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[*N*,*N*′-Ethylenebis(salicylideneiminato)]nickel(II),* [Ni($C_{16}H_{14}N_2O_2$)]. A Redetermination

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Abstract. $M_r = 325{\cdot}0$, orthorhombic, *Pbca*, $a = 13{\cdot}831\,(3)$, $b = 26{\cdot}155\,(5)$, $c = 7{\cdot}482\,(2)$ Å, $Z = 8$, $D_x = 1{\cdot}595$ Mg m^{-3}, $F(000) = 1344$, $\mu = 2{\cdot}08$ mm^{-1} [λ(Cu $K\alpha$)], $T = 298$ K. The structure has been refined by full-matrix least-squares methods to a final $R = 0{\cdot}042$ for 1975 independent significant reflections. All H atoms have been directly located. The geometry of the molecule, as a whole, is in agreement with that found by Shkol'nikova, Yumal', Shugam & Voblikova [*Zh. Strukt. Khim.* (1970). **5**, 886–890] in a previous determination, but the precision of the analysis is now high enough to allow a detailed description of the molecular conformation.

Introduction. The crystal structure of the title compound was determined to define the details of its conformation which could not be obtained from the analysis by Shkol'nikova, Yumal', Shugam & Voblikova (1970) and which, even if correct, were not accurate enough for this purpose.

Experimental. Cell parameters and intensity data measured on a Siemens AED autodiffractometer, Ni-filtered Cu $K\alpha$ radiation (1·54178 Å); accurate lattice parameters from least-squares refinement of 20 reflections ($35° < 2\theta < 62°$); crystal used was approximately cylindrical, mean radius 0·11 mm; one reflection remeasured after 20 reflections as a check on crystal and instrument stability showed no significant change; 2566 independent reflections ($2\theta_{\max}$ 140°), 585 of which were considered unobserved [$I < 2\sigma(I)$]; structure solved, independently of earlier work, by heavy-atom method; full-matrix least-squares refinement of positional and anisotropic thermal parameters for non-hydrogen atoms converged with $R = 4{\cdot}8\%$; all H atoms located from a difference Fourier synthesis and introduced in further refinement as fixed-atom contributions ($B_{\rm iso} = 6{\cdot}3$ Å^2); final convergence reached with $R = 4{\cdot}2\%$, $R_w = 4{\cdot}8\%$; $\sum w|\Delta F|^2$ minimized with $w = 1/[\sigma^2(F_o) + 0{\cdot}008328\,F_o^2]$; in the final cycle no shift-over-error ratio, Δ/σ, was greater than 0·3; overdetermination ratio was NO:NV = 1975:246 = 8:1; final difference Fourier map revealed no unusual features; atomic scattering factor tables for Ni from *International Tables for X-ray Crystallography* (1974), those for O, N, C from Cromer & Mann (1968) and those for H from Stewart, Davidson & Simpson (1965).

Discussion. Final positional parameters for all atoms and isotropic $B_{\rm eq}$ for non-hydrogen atoms are reported in Table 1.† Bond lengths and bond angles are given in Table 2. The numbering scheme adopted is shown in Fig. 1.

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* The 'salen' ligand is also known as 'salicylideneaminate'.

† Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38383 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Fractional atomic coordinates* (×10^4) *and equivalent isotropic thermal parameters for non-hydrogen atoms*

B_{eq} is that defined by Hamilton (1959).

	x	*y*	*z*	B_{eq}(Å^2)
Ni	4520·6 (3)	5115·0 (1)	1904·7 (5)	2·75 (1)
O(1)	3630 (1)	5600 (1)	1178 (3)	3·25 (4)
O(2)	3666 (1)	4640 (1)	961 (3)	3·13 (4)
N(1)	5356 (1)	5589 (1)	2906 (3)	3·15 (5)
N(2)	5414 (1)	4628 (1)	2571 (3)	3·17 (5)
C(1)	3712 (2)	6099 (1)	1251 (3)	3·03 (5)
C(2)	4450 (2)	6353 (1)	2201 (4)	3·53 (6)
C(3)	4450 (2)	6898 (1)	2290 (5)	4·72 (8)
C(4)	3758 (3)	7181 (1)	1463 (5)	5·52 (10)
C(5)	3054 (2)	6931 (1)	437 (4)	4·43 (8)
C(6)	3027 (2)	6404 (1)	339 (4)	3·61 (6)
C(7)	5250 (2)	6080 (1)	2966 (3)	3·45 (6)
C(8)	3707 (2)	4141 (1)	1099 (3)	3·13 (6)
C(9)	4445 (2)	3878 (1)	2024 (3)	3·53 (7)
C(10)	4398 (2)	3338 (1)	2171 (5)	4·86 (9)
C(11)	3665 (3)	3064 (1)	1424 (5)	5·48 (9)
C(12)	2966 (2)	3318 (1)	420 (4)	4·62 (8)
C(13)	2977 (2)	3845 (1)	254 (4)	3·57 (6)
C(14)	5296 (2)	4135 (1)	2630 (4)	3·54 (6)
C(15)	6385 (2)	4842 (1)	2954 (4)	3·95 (7)
C(16)	6226 (2)	5368 (1)	3763 (4)	3·79 (6)

