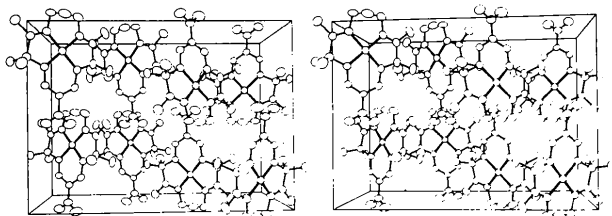


Fig. 3. Stereoscopic view showing molecular packing in the orthorhombic unit cell.

Table 3. Bond distances (\AA) and angles ($^{\circ}$) involving hydrogen atoms

O(1)-H(OO)	1.198 (14)	O(1)-H(OO)-O(2)	170.8 (8)
O(2)-H(OO)	1.200 (14)	1H(5)-C(5)-N(4)	119.7 (6)
C(5)-1H(5)	1.092 (9)	1H(5)-C(5)-C(6)	116.6 (6)
C(7)-1H(7)	1.081 (10)	1H(7)-C(7)-N(3)	120.4 (6)
C(8)-1H(8)	1.02 (2)	1H(7)-C(7)-C(6)	116.6 (6)
C(8)-2H(8)	1.03 (2)	1H(8)-C(8)-2H(8)	106 (1)
C(8)-3H(8)	1.03 (2)	1H(8)-C(8)-3H(8)	109 (1)
C(9)-1H(9)	1.04 (2)	2H(8)-C(8)-3H(8)	108 (1)
C(9)-2H(9)	1.00 (2)	1H(9)-C(9)-2H(9)	107 (1)
C(9)-3H(9)	1.01 (2)	1H(9)-C(9)-3H(9)	106 (1)
C(10)-1H(10)	1.09 (1)	2H(9)-C(9)-3H(9)	106 (1)
C(10)-2H(10)	1.08 (2)	1H(10)-C(10)-2H(10)	104.5 (9)
C(10)-3H(10)	1.06 (1)	1H(10)-C(10)-3H(10)	108.9 (8)
C(11)-1H(11)	1.08 (1)	2H(10)-C(10)-3H(10)	110.9 (9)
C(11)-2H(11)	1.06 (2)	1H(11)-C(11)-2H(11)	108 (1)
C(11)-3H(11)	1.06 (2)	1H(11)-C(11)-3H(11)	108 (1)
C(12)-1H(12)	1.07 (1)	2H(11)-C(11)-3H(11)	109 (1)
C(12)-2H(12)	1.04 (2)	1H(12)-C(12)-2H(12)	106 (1)
C(12)-3H(12)	1.08 (2)	1H(12)-C(12)-3H(12)	104 (1)
C(13)-1H(13)	1.08 (2)	2H(12)-C(12)-3H(12)	110 (1)
C(13)-2H(13)	1.06 (2)	1H(13)-C(13)-2H(13)	107.4 (9)
C(13)-3H(13)	1.08 (2)	1H(13)-C(13)-3H(13)	109.1 (9)
		2H(13)-C(13)-2H(13)	107.3 (9)

264 anisotropic temperature factors. No corrections were made for secondary-extinction effects. There were no changes greater than 0.1σ in any of the 397 parameters varied in the final refinement cycle. A final difference map revealed no significant negative or positive nuclear-scattering density. The atomic coordinates together with the equivalent values of the anisotropic temperature factors (B_{eq}), calculated by the method of Hamilton (1959), are given in Table 2.* The thermal motion as ellipsoids and atomic notation are shown in Fig. 1.

Interatomic distances and angles involving nonhydrogen atoms are given in Figs. 1 and 2 along with the corresponding values obtained from a low-temperature X-ray study (Hussain, Murmann & Schlemper, 1980) of the monoclinic form of this compound. A stereoscopic view of the molecular packing appears in Fig. 3. The bond distances and angles involving H atoms are listed in Table 3.

Discussion

The low-temperature X-ray structural analysis of the monoclinic form (space group $P2_1/a$) of the title compound has been reported recently (Hussain, Murmann & Schlemper, 1980). The primary interest in the neutron diffraction analysis of the orthorhombic form was to examine any structural differences between the two forms and for precise location of the H atoms, particularly in the short intramolecular hydrogen bond.

