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Neutron and X-ray Diffraction Study of a Macrocyclic Nickel(II) Complex with Ni^{II} in a Pseudoaromatic Chelate Ring

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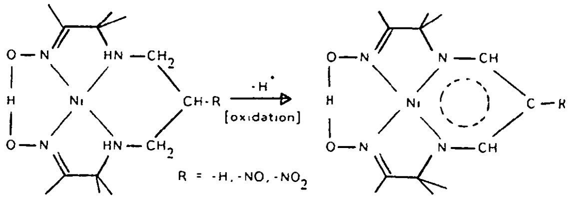
Abstract. [3,3′-Dimethyl-3,3′-(2-nitrosopropanediylidenediamino)bis(2-butanone oximato)-*N,N′,N″,N‴*]-nickel(II), [Ni(pnao–7H)NO], $[Ni(C_{13}H_{21}N_5O_3)]$, $M_r = 354{\cdot}1$, monoclinic, $P2_1/c$, $a = 10{\cdot}160\,(3)$, $b = 11{\cdot}305\,(3)$, $c = 14{\cdot}053\,(3)$ Å, $\beta = 107{\cdot}9\,(2)°$, $V = 1536{\cdot}3\,(3)$ Å^3, $Z = 4$, $D_m = 1{\cdot}530\,(6)$, $D_x = 1{\cdot}539$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}7107$, $\lambda(\text{neutron}) = 1{\cdot}058$ Å, $\mu = 12{\cdot}86$ (X-ray), $0{\cdot}084$ cm^{-1} (neutron), $F(000) = 744$, room temperature, $R = 0{\cdot}039$ (X-ray), 0·074 (neutron), unique reflections: 2004 (X-ray), 2315 (neutron). A combined X-ray/neutron diffraction study was carried out to investigate the aromatic behaviour of the six-membered heterocyclic chelate ring and the intramolecular hydrogen bonding. The H atoms were located precisely from the neutron data. The aromaticity of the six-membered chelate ring is suggested by its planarity and the relative shortness of the C—N and C—C bond distances in the ring. The short intramolecular O···O hydrogen bond [2·411 (3) Å] is symmetric.

Introduction. Oxidation of the [Ni(pnao—H)]$^+$ ion (structure *A*†) in basic solution easily yields a quasi-aromatic system [Ni(pnao—7H)*R*] (structure *B*) in which the central carbon atom in the six-membered heterocyclic ring exhibits a relatively high electron density (Urban & Vassian, 1979). Thus, this ring behaves like a phenol or aromatic amine with respect to the attachment of various functional groups while the rest of the molecule remains unreactive. This reactivity of the heterocyclic ring in these pseudoaromatic metal complexes has been utilized to connect two parent molecules having structure (*B*) through a (—CH—)$_3$ or a [—CH—C(CH$_3$)—CH—] linkage at the central carbon to form a highly conjugated dinuclear species with considerable kinetic stability (Ghiron, Murmann & Schlemper, 1986). The benzene-like behaviour of the six-membered chelate ring is reflected in the planar nature of complex (*B*) and the short bond length in the ring. We reported the first structure determination of the monoclinic and orthorhombic forms of the planar C(12)—NO$_2$ derivative of complex (*B*) at low temperature by X-ray diffraction and at room temperature by neutron diffraction (Hussain, Murmann & Schlemper, 1980; Hussain, Schlemper & Yelon, 1981).



[Ni(pnao-H)]$^+$ [Ni(pnao-7H)R]

(*A*) (*B*)

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† pnao = 3,3′-dimethyl-3,3′-(1,3-propanediylamino)bis(2-butanone oxime).

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In the present paper a combined X-ray and neutron diffraction analysis of the C(12)—NO derivative, is presented for the precise location of H atoms and to establish the degree of unsaturation and the extent of planarity in yet another quasi-aromatic system. The structures of these parent complexes are important because they provide an understanding of the synthetic pathways of a wide variety of dimeric (and probably polymeric) complexes which may lead to the subsequent building of structures resembling biological molecules (Korybat-Daszkiewicz *et al.*, 1984).