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

Ni–O(1)	1·850 (2)	C(2)–C(7)	1·436 (4)
Ni–O(2)	1·855 (2)	C(3)–C(4)	1·359 (5)
Ni–N(1)	1·853 (2)	C(4)–C(5)	1·402 (5)
Ni–N(2)	1·843 (2)	C(5)–C(6)	1·381 (4)
O(1)–C(1)	1·311 (4)	C(8)–C(9)	1·412 (4)
O(2)–C(8)	1·310 (4)	C(8)–C(13)	1·421 (4)
N(1)–C(7)	1·293 (4)	C(9)–C(10)	1·418 (4)
N(1)–C(16)	1·481 (3)	C(9)–C(14)	1·429 (4)
N(2)–C(14)	1·301 (4)	C(10)–C(11)	1·362 (5)
N(2)–C(15)	1·483 (3)	C(11)–C(12)	1·393 (5)
C(1)–C(2)	1·410 (4)	C(12)–C(13)	1·384 (4)
C(1)–C(6)	1·414 (4)	C(15)–C(16)	1·519 (4)
C(2)–C(3)	1·427 (4)		

N(1)–Ni–N(2)	86·3 (1)	C(8)–C(9)–C(14)	121·4 (2)
O(2)–Ni–N(2)	93·9 (1)	C(9)–C(14)–N(2)	124·0 (2)
O(1)–Ni–N(1)	94·3 (1)	N(1)–C(16)–C(15)	107·4 (2)
O(1)–Ni–O(2)	85·6 (1)	N(2)–C(15)–C(16)	106·7 (2)
Ni–O(1)–C(1)	127·8 (2)	C(2)–C(1)–C(6)	117·5 (2)
Ni–O(2)–C(8)	127·6 (2)	C(1)–C(2)–C(3)	119·6 (3)
Ni–N(1)–C(7)	127·4 (2)	C(2)–C(3)–C(4)	121·5 (3)
Ni–N(1)–C(16)	114·9 (2)	C(3)–C(4)–C(5)	119·0 (3)
C(7)–N(1)–C(16)	117·7 (2)	C(4)–C(5)–C(6)	120·9 (3)
Ni–N(2)–C(14)	127·6 (2)	C(1)–C(6)–C(5)	121·3 (3)
Ni–N(2)–C(15)	113·5 (2)	C(9)–C(8)–C(13)	117·8 (2)
C(14)–N(2)–C(15)	118·8 (2)	C(8)–C(9)–C(10)	119·3 (2)
O(1)–C(1)–C(2)	123·5 (2)	C(9)–C(10)–C(11)	121·8 (3)
C(1)–C(2)–C(7)	121·6 (3)	C(10)–C(11)–C(12)	119·2 (3)
C(2)–C(7)–N(1)	124·5 (2)	C(11)–C(12)–C(13)	121·1 (3)
O(2)–C(8)–C(9)	123·7 (2)	C(8)–C(13)–C(12)	120·7 (3)

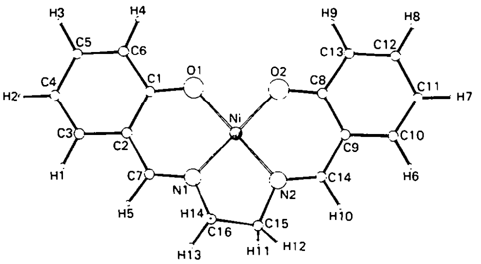

Fig. 1. Perspective drawing of the molecule showing the atom-numbering scheme.

Coordination around the metal is not strictly planar: all atoms are tetrahedrally displaced from the mean coordination plane by 0·023 (2) Å. The average values of the distances Ni–O [1·853 (3) Å] and Ni–N [1·848 (3) Å] are not significantly different from those found by Bresciani Pahor, Calligaris, Delise, Nardin, Randaccio, Zotti, Fachinetti & Floriani (1976) in the macrocation $[\{Ni(salen)\}_2Na(NCMe)_2]^+$ [Ni–O = 1·860 (3), Ni–N = 1·848 (2) Å] and this indicates that the presence of Na in the coordination sphere does not appreciably influence the geometry in the coordination plane.

The two halves of the Schiff-base ligand have the same geometry and are related by a non-crystallographic twofold axis running through Ni and the midpoint of the bond C(15)–C(16). The two benzene rings are slightly but significantly puckered, total puckering amplitudes, calculated following Cremer & Pople (1975), being 0·039 (3) and 0·044 (3) Å for the rings C(1)–C(6) and C(8)–C(13) respectively. The deviations from planarity suggest a deformation of the rings toward the boat model, in agreement with the asymmetry parameters (Duax, Weeks & Rohrer, 1976) ΔC_s[C(2)–C(3)] = 0·7 (4)° and ΔC_s[C(9)–C(10)] = 0·6 (5)° and could be attributed to coordination effects. In fact, in the free Schiff-base H_2salen (Bresciani Pahor, Calligaris, Nardin & Randaccio, 1978) the two rings are practically planar, the total puckering parameters being Q = 0·010 (3) and 0·014 (3) Å respectively for the two rings. Bond distances and angles in the chelating moieties of the molecule are significantly different from those present in the free ligand. In particular the distances C–O and C–C (adjacent to the N–CH bonds) are shorter than those found in H_2salen while the N–CH distances are longer. This trend, already observed in other salen complexes (Calligaris, Nardin & Randaccio, 1972), shows that an extended conjugation is present in the coordinated ligand (Bresciani Pahor *et al.*, 1978, and references therein).

