

Fig. 2. Unit-cell packing diagram; dotted lines indicate hydrogen bonds.

Fig. 2 shows the crystal packing diagram. The structure is stabilized by a network of hydrogen bonds involving the N—H groups (Table 3). In ClO<sub>4</sub><sup>-</sup>, two O atoms [O(7) and O(8)] have higher thermal parameters than the other two [O(5) and O(6)], which are associated with hydrogen bonds.

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Table 3. Possible hydrogen bonds, distances (Å) and angles (°) with e.s.d.'s in parentheses

	N...O	∠N—H...O	Position of O
N(3)—H(9)...O(3)	2.92 (3)	153.7 (8)	x, 1-y, ½-z
N(4)—H(5)...O(4)	2.78 (3)	157.6 (8)	x, y, ½-z
N(1)—H(1)...O(3)	2.92 (4)	149.9 (9)	x, y, ½-z
N(1)—H(2)...O(4)	3.29 (5)	147.2 (10)	x, y, ½-z
N(2)—H(8)...O(5)	3.14 (4)	135.4 (10)	x, y, z
N(2)—H(7)...O(6)	3.08 (3)	146.5 (9)	x, y, ½-z

#### References

- COLEMAN, P. F., LEGG, J. I. & STEELE, J. (1970). *Inorg. Chem.* **9**, 937–944.  
*International Tables for X-ray Crystallography* (1962). Vol. III, p. 273. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)  
*International Tables for X-ray Crystallography* (1974). Vol. IV, pp. 99, 149. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)  
KURODA, B. K. & WATANABE, K. (1971). *Bull. Chem. Soc. Jpn*, **44**, 1034–1039.  
LEGG, J. I., COOKE, D. W. & DOUGLAS, B. E. (1967). *Inorg. Chem.* **6**, 700–706.  
MOTHERWELL, W. D. S. & CLEGG, W. (1978). *PLUTO78*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.  
SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.  
SHELDRICK, G. M. (1986). *SHELX86*. Program for crystal structure determination. Univ. of Cambridge, England.

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## Structure of Dichlorobis(triphenylphosphine)nickel(II)

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**Abstract.** [NiCl<sub>2</sub>[(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P]<sub>2</sub>], *M<sub>r</sub>* = 654.20, monoclinic, *P*2/*c* (No. 13), *a* = 11.580 (2), *b* = 8.094 (1), *c* = 17.220 (3) Å, β = 107.20 (2)°, *V* = 1541.8 (5) Å<sup>3</sup>, *Z* = 2, *D<sub>x</sub>* = 1.409 g cm<sup>-3</sup>, graphite-monochromated X-radiation (λ = 0.71073 Å), μ(Mo Kα) = 9.29 cm<sup>-1</sup>, *F*(000) = 676, *T* = 94 (5) K though held constant to within ±1 K, final *R*(*F*) = 0.038 for 8615 observed reflections [*F* > 3σ(*F*), (sin θ)/λ < 1.0 Å<sup>-1</sup>]. The crystal structure requires the [NiCl<sub>2</sub>[(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P]<sub>2</sub>] molecule to have *C*<sub>2</sub> symmetry. Coordination about the central Ni atom is approximately tetrahedral in accord with the observed paramagnetism of the molecule. A significant opening of the Cl—Ni—Cl angle from an ideal tetrahedral value to 127.9 (1)° is noted. In addition, a long Ni—P separation of 2.1380 (2) Å, and somewhat short

P—C(Ph) distances of 1.810–1.819 (1) Å are observed, consistent with a π back-bonding model which incorporates P—C σ\* orbitals in the acceptor role.

**Introduction.** It was first observed by Venanzi (1962) that dichlorobis(triphenylphosphine)nickel(II) is paramagnetic. A crystal structure analysis based on visual estimates of intensities from zero-level Weissenberg photographs allowed distinction between the possible tetrahedral and *cis*-planar structures (Garton, Henn, Powell & Venanzi, 1963). However, refinement to *R* = 0.22 left structural parameters poorly defined and some ambiguity over the space group (*P*2/*c* vs *Pc*). A later crystallographic study (Bruins Slot, Van Havare, Noordik, Beurskens & Royo, 1984) based on



Table 1. Atomic coordinates and equivalent isotropic vibrational parameters ( $\text{\AA}^2$ ) with estimated standard deviations