Experimental. Compound prepared by the method of Vassian & Murmann (1967). Crystals were obtained from anhydrous CH_3CN solution. All calculations with the neutron data were performed using cell constants determined from the X-ray data. The neutron data were collected on a PDP 11/03 computer-controlled four-circle diffractometer developed at the University of Missouri, Research Reactor Facility. Detailed procedure for collection and reduction of neutron data described earlier (Hussain & Schlemper, 1979*a*,*b*). Because of the relatively small size of the crystal and the high thermal motion of the methyl H atoms, the number of significant observations (and thus the precision of the neutron results) is limited. The neutron structure was refined starting from X-ray parameters for non-H atoms and the H atoms were located from the ΔF map from the neutron data. In the final neutron refinement all atoms were refined anisotropically. In the X-ray refinement the initial positional parameters for the H atoms were refined isotropically starting with the values from the neutron data while the non-H atoms were refined anisotropically. Final ΔF map for neutron data revealed no significant negative nuclear scattering density for H atoms nor any positive density for non-H atoms. The maximum height in the X-ray ΔF map was $<0{\cdot}21$ e Å^{-3}. The X-ray and neutron data collection and refinement parameters are given in Table 1. Positional parameters are listed in Table 2.*

Discussion. The crystals contain discrete, neutral monomeric units of the title compound shown in Fig. 1. The bond distances and angles are listed in Tables 3 and 4 and results showing the planarity of the molecule are given in Table 5.

Table 1. *Neutron and X-ray data collection and structure refinement parameters for the title compound*

	X-ray data	Neutron data
Crystal shape and size (mm)	Plate-like 0·17 × 0·20 × 0·25	Rectangular 1·0 × 1·3 × 2·0
Method of measuring D_m	Flotation	
Diffractometer used	CAD-4	Locally developed
Method of intensity measurement	ω–2θ	ω–2θ
No. and 2θ range of reflections for lattice parameters	25 >23°	–
Absorption coefficient (μ) (cm^{-1})	12·86	0·084
Maximum transmission factor	96·3	97·3
Minimum transmission factor	92·2	91·4
Max. value of $(\sin\theta)/\lambda$ (Å^{-1})	1·193	0·9416
Range of *h*, *k* and *l*	0→14, 0→14, −15→15	0→14, 0→15, −15→15
Interval, std reflections measured	100	85
Total No. of reflections measured	2769	4970
No. of unique reflections	2004	2315
No. of observed reflections	1529	1266
Criterion for observed reflections	$I > \sigma(I)$	$I > 1{\cdot}5\sigma(I)$
Methods used to solve structure	*MULTAN**	*MULTAN**
Use of F or F^2 in LS refinement	F	F
Method of locating hydrogens	Neutron positions	ΔF map
Weighting scheme	unit weight	unit weight
Parameters refined	283	389
Value of R	0·039	0·074
Value of wR	0·043	0·055
Ratio of max. LS shift to e.s.d. (Δ/σ)	0·44	0·13
Error in an observation of unit weight (S)	1·209	1·41
Extinction coefficient	No correction	3·3 (5) × 10^{-5}
Sources of atomic scattering factors and f', f'' values	*International Tables for X-ray Crystallography* (1974)	*International Tables for X-ray Crystallography* (1974)
Computer programs used	*SDP*82†	*SDP*82†

* Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson (1982).
† Enraf–Nonius (1982).

The coordination geometry around the nickel(II) atom is square planar with the average value of the N—Ni—N angles in the six-membered rings about 14° larger than the similar angle in the five-membered chelate rings. Similar differences in these angles were observed in the corresponding α-amine–oxime complexes of nickel(II) and palladium(II) (Hussain & Schlemper, 1979*a*,*b*). The internal angles of the chelate rings in the present compound are consistent with our earlier conclusions regarding the relatively less constraining steric requirements of pnao in comparison with the other α-amine–oximes (Hussain & Schlemper, 1979*a*,*b*). The average Ni—N(amine) distance exceeds the Ni—N(oxime) distance by about 0·03–0·07 Å in the unoxidized nickel(II) complexes in contrast to the oxidized forms where the average Ni—N(oxime) > Ni—N(amine) by about 0·02 Å. The average C—N and C—C distances within the aromatic ring are shorter by 0·19 and 0·11 Å, respectively, than the corresponding single bonds in the unoxidized form. The C—N bond distance in the ring averages 1·298 (6) Å while the C—N bond in the aliphatic portion averages 1·484 (5) Å and the double-bonded C—N distances average 1·276 (5) Å. In a related macrocyclic complex (Corfield, Mokren, Hipp & Busch, 1973) with the six-membered chelate ring in a boat configuration and a bonding scheme consistent with localized double bonds, the average C—N and C—C distances are 1·28 and 1·46 Å, respectively. The internal angles within the pseudoaromatic ring (excluding the N—Ni—N angle) average 124·7 (4)°. These variations in the distances and angles for the heterocyclic ring can be interpreted in terms of delocalized

