partial double bond of 1·671 (8) Å observed in the free ligand (Form, Raper & Downie, 1976), but is much shorter than the 1·79 Å quoted in *cis*-bis[2(3*H*)-benzimidazolethione]tetrachlorotellurium(IV)–dioxane (Deuten, Schnabel & Klar, 1979). This S—C bond length also agrees with those obtained for similar compounds referred to in *Introduction*. The C(2)—N(3) and C(2)—N(4) bond lengths [1·337 (6) and 1·346 (6) Å] do not show significant variation in keeping with the thione structure and agree with the value [1·362 (6) Å] quoted in the free ptu crystal structure and with the 1·353 (14) and 1·317 (13) Å in the 2(3*H*)-benzimidazolethione–Te^{IV} complex (Deuten, Schnabel & Klar, 1979). Hence the bond parameters obtained for our compound clearly indicate the presence of thione form (III). C—C bond lengths are in the range 1·370 (8) to 1·400 (9) Å and C—C—C angles are in the range 116·7 (4) to 122·9 (5)°. The average N—H and C—H bond lengths in the ptu ligand are 0·84 (5) and 0·88 (6) Å respectively. The ptu group is planar within a maximum deviation of 0·041 (4) Å from the least-squares plane.

The thiourea SCN_2 moiety is planar with the maximum deviation from the least-squares plane through the atoms being 0·028 (5) Å. The S—C bond length [1·734 (6) Å] and C—N partial double bonds [1·329 (8) and 1·311 (8) Å] are normal for thiourea ligands. The average N—H bond is 0·87 (2) Å.

The Cl^- ions remain outside the coordination sphere of the Te atom, Te—Cl being 5·618 (2) Å. However, the Cl^- ion remains approximately in the least-squares plane of the SCN_2 thiourea and ptu groups, the deviation of the ion from these two planes being 0·014 (1) and 0·855 (1) Å respectively. Two N atoms of the thiourea group are involved in hydrogen bonding with the Cl^- ion, as revealed by the distances 3·292 (6) and 3·453 (6) Å. Furthermore, the same Cl^- ion participates in hydrogen bonding with the NH group of the ptu ligand also, with distances of 3·225 (4) and 3·214 (4) Å. There is a short intermolecular S···S van der Waals interaction [S(2)···S(2)($1-x$, $-y$, $-z$) = 3·207 (2) Å].

References

Alcock, N. W. (1972). *Adv. Inorg. Chem. Radiochem.* **15**, 1–53.

Anderson, O. P. (1971). *Acta Chem. Scand.* **25**, 3593–3608.

Ase, K. (1969). *Acta Chem. Scand.* **23**, 3206–3216.

Ase, K., Moe, K. M. & Solheim, J. O. (1971). *Acta Chem. Scand.* **25**, 2467–2475.

Ase, K. & Roti, I. (1974). *Acta Chem. Scand. Ser. A*, **28**, 104–112.

Ault, H. K. & Husebye, S. (1978). *Acta Chem. Scand. Ser. A*, **32**, 157–162.

Barnard, P. W. C., Donaldson, J. W., Grimsey, R. M. A., Dennes, G., Russo, U. & Calogero, S. (1981). *Inorg. Chim. Acta*, **51**, 217–223.

Cromer, D. T. & Liberman, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.

Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* A**24**, 321–324.

Deuten, K. V., Schnabel, W. & Klar, G. (1979). *Cryst. Struct. Commun.* **8**, 679–684.

Elder, R. C., Marcuso, T. & Boolchand, P. (1977). *Inorg. Chem.* **16**, 2700–2704.

Form, G. R., Raper, E. S. & Downie, T. C. (1976). *Acta Cryst.* B**32**, 345–348.

Fosheim, K., Foss, O., Scheie, A. & Solheimsnes, S. (1965). *Acta Chem. Scand.* **19**, 2336–2348.

Foss, O. (1970). *Pure Appl. Chem.* **24**, 31–48.

Foss, O., Lyssandtrae, N., Moe, K. M. & Tysseland, M. (1973). *Acta Chem. Scand.* **27**, 218–228.

