Complexes with Sulphur and Selenium Donor Ligands. Part 7.[1] The Crystal and Molecular Structure of Bis(diphenylphosphinodithioato)-cobalt(II)–Quinoline (1/1)

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The title complex has been characterised and its crystal and molecular structure solved by diffractometric methods. Turquoise crystals of formula $[Co(S_2PPh_2)_2]\cdot C_9H_7N$ obtained from chloroform solution are orthorhombic, space group *Fdd*2, with unit-cell dimensions $a = 23.528(2)$, $b = 28.690(2)$, $c = 9.571(1)$ Å, and $Z = 8$. The structure has been refined by least-squares methods using 964 independent reflections, to a conventional R of 0.065. The structure is monomeric and the co-ordination about the cobalt is slightly distorted trigonal bipyramidal, the quinoline molecule lying in the equatorial plane. The axial and equatorial Co–S distances are very different, $(Co-S_{ax.}) - (Co-S_{eq.}) = 0.30$ Å (3σ 0.018 Å). This difference is reflected in the shorter $P-S_{ax.}$ distance, which although just statistically significant (0.04 Å shorter than $P-S_{eq.}$, 3σ 0.018 Å), leads to an observable difference in the $\nu_{asym}(PS)$ band in the i.r. spectrum of the quinoline adduct and the parent $[Co(S_2PPh_2)_2]$. The electronic spectra and magnetism of the complex are briefly discussed.

PHOSPHORODITHIOATE and phosphinodithioate complexes of transition-metal ions are of continuing interest [2] since the initial work of Kuchen and Hertel [3] and Jørgensen.[4] The formation of adducts by nickel(II) complexes, such as $[Ni\{S_2P(OEt)_2\}_2]$, has been a popular topic. The above complex forms 1 : 1 adducts with unidentate bases [5] and with PPh_3,[6] both types of complex being square-pyramidal and high spin, despite the presence of an $[NiS_4P]$ chromophore in the latter.[7] More stable six-co-ordinate complexes of chromophore $[NiS_4N_2]$ are very common, and crystal structures of both *cis* and *trans* octahedral stereochemistries have been reported.[8, 9]

Much less is known of the cobalt(II) analogues. Kuchen first reported a $[CoS_4N_2]$ chromophore, in $[Co(S_2PPh_2)_2]\cdot 2py$,[3] and similar complexes were later reinvestigated.[10] It was found that pyridine, 4-methylpyridine, and isoquinoline gave 1 : 2 adducts, whilst 2- and 3-methylpyridine, 2-aminopyridine, and quinoline formed only 1 : 1 adducts. The structures were assigned on the basis of only fragmentary data.

Given the lack of structural information available for these complexes, we have carried out a crystal-structure analysis of the complex $[Co(S_2PPh_2)_2]\cdot$quinoline.

EXPERIMENTAL

The complex was prepared by the reaction between cobalt(II) chloride, $Na[S_2PPh_2]$ (prepared by the reaction between PPh_2Cl and elemental sulphur, followed by reaction of the product with Na[HS] [11]), and quinoline (excess) in water. The turquoise precipitate obtained was crystallised by slow evaporation of a chloroform solution containing a few drops of quinoline. Crystallisation from neat quinoline gave the same product (Found: C, 56.2; H, 3.7; N, 2.2; S, 8.7. Calc. for $C_{33}H_{27}CoNP_2S_4$: C, 57.75; H, 3.95; N, 2.05; S, 9.0%).

Crystal Data.—$[Co(S_2PPh_2)_2]\cdot C_9H_7N$, $M = 686.5$, Orthorhombic, $a = 23.528(2)$, $b = 28.690(2)$, $c = 9.571(1)$ Å, $U = 6\,460.6$ Å^3, $D_m = 1.42$, $Z = 8$, $D_c = 1.41$ g cm^{-3}, $F(000) = 2\,824$, Mo-K_α radiation, $\lambda = 0.710\,7$ Å, μ(Mo-K_α) = 9.21 cm^{-1}, space group *Fdd*2 (from systematic absences).