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43073 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

multiple bonding among the atoms of the ring. The aromaticity of the ring is also consistent with the angles around N(1) and N(3), both of which are planar within experimental error in contrast to the pyramidal angles (340°) in the unoxidized counterpart and related complexes. Thus the significant conjugation explains the aromatic behaviour of the complex towards various electrophiles.

The 14-membered macrocylic ring in this complex is highly planar (Table 5) which is common to all the oxidized species. All atoms except terminal methyl groups are within 0·165 (5) Å of the least-squares plane defined by the atoms in the 14-membered ring. The N(5) and O(3) atoms of the –NO group are −0·348 and −0·437 Å, respectively, from the least-squares plane of the macrocycle. The N(5)–O(3) bond distance of 1·166 (8) Å is significantly shorter than the average of 1·356 (4) Å for N(3)–O(1) and N(4)–O(2) distances, consistent with the expected 'triple-bond' nature. The maximum deviation of any atom in the macrocyclic ring from the NiN_4 plane is −0·194 (5) Å. In contrast to the chair configuration in the unoxidized form the six-membered aromatic ring in the present compound is planar with a maximum deviation of 0·051 (1) Å from the least-squares plane defined by the six atoms of the chelate ring.

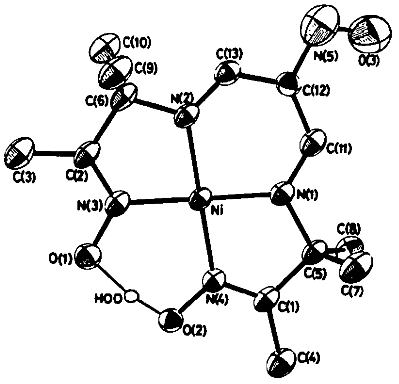

Fig. 1. A perspective view of the title compound showing atom-labelling scheme and thermal ellipsoids. The hydrogen atoms are omitted for clarity.

Table 2. *Positional parameters from neutron and X-ray data sets for all atoms in the title compound; hydrogen atoms were refined isotropically*

