bonds [Ta(3)–O(34) = 2·03 (2) Å]. The Ta–O distance in the central unit [1·76 (2) Å] indicates a double-bond interaction; the O bridges are thus unsymmetrical, although essentially linear [Ta(3)–O(34)–Ta(4) = 178·4 (15)°] (Prout & Daran, 1979).

As a result of the *trans* influence of the oxo groups, the Cl atoms *trans* to the Ta(4)–O(34) and Ta(4′)–O(34′) bonds show a relatively weak interaction with Ta(4) and Ta(4′), respectively [the corresponding bond distance is 2·672 (9) Å]. Accordingly, the Cl atoms *trans* to the Ta(3)–O(34) and Ta(3′)–O(34′) dative bonds show relatively short Ta–Cl distances at 2·30 (1) Å.

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References

BUNKER, M. J., DE CIAN, A., GREEN, M. L. H., MOREAU, J. J. E. & SINGANPORIA, N. (1980). *J. Chem. Soc. Dalton Trans.* pp. 2155–2160.

CARRUTHERS, J. R. & WATKIN, D. J. (1979). *Acta Cryst.* A**35**, 698–699.

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

GREEN, J. C., OVERTON, C. P., PROUT, K. & MARÍN, J. M. (1983). *J. Organomet. Chem.* **241**, C21–C23.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

LABINGER, J. A. (1982). *Comprehensive Organometallic Chemistry*, Vol. 3. Oxford: Pergamon Press.

MACLAIN, S. J., WOOD, C. D. & SCHROCK, R. R. (1979). *J. Am. Chem. Soc.* **101**, 4558–4570.

NORTH, A. C. T., PHILLIPS, D. S. & MATHEWS, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

PROUT, C. K. & DARAN, J. C. (1979). *Acta Cryst.* B**35**, 2882–2888.

WATKIN, D. J. & CARRUTHERS, J. R. (1981). *CRYSTALS User Guide*. Chemical Crystallography Laboratory, Univ. Oxford.

Acta Cryst. (1985). C**41**, 58–60

Bis[(*N*,*N*′-diethyldithiocarbamato)bis(diphenylphosphinito)platinato-*O*,*O*′]cobalt(II) Chloroform (1/2), $Co[(C_{12}H_{10}OP)_2Pt(C_5H_{10}NS_2)]_2.2CHCl_3$

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Abstract. $M_r = 1789{\cdot}11$, triclinic, $P\bar{1}$, $a = 11{\cdot}31$ (3), $b = 14{\cdot}085$ (4), $c = 24{\cdot}701$ (8) Å, $\alpha = 80{\cdot}20$ (3), $\beta = 76{\cdot}73$ (3), $\gamma = 66{\cdot}32$ (2)°, $V = 3493{\cdot}9$ Å^3, $Z = 2$, $D_x = 1{\cdot}70$, $D_m = 1{\cdot}65$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 49{\cdot}13$ cm^{-1}, $F(000) = 1754$, $T = 291$ K, $R = 0{\cdot}0914$ for 3979 unique observed reflections. The molecule has the Co atom at the centre with the Pt atoms and the associated ligands either side of it. The coordination about each Pt atom is square-planar, with Pt–S 2·38, Pt–P 2·25 Å, and tetrahedral about the Co atom, with Co–O 1·95–1·97 Å.

Introduction. The crystal-structure determination was undertaken as part of a wider study of the metal complexes of sulphur ligands. The reaction of $[Pt(S_2CNEt_2)(Ph_2PO)_2H]$ with some first-row transition-metal acetylacetonates, in this case cobalt, yielded the heterobimetallic complex whose structure is reported here. The structure analysis was undertaken to confirm the proposed tetrahedral coordination about the Co atom and the square-planar environment of the Pt atoms. To the best of our knowledge this structure is the first of its kind to be reported.