Preliminary crystal data were determined from rotation and Weissenberg photographs and the quoted cell dimensions were obtained by least-squares refinement of the 2θ values of 20 reflections ($2\theta > 22°$) accurately measured on a Siemens A.E.D. single-crystal diffractometer.

Intensity-data Collection.—Three-dimensional intensity data were taken from a prismatic crystal of dimensions 0.13 × 0.16 × 0.34 mm, aligned with its [100] axis along the axis of the Siemens diffractometer. All the reflections with $5 < 2\theta < 58°$ were measured using the moving counter–moving crystal scan technique with a drive speed related to the number of counts on the peak (lowest speed, 2.5° min^{-1}). A standard reflection monitored every 20 reflections was used to check for any decomposition or change in the alignment of the crystal; no significant change in the measured intensity of this reflection was observed during data collection. The ' five-point ' method was used for measuring intensities and background. Of 2 230 independent reflections, 964 having $I > 2\sigma(I)$ were considered observed and were used in the analysis. Lorentz and polarisation corrections were applied and structure amplitudes derived. Absorption corrections were not applied in view of the low absorption of the sample ($\mu\bar{r} \simeq 0.1$).

Reflectance spectra were recorded against MgO as reference on a Beckman DK2A spectrophotometer and

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[1] Part 6; E. Borghi, V. Di Castro, F. Monacelli, and A. A. G. Tomlinson, *J.C.S. Dalton*, preceding paper.

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[5] C. Furlani, *Co-ordination Chem. Rev.*, 1968, **3**, 141.

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solution spectra on a Cary 14 instrument. Infrared spectra were obtained on Perkin-Elmer 621 and 180 instruments as Nujol mulls. Magnetic susceptibility measurements at intermediate temperatures (liquid N_2) were carried out on a Gouy balance; Co[Hg(SCN)$_4$] was used as a calibrant.

Structure Determination and Refinement.—The structure was solved by the heavy-atom technique, the cobalt atom being assumed to lie on a two-fold axis, as indicated by the number of molecules in the unit cell ($Z = 8$). The Fourier map confirmed this assumption and revealed all the atoms of the phosphinodithioate group and the presence of a quinoline molecule. The latter is distributed in a disordered fashion over two positions related by the two-fold axis.