	x	*y*	*z*	B_{eq}(Å^2)
Parameters from neutron data set				
Ni	0·2024 (4)	0·0830 (3)	0·1357 (3)	2·85 (7)
O(1)	0·2238 (7)	−0·0094 (7)	−0·0472 (5)	4·3 (2)
O(2)	0·0356 (7)	0·1273 (6)	−0·0646 (5)	3·7 (2)
O(3)	0·248 (1)	0·139 (1)	0·5095 (8)	10·1 (3)
N(1)	0·1301 (4)	0·1747 (4)	0·2181 (3)	3·32 (9)
N(2)	0·3440 (4)	0·0147 (4)	0·2374 (3)	3·20 (9)
N(3)	0·2790 (4)	−0·0065 (4)	0·0540 (3)	3·46 (9)
N(4)	0·0613 (4)	0·1529 (4)	0·0347 (3)	3·14 (9)
N(5)	0·3189 (6)	0·4125 (6)	0·9791 (4)	6·8 (2)
C(1)	−0·0140 (5)	0·2325 (5)	0·0565 (4)	3·0 (1)
C(2)	0·3875 (5)	−0·0683 (5)	0·0934 (4)	3·5 (1)
C(3)	0·4548 (6)	−0·1444 (6)	0·0351 (5)	4·4 (2)
C(4)	−0·1177 (6)	0·3011 (6)	−0·0193 (5)	4·1 (2)
C(5)	0·0180 (5)	0·2569 (5)	0·1679 (4)	3·1 (1)
C(6)	0·4466 (5)	−0·0577 (5)	0·2067 (4)	3·4 (1)
C(7)	0·0674 (7)	0·3851 (6)	0·1871 (5)	4·7 (2)
C(8)	−0·1102 (6)	0·2371 (6)	0·2001 (4)	4·2 (1)
C(9)	0·5827 (5)	0·0034 (6)	0·2327 (5)	4·3 (1)
C(10)	0·4624 (7)	−0·1801 (6)	0·2555 (5)	4·9 (2)
C(11)	0·1690 (5)	0·1686 (5)	0·3153 (4)	3·4 (1)
C(12)	0·2779 (6)	0·0977 (6)	0·3720 (4)	4·1 (2)
C(13)	0·3633 (6)	0·0276 (5)	0·3333 (4)	4·0 (1)
H(OO)	0·125 (1)	0·058 (1)	−0·0607 (8)	4·8 (3)
H1C(3)	0·446 (2)	−0·233 (1)	0·050 (1)	11·4 (5)
H2C(3)	0·412 (2)	−0·136 (2)	−0·038 (1)	10·9 (5)
H3C(3)	0·556 (2)	−0·129 (2)	0·050 (2)	13·1 (6)
H1C(4)	−0·181 (2)	0·354 (2)	0·009 (1)	10·3 (5)
H2C(4)	−0·070 (2)	0·358 (2)	−0·059 (1)	9·3 (5)
H3C(4)	−0·181 (2)	0·246 (2)	−0·078 (1)	10·8 (6)
H1C(7)	0·153 (1)	0·401 (1)	0·160 (1)	6·3 (4)
H2C(7)	−0·012 (2)	0·444 (1)	0·152 (1)	7·1 (4)
H3C(7)	0·101 (2)	0·403 (1)	0·272 (1)	7·5 (4)
H1C(8)	−0·195 (1)	0·290 (2)	0·155 (1)	7·4 (4)
H2C(8)	−0·090 (1)	0·262 (2)	0·2791 (7)	6·9 (4)
H3C(8)	−0·141 (1)	0·146 (1)	0·188 (1)	7·4 (4)
H1C(9)	0·571 (2)	0·095 (1)	0·201 (1)	7·5 (4)
H2C(9)	0·655 (1)	−0·040 (1)	0·199 (1)	7·6 (4)
H3C(9)	0·630 (1)	0·012 (2)	0·3121 (9)	6·7 (4)
H1C(10)	0·524 (2)	−0·236 (1)	0·225 (1)	7·2 (4)
H2C(10)	0·361 (2)	−0·225 (1)	0·240 (1)	7·9 (4)
H3C(10)	0·506 (2)	−0·178 (1)	0·335 (1)	7·6 (4)
HC(11)	0·121 (1)	0·227 (1)	0·3588 (8)	5·4 (3)
HC(13)	0·447 (1)	−0·017 (1)	0·3877 (8)	5·5 (3)