Experimental. The preparation of, and the spectral and magnetic data for the blue compound $Co[(OPPh_2)_2Pt(S_2CNEt_2)]_2$ have been previously reported (Allan, Milburn, Stephenson & Veitch, 1983). Recrystallization from $CHCl_3$ produced the compound $Co[(OPPh_2)_2Pt(S_2CNEt_2)]_2.2CHCl_3$ whose X-ray structure analysis is reported here. D_m measured by flotation in chloroform and 1,3-dibromopropan-2-ol. Crystals: dark-blue needles, dimensions 0·4 × 0·4 × 0·2 mm. They decomposed in air through loss of solvent and the

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Table 1. *Atomic coordinates (fractional* $\times 10^5$ *for* Pt, $\times 10^4$ *for remaining atoms) and thermal vibration parameters* (Å^2 $\times 10^3$) *with e.s.d.'s in parentheses*

Isotropic temperature factor = $\exp(-U\sin^2\theta/\lambda^2)$.

	x	y	z	U_{iso}
Pt(2)	12650 (10)	22352 (8)	8310 (4)	44 (01)*
Pt(1)	−6691 (10)	27656 (8)	41688 (4)	44 (07)*
Co(1)	773 (4)	2497 (3)	2497 (2)	49 (02)*
S(1)	−1669 (9)	4065 (6)	4814 (4)	83 (06)*
S(2)	−2210 (7)	2245 (6)	4834 (3)	58 (05)*
S(3)	2221 (9)	947 (5)	184 (4)	80 (06)*
S(4)	−135 (7)	2757 (6)	157 (3)	62 (05)*
O(2)	49 (16)	1579 (11)	3037 (7)	49 (4)
O(3)	−312 (18)	3409 (12)	1962 (8)	59 (5)
O(1)	1130 (17)	3243 (12)	3002 (7)	58 (5)
O(4)	2379 (18)	1744 (12)	1997 (8)	60 (5)
N(1)	−3355 (23)	3576 (19)	5666 (12)	85 (8)
C(2)	959 (29)	1703 (21)	−174 (13)	63 (8)
C(1)	−2541 (29)	3312 (20)	5157 (12)	61 (8)
N(2)	843 (24)	1464 (18)	−649 (11)	79 (8)
C(21)	1849 (38)	569 (27)	−956 (17)	129 (15)
C(22)	2678 (50)	964 (37)	−1457 (22)	168 (21)
C(23)	−183 (35)	2136 (27)	−987 (16)	107 (24)
C(24)	−1195 (52)	1604 (43)	−865 (28)	192 (24)
C(11)	−3647 (44)	4557 (25)	5934 (17)	127 (15)
C(12)	−2946 (56)	4157 (39)	6447 (22)	171 (21)
C(13)	−4038 (34)	2857 (25)	5976 (17)	118 (14)
C(14)	−5459 (32)	3409 (39)	5848 (26)	181 (23)
C(4)	−1310 (27)	609 (22)	2472 (13)	106 (12)
Cl(4)	−782 (11)	1088 (9)	1796 (5)	123 (9)*
Cl(5)	−457 (15)	−788 (9)	2546 (7)	163 (11)*
Cl(6)	−2995 (11)	893 (12)	2580 (6)	151 (10)*
C(3)	3222 (30)	5601 (18)	7464 (16)	90 (11)*
Cl(1)	4535 (12)	5860 (12)	7582 (5)	147 (10)*
Cl(2)	3682 (14)	4234 (10)	7529 (7)	166 (12)*
Cl(3)	2880 (10)	6066 (9)	6786 (5)	121 (8)*
P(1)	656 (7)	3489 (5)	3615 (3)	49 (4)*
P(2)	178 (7)	1383 (5)	3656 (3)	47 (4)*
C(51)	1906 (15)	639 (13)	3695 (8)	42 (6)
C(52)	2351 (15)	483 (13)	4197 (8)	81 (10)