The equivalent isotropic vibrational parameter is defined as  $U_{eq} = \frac{1}{3}[U_{22} + 1/\sin^2\beta(U_{11} + U_{33} + 2U_{13}\cos\beta)]$ .

	x	y	z	$U_{eq}(\text{\AA}^2)$
Ni	0.500	0.28635 (2)	0.750	0.01500 (3)
Cl	0.50870 (2)	0.16671 (3)	0.63668 (1)	0.02466 (5)
P	0.32698 (2)	0.44765 (3)	0.70994 (1)	0.01444 (4)
C(1)	0.20055 (8)	0.3084 (1)	0.66840 (6)	0.0184 (2)
C(2)	0.19212 (9)	0.1660 (1)	0.71244 (7)	0.0242 (2)
C(3)	0.0941 (1)	0.0597 (2)	0.68425 (8)	0.0314 (3)
C(4)	0.0054 (1)	0.0946 (2)	0.6120 (1)	0.0381 (3)
C(5)	0.0140 (1)	0.2338 (2)	0.5678 (1)	0.0390 (4)
C(6)	0.1114 (1)	0.3415 (2)	0.59555 (8)	0.0280 (3)
C(7)	0.31922 (8)	0.5944 (1)	0.62921 (5)	0.0165 (2)
C(8)	0.35154 (9)	0.5397 (1)	0.56142 (6)	0.0204 (2)
C(9)	0.3489 (1)	0.6476 (1)	0.49825 (6)	0.0231 (2)
C(10)	0.3162 (1)	0.8120 (1)	0.50282 (7)	0.0232 (2)
C(11)	0.2847 (1)	0.8675 (1)	0.57030 (7)	0.0234 (2)
C(12)	0.28555 (9)	0.7592 (1)	0.63324 (6)	0.0201 (2)
C(13)	0.28416 (7)	0.5641 (1)	0.78745 (5)	0.0160 (2)
C(14)	0.36650 (9)	0.6777 (1)	0.83408 (6)	0.0203 (2)
C(15)	0.3387 (1)	0.7686 (1)	0.89477 (7)	0.0232 (2)
C(16)	0.2279 (1)	0.7466 (1)	0.90906 (6)	0.0239 (2)
C(17)	0.14475 (9)	0.6351 (2)	0.86248 (7)	0.0272 (3)
C(18)	0.17257 (8)	0.5439 (1)	0.80187 (6)	0.0223 (2)

Table 2. Bond distances ( $\text{\AA}$ ) and selected bond angles ( $^\circ$ ) and torsion angles ( $^\circ$ )

Ni—Cl	2.2075 (2)	C(7)—C(12)	1.398 (1)
Ni—P	2.3180 (2)	C(8)—C(9)	1.389 (1)
P—C(1)	1.8175 (9)	C(9)—C(10)	1.392 (1)
P—C(7)	1.8104 (8)	C(10)—C(11)	1.391 (1)
P—C(13)	1.8189 (8)	C(11)—C(12)	1.392 (1)
C(1)—C(2)	1.400 (1)	C(13)—C(14)	1.396 (1)
C(1)—C(6)	1.394 (2)	C(13)—C(18)	1.395 (1)
C(2)—C(3)	1.392 (1)	C(14)—C(15)	1.392 (1)
C(3)—C(4)	1.388 (2)	C(15)—C(16)	1.387 (1)
C(4)—C(5)	1.380 (2)	C(16)—C(17)	1.389 (2)
C(5)—C(6)	1.393 (2)	C(17)—C(18)	1.391 (1)
C(7)—C(8)	1.399 (1)		
Cl—Ni—C(1)'	127.95 (1)	Ni—P—C(7)	116.12 (3)
Cl—Ni—P	104.210 (9)	Ni—P—C(13)	118.21 (3)
C(1)—Ni—P'	104.411 (8)	C(1)—P—C(7)	104.68 (4)
P—Ni—P'	111.42 (1)	C(1)—P—C(13)	104.34 (4)
Ni—P—C(1)	106.96 (3)	C(7)—P—C(13)	105.14 (4)
		Ni—P—C(1)—C(2)	47.25 (8)
		Ni—P—C(7)—C(8)	45.40 (8)
		Ni—P—C(13)—C(14)	58.26 (8)

diffractometer data collected at room temperature led to only  $R = 0.104$ , and was suspected of containing a small amount of  $[\text{Ni}(\text{CO})_2(\text{Ph}_3\text{P})_2]$  as an impurity. This study was undertaken to establish an accurate structural characterization of the title compound. A charge density study of this compound is now in progress.