	x	*y*	*z*	B_{eq}(Å^2)
Parameters from X-ray data set				
Ni	0·20264 (5)	0·08278 (53)	0·13596 (4)	2·50 (1)
O(1)	0·2242 (3)	−0·0086 (3)	−0·0467 (2)	3·76 (8)
O(2)	0·0354 (3)	0·1271 (3)	−0·0635 (2)	3·26 (7)
O(3)	0·2515 (6)	0·1389 (6)	0·5151 (4)	9·9 (2)
N(1)	0·1304 (3)	0·1737 (3)	0·2184 (3)	2·79 (8)
N(2)	0·3448 (3)	0·0146 (3)	0·2372 (3)	2·81 (8)
N(3)	0·2799 (4)	−0·0062 (3)	0·0542 (3)	2·92 (8)
N(4)	0·0616 (4)	0·1530 (3)	0·0349 (2)	2·71 (8)
N(5)	0·3213 (5)	0·0820 (5)	0·4808 (3)	7·3 (1)
C(1)	−0·0127 (4)	0·2326 (4)	0·0571 (3)	2·8 (1)
C(2)	0·3874 (4)	−0·0688 (4)	0·0941 (3)	2·9 (1)
C(3)	0·4544 (5)	−0·1442 (5)	0·0350 (4)	4·2 (1)
C(4)	−0·1184 (5)	0·3010 (5)	−0·0193 (4)	4·0 (1)
C(5)	0·0183 (4)	0·2580 (4)	0·1672 (3)	2·8 (1)
C(6)	0·4444 (4)	−0·0585 (4)	0·2055 (3)	3·0 (1)
C(7)	0·0676 (5)	0·3854 (5)	0·1879 (4)	4·4 (1)
C(8)	−0·1097 (5)	0·2368 (6)	0·2003 (4)	4·0 (1)
C(9)	0·5842 (5)	0·0053 (5)	0·2328 (4)	4·5 (1)
C(10)	0·4593 (5)	−0·1811 (5)	0·2531 (4)	4·6 (1)
C(11)	0·1704 (5)	0·1692 (4)	0·3154 (4)	3·3 (1)
C(12)	0·2778 (5)	0·0973 (5)	0·3726 (3)	3·4 (1)
C(13)	0·3620 (5)	0·0271 (4)	0·3320 (3)	3·3 (1)
H(OO)	0·113 (5)	0·064 (5)	−0·065 (4)	6 (1)
H1C(3)	0·437 (5)	−0·224 (5)	0·045 (4)	7 (1)
H2C(3)	0·403 (5)	−0·137 (5)	−0·033 (1)	7 (1)
H3C(3)	0·548 (6)	−0·133 (5)	0·049 (4)	9 (2)
H1C(4)	−0·186 (5)	0·335 (5)	0·006 (4)	8 (1)
H2C(4)	−0·081 (5)	0·343 (5)	−0·056 (7)	7 (1)
H3C(4)	−0·172 (5)	0·253 (5)	−0·073 (3)	6 (1)
H1C(7)	0·142 (4)	0·401 (4)	0·163 (3)	3·0 (9)
H2C(7)	−0·004 (4)	0·441 (4)	0·155 (3)	4 (1)
H3C(7)	0·103 (5)	0·401 (4)	0·259 (4)	6 (1)
H1C(8)	−0·176 (4)	0·286 (3)	0·162 (3)	2·7 (9)
H2C(8)	−0·096 (5)	0·258 (5)	0·280 (4)	6 (1)
H3C(8)	−0·129 (5)	0·154 (5)	0·190 (4)	7 (1)
H1C(9)	0·567 (4)	0·085 (4)	0·205 (3)	4 (1)
H2C(9)	0·653 (4)	−0·038 (4)	0·207 (3)	5 (1)
H3C(9)	0·630 (5)	0·011 (5)	0·303 (4)	8 (1)
H1C(10)	0·524 (4)	−0·221 (4)	0·232 (3)	5 (1)
H2C(10)	0·371 (5)	−0·215 (4)	0·238 (3)	5 (1)
H3C(10)	0·493 (4)	−0·179 (4)	0·314 (3)	2·9 (9)
HC(11)	0·130 (4)	0·216 (4)	0·347 (3)	4 (1)
HC(13)	0·430 (4)	−0·011 (4)	0·377 (3)	4 (1)

The intramolecular hydrogen bond is not significantly affected by the substituent on the carbon at position 12. The O···O distance [2·411 (3) Å] is similar to the corresponding distances in the other oxidized forms (Table 6). The positions of hydrogen atoms were precisely determined from neutron data. The H atom H(OO) is coplanar with the macrocyclic ring and is nearly midway between the O(1) and O(2) atoms [average O—H distance 1·208 (20) Å] forming a nearly linear symmetrical O—H—O bond [O(1)—H(OO)—O(2) angle 173 (1)°]. In contrast to this, the X-ray data show a more asymmetric O—H—O bond with O(1)—H(OO) distance 0·28 (6) Å longer than O(2)—H(OO). The discrepancies between X-ray and neutron analysis give an indication of fairly low accuracy in the positions of H atoms determined from X-ray diffraction. Such differences were also observed earlier (Ching & Schlemper, 1975; Fair & Schlemper, 1978). The C—H distances determined by neutron data (Table 4) range from 1·00 (3) to 1·12 (3) Å and are 0·1–0·2 Å longer than those obtained from the X-ray data. The average H—C—H angle for the terminal methyl groups is very close to the tetrahedral angle.

