Crystal and Molecular Structure of the Five-co-ordinate High-spin Complex {[2-{[2-(Diethylamino)ethyl]amino}ethyl]diphenylphosphine oxide} di-isothiocyanatocobalt(II)

By **C. A. Ghilardi** * and **A. Bianchi Orlandini**, Istituto di Chimica Generale dell'Università di Firenze, Laboratorio del C.N.R., 41 via Jacopo Nardi, 50132 Firenze (Italy)

The crystal and molecular structure of the title compound has been determined by *X*-ray diffraction techniques, from 1258 reflections collected by photographic methods. The complex crystallises in the monoclinic space group $P2_1/c$, with $a = 9{\cdot}518(1)$, $b = 16{\cdot}310(1)$, $c = 16{\cdot}532(1)$ Å, $\beta = 100{\cdot}59(1)^\circ$, $Z = 4$. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares procedures to R 9·5%.

The structure consists of distorted trigonal bipyramids, with two nitrogen and one oxygen atoms forming the equatorial plane and two nitrogen atoms at the apices.

DURING studies to clarify the relationship between the nature of the donor set and the spin state in five-co-ordinate Co^{II} and Ni^{II} complexes, we have prepared several series of such complexes with multidentate ' hybrid ' ligands containing in turn nitrogen, oxygen, phosphorus, arsenic, and sulphur as donor atoms.[1] The influence of the co-ordination geometry on the spin-state of the metal-complex has also been studied through a crystallographic investigation carried out on several complexes where the donor set has been systematically varied.

The crystal structure of the high-spin complex $Co(nno)(NCS)_2$, where (nno) is the terdentate ligand [2-{[2-(diethylamino)ethyl]amino}ethyl]diphenylphosphine oxide, $Et_2N{\cdot}[CH_2]_2{\cdot}NH{\cdot}[CH_2]_2{\cdot}P(\dot{:}O)Ph_2$ has therefore been determined. The presence of a phosphine oxide provides additional interest in the study of this compound, since few structures of such complexes have been reported.

EXPERIMENTAL

Crystal Data.—$C_{22}H_{29}CoN_4OPS_2$, $M = 519{\cdot}55$, Monoclinic, $a = 9{\cdot}518(1)$, $b = 16{\cdot}310(1)$, $c = 16{\cdot}532(1)$ Å, $\beta = 100{\cdot}59(1)^\circ$, $U = 2522{\cdot}8$ Å^3, D_m (by flotation) $= 1{\cdot}36$, $Z = 4$, $D_c = 1{\cdot}376$, $F(000) = 1084$. Fe-K_α radiation, $\lambda = 1{\cdot}9373$ Å; $\mu(\text{Fe-}K_\alpha) = 61{\cdot}8$ cm^{-1}. Space group, $P2_1/c$ from systematic absences: $0k0$ for $k = 2n + 1$ and $h0l$ for $l = 2n + 1$.

Data Collection.—Dark blue crystals with elongated prismatic shape were obtained.[2] The crystal used for *X*-ray analysis had dimensions 0·46 × 0·12 × 0·12 mm. Unit-cell parameters and their estimated standard deviations were determined by a least-squares fit of 18 2θ values ($+2\theta$, -2θ technique), measured on an automatic Hilger four-circle diffractometer. Double integrated Weissenberg photographs of the layers 0—5kl were taken on a Nonius integrating camera, by the multiple-film equi-inclination technique with manganese-filtered Fe-K_α radiation. The intensities of 1258 reflections were measured on a Nonius microdensitometer and the various levels roughly scaled by means of two Weissenberg photographs containing 30° samples from each level. The intensities were corrected for Lorentz and polarization effects. No correction was made for absorption or for anomalous dispersion. The atomic scattering factors for cobalt, sulphur, phosphorus, oxygen, nitrogen, and carbon were taken from ref. 3.

Structure Determination.—The structure was solved by the heavy-atom technique: the positions of the cobalt and

---

[1] L. Sacconi, *Pure Appl. Chem.*, 1971, **27**, 161, and references therein.

[2] R. Morassi and L. Sacconi, to be published.