Foss, O., Maroy, K. & Husebye, S. (1965). *Acta Chem. Scand.* **19**, 2361–2368.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

Sheldrick, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Takahashi, Y. & Yabe, K. (1969). *Bull. Chem. Soc. Jpn*, **42**, 3064–3072.

Acta Cryst. (1984). C**40**, 965–967

Structure of Chloro(diethyldithiocarbamato)(triphenylphosphine)nickel(II), $[NiCl(C_5H_{10}NS_2)\{P(C_6H_5)_3\}]$

By K. Ramalingam and G. Aravamudan

Department of Chemistry, Indian Institute of Technology, Madras-600 036, *India*

and M. Seshasayee and Ch. Subramanyam

Department of Physics, Indian Institute of Technology, Madras-600 036, *India*

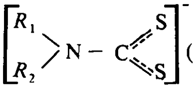
(*Received* 4 *November* 1983; *accepted* 13 *February* 1984)

Abstract. $M_r = 504{\cdot}69$, triclinic, $P\bar{1}$, $a = 9{\cdot}808$ (2), $b = 11{\cdot}690$ (2), $c = 14{\cdot}026$ (2) Å, $\alpha = 97{\cdot}63$ (1), $\beta = 118{\cdot}35$ (1), $\gamma = 108{\cdot}81$ (1)°, $V = 1258{\cdot}4$ Å^3, $Z = 2$, $D_x = 1{\cdot}33$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 1{\cdot}049$ mm^{-1}, $T = 300$ K, $F(000) = 524$, final $R = 0{\cdot}052$ for 1773 reflections. Ni^{II} displays planar fourfold coordination with the following parameters: Ni—S(*trans* to Cl) = 2·170 (4), Ni—S(*trans* to P)

0108-2701/84/060965-03$01.50

= 2·232 (3), Ni—Cl = 2·187 (3), Ni—P = 2·204 (3) Å, S(1)—Ni—S(2) = 78·4 (1), S(2)—Ni—Cl = 93·2 (1), Cl—Ni—P = 93·7 (1), P—Ni—S(1) = 94·7 (1)°. There are no significant intermolecular interactions.

Introduction. The structure and reactivity of metal dithiolates, especially of dithiocarbamates, have evoked



(=L),

interest in recent years (Burns, McCullough & McAuliffe, 1980; Coucouvanis, 1970, 1979). The d^8 divalent transition-metal ions form stable dithiocarbamates of the type ML_2 (M = Ni, Pd, Pt) which are generally resistant to attack by hard Lewis bases. However, by suitably choosing R_1 and R_2 (*e.g.* $R_1 = R_2 = C_2H_4OH$), it has recently been shown that NiL_2 complexes can be readily broken up with ethylenediamine (Aravamudan, Ramalingam, Radha & Seshasayee, 1984). The ML_2 dithiocarbamates are also opened up by π-acceptor ligands such as substituted phosphines (Maxfield, 1970). These phosphine dithiocarbamate complexes of Ni^{II}, Pd^{II} and Pt^{II} have shown interesting NMR, electronic spectral and electrochemical characteristics (Fackler, Lin & Andrews, 1977; Bowmaker, Boyd, Campbell, Hope & Martin, 1982). In addition, the Ni^{II} complexes also give rise to Ni^{I} and Ni^{III} species on γ irradiation, which have interesting ESR features (Muralikrishna & Subramanian, 1984; Bowmaker, Boyd & Campbell, 1982). Structural work on these Ni complexes is, however, sparse. Here we report the crystal structure of the title compound. The structure of its triethylphosphine analogue was reported (Chan, Chen, Fackler, Masters & Pan, 1982) when this work was in progress.