In conclusion, the unusual reactivity of the present and other similar pseudoaromatic complexes towards various electrophiles can be explained on the basis of the aromatic nature of the six-membered chelate ring which in turn results in the unusual planarity of the macrocyclic ring. Such planarity is introduced as a result of oxidation of the aliphatic precursor molecule.

Table 3. *Intramolecular bond distances* (Å) *and angles* (°) *for non-hydrogen atoms from X-ray data*

Ni—N(1)	1·860 (3)	N(1)—C(11)	1·298 (6)
Ni—N(2)	1·856 (4)	N(2)—C(13)	1·297 (6)
Ni—N(3)	1·872 (4)	C(1)—C(5)	1·508 (6)
Ni—N(4)	1·858 (4)	C(2)—C(6)	1·497 (6)
O(1)—N(3)	1·356 (4)	C(1)—C(4)	1·482 (7)
O(2)—N(4)	1·357 (4)	C(2)—C(3)	1·494 (7)
O(3)—N(5)	1·166 (8)	C(5)—C(7)	1·524 (7)
N(1)—C(5)	1·490 (5)	C(5)—C(8)	1·528 (7)
N(2)—C(6)	1·478 (5)	C(6)—C(9)	1·533 (7)
N(3)—C(2)	1·278 (5)	C(6)—C(10)	1·526 (7)
N(4)—C(1)	1·274 (5)	C(11)—C(12)	1·400 (7)
N(5)—C(12)	1·458 (6)	C(13)—C(12)	1·409 (7)

N(1)—Ni—N(2)	96·6 (2)	C(2)—N(3)—Ni	119·4 (3)
N(1)—Ni—N(4)	83·1 (2)	C(11)—C(12)—N(5)	126·9 (4)
N(4)—Ni—N(3)	97·5 (2)	N(5)—C(12)—C(13)	109·1 (4)
N(2)—Ni—N(3)	82·7 (2)	C(12)—N(5)—O(3)	109·8 (5)
Ni—N(1)—C(11)	125·2 (3)	N(4)—C(1)—C(4)	122·9 (5)
N(1)—C(11)—C(12)	124·3 (5)	C(4)—C(1)—C(5)	115·6 (4)
C(11)—C(12)—C(13)	124·0 (4)	N(3)—C(2)—C(3)	123·1 (5)
C(12)—C(13)—N(2)	124·7 (5)	C(3)—C(2)—C(6)	122·0 (5)
C(13)—N(2)—Ni	124·8 (3)	C(6)—N(2)—C(13)	118·8 (4)
Ni—N(3)—O(1)	122·3 (3)	C(5)—N(1)—C(11)	118·6 (4)
N(3)—O(1)—H(OO)	104 (2)	C(1)—C(5)—C(7)	109·2 (4)
O(1)—H(OO)—O(2)	168 (5)	C(1)—C(5)—C(8)	110·6 (4)
H(OO)—O(2)—N(4)	104 (2)	N(1)—C(5)—C(7)	110·7 (4)
O(2)—N(4)—Ni	123·4 (3)	N(1)—C(5)—C(8)	110·4 (4)
Ni—N(1)—C(5)	116·2 (3)	C(7)—C(5)—C(8)	110·5 (5)
C(1)—N(4)—Ni	119·4 (3)	C(2)—C(6)—C(9)	109·2 (4)
Ni—N(2)—C(6)	116·4 (3)	N(2)—C(6)—C(10)	111·2 (4)
N(2)—C(6)—C(2)	106·1 (4)	C(9)—C(6)—C(10)	111·0 (5)
C(6)—C(2)—N(3)	114·9 (4)		

Table 4. *Bond distances* (Å) *and angles* (°) *involving hydrogen atoms from neutron data*