[3] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

one sulphur atom were determined from a three-dimensional Patterson synthesis. A series of Fourier synthesis showed the positions of all non-hydrogen atoms. At this point R was 23%. Block-diagonal least-squares cycles with isotropic temperature factors reduced R to 17%. These calculations were performed on the IBM 1130.[4] Refinement was then continued using the full-matrix least-squares program of Busing and Levy adapted for the IBM 7090 by Stewart.[5] The function minimized was $\Sigma w(|F_o| - |F_c|)^2$. The F values were weighted according to Hughes scheme: $w = 1$ for reflections with $F_o \leqslant 15$ and $\sqrt{w} = 15/F_o$ for reflections with $F_o > 15$. Three cycles of isotropic refinement on all atoms led to R 13·9%. At this point cycles of isotropic refinement on carbon atoms and cycles of anisotropic refinement on heavy atoms were alternated to convergence. The final R was 9·5%. Hydrogen atoms were not introduced. Scale level factors were also refined in each cycle except during the anisotropic refinement. A difference-Fourier map calculated at this stage showed no particular features. Final values of the atomic parameters and their standard deviations are reported in Tables 1 and 2. Standard deviations were calculated according to the expression: $\sigma_j = [\Sigma w \Delta F^2 a^{jj}/(m - n)]^{1/2}$, where m is the number of reflections, n the number of the parameters refined, and a^{jj} the jj^{th} element of the inverse least-squares matrix. Standard deviations were corrected by the factor: $K = [(m - n_o)/(m - n_t)]^{1/2}$, where m is the number of the reflections, n_o the number of the refined parameters, and n_t the number of the total parameters. This correction was applied to take account of the fact that the refinement was carried out in two stages. However, standard deviations are probably underestimated because corrections for absorption and anomalous dispersion were not applied. Bond lengths and angles with their estimated standard deviations are given in Table 3. The final values of the

TABLE 1

Positional parameters ($\times 10^4$), isotropic thermal parameters, and estimated standard deviations

Atom	x/a	y/b	z/c	$B/\text{Å}^2$
Co	1086(2)	2662(1)	2957(1)	*
S(1)	2690(7)	5004(3)	4545(3)	*
S(2)	−1122(7)	4616(4)	1073(4)	*
P	3404(5)	1482(2)	2357(2)	*
O	2873(11)	2063(6)	2958(6)	*
N(1)	17(17)	1575(9)	2311(12)	*
N(2)	−622(18)	2460(8)	3594(8)	*
N(3)	2018(15)	3576(7)	3677(7)	*
N(4)	305(16)	3319(9)	1964(8)	*
C(1)	1960(21)	847(10)	1820(10)	5·8(4)
C(2)	553(27)	1263(15)	1629(15)	8·9(6)
C(3)	−1349(24)	1557(13)	2422(13)	7·6(5)
C(4)	−1593(24)	1822(13)	3245(13)	7·8(5)
C(5)	−1547(27)	3332(15)	3392(13)	8·9(6)
C(6)	−2715(34)	3422(19)	3840(19)	13·4(8)
C(7)	−186(29)	2473(16)	4515(17)	11·3(7)
C(8)	1240(27)	1910(13)	4721(13)	8·5(6)
C(9)	2302(18)	4167(9)	4037(9)	4·3(3)
C(10)	−285(22)	3894(11)	1575(11)	6·4(4)
C(11)	4706(18)	804(9)	2876(9)	4·3(3)
C(12)	5515(19)	285(9)	2477(9)	4·5(3)
C(13)	6576(22)	−213(10)	2913(11)	5·9(4)
C(14)	6826(23)	−177(12)	3763(13)	7·1(5)
C(15)	6027(20)	302(10)	4180(10)	5·2(4)
C(16)	4973(19)	826(9)	3759(10)	4·8(4)
C(17)	4271(18)	2032(8)	1655(9)	4·1(3)
C(18)	4408(21)	1669(11)	908(11)	6·2(4)
C(19)	5180(29)	2120(17)	382(17)	10·0(7)
C(20)	5876(24)	2873(12)	651(12)	7·1(5)
C(21)	5635(23)	3195(11)	1388(12)	6·8(5)
C(22)	4847(19)	2793(10)	1895(10)	4·9(4)

* Anisotropic parameters in Table 2.