The configuration of the molecule is 'stepped'; the dihedral angle between the planes defined by the two salicylideneimine residues is 6·6 (1)° and those these planes form with the coordination plane are 5·1 (1) and 9·5 (1)°. The torsion angle around the C(15)–C(16) ethylene bridge is −34·0 (3)° and these two atoms are displaced by 0·07 and 0·42 Å on opposite sides from the NiNN plane.

It is noteworthy that, while in many salen complexes the CH_2–CH_2 group is disordered and therefore appears more or less flattened, in the present compound this group is well defined and no indication of disorder is observed.

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Structure of η^3-Allyl[1,2-bis(dimethylphosphino)ethane]-η^6-toluenetungsten Hexafluorophosphate, $[W(C_3H_5)(C_7H_8)(C_6H_{16}P_2)]PF_6$

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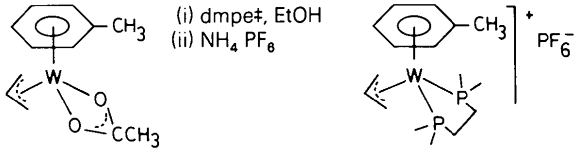
Abstract. $M_r = 612\cdot2$, orthorhombic, $Pbc2_1$, $a = 8\cdot680\,(5)$, $b = 16\cdot230\,(4)$, $c = 30\cdot453\,(8)$ Å, $U = 4290$ Å^3, room temperature, $D_x = 1\cdot89$ Mg m^{-3} for $Z = 8$, $\mu = 5\cdot98$ mm^{-1}, $F(000) = 2384$, $\lambda(\text{Mo } K\alpha) = 0\cdot71069$ Å. $R = 0\cdot051$ for 2273 observed reflexions. The asymmetric unit contains two crystallographically independent cations $C_{16}H_{29}P_2W^+$ together with two partially disordered PF_6^- anions. The W atoms are surrounded by a quasi planar π-toluene ligand, a π-allyl group and a chelated diphosphine ligand disordered in one of the cations.

Introduction. The crystal structure of the title compound, synthesized in accordance with the scheme below, has been determined as part of a broad study of η^6-arenetungsten complexes.



The synthesis of the starting material has been reported in a previous paper (Prout, Gourdon, Couldwell, Meunier, Miao & Woolcock, 1982).

Experimental. Small green plates of the title compound, supplied by Dr M. L. H. Green and co-workers, were very sensitive to air and moisture and were mounted for X-ray examination in argon-filled capillary tubes. It was not possible to measure their density. After survey photography by precession techniques, the selected crystal was set up on an Enraf–Nonius CAD-4F diffractometer. Cell dimensions and the orientation matrix were obtained by least squares from the setting angles of 25 reflexions. Data collection: $\sin\theta/\lambda < 0\cdot55$ Å^{-1}, h 0–9, k 0–17, l 0–32, $\omega/2\theta$ scans, ω-scan angle $(0\cdot9 + 0\cdot35 \tan\theta)^\circ$, graphite-monochromated Mo $K\alpha$ radiation. Reflexions with $I < 3\sigma(I)$ [$\sigma(I)$ from simple counting statistics] were omitted in subsequent calculations. Lorentz–polarization corrections and an empirical absorption correction (North, Phillips & Mathews, 1968) were applied to a set of 2277 independent observed structure amplitudes. Final weighting $w = 1/[1 + (|F_o|-4000)^2]/3000$.

Heavy-atom techniques revealed two heavy atoms per asymmetric unit. The refinement was carried out in the non-centrosymmetric $Pbc2_1$ [$\sum w(\Delta F)^2$ minimized] with two molecules of the title compound per asymmetric unit. Subsequent F_o syntheses indicated that both PF_6^- anions and one of the dmpe ligands were partially disordered. The existence of six peaks at *ca* 1·90 Å from P(11) led us to conclude that each of the three C atoms bonded to P(11) could occupy two sites as shown in Fig. 1: C(111), C(112), C(113) and C(511), C(512) and C(513). In order to avoid ill-conditioned normal matrices, slack constraints (Waser, 1963; Rollett, 1969) were applied to both the PF_6^- anions and the dmpe group. Refinement led to occupation factors of 0·54 for C(111), C(112), C(113) and 0·46 for C(511), C(512), C(513).

For no ligand could the H atoms be found. The W and P atoms were refined anisotropically and the F and C atoms isotropically. Refinement was by least squares with a large-block approximation to the normal matrix:

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‡ dmpe is $(CH_3)_2PCH_2CH_2P(CH_3)_2$.

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