O(1)—H(OO)	1·23 (2)	C(7)—H2C(7)	1·05 (2)
O(2)—H(OO)	1·19 (2)	C(7)—H3C(7)	1·16 (2)
C(11)—HC(11)	1·12 (2)	C(8)—H1C(8)	1·08 (2)
C(13)—HC(13)	1·08 (2)	C(8)—H2C(8)	1·10 (2)
C(3)—H1C(3)	1·03 (3)	C(8)—H3C(8)	1·07 (3)
C(3)—H2C(3)	1·00 (3)	C(9)—H1C(9)	1·12 (2)
C(3)—H3C(3)	1·01 (3)	C(9)—H2C(9)	1·10 (2)
C(4)—H1C(4)	1·04 (2)	C(9)—H3C(9)	1·08 (2)
C(4)—H2C(4)	1·07 (3)	C(10)—H1C(10)	1·07 (2)
C(4)—H3C(4)	1·08 (2)	C(10)—H2C(10)	1·11 (2)
C(7)—H1C(7)	1·07 (3)	C(10)—H3C(10)	1·07 (2)

N(4)—O(2)—H(OO)	100·9 (8)	H2C(7)—C(7)—H3C(7)	108 (1)
O(2)—H(OO)—O(1)	172 (1)	H1C(8)—C(8)—H2C(8)	108 (1)
N(3)—O(1)—H(OO)	101·7 (6)	H1C(8)—C(8)—H3C(8)	108 (2)
H1C(3)—C(3)—H2C(3)	106 (2)	H2C(8)—C(8)—H3C(8)	111 (1)
H1C(3)—C(3)—H3C(3)	106 (2)	H1C(9)—C(9)—H2C(9)	105 (1)
H2C(3)—C(3)—H3C(3)	107 (2)	H1C(9)—C(9)—H3C(9)	106 (2)
H1C(4)—C(4)—H2C(4)	108 (2)	H2C(9)—C(9)—H3C(9)	110 (1)
H1C(4)—C(4)—H3C(4)	109 (2)	H1C(10)—C(10)—H2C(10)	106 (2)
H2C(4)—C(4)—H3C(4)	102 (2)	H1C(10)—C(10)—H3C(10)	109 (1)
H1C(7)—C(7)—H2C(7)	109 (2)	H2C(10)—C(10)—H3C(10)	106 (2)
H1C(7)—C(7)—H3C(7)	109 (2)		

Table 5. *Least-squares planes depicting the overall molecular planarity and that of the pseudoaromatic six-membered chelate ring*

LS plane for 14-membered macrocyclic ring:

$$0{\cdot}6535x + 0{\cdot}7853y - 0{\cdot}0587z - 1{\cdot}5132 = 0$$

Plane-defining atoms and their distance from the plane (Å)

O(1)	–0·050 (3)	C(2)	0·061 (5)
O(2)	–0·089 (3)	C(5)	0·165 (5)
N(1)	0·023 (4)	C(6)	0·164 (5)
N(2)	0·025 (4)	C(11)	–0·067 (5)
N(3)	0·011 (4)	C(12)	–0·154 (5)
N(4)	–0·014 (4)	C(13)	–0·064 (5)
C(1)	0·101 (5)	H(OO)	–0·112 (51)

Distances of other atoms (Å)

Ni	–0·007 (1)	C(8)	–0·976 (5)
N(5)	–0·348 (5)	O(3)	–0·437 (6)
C(7)	1·515 (5)	C(9)	1·550 (5)
C(10)	–0·940 (6)		

Table 6. *A comparison of bond distances* (Å) *and angles* (°) *in the six-membered pseudoaromatic chelate rings*

Reference	[Ni(pnao–7H)NO$_2$] Monoclinic form X-ray (*a*)	[Ni(pnao–7H)NO$_2$] Orthorhombic form Neutron (*b*)	[Ni(pnao–7H)NO] Present complex X-ray (*c*)	[Ni(pnao–H] Unoxidized form Neutron (*d*)
Ni—N(1)	1·869 (4)	1·856 (3)	1·860 (3)	1·935 (5)
Ni—N(2)	1·863 (4)	1·857 (3)	1·856 (4)	1·939 (5)
N(1)—C(11)	1·308 (5)	1·311 (4)	1·298 (6)	1·478 (7)
C(11)—C(12)	1·416 (6)	1·416 (5)	1·400 (7)	1·514 (8)
C(12)—C(13)	1·424 (6)	1·413 (6)	1·409 (7)	1·521 (8)
C(13)—N(2)	1·304 (6)	1·296 (4)	1·297 (6)	1·486 (7)
O···O	2·427 (5)	2·390 (8)	2·411 (3)	2·409 (6)
N(1)—Ni—N(2)	96·1 (2)	96·5 (2)	96·6 (2)	97·7 (2)
Ni—N(1)—C(11)	125·9 (4)	125·9 (3)	125·2 (3)	120·0 (3)
N(1)—C(11)—C(12)	123·5 (5)	123·0 (4)	124·3 (5)	112·5 (5)
C(11)—C(12)—C(13)	124·9 (4)	124·9 (5)	124·0 (4)	112·5 (5)
C(12)—C(13)—N(2)	122·8 (4)	123·6 (4)	124·7 (5)	112·1 (5)