Both forms have discrete monomeric neutral complex units and all corresponding and chemically equivalent distances and angles are identical. The 14-membered macrocycle is planar and the values for distances and angles are internally consistent with C_{2v} point symmetry for the molecule. The main differences between the crystal structures of the two forms are in the packing of the complex. While the monoclinic form ($P2_1/a$) has four formula units in the unit cell, the orthorhombic ($Pbca$) has eight. The unit-cell volume [$3171 (7) \text{\AA}^3$] of the latter form is significantly (29\AA^3) greater than twice the volume of the former (3142\AA^3). A comparison of the intermolecular distances in both modifications is given in Table 4. All contact distances in the monoclinic form are consistently shorter than the corresponding distances in the orthorhombic form, as expected from the smaller volume of the former. The O(1) and O(2) atoms in the monoclinic modification have six intermolecular contacts shorter than 3.5\AA

* Tables containing anisotropic thermal parameters, least-squares-planes calculations and a list of structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35710 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

which would tend to lengthen the $\text{O}\cdots\text{O}$ distance compared to that in the orthorhombic form which has only one contact shorter than 3.5 Å. The observed differences, in the orientation of the nitro group and in the $\text{O}\cdots\text{O}$ distance, of the two forms probably reflect the variation in their packing patterns. The plane of the nitro group makes an angle of 6° with the molecular plane compared to the 16° observed in the monoclinic form. The 14-membered macrocycle is planar in both forms and is not affected by the change in packing pattern. The smaller tilt of the nitro group in the orthorhombic form appears to be the result of packing considerations. As pointed out earlier (Hussain, Murmann & Schlemper, 1980) such solid-state effects will not be reflected in the solution $^1\text{H-NMR}$ spectrum of the compounds where both protons [1H(5) and 1H(7)] appear equivalent (Urban & Vassain, 1979). The C–N(nitro) distance [1.419 (5) Å] is significantly shorter than the corresponding distance in 4-nitropyridine *N*-oxide, 1.454 (2) Å (Coppens & Lehmann, 1976) indicating some multiple bonding in this bond. However, this shortening is significantly less than expected for a true N–C double bond, the presence of which would be expected to favor even more strongly coplanarity of the six-membered chelate ring and the nitro group.

The $\text{O}\cdots\text{O}$ distance [2.390 (8) Å] observed in the present study is significantly shorter than the corresponding distance [2.427 (5) Å] for the monoclinic form. It is one of the shortest $\text{O}\cdots\text{O}$ distances

Table 4. *A comparison of some of the intermolecular contacts in both forms of $[\text{Ni}\{\text{(pnao)} - 6\text{H}(\text{NO}_2)\}]$*

The first atom is at the coordinates listed in Table 2; the listed symmetry positions are for the second atom.

	Monoclinic form		Orthorhombic form	
	Symmetry position*	Distance (Å)	Symmetry position*	Distance (Å)
$\text{O}(1)\cdots\text{O}(2)^\dagger$	1	2.427 (5)	1	2.390 (8)
$\text{O}(1)\cdots\text{O}(3)$	4	3.225 (6)	5	3.776 (9)
$\text{O}(1)\cdots\text{N}(1)$	2	3.315 (5)	–	–
$\text{O}(1)\cdots\text{C}(7)$	4	3.315 (5)	5	3.734 (7)
$\text{O}(1)\cdots\text{C}(13)$	4	3.486 (6)	–	–
$\text{O}(2)\cdots\text{C}(13)$	2	3.414 (6)	–	–
$\text{O}(2)\cdots\text{C}(1)$	2	3.449 (6)	–	–
$\text{O}(2)\cdots\text{C}(10)$	–	–	2	3.266 (8)
$\text{O}(3)\cdots\text{N}(1)$	4	2.966 (6)	5	3.753 (8)
$\text{O}(3)\cdots\text{C}(1)$	4	3.196 (7)	6	3.610 (7)
$\text{O}(4)\cdots\text{O}(4)$	2	2.906 (8)	2	3.099 (9)
$\text{O}(4)\cdots\text{C}(5)$	2	3.299 (6)	2	3.421 (7)
$\text{O}(4)\cdots\text{C}(8)$	4	3.406 (7)	6	3.543 (9)
$\text{O}(4)\cdots\text{N}(5)$	2	3.419 (6)	2	3.691 (7)
$\text{O}(4)\cdots\text{C}(9)$	3	3.471 (6)	5	3.534 (9)

* The symmetry positions are as follows: (1) = x, y, z ; (2) = $-x, -y, -z$; (3) = $\frac{1}{2} - x, \frac{1}{2} + y, -z$; (4) = $\frac{1}{2} + x, \frac{1}{2} - y, z$; (5) = $\frac{1}{2} + x, \frac{1}{2} - y, -z$; (6) = $\frac{1}{2} + x, y, \frac{1}{2} - z$.

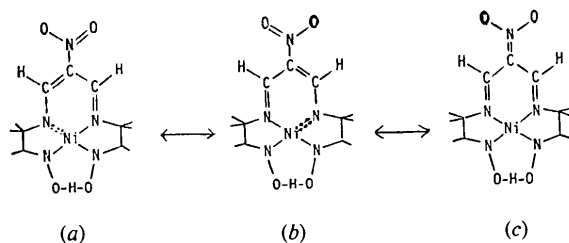
† The intramolecular hydrogen bond.