C(53)	3684 (15)	−42 (13)	4216 (8)	97 (11)
C(54)	4572 (15)	−411 (13)	3732 (8)	112 (13)
C(55)	4127 (15)	−254 (13)	3230 (8)	125 (14)
C(56)	2794 (15)	270 (13)	3212 (8)	86 (10)
C(511)	−630 (16)	490 (11)	3929 (8)	37 (6)
C(512)	−1953 (16)	839 (11)	3891 (8)	63 (8)
C(513)	−2648 (16)	190 (11)	4096 (8)	76 (9)
C(514)	−2020 (16)	−808 (11)	4338 (8)	60 (8)
C(515)	−697 (16)	−1157 (11)	4376 (8)	68 (8)
C(516)	−2 (16)	−508 (11)	4171 (8)	67 (8)
C(61)	−94 (21)	4905 (12)	3595 (9)	67 (8)
C(62)	−764 (21)	5429 (12)	3157 (9)	93 (11)
C(63)	−1379 (21)	6512 (12)	3122 (9)	113 (13)
C(64)	−1322 (21)	7070 (12)	3525 (9)	122 (14)
C(65)	−651 (21)	6545 (12)	3962 (9)	95 (11)
C(66)	−37 (21)	5463 (12)	3998 (9)	86 (10)
C(611)	2099 (17)	3158 (15)	3905 (8)	62 (8)
C(612)	3303 (17)	2907 (15)	3541 (8)	82 (10)
C(613)	4456 (17)	2633 (15)	3748 (8)	107 (12)
C(614)	4405 (17)	2610 (15)	4319 (8)	96 (12)
C(615)	3202 (17)	2862 (15)	4684 (8)	82 (10)
C(616)	2049 (17)	3136 (15)	4475 (8)	63 (8)
P(3)	217 (6)	3620 (5)	1338 (3)	45 (4)*
P(4)	2778 (7)	1517 (6)	1388 (3)	50 (4)*
C(41)	3382 (21)	113 (11)	1392 (9)	66 (8)
C(42)	2775 (22)	−393 (11)	1832 (9)	87 (10)
C(43)	3180 (22)	−1474 (11)	1872 (9)	118 (14)
C(44)	4190 (22)	−2048 (11)	1473 (9)	110 (13)
C(45)	4797 (22)	−1542 (11)	1033 (9)	98 (11)
C(46)	4393 (22)	−461 (11)	993 (9)	94 (11)
C(411)	4175 (17)	1856 (15)	1106 (9)	66 (8)
C(412)	4788 (17)	2101 (15)	1461 (9)	81 (10)
C(413)	5881 (17)	2362 (15)	1244 (9)	104 (12)
C(414)	6362 (17)	2378 (15)	671 (9)	101 (12)
C(415)	5749 (17)	2132 (15)	315 (9)	101 (12)
C(416)	4656 (17)	1871 (15)	533 (9)	91 (11)
C(31)	−1225 (14)	4521 (12)	1074 (8)	56 (7)
C(32)	−1335 (14)	5510 (12)	821 (8)	56 (7)
C(33)	−2466 (14)	6157 (12)	610 (8)	108 (12)
C(34)	−3486 (14)	5816 (12)	652 (8)	70 (9)
C(35)	−3376 (14)	4828 (12)	905 (8)	64 (8)
C(36)	−2245 (14)	4180 (12)	1116 (8)	48 (7)
C(311)	1264 (18)	4349 (14)	1299 (10)	65 (8)
C(312)	2017 (18)	4523 (14)	788 (10)	87 (10)
C(313)	2842 (18)	5054 (14)	757 (10)	81 (10)
C(314)	2914 (18)	5412 (14)	1237 (10)	85 (10)
C(315)	2161 (18)	5239 (14)	1748 (10)	117 (13)
C(316)	1336 (18)	4707 (14)	1779 (10)	92 (11)

* Equivalent values U_{eq} of the anisotropic-temperature-factor coefficients. $U_{eq} = \frac{1}{3}$(trace of the orthogonalized U_{ij} tensor).

crystal used for data collection was mounted in a sealed capillary tube in the manner commonly used for proteins (Blundell & Johnson, 1976).