TABLE 2

Anisotropic thermal parameters ($\times 10$ Å^2) with their estimated standard deviations

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Co	50(2)	43(1)	51(1)	−3(1)	7(1)	−5(1)
S(1)	134(5)	41(2)	58(2)	−7(2)	−22(2)	−11(2)
S(2)	78(5)	100(4)	99(4)	−3(3)	−15(3)	47(3)
P	33(3)	42(2)	41(2)	2(2)	1(2)	−12(1)
O	49(8)	54(6)	52(6)	6(5)	8(4)	−23(4)
N(1)	46(12)	83(9)	145(14)	−5(8)	33(9)	−79(10)
N(2)	84(12)	79(9)	39(7)	−48(8)	10(6)	−4(6)
N(3)	57(10)	45(7)	48(7)	−4(6)	6(6)	−6(4)
N(4)	66(11)	76(9)	53(8)	−1(7)	10(6)	4(7)

The temperature factor is defined as:

$$\exp(-\tfrac{1}{4}\sum_{i=1}\sum_{j=1} B_{ij}h_ih_ja_i^*a_j^*).$$

TABLE 3

Bond lengths (Å) and angles (°) with estimated standard deviations in parentheses

(*a*) Bond lengths

Co–O	1·96(1)	N(1)–C(2)	1·41(3)
Co–N(1)	2·22(2)	N(1)–C(3)	1·35(3)
Co–N(2)	2·12(2)	N(2)–C(4)	1·44(3)
Co–N(3)	2·01(1)	N(2)–C(5)	1·67(3)
Co–N(4)	1·99(1)	N(2)–C(7)	1·50(3)
S(1)–C(9)	1·61(2)	N(3)–C(9)	1·14(2)
S(2)–C(10)	1·57(2)	N(4)–C(10)	1·21(2)
P–O	1·52(1)	C(1)–C(2)	1·48(3)
P–C(1)	1·82(2)	C(3)–C(4)	1·49(3)
P–C(11)	1·76(2)	C(5)–C(6)	1·45(4)
P–C(17)	1·78(2)	C(7)–C(8)	1·62(4)

(*b*) Bond angles

O–Co–N(1)	85·6(0·5)	Co–N(2)–C(4)	114·0(1·2)
O–Co–N(2)	131·8(0·5)	Co–N(2)–C(5)	101·1(1·0)
O–Co–N(3)	94·6(0·5)	Co–N(2)–C(7)	114·0(1·4)
O–Co–N(4)	117·5(0·5)	C(4)–N(2)–C(5)	105·0(1·5)
N(1)–Co–N(2)	77·8(0·6)	C(4)–N(2)–C(7)	117·0(1·6)
N(1)–Co–N(3)	172·6(0·6)	C(5)–N(2)–C(7)	103·1(1·5)
N(1)–Co–N(4)	88·0(0·6)	Co–N(3)–C(9)	166·9(1·3)
N(2)–Co–N(3)	96·7(0·5)	Co–N(4)–C(10)	156·9(1·4)
N(2)–Co–N(4)	106·8(0·6)	P–C(1)–C(2)	114·5(1·4)
N(3)–Co–N(4)	98·4(0·5)	N(1)–C(2)–C(1)	116·0(1·9)
O–P–C(1)	111·2(0·7)	N(1)–C(3)–C(4)	115·8(1·9)
O–P–C(11)	111·1(0·7)	N(2)–C(4)–C(3)	112·4(1·8)
O–P–C(17)	111·1(0·6)	N(2)–C(5)–C(6)	114·1(1·9)
C(1)–P–C(11)	106·3(0·8)	N(2)–C(7)–C(8)	105·6(1·8)
C(1)–P–C(17)	111·6(0·7)	S(1)–C(9)–N(3)	179·6(1·5)
C(11)–P–C(17)	105·4(0·8)	S(2)–C(10)–N(4)	177·2(1·8)
Co–O–P	134·4(0·7)	P–C(11)–C(12)	123·5(1·2)
Co–N(1)–C(2)	118·1(1·3)	P–C(11)–C(16)	117·2(1·2)
Co–N(1)–C(3)	108·7(1·3)	P–C(17)–C(18)	119·4(1·2)
C(2)–N(1)–C(3)	126·8(1·9)	P–C(17)–C(22)	118·0(1·2)