observed for the α -amine complexes studied so far, but is significantly longer than the shortest reported $\text{O}\cdots\text{O}$ distances observed in the X-ray analyses of a Cu^{II} complex of a Schiff base [2.31 (1) Å, Bertrand, Black, Ellen, Helm & Mahmood, 1976] and the bihydroxide anion $(\text{H}_3\text{O}_2)^-$ [2.29 (2) Å, Abu Dari, Raymond & Freyberg, 1979]. The H atom, H(OO), is coplanar with the macrocyclic ring and is exactly midway between the O atoms [average O–H distance 1.199 (14) Å] forming a nearly linear [O–H–O angle 170.8 (8)°], symmetric O–H–O bond. This is in contrast to the apparently asymmetric O–H \cdots O bond observed in the low-temperature X-ray study of the monoclinic form. Similar discrepancies between X-ray and neutron studies were observed in the case of $[\text{Ni}(\text{enao}) - \text{H}]^+$ (Ching & Schlemper, 1975; Fair & Schlemper, 1978), again indicating the fairly low accuracy in the positions of the H atoms determined by X-ray diffraction, even when direct location of these atoms is made from difference Fourier maps. All other distances (Table 3) involving H atoms range from 1.01 (2) to 1.08 (2) Å, and the H–C–H angles are in the range 106–109°, as expected for sp^3 C atoms. As usual the corresponding C–H distances measured in the low-temperature X-ray study of the monoclinic form are 0.1–0.2 Å shorter than the values observed here by neutron diffraction. When rigid-body thermal parameters for the individual atoms in the O–H \cdots O bridge are subtracted, the r.m.s. amplitude of the difference ellipsoid (neglecting the screw motion) of the H atom was 0.033 (7) Å² along the hydrogen-bond axis. The average value in the two directions perpendicular to the O–H \cdots O axis was close to zero. The elongation in the O–H \cdots O direction suggests a broad single-minimum potential similar to those observed for $[\text{Ni}(\text{ao})_2 - \text{H}]^+$ (Schlemper, Hamilton & LaPlaca, 1971) and $[\text{Ni}(\text{pnao}) - \text{H}]^+$ (Hussain & Schlemper, 1979). The differences between the nuclear thermal ellipsoids derived from the β_{ij} values and those calculated from rigid-body parameters for the O(1) and O(2) atoms were very small with an average r.m.s. value of 0.007 Å.

An analysis of bond summation for the oxime O atoms using the approach of Brown & Shannon (1973) including all contacts less than 3.0 Å gave summation (S_i) values of 2.008 for O(1) and 1.996 for O(2), which are very close to the expected value of two for these atoms. An examination of bond summations for a series of these short hydrogen-bond systems shows an apparent trend for the oxime O atoms to achieve a constant summation. Similar calculations for the strengths of bonds involving the H atom in the hydrogen bond using the O(1)–H(OO) and O(2)–H(OO) distances of 1.198 and 1.200 Å gave an S_i value of 0.973 compared to the expected value of one.

In contrast to all α -amine-oximes (Hussain & Schlemper, 1979) and Hpre (Saarinen, Korvenranta & Näsäkkälä, 1979) complexes studied so far, the

Ni–N(amine) distances [av. 1.856 (3) Å] in both forms are significantly shorter than the Ni–N(oxime) distances [av. 1.879 (4) Å] due to the aromaticity in the six-membered chelate ring, suggesting contributions from the three resonance forms (a) to (c).



Considerable multiple bonding, also consistent with aromaticity, in the N(amine)–C, C–C and C–N(nitro) bonds of the six-membered chelate ring is evident from the various bond distances, from the sum of the angles around N and C atoms, and from the planarity of the ring. The C(5) and C(7) atoms are sp^2 hybridized with coplanar H atoms, 1H(5) and 1H(7). In a related macrocyclic complex (Corfield, Mokren, Hipp & Busch, 1973) with a six-membered chelate ring in the boat configuration and a bonding scheme consistent with localized double bonds, the average N–C and C–C distances are 1.28 and 1.46 Å compared to 1.304 and 1.415 Å, respectively, in the present complex. The observed lengthening in the N–C distance and shortening in the C–C distance is expected on the basis of the charge delocalization in the chelate ring. Unusual chemical reactivity towards various electrophiles and NMR evidence also suggest aromatic nature of the six-membered ring.

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The Structure of Chlorobis(1,10-phenanthroline)copper(II) Perchlorate

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Abstract

$C_{24}H_{16}ClCuN_4^+ \cdot ClO_4^-$, $[Cu^{II}Cl(phen)_2]^+ \cdot ClO_4^-$, $M_r = 558.85$, monoclinic, $P2_1/c$, $a = 12.668$ (1), $b = 11.247$ (1), $c = 17.222$ (1) Å, $\beta = 111.50$ (1)°, $V = 2283.0$ (1) Å³, $Z = 4$, $D_m = 1.625$, $D_c = 1.635$ Mg

m^{-3} . The structure was refined to $R = 0.072$ for 2573 reflections with $I > 2\sigma(I)$. The metal ion is pentacoordinated to the four N atoms of the bidentate chelates and to the chloride ion. The ligand atoms are arranged about the Cu atom in what can be best regarded as a distorted trigonal-bipyramidal con-

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