(*a*) Hussain, Murmann & Schlemper (1980). (*b*) Hussain, Schlemper & Yelon (1981). (*c*) This work. (*d*) Hussain & Schlemper (1979*a*,*b*).

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Structure of *trans*-Diiodobis[tris(pentafluorophenyl)phosphine]platinum(II)–Dichloromethane (1/2)

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Abstract. $[\mathrm{PtI_2(C_{18}F_{15}P)_2}].2\mathrm{CH_2Cl_2}$, $M_r = 1683{\cdot}2$, monoclinic, $P2_1/a$, $a = 19{\cdot}424\,(7)$, $b = 13{\cdot}719\,(4)$, $c = 9{\cdot}426\,(6)$ Å, $\beta = 111{\cdot}94\,(5)°$, $V = 2330\,(2)$ Å^3, $Z = 2$, $D_x = 2{\cdot}399$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 45{\cdot}3$ cm^{-1}, $F(000) = 1568$, $T = 293$ K, $R = 0{\cdot}061$ for 1776 unique reflections with $I \geq 3\sigma(I)$. The Pt atoms lie on sites of $\bar{1}$ symmetry and display slightly distorted square-planar coordination with P—Pt—I $= 85{\cdot}1\,(2)°$. The Pt—I and Pt—P distances of $2{\cdot}626\,(2)$ and $2{\cdot}292\,(6)$ Å are not lengthened appreciably by overcrowding of the bulky iodo and phosphine ligands.

Introduction. According to Tolman (1977) $(\mathrm{C_6F_5})_3\mathrm{P}$ is one of the most bulky of phosphine ligands, with a cone angle of 184°. Consistent with this, metal complexes of $(\mathrm{C_6F_5})_3\mathrm{P}$ display rotational isomerism (Kemmitt, Nichols & Peacock, 1967). In particular, spectroscopic studies suggest that the title complex may exist as eclipsed and staggered rotamers in solution (Docherty, Rycroft, Sharp & Webb, 1979). This analysis was carried out to establish the rotameric form of the solid compound and the extent of any distortion of the metal coordination arising from the presence of the bulky phosphine and iodo ligands.

Experimental. Red, transparent needle grown from dichloromethane by solvent extraction at 277 K; forms exhibited and face–centroid distances (mm): {110} 0·037, {001} 0·117; Enraf–Nonius CAD-4F diffractometer, Mo X-rays, graphite monochromator; cell dimensions by least-squares fit to the setting angles of 25 automatically centred reflections with $10 < \theta < 16°$; intensities of 3634 reflections, with $2 \leq \theta(\mathrm{Mo}\,K\alpha) \leq 25°$ and $h\,0{\to}23$, $k\,0{\to}16$, $l\,{-11}{\to}11$, measured from continuous $\theta/2\theta$ scans of 0·80° in θ increased by 25% at each end to assess background effects; corrections for Lp, crystal decomposition (up to 28% of I based on intensities of 200 and 020 standard reflections) and absorption effects (Gaussian quadrature, 192 grid points, transmission factors on F^2 0·66–0·77), no correction required for extinction; R_{int} 0·066 for 150 independent reflections measured at least twice; 3278 independent structure amplitudes; of these 1776 with $I \geq 3\sigma(I)$ used in the structure analysis. Patterson and difference syntheses; full-matrix least-squares refinement on F; $w^{-1} = \sigma^2(F) + 4 \times 10^{-4}F^2$; H atoms riding on bonded C atoms with C—H = 1·08 Å; final adjustment of 349 parameters (anisotropic U_{ij} for all non-H atoms) gave $R = 0{\cdot}061$, $wR = 0{\cdot}060$, S

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