(*c*) Phenyl rings

	Mean value	Mean devn.	Max. devn.
(i) Bond lengths			
Ring (A)	1·39	0·02	0·03
Ring (B)	1·40	0·03	0·03
(ii) Bond angles			
Ring (A)	120·0	1·6	1·9
Ring (B)	119·9	1·8	2·1

---

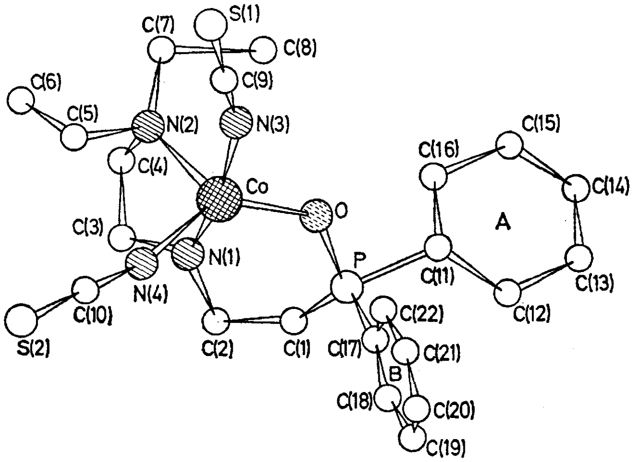
[4] Series of programmes from the A.R.C. Unit of Structural Chemistry, University College, London, for the IBM 1130 Computer.

[5] '*X*-Ray '63' System of Programs, J. M. Stewart, Technical Report TR 64 6, University of Maryland, Computer Science Center, 1964.

observed and calculated structure factors are listed in Supplementary Publication No. SUP 20421 (2 pp., 1 microfiche).*

DISCUSSION

The structure consists of discrete molecules of Co(nno)$(NCS)_2$ in which the cobalt atom exhibits a distorted trigonal bipyramidal co-ordination, with an axial angle of 172·6°. The cobalt atom is five-co-ordinated by four nitrogen atoms and one oxygen atom. The two nitrogen atoms from the isothiocyanate groups occupy an axial and an equatorial position; the oxygen atom co-ordinates in the equatorial plane, the remaining two positions being occupied by the two nitrogen atoms of the ligand. The Figure shows a perspective view of the molecule and the atom numbering system used.



A perspective view of the configuration of the complex Co(nno)$(NCS)_2$

The cobalt atom is 0·23 Å out of the equatorial plane toward the NCS ligand. The equation of the plane through atoms N(4), O, and N(2) in monoclinic co-ordinates is: $2{\cdot}919x + 12{\cdot}493y + 8{\cdot}249z = 5{\cdot}856$. It follows that the N(3)–Co–L(eq) angles are larger than the theoretical value of 90°. Furthermore the Co–N(1) axial bond is 0·1 Å longer than the Co–N(2) equatorial bond. This type of distortion, although not very enhanced, recalls the trend, previously noticed [6] in some high-spin trigonal bipyramidal Co^{II} complexes, toward tetrahedral geometry.