Experimental. Preparation according to Maxfield (1970); purple crystals isolated were sensitive to hydrolysis leading to the formation of bis(diethyldithiocarbamato)nickel(II), nickel chloride and triphenylphosphine; single crystals, however, obtained by dissolving the compound in ethyl acetate–dichloromethane and evaporating the solution under anhydrous conditions. D_m not determined. Crystal 0·4 × 0·08 × 0·3 mm. CAD-4 diffractometer, graphite filter, Mo $K\alpha$ radiation. Lattice constants: 24 high-angle reflections. ω–2θ scan technique, $1 < \theta < 27°$ (h: 0 to 10, k: 12 to −12, l: 15 to −15). 4776 reflections recorded. 1773 unique with $I > 3\sigma(I)$ used in structure refinement. No absorption correction. Two standards: intensity variation < 5%. Space group $P\bar{1}$ assumed, and later proved to be correct. Coordinates of Ni, P and Cl atoms from Patterson map and other non-hydrogen atom positions revealed by successive difference Fourier maps. 17 of the 25 H atoms appeared in difference Fourier maps; positions of the eight H atoms attached to C(3), C(4) and C(5) atoms were deduced using geometrical constraints (*AFIX* routine of the program *SHELX76*, Sheldrick, 1976). Full-matrix least-squares refinements on F with anisotropic thermal parameters for non-hydrogen atoms and isotropic for H converged to $R = 0·052$, $R_w = 0·055$ with $w = 1·000/[\sigma^2(F_o) + 0·161\,|F_o|^2]$. $(\Delta/\sigma)_{max} = 0·967$. Final $\Delta\rho$ map featureless, max. peak being 0·41 e Å^{-3}. No correction for secondary extinction.

Discussion. Positional and thermal parameters are listed in Table 1.* Bond parameters are given in Table 2. Fig. 1 gives the *ORTEP* plot (Johnson, 1976) of the molecule. The title compound, [NiCl(dtc)(PPh_3)] (I), is monomeric with no significant (< 3·5 Å) intermolecular contacts. Ni, S(1), S(2), P and Cl atoms are planar to within 0·003 Å. The planarity of the coordination around Ni^{II} is also manifested in the observed diamagnetism of the compound. The deviation of this plane from a perfect square is caused by the small bite angle subtended by the S atoms of the chelating dtc at the Ni position. NiCl(dtc)(PEt_3) (II) displays a similar geometry around Ni (Chan, Chen, Fackler, Masters & Pan, 1982).

The Ni—S distances in (I) and in (II) are quite different, in contrast to Ni(dtc)$_2$ (III) [2·195 (2) and 2·207 (2) Å] (Bonamico, Dessy, Mariani, Vaciago & Zambonelli, 1965). This is ascribed to the different *trans* influences of phosphine and Cl^-. Triphenylphosphine being a good π acceptor has a greater *trans* influence and hence the Ni—S bond *trans* to P is longer than that *trans* to Cl [Ni—S *trans* to P = 2·232 (3) Å, Ni—S *trans* to Cl = 2·170 (4) Å]. Asymmetry in the Ni—S bonds in (I) leads to an increase in Ni—S—C angle [87·4 (4)° in (I); 85·3 (4)° in (III)] and a contraction in S—C—S angle [108·7 (7)° in (I); 110·5 (4)° in (III)].

The bond parameters of the dtc moiety are found to be normal. Chan *et al.* (1982) reported that the C—N bond order in (II) is slightly different from that of (III) based on spectroscopic data, though they state that there is no X-ray evidence for this. However, we find that the ν(C—N) frequency for (I) and (III) appears at the same value, *viz* 1525 cm^{-1}, implying no change in bond order. X-ray evidence for the change in C—N bond length of (I) with respect to (III) is also not apparent.

Compounds (I) and (II) are rare examples of square-planar Ni^{II} complexes featuring Cl^- as a ligand. This is forced through the square-planar geometry

---

* 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 39272 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional* ($\times 10^4$) *and equivalent isotropic thermal parameters* ($\times 10^3$) *for non-*H *atoms with e.s.d.'s in parentheses*