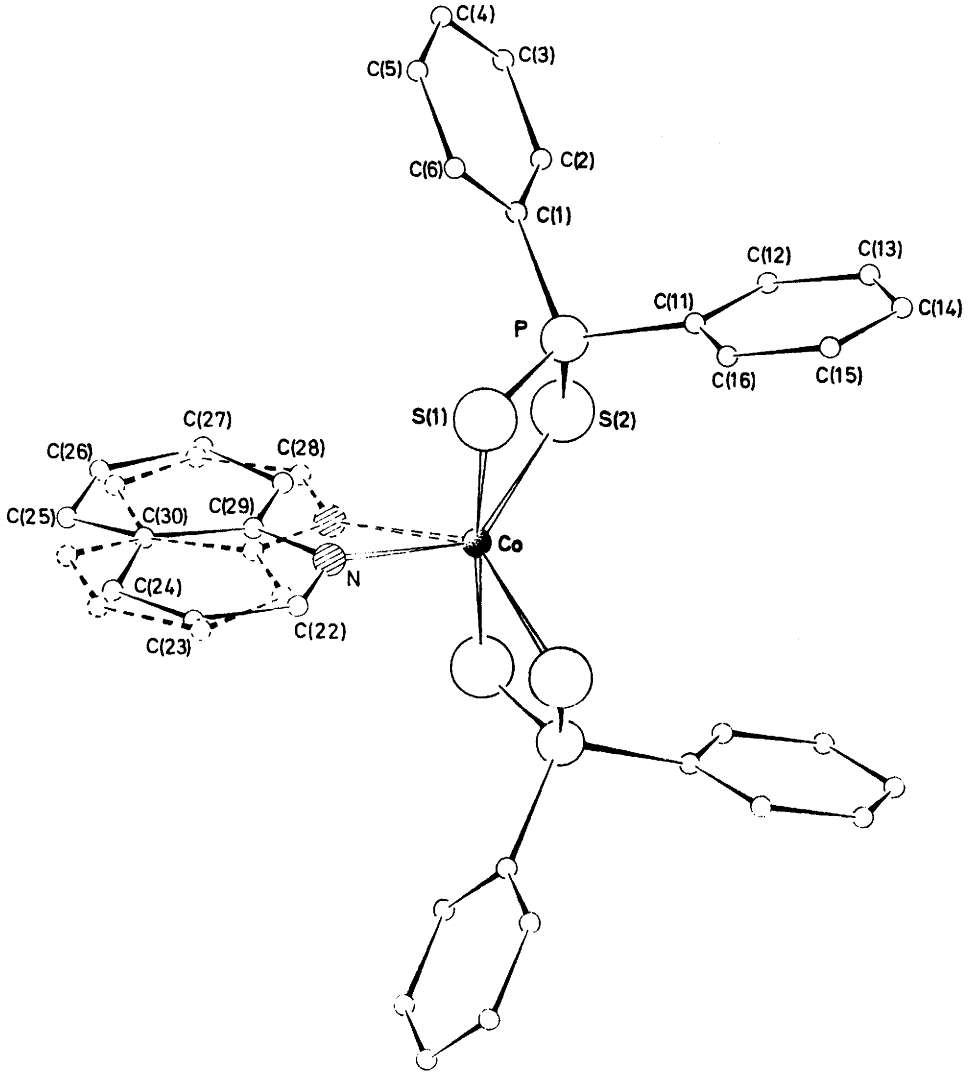

FIGURE 1 Clinographic [100] projection of the molecule

Refinement was by full-matrix least-squares applying a bond-length constraint to the pairs of atoms C(22)–C(23), C(23)–C(24), C(25)–C(26), and C(26)–C(27) of the quinoline and a 'rigid-body' constraint to the phenyl rings. The Co, S, and P atoms were refined anisotropically. The function minimised in the least-squares calculation was $\Sigma w(\Delta F)^2$ with unit weights. The final R was 0.065. No attempt was made to locate the hydrogen atoms.

The atomic scattering factors used were those of Cromer and Mann [12] for S, P, N, and C, and those in ref. 13 for Co. All the calculations were performed on the CYBER 7600 computer of the Centro di Calcolo Interuniversitario dell'Italia Nord-Orientale, Bologna, Italy, using the SHELX system of computer programs.[14] Table 1 lists the final atomic co-ordinates. Observed and calculated structure factors and thermal parameters are listed in Supplementary Publication SUP No. 22224 (11 pp.).* Bond distances and angles are shown in Table 2.

RESULTS AND DISCUSSION

Description of the Structure.—Figure 1 shows a clinographic [100] projection of the molecule; the quinoline

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

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[13] 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1969, vol. 4, p. 99.

[14] G. Sheldrick, SHELX System of Computer Programs, Cambridge, 1975.

molecule related by the two-fold axis is indicated by broken lines.

TABLE 1

Final positional parameters (× 10^4) with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c
Co	0	0	0
S(1)	874(2)	569(1)	−64(6)
S(2)	−441(2)	610(1)	−1 164(5)
P	320(2)	937(1)	−1 166(5)
C(1)	224(5)	1 518(3)	−484(12)
C(2)	−265(5)	1 771(3)	−809(12)
C(3)	−337(5)	2 220(3)	−283(12)
C(4)	80(5)	2 417(3)	570(12)
C(5)	569(5)	2 164(3)	896(12)
C(6)	641(5)	1 715(3)	369(12)
C(11)	556(5)	1 019(4)	−2 958(9)
C(12)	182(5)	1 212(4)	−3 929(9)
C(13)	345(5)	1 256(4)	−5 324(9)
C(14)	882(5)	1 107(4)	−5 748(9)
C(15)	1 257(5)	914(4)	−4 777(9)
C(16)	1 094(5)	870(4)	−3 382(9)
N	205(8)	−92(7)	2 027(24)
C(22)	695(25)	−303(20)	2 444(38)
C(23)	821(14)	−374(12)	3 854(31)
C(24)	487(12)	−242(10)	4 965(34)
C(25)	−416(12)	94(12)	5 620(39)
C(26)	−903(11)	318(10)	5 163(30)
C(27)	−1 039(15)	420(12)	3 771(31)
C(28)	−650(25)	265(20)	2 670(50)
C(29)	−151(12)	52(12)	3 056(30)
C(30)	0	0	4 542(24)
N′ *	−205(8)	92(7)	2 027(24)
$N_{av.}$ *	0(8)	0(7)	2 027(24)