X-ray intensity data collected on a Nonius CAD-4 diffractometer, lattice parameters obtained from least-squares refinement of 14 reflections ($4 < \theta < 13°$). $(\sin\theta/\lambda)_{max} = 0{\cdot}481$ Å^{-1} ($2 \le \theta \le 20°$), range of h, k and l 0→10, −13→13 and −23→23. 7076 reflections including intensity controls measured, 5307 unique. Three standard reflections showed an intensity variation of 10817→8329, 14157→11908, 1417→959 with respective percentage decays of 23%, 16% and 32% over the 90 h exposure, giving an average decomposition of 24%. A linear correction for intensity fall-off based on the average of the decay of these three reflections was applied (North, Phillips & Mathews, 1968). $R_{int} = 0{\cdot}0135$, 1328 reflections with $I < 3\sigma(I)$ considered unobserved. Structure solved by Patterson and difference Fourier techniques. Least-squares refinement on $|F|$. H atoms not included in refinement. Following parameters refined: scale factor, x, y, z for all non-H atoms, isotropic temperature factors for all atoms except Pt, Co, Cl, P and S. Benzene rings refined as rigid groups and chloroform molecules restrained as were the C—N distances in the dithiocarbamate ligand. Final $R = 0{\cdot}0914$, $wR = 0{\cdot}1144$; w calculated from $1{\cdot}0000/[\sigma^2(F) + 0{\cdot}02743F^2].(\Delta/\sigma)_{max}$ in final cycle of refinement 0·0033. Max. and min. peak heights in final difference Fourier synthesis 4·2 and −4·5 e Å^{-3}, close to heavy-atom positions. We suggest this arises from the instability of the crystals. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Programs used: *SHELX*76 (Sheldrick, 1976) for crystallographic calculations, *PLUTO* (Motherwell, 1978) for the diagram and *FGEOM* (M. J. Barrow, unpublished) for calculations of torsion angles, mean planes and interatomic distances.

Discussion. The final atomic parameters are given in Table 1.*

* Lists of structure factors, anisotropic thermal parameters, intermolecular non-bonded distances, constrained data and results of a final refinement including an empirical absorption correction, together with diagrams giving all bond distances and angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39776 (59 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

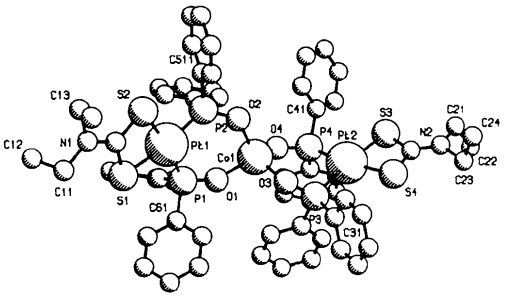

Fig. 1. General view of the molecule showing the coordination of the Pt and Co atoms. The $CHCl_3$ solvate molecules have been omitted for clarity.

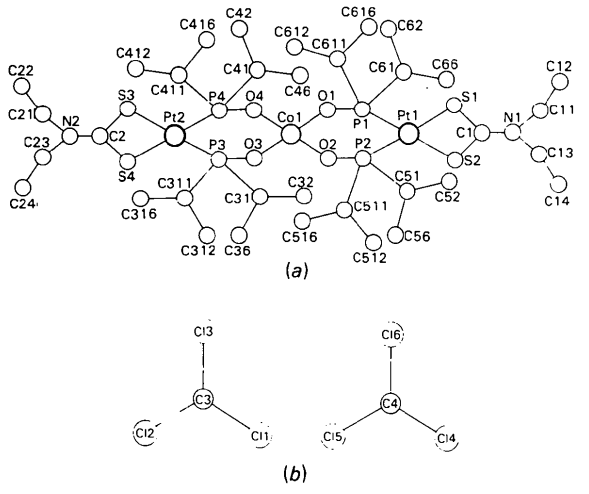

Fig. 2. Schematic diagram showing the numbering scheme of (*a*) the metal complex and (*b*) the solvate molecules. The three distal C atoms of the benzene rings have been omitted.

The computer-generated drawing (Fig. 1) of this crystal structure shows that each of the Pt atoms is coordinated to two S atoms (from the dithiocarbamate portion of the molecule) and the two P atoms (from the diphenylphosphinito groups) in a square-planar arrangement. The complete atomic-numbering scheme is shown in Fig. 2. The bond lengths and angles about the metal atoms are given in Table 2. The Pt—S bond distances and the S—Pt—S bond angles are similar to those reported for the compound $Pt(S_2CNEt_2)_2$ (Amanov, Kukina & Porai-Koshits, 1967).