The factors, which are generally supposed to be responsible for distortions in the co-ordination geometry, leave unexplained the difference between the mean value of the N(1)–Co–L(eq) angles (83·8°) and the mean of the N(3)–Co–L(eq) angles (96·6°): *i.e.* (*a*) the stereochemical activity of the *d* electrons for a d^7 high spin system in C_{3v} symmetry is small, owing to the single occupancy of d_{xy}, $d_{x^2-y^2}$, and d_{z^2} orbitals; (*b*) ligand–ligand repulsion should be more effective on the N(1) than N(3) atom [N(3) forms with all the equatorial ligands angles larger than 90°], but only the elongation of the axial Co–N(1) bond may be regarded as a result of this effect; and (*c*) steric constraints play an important role in complexes with multidentate ligands. In the present case this factor has little effect, because the ligand forms both five- and six-membered rings. Five-membered chelate rings form ' bite ' angles smaller than and six-membered chelate rings angles larger than 90°.[7,8]

Another feature of this co-ordination is that one of the equatorial angles is considerably larger than the others [O–Co–N(2) 131·8, O–Co–N(4) 117·5, and N(2)–Co–N(4) 106·8]. This distortion probably cannot be attributed to packing effects: no relevant inter- or intra-molecular contacts have been found. A similar value of 129·8° has been reported for the high-spin complex $Co(C_6H_7NO)_5(ClO_4)_2$.[9] The Co–O distance value [1·96(1) Å] is in good agreement with the mean value [1·975(8) Å] for equatorial bonds, which has been found in the $Co(C_6H_7NO)(ClO_4)_2$ complex.[9] Bond distances and angles in the two isothiocyanate groups are slightly different, but still in the range of those reported.[10-13] The values [1·99(1) and 2·01(1) Å] for the Co–N distances involving the isothiocyanate groups are not significantly different from those [1·97(1) and 1·99(1) Å] found in the complex Co(ns)$(NCS)_2$,[10] † which has a very similar co-ordination geometry. The values of the Co–N bond distance [2·22(2) and 2·12(2) Å] are also comparable with those [2·24(1) and 2·15(1) Å] found for apical and equatorial Co–N bonds in the Co(ns)$(NCS)_2$ complex,[10] where the two nitrogen atoms are in the same sp^3 hybridization. The P–O bond length of 1·52(1) Å is slightly longer than that found in free triphenylphosphine oxide [1·46(1) Å] [14] and may be indicative of a lower bond-order. Values of 1·51(2) and 1·50 Å for co-ordinated phosphine oxide have been reported.[15,16] Some poor values of bond distances in the ligand, especially for the ethyl chains, and the high thermal parameters for the carbon atoms may be indicative of disorder.

We thank Professor L. Sacconi for suggestions and continuous interest and D. Masi for technical assistance.

[1/2484 *Received, 29th December*, 1971]

---

* See note about Supplementary Publications in Notice to Authors, No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp are supplied as full size copies.

† The ligand ns is *NN*-bis-[2-(diethylamino)ethyl]-2-(methylthio)ethylamine, $(Et_2N{\cdot}[CH_2]_2)_2N([CH_2]_2{\cdot}SMe)$.

[6] L. Sacconi, M. Di Vaira, and A. Bianchi, *J. Amer. Chem. Soc.*, 1970, **92**, 4465; P. Dapporto, G. Fallani, and L. Sacconi, *J. Co-ordination Chem.*, 1971, **1**, 269.

[7] L. P. Haugen and R. Eisenberg, *Inorg. Chem.*, 1969, **8**, 1072.

[8] S. Biagini and M. Cannas, *J. Chem. Soc.* (*A*), 1970, 2398.

[9] Bernard A. Coyle and James A. Ibers, *Inorg. Chem.*, 1970, **9**, 767.

[10] P. Dapporto and M. Di Vaira, *J. Chem. Soc.* (*A*), 1971, 1891.

[11] Prem C. Jain and E. C. Lingafelter, *J. Amer. Chem. Soc.*, 1967, **89**, 6131.

[12] A. Ferrari, A. Braibanti, G. Bigliardi, and A. M. Lanfredi, *Acta Cryst.*, 1965, **18**, 367.

[13] M. Di Vaira, *J. Chem. Soc.* (*A*), 1971, 148.

[14] G. Bandoli, G. Bartolozzo, D. A. Clemente, U. Croatto, and C. Panattoni, *J. Chem. Soc.* (*A*), 1970, 2778.

[15] J. A. Bertrand, *Inorg. Chem.*, 1967, **6**, 495.

[16] M. Mathew and Gus J. Palenik, *Canad. J. Chem.*, 1969, **47** 1094.