* N′ is symmetry-related to N by the two-fold axis; $N_{av.}$ represents the intermediate between N and N′.

Unlike the structures reported for $[Ni(S_2PPh_2)_2]\cdot C_9H_7N$ and $[Ni\{S_2P(OMe)_2\}_2]\cdot 2,9Me_2$-phen (phen = 1,10-phenanthroline), the first of which is close to square pyramidal (s.p.) and the second so distorted that it may be considered as intermediate between s.p. and trigonal bipyramidal (t.b.p.),[8] $[Co(S_2PPh_2)_2]\cdot C_9H_7N$ appears to have a stereochemistry close to a t.b.p. Thus, the N, S(2), S(2′), and Co atoms lie strictly in a plane and the in-plane angles are S(2)–Co–N(intermediate) = 119° and S(2)–Co–S(2′) = 122°. In addition, S(1)–Co–S(1′) = 177.3°, not too distant from the expected angle of 180°. This description is further supported by the difference in axial and equatorial Co–S distances. So far as we are aware, this difference, $(Co\text{–}S_{ax.}) - (Co\text{–}S_{eq.}) = 0.30$ Å, is the largest yet found for a high-spin cobalt(II) complex, although comparisons can be made only with *O*- or *N*-bonding ligands;[15] few d^7 t.b.p. complexes with *S*-bonding ligands have been reported.[1] The sum of the Pauling radii for octahedral Co^{II} and S is 2.36 Å,[16] which underlines the weak character of the $Co\text{–}S_{ax.}$ bond. Indeed, when lengthening of a M–L bond of similar magnitude has been observed in complexes of the type [Co(tripod ligand)X]Y, the co-ordination geometry

TABLE 2

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

Co–S(1)	2.626(5)	P–C(1)	1.80(1)
C–S(2)	2.320(5)	P–C(11)	1.82(1)
Co–N	2.026(23)	N–C(22)	1.36(6)
P–S(1)	1.981(6)	N–C(29)	1.36(4)
P–S(2)	2.021(6)		
	Mean C–C(phenyl)	1.40 ± 0.02	
	Mean C–C(quin)	1.41 ± 0.06	
S(1)–Co–S(2)	82.5(2)	Co–S(2)–P	87.4(2)
S(1)–Co–S(1′)	177.3(2)	S(1)–P–S(2)	109.6(2)
S(2)–Co–S(2′)	122.6(2)	S(1)–P–C(1)	112.5(5)
S(1)–Co–N	85.2(6)	S(1)–P–C(11)	111.7(5)
S(2)–Co–N	131.9(6)	S(2)–P–C(1)	108.5(4)
S(2′)–Co–N	104.9(6)	S(2)–P–C(11)	109.4(5)
Co–S(1)–P	80.1(2)	C(1)–P–C(11)	105.1(5)
	Mean C–C–C(phenyl)	120 ± 1	
	Mean C–C–C(quin)	120 ± 3	