**Experimental.** Dark blue-green crystals of  $[\text{NiCl}_2\{(\text{C}_6\text{H}_5)_3\text{P}\}_2]$  were grown under a nitrogen atmosphere by slow evaporation from a solution of the compound in absolute ethanol. A crystal of dimensions  $0.47 \times 0.33 \times 0.38$  mm was used for data collection. Measurements were made using an Enraf-Nonius CAD-4

diffractometer with a locally modified low-temperature device. Lattice parameters were determined by a least-squares fit of 25 reflections with  $48 < 2\theta < 56^\circ$ . A total of 25248 intensity data were collected (excluding standard reflections  $\bar{1}20$ ,  $0\bar{3}3$ ,  $30\bar{4}$ ,  $\bar{1}3\bar{2}$ ,  $14$ ,  $8,7,10$ ,  $6,2,2\bar{1}$  which were measured every 2 h during data collection; no significant decay was observed, though some fluctuation was taken account of by use of a curve-fitting procedure). Data were collected in the range  $0 < 2\theta < 90^\circ$ ;  $-23 \leq h \leq 23$ ,  $-11 \leq k \leq 16$ ,  $-34 \leq l \leq 34$ . Corrections for Lorentz and polarization factors were made; correction for absorption was based on indexed faces  $[(100)$ ,  $(\bar{1}00)$ ,  $(010)$ ,  $(0\bar{1}0)$ ,  $(00\bar{1})$ ,  $(10\bar{2})$ ,  $(\bar{1}\bar{1}9)$ , max. and min. transmission coefficients 0.783 and 0.646]. Averaging yielded 13288 independent reflections, of which 8615 with  $I > 1.5\sigma(I)$  were used in subsequent structure solution and refinement ( $R_{\text{int}} = 0.019$  for observed reflections).

The structure was solved using the *MULTAN*11/82 series of programs (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) to locate the unique Ni, Cl and P atoms. Remaining non-H atoms were located from difference Fourier maps. H atoms were placed in calculated positions, using a C—H distance of 0.95  $\text{\AA}$ . Full-matrix least-squares refinements based on  $F$  were carried out for 186 parameters. Positional and anisotropic vibrational parameters were refined for all non-H atoms. H atoms were refined using a riding model, their isotropic vibrational parameters fixed at 1.2 times the equivalent isotropic parameter for the attached C atoms. Final  $R = 0.038$ ,  $wR = 0.052$ , where  $w = 1/\sigma^2(F)$  and  $\sigma^2(F^2) = [\sigma_c^2(I) + (0.05)^2(F^2)^2]$ ,  $S = 1.28$ . In the final cycle of refinement  $(\Delta/\sigma)_{\text{max}} < 0.01$ . Maximum and minimum peaks in the electron density difference map were 0.94 and  $-1.10 \text{ e}\text{\AA}^{-3}$  respectively. Scattering factors, corrected for anomalous dispersion, were taken from *International Tables for X-ray Crystallography* (1974). Calculations were carried out using the *SDP* program package (Frenz, 1978).

**Discussion.** Final atomic coordinates are listed in Table 1.\* Bond lengths and selected bond angles and torsion angles are given in Table 2.† The molecular structure of

\* Lists of structure factors, anisotropic vibrational parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51444 (130 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

† It should be noted that the low estimated standard deviation values obtained for the refined structural parameters reflect the precision of the data, being collected to high resolution and being determined from the averaging of many symmetry-equivalent data, rather than being realistic of the total error associated with the refined parameters. More realistic e.s.d.'s would be somewhat larger.



$[\text{NiCl}_2(\text{Ph}_3\text{P})_2]$  is depicted in Fig. 1 along with the atomic labelling scheme.

The molecule's approximate tetrahedral geometry is readily established by examination of the bond angles at nickel. It is noted that the Cl–Ni–Cl angle, at  $127.95(1)^\circ$ , is considerably larger than the other interligand angles. While this may be in part a result of Jahn–Teller distortion, which is suggested by Dunitz & Orgel (1959) to occur in tetrahedral  $\text{Ni}^{\text{II}}$  complexes, it is likely to be mostly due to the repulsive effect between the chlorine ligands which lie some  $0.11 \text{ \AA}$  closer to the metal than the P atoms.