The r.m.s. deviations from the planes Pt(1),S(1),S(2),P(1),P(2) and Pt(2),S(3),S(4),P(3),P(4) are 0·07 and 0·08 Å respectively. The angle between the normals to the two Pt atom planes is 92 (1)°, giving a Pt—Co—Pt angle of 165 (1)°. The Co atom, which lies significantly out of both of these planes, is coordinated to two O atoms of each of the diphenylphosphinito ligands. The atoms Pt(1), P(1), P(2), O(1), O(2) and Pt(2), P(3), P(4), O(3), O(4) are non-planar and form distorted boats. The tetrahedral environment of the Co atom and the square-planar environment of the Pt atoms are in agreement with the spectral and magnetic data previously recorded for this compound.

Attempts to improve the refinement of the structure by applying an additional absorption-correction technique of Walker & Stuart (1983) led to a 2% decrease in agreement index but no significant change in the overall geometry. This final cycle of refinement has been deposited for reference but is not considered suitable for publication.* The data in the paper relate to the final cycle of refinement referred to in the *Experimental.*

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Table 2. *Bond lengths* (Å) *and angles* (°) *about the* Pt *and* Co *atoms*

The standard deviations of all the bond lengths lie between 0·007 (Pt—P) and 0·083 Å (C—C) with an average value of 0·02 Å. The standard deviations of all the angles lie between 0·3 (S—Pt—S) and 3° (N—C—C) with an average value of 1·3°.

Pt(1)–S(1)	2·381 (9)	Pt(2)–S(3)	2·374 (9)
Pt(1)–S(2)	2·361 (8)	Pt(2)–S(4)	2·383 (9)
Pt(1)–P(1)	2·229 (8)	Pt(2)–P(3)	2·252 (7)
Pt(1)–P(2)	2·258 (8)	Pt(2)–P(4)	2·250 (8)
Co(1)–O(1)	1·960 (22)	Co(1)–O(3)	1·951 (18)
Co(1)–O(2)	1·970 (17)	Co(1)–O(4)	1·954 (16)
S(1)–Pt(1)–S(2)	74·0 (3)	S(3)–Pt(2)–S(4)	73·9 (3)
P(1)–Pt(1)–P(2)	91·0 (3)	P(3)–Pt(2)–P(4)	91·1 (3)
S(1)–Pt(1)–P(1)	96·7 (3)	S(4)–Pt(2)–P(3)	98·2 (3)
S(2)–Pt(1)–P(2)	98·2 (3)	S(3)–Pt(2)–P(4)	97·0 (3)
O(1)–Co(1)–O(2)	100·9 (8)	O(1)–Co(1)–O(4)	110·9 (9)
O(3)–Co(1)–O(4)	101·1 (7)	O(2)–Co(1)–O(3)	117·1 (8)

* See deposition footnote.

References

ALLAN, J. R., MILBURN, G. H. W., STEPHENSON, T. A. & VEITCH, P. M. (1983). *J. Chem. Res.* (*S*), pp. 2–5; (*M*), pp. 2009–2022.

AMANOV, A. Z., KUKINA, G. A. & PORAI-KOSHITS, M. A. (1967). *Zh. Strukt. Khim.* **8**(1), 174–175.

BLUNDELL, T. L. & JOHNSON, L. N. (1976). *Protein Crystallography*, p. 81. London: Academic Press.

International Tables for Crystallography (1974). Vol. IV, pp. 99–101. Birmingham: Kynoch Press.

MOTHERWELL, W. D. S. (1978). *PLUTO.* Program for plotting molecular and crystal structures. Univ. of Cambridge, England.

NORTH, A. C. T., PHILLIPS, D. C. & MATHEWS, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

SHELDRICK, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.

WALKER, N. & STUART, D. (1983). *Acta Cryst.* A**39**, 158–166.