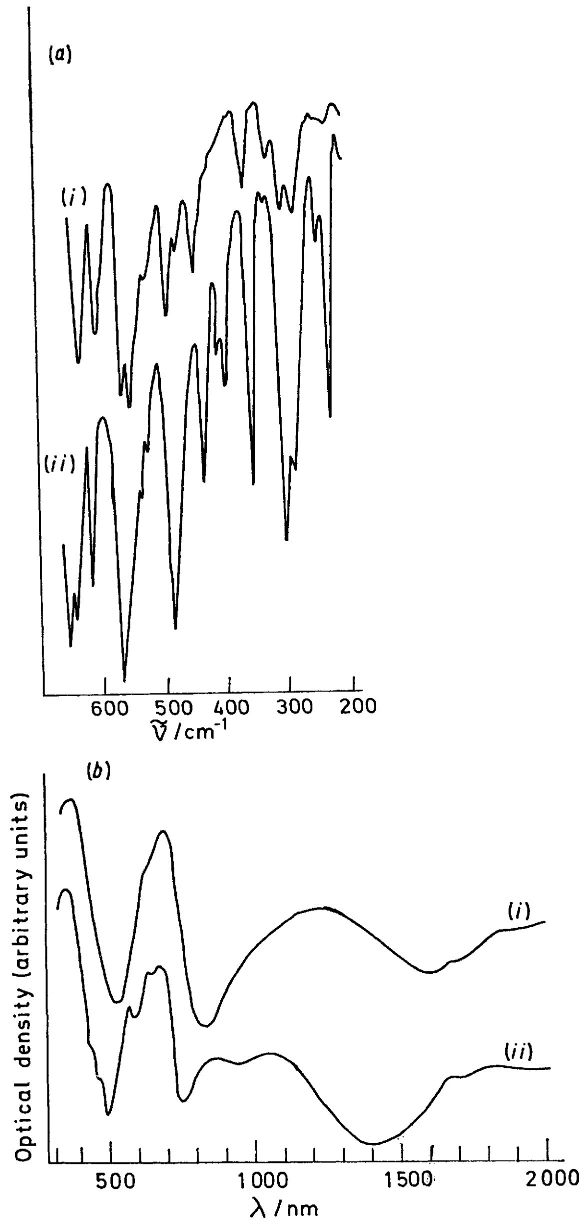

FIGURE 2 Infrared (*a*) and electronic spectra (reflectance) (*b*) of (*i*) $[Co(S_2PPh_2)_2]$ and (*ii*) $[Co(S_2PPh_2)_2]\cdot C_9H_7N$

[15] B. A. Coyle and J. A. Ibers, *Inorg. Chem.*, 1970, **9**, 767.

[16] L. Pauling, 'The Nature of the Chemical Bond,' Cornell University Press, 2nd edn., 1964, pp. 164 and 182.

has been regarded as intermediate between t.b.p. and four-co-ordinate tetrahedral.[17] Presumably, $[Co(S_2PPh_2)_2]\cdot C_9H_7N$ may also be considered as having an intermediate geometry between t.b.p and trigonal planar. Whether this is a good description or not, it is usually assumed that the *d* electrons in high-spin d^7 t.b.p. complexes are likely to have little stereochemical effect since they are distributed uniformly in the σ anti-bonding orbitals $d_{x^2-y^2}$, d_{xy}, and d_{z^2}. The major stereochemical effect, *i.e.* elongation, is therefore presumably caused by ligand repulsion (which is higher for axial than for equatorial ligands).[18]

The Co–S axial lengthening is reflected in the shorter S(1)–P distance [0.04 Å shorter than S(2)–P, 3σ 0.018 Å] which may be compared with the S=P distance in the ' dangling ' $[S_2P(OMe)_2]^-$ in $[Ni\{S_2P(OMe)_2\}_2]\cdot 2,9Me_2$-phen of 1.94(1) Å, and with the difference in S–P bond lengths for the bidentate phosphorodithioate ligand [S–P 1.97(1), S=P 1.91(1) Å] in the same structure.[8] {The S–P distance present in the ' dangling ' $[S_2PPh_2]^-$ in $[Pd(S_2PPh_2)_2]\cdot PPh_3$, 2.13 Å, seems too inaccurate to allow comparisons to be made.[19]} Although the above structures are of only relatively low accuracy, it does appear that, when the ligand is unidentate with a ' dangling ' sulphur atom, in phosphoro- and phosphinodithioates there is a greater delocalisation of charge over the S_2P group than when the group is bidentate but with widely differing M–S bonds.

The structure contains no intermolecular contacts shorter than 3.5 Å.