The Ni–P distance of  $2.3180(2) \text{ \AA}$  is quite long. In a comprehensive statistical analysis of interatomic distances from accurately determined structures of inorganic and organometallic complexes, Allen, Kennard, Watson, Brammer, Orpen & Taylor (1989) have observed that Ni–P distances fall into two fairly well defined groups with mean values of  $2.187$  and  $2.321 \text{ \AA}$  respectively, though no common chemical distinction between long and short bonds is apparent. In this structure the long Ni–P bond may be the result of weak back-donation from nickel due to the electron-withdrawing effect of the chlorine ligands. Perhaps directly related to this observation are the short P–C distances of  $1.810$ – $1.819 \text{ \AA}$  [see Allen *et al.* (1988), mean P–C(Ph) distance in metal complexes =

$1.828 \text{ \AA}$ ]. The two observations are consistent based on the argument that the phosphine acceptor orbitals for  $\pi$  back-donation are not pure phosphorus  $3d$  orbitals but a combination of these with P–C  $\sigma^*$  orbitals. Hence, increased  $\pi$  back-donation would lead to weakening and lengthening of the P–C bonds. In this structure it is suggested that weak  $\pi$  back-donation has resulted in strong and quite short P–C bonds. Strong support for this bonding description comes from theoretical studies of the interaction of  $\text{PX}_3$  molecules with metal atoms (Xiao, Trogler, Ellis & Berkovich-Yellin, 1983; Marynick, 1984) and from direct structural evidence (Orpen & Connelly, 1985). One might also suggest that a misplaced P atom would manifest the same results. However, the accuracy of this structure is sufficient to dismiss that argument.

The Ni–Cl distance of  $2.2075(3) \text{ \AA}$  compares well with the mean distance of  $2.217 \text{ \AA}$  calculated by Allen *et al.* (1988), based on structures of 18 four-coordinate  $\text{Ni}^{\text{II}}$  complexes. By contrast, mean Ni–Cl distances for five- and six-coordinate  $\text{Ni}^{\text{II}}$  complexes were  $2.308$  and  $2.441 \text{ \AA}$ , respectively. The only other structural features of interest are to note that the P–C(7) distance, at  $1.810(1) \text{ \AA}$ , is some  $0.008(1) \text{ \AA}$  shorter than the other two P–C(Ph) distances. In addition the Ni–P–C(1) angle is approximately  $10^\circ$  less than its counterparts for the other two rings. This distortion may be electronic in origin as a similarity in Ni–P–C–C torsion angles for the three rings suggests no major steric demand as this is a common orientation for triphenylphosphine moieties (Bye, Schweizer & Dunitz, 1982).

Comparison with the room-temperature structure determination by Bruins Slot *et al.* shows some substantial differences. Most notable are the larger Ni–Cl distance of  $2.360(3) \text{ \AA}$  [*cf.*  $2.2075(3) \text{ \AA}$ ] and the smaller Cl–Ni–Cl angle of  $120.9(1)^\circ$  [*cf.*  $127.95(1)^\circ$ ]. These differences appear to be too large to attribute to the difference in temperature of the two studies. It seems more likely that the suggested carbonyl impurity is responsible for an inaccurately determined chlorine position in the room-temperature structure.

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#### References

- ALLEN, F. A., KENNARD, O., WATSON, D. G., BRAMMER, L., ORPEN, G. & TAYLOR, R. (1989). *J. Chem. Soc. Dalton Trans.* In the press.