$$U_{\rm eq} = \tfrac{1}{3}\textstyle\sum_i U_{ii}.$$

	x	y	z	$U_{\rm eq}$(Å^2)
Ni	4653 (2)	1119 (1)	2818 (1)	43 (1)
Cl	7148 (3)	1637 (2)	3017 (2)	55 (1)
S(1)	2247 (4)	392 (3)	2731 (3)	77 (1)
S(2)	4716 (3)	−541 (2)	3431 (2)	59 (1)
P	4235 (3)	2641 (2)	2114 (2)	39 (1)
N	1801 (11)	−1657 (8)	3422 (8)	85 (2)
C(1)	2782 (12)	−753 (9)	3242 (8)	63 (2)
C(2)	−36 (15)	−1782 (12)	3044 (12)	109 (2)
C(3)	220 (18)	−815 (15)	4070 (14)	155 (2)
C(4)	2379 (15)	−2589 (11)	3885 (11)	108 (2)
C(5)	1513 (22)	−3838 (13)	2905 (17)	172 (2)
C(6)	2063 (10)	2548 (8)	1553 (8)	45 (2)
C(7)	1680 (11)	2810 (9)	2377 (8)	56 (2)
C(8)	19 (12)	2652 (10)	2010 (10)	71 (2)
C(9)	−1155 (12)	2315 (11)	887 (11)	74 (2)
C(10)	−802 (13)	2064 (13)	87 (10)	84 (2)
C(11)	839 (13)	2178 (11)	411 (9)	67 (2)
C(12)	4443 (11)	2552 (9)	886 (8)	53 (2)
C(13)	5279 (13)	3620 (10)	714 (9)	85 (2)
C(14)	5406 (16)	3481 (13)	−235 (11)	127 (2)
C(15)	4672 (16)	2273 (14)	−1018 (10)	123 (2)
C(16)	3824 (15)	1254 (12)	−870 (9)	91 (2)
C(17)	3729 (13)	1350 (10)	90 (9)	70 (2)
C(18)	5689 (10)	4305 (8)	3126 (7)	41 (1)
C(19)	5171 (12)	5269 (9)	3002 (9)	61 (2)
C(20)	6290 (14)	6511 (9)	3823 (10)	76 (2)
C(21)	7893 (13)	6789 (9)	4732 (9)	62 (2)
C(22)	8380 (13)	5811 (10)	4837 (9)	63 (2)
C(23)	7290 (12)	4574 (9)	4043 (8)	39 (1)

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

Ni–Cl	2·187 (3)	Ni–S(1)	2·170 (4)
Ni–P	2·204 (3)	Ni–S(2)	2·232 (3)
C(1)–S(1)	1·712 (12)	C(1)–S(2)	1·713 (13)
C(1)–N	1·323 (16)	N–C(2)	1·565 (19)
C(2)–C(3)	1·566 (26)	N–C(4)	1·473 (17)
C(4)–C(5)	1·517 (20)	P–C(6)	1·845 (11)
C(6)–C(7)	1·401 (18)	C(7)–C(8)	1·393 (16)
C(8)–C(9)	1·335 (16)	C(9)–C(10)	1·346 (24)
C(10)–C(11)	1·401 (19)	P–C(12)	1·823 (13)
C(12)–C(13)	1·377 (16)	C(13)–C(14)	1·388 (23)
C(14)–C(15)	1·379 (19)	C(15)–C(16)	1·320 (21)
C(16)–C(17)	1·386 (21)	P–C(18)	1·841 (7)
C(18)–C(19)	1·377 (16)	C(19)–C(20)	1·403 (12)
C(20)–C(21)	1·364 (14)	C(21)–C(22)	1·373 (18)
C(22)–C(23)	1·385 (12)		
Cl–Ni–S(2)	93·2 (1)	Cl–Ni–P	93·7 (1)
S(1)–Ni–S(2)	78·4 (1)	S(1)–Ni–P	94·7 (1)
Cl–Ni–S(1)	171·6 (1)	S(2)–Ni–P	172·7 (1)
Ni–S(1)–C(1)	87·4 (4)	Ni–S(2)–C(1)	85·4 (4)
S(1)–C(1)–S(2)	108·7 (7)	S(1)–C(1)–N	124 (1)
S(2)–C(1)–N	127 (1)	C(1)–N–C(2)	119 (1)
N–C(2)–C(3)	106 (1)	C(1)–N–C(4)	120 (1)
N–C(4)–C(5)	109 (1)	P–C(6)–C(7)	116·0 (6)
P–C(6)–C(11)	124 (1)	C(6)–C(7)–C(8)	119·2 (9)
C(7)–C(8)–C(9)	120 (1)	C(8)–C(9)–C(10)	122 (1)
C(9)–C(10)–C(11)	121 (1)	C(10)–C(11)–C(6)	118 (1)
C(11)–C(6)–C(7)	120 (1)	P–C(12)–C(13)	123·3 (8)
P–C(12)–C(17)	118·2 (9)	C(12)–C(13)–C(14)	120 (1)
C(13)–C(14)–C(15)	120 (1)	C(14)–C(15)–C(16)	120 (1)
C(15)–C(16)–C(17)	122 (1)	C(16)–C(17)–C(12)	120 (1)
C(17)–C(12)–C(13)	119 (1)	P–C(18)–C(19)	121·3 (6)
P–C(18)–C(23)	119·1 (8)	C(18)–C(19)–C(20)	119·4 (9)
C(19)–C(20)–C(21)	121 (1)	C(20)–C(21)–C(22)	118·2 (8)
C(21)–C(22)–C(23)	121·5 (9)	C(22)–C(23)–C(18)	120 (1)
C(23)–C(18)–C(19)	119·6 (7)		