Spectra and Magnetism.—The just statistically significant difference in S–P distances in the adduct would be expected to lead to some differences in the i.r. spectra of $[Co(S_2PPh_2)_2]$ and its quinoline adduct in the 400—650 cm^{-1} region, where all the vibrations involving the S_2P group are believed to appear.[20] Müller *et al.*[20] assigned bands at 619—648 cm^{-1} to ν_{asym}(PS) and at 523—566 cm^{-1} to ν_{sym}(PS) for many complexes in which the phosphinodithioate ligand is bidentate. Although there is a distinct splitting in ν_{asym}(PS) in the adduct, the ν_{sym}(PS) band at 564 cm^{-1} in the adduct is single whereas in $[Co(S_2PPh_2)_2]$ itself it is split. Band splittings do not therefore seem useful for diagnostic purposes. However, support for the asymmetric nature of the S_2P group comes from the position of the ν_{asym}(PS) band, which lies at 640 cm^{-1} (average) in the quinoline adduct and at 632 cm^{-1} in the parent $[Co(S_2PPh_2)_2]$. These values give $\frac{1}{2}(\nu_{asym}+\nu_{sym})$ values of 594 cm^{-1} for $[Co(S_2PPh_2)_2]$ and 601 cm^{-1} for the quinoline adduct; Müller *et al.* used this parameter as a measure of the symmetrical character of the S_2P group, the value for the quinoline adduct being close to that for $Na[S_2PPh_2]$.[20]

In the quinoline adduct there is a split band centred at 400 cm^{-1} (394, 401) which is not present in the parent complex. We assign this to the asym and sym Co–N stretching modes. The Co–S region is more complicated than expected; $[Co(S_2PPh_2)_2]$ has three bands at 282, 300, and 310 cm^{-1}. Co–S stretching vibrations in tetrahedral cobalt(II) complexes have been assigned at *ca.* 300 cm^{-1}.[21] In the quinoline adduct, two bands are still present at 282 and 300 cm^{-1} and these are assigned to Co–S stretches. In the adduct, a strong band also appears at 226 cm^{-1} (see Figure 2). It is tempting to assign this to a Co–S stretching vibration of the ' long ' Co–S bond, although it may also be due to a Co–N deformation mode.

The electronic spectrum of the quinoline adduct shows significant differences from that of $[Co(S_2PPh_2)_2]$ only below *ca.* 13 000 cm^{-1}. A two-component band, presumably due to transitions to the t.b.p. energy level $b^4E(F)$,[22] split by the C_{2v} field, lies at 13 200 and 10 600 cm^{-1}. Given that a C_{2v} perturbation of the energy level $^4B_1$ derived from a C_{4v} stereochemistry (which lies in the same energy range) does not split on lowering the symmetry,[7] the presence of the component at 13 200 cm^{-1} is yet further evidence that such a band is characteristic of t.b.p. geometry (or close to it).[23] On the other hand, bands further to the visible are not useful for diagnostic purposes, since they derive from splitting of the $^4E(F)$ and $^4E(P)$ transitions in D_{3h} symmetry.[22] This will lead to four (or less, because of overlap) closely spaced components, as observed (Figure 2). Similar splittings would be given in this region by a structure derived from C_{4v} symmetry. Ignoring the near-i.r. region will then give an incorrect assignment of stereochemistry, which has indeed occurred for adducts of $[Co(S_2PPh_2)_2]$;[10] square-based pyramidal structures were proposed. The same point should be kept in mind when using electronic spectra of high-spin Co^{II} as a ' structure-function ' marker in metalloproteins.[24]

Despite the distortion present, the magnetic moment is, if anything, on the high side of the usual values for non-octahedral high-spin Co^{II}:[17] $\mu = 4.69 \pm 0.03$ B.M.* The Curie–Weiss law is followed and the complex is magnetically dilute, $\theta = -15 \pm 1$ K.

Since attack of a unidentate base on a tetrahedral phosphinodithioatometal complex gives a stereochemistry different than attack on a square-planar complex, the stereochemistries of other adducts with bidentate bases would be of interest.

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* Throughout this paper: 1 B.M. ≈ 9.27×10^{-24} A m^2.

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