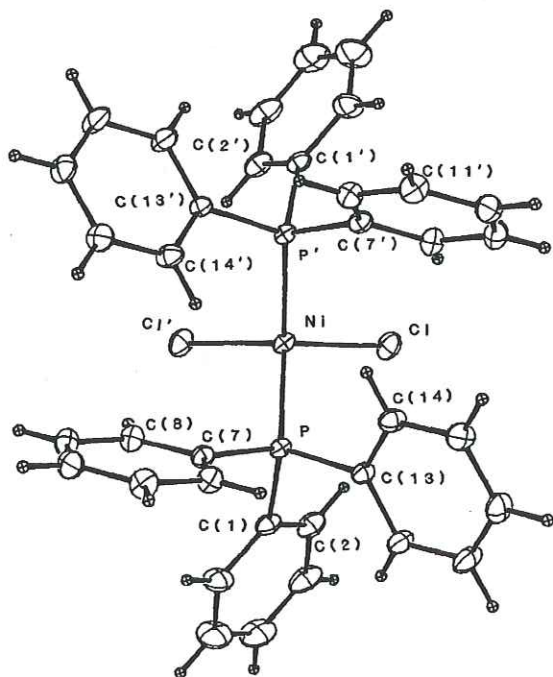


Fig. 1. Molecular structure with atomic labelling scheme. All non-H atoms are shown with 50% probability ellipsoids.

- BRUINS SLOT, H. J., VAN HAVARE, W. K. L., NOORDIK, J. H., BEURSKENS, P. T. & ROYO, P. (1984). *Cryst. Spectrosc. Res.* **14**, 623.
- BYE, E., SCHWEIZER, B. W. & DUNITZ, J. D. (1982). *J. Am. Chem. Soc.* **104**, 5893–5898.
- DUNITZ, J. D. & ORGEL, L. E. (1957). *J. Phys. Chem. Solids*, **3**, 20–29.
- FRENZ, B. A. (1978). *The Enraf-Nonius CAD-4 SDP – A Real-time System for Concurrent X-ray Data Collection and Crystal Structure Solution*. In *Computing in Crystallography*, edited by H. SCHENK, R. OLTROF-HAEKAMP, H. VAN KONINGSVELD & G. C. BASSI. Delft Univ. Press.
- GARTON, G., HENN, D. E., POWELL, H. M. & VENANZI, L. M. (1963). *J. Chem. Soc.* pp. 3625–3629.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
- MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1982). *MULTAN11/82. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
- MARYNICK, D. S. (1984). *J. Am. Chem. Soc.* **106**, 4064–4065.
- ORPEN, A. G. & CONNELLY, N. G. (1985). *J. Chem. Soc. Chem. Commun.* pp. 1310–1311.
- VENANZI, L. M. (1962). *J. Chem. Soc.* pp. 719–724.
- XIAO, S.-X., TROGLER, W. C., ELLIS, D. E. & BERKOVICH-YELLIN, Z. (1983). *J. Am. Chem. Soc.* **105**, 7033–7037.

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# Structure of {N-[2-(2-Aminoethylamino)ethyl]salicylideneaminato-O,N,N',N''}-palladium(II) Perchlorate

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**Abstract.** [Pd(C<sub>11</sub>H<sub>16</sub>N<sub>3</sub>O)]ClO<sub>4</sub>,  $M_r = 412.12$ , monoclinic,  $P2_1/c$ ,  $a = 8.960$  (3),  $b = 13.541$  (6),  $c = 11.887$  (2) Å,  $\beta = 98.88$  (2)°,  $V = 1424.9$  (8) Å<sup>3</sup>,  $Z = 4$ ,  $D_m = 1.913$  (3),  $D_x = 1.921$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 1.50$  mm<sup>-1</sup>,  $F(000) = 824$ ,  $T = 296$  K,  $R = 0.047$  for 2776 unique observed reflections. The [Pd<sup>II</sup>(C<sub>11</sub>H<sub>16</sub>N<sub>3</sub>O)]<sup>+</sup> complex cation with the saden ligand contains two five-membered and two six-membered rings. The coordination polyhedron around the Pd atom is a slightly distorted square (one O and three N) with Pd–O = 1.980 (4) Å and Pd–N in the range 1.951 (4)–2.075 (6) Å. The perchlorate anion is disordered. The structure is predominantly held together by electrostatic interactions.

**Introduction.** Some complexes containing tetradentate Schiff bases have received a great deal of attention owing to their ability to undergo reversible adduct formation with oxygen and serve as simple models for various metalloenzymes. As a rule the tetradentate Schiff bases which have been utilized up till now are symmetric, they are coordinated as anions with charge 2–. On the other hand, complexes with non-symmetrical tetradentate Schiff bases are almost unknown, owing to the difference in their charge as well as to the number of donor atoms that can suitably modify the properties of the complexes. So far two structures of Ni<sup>II</sup> complexes with the saden ligand, {N-[2-(2-aminoethylamino)ethyl]salicylideneaminato-O,N,N',N''},

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