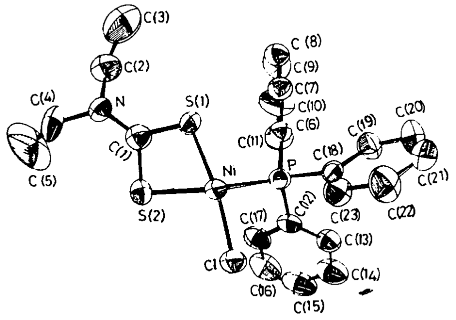


Fig. 1. *ORTEP* plot of the molecule.

imposed on Ni$^{\rm II}$ by the other two ligands, *viz* dtc and PPh$_3$, which would induce large crystal-field effects.

The Ni–P distances observed in (I) and (II) [2·204 (3) Å in (I); 2·188 (2) Å in (II)] are two of the shortest distances reported for divalent Ni–phosphine complexes. Comparison of the non-bonded distances and angles in (I) and (II) shows the effect of introducing bulky triphenylphosphine in the place of triethylphosphine. There is a considerable decrease in S(1)···Ni···P, S(2)···Ni···Cl angles and increase in P···Ni···Cl in (I) with respect to (II). The three phenyl rings in PPh$_3$ are 'pitched' to varying extents with respect to their corresponding Ni, P, C planes [dihedral angles Ni–P–C–C = 69·0 (6), 42·0 (6), 27·3 (5)°]; 'pitching' apparently relieves steric strain as has been explained in the species [Ni(I$_3$)(PPh$_3$)]$^-$ by Taylor, Templeton, Zalkin & Horrocks (1968).

References

ARAVAMUDAN, G., RAMALINGAM, K., RADHA, K. & SESHASAYEE, M. (1984). To be published.

BONAMICO, M., DESSY, G., MARIANI, C., VACIAGO, A. & ZAMBONELLI, C. (1965). *Acta Cryst.* **19**, 619–626.

BOWMAKER, G. A., BOYD, P. D. W. & CAMPBELL, G. K. (1982). *Inorg. Chem.* **21**, 2403–2412.

BOWMAKER, G. A., BOYD, P. D. W., CAMPBELL, G. K., HOPE, J. M. & MARTIN, R. L. (1982). *Inorg. Chem.* **21**, 1152–1159.

BURNS, R. P., MCCULLOUGH, F. P. & MCAULIFFE, C. A. (1980). *Adv. Inorg. Chem. Radiochem.* **23**, 211–280.

CHAN, L. T., CHEN, H. W., FACKLER, J. P. JR, MASTERS, A. F. & PAN, W. H. (1982). *Inorg. Chem.* **21**, 4291–4295.

COUCOUVANIS, D. (1970). *Prog. Inorg. Chem.* **11**, 233–371.

COUCOUVANIS, D. (1979). *Prog. Inorg. Chem.* **26**, 301–469.

FACKLER, J. P. JR, LIN, I. J. B. & ANDREWS, J. (1977). *Inorg. Chem.* **16**, 450–457.

JOHNSON, C. K. (1976). *ORTEP*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.

MAXFIELD, P. L. (1970). *Inorg. Nucl. Chem. Lett.* **6**, 693–696.

MURALIKRISHNA, C. & SUBRAMANIAN, S. (1984). To be published.

SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

TAYLOR, R. P., TEMPLETON, D. H., ZALKIN, A. & HORROCKS, D. H. (1968). *Inorg. Chem.* **7**, 2629–2636.