Synthesis, stereochemistry and crystal structures of cobalt(III) complexes containing 5,8-diphenyl-2,11-dithia-5,8-diphosphadodecane or 5,9-diphenyl-2,12-dithia-5,9-diphosphatridecane

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Twelve new cobalt(III) complexes containing a tetradentate phosphine ligand of the type $MeS(CH_2)_2PPh(CH_2)_nPPh(CH_2)_2SMe$ (n = 2 L^1 or 3 L^2) were prepared. Their structures were assigned on the basis of electronic absorption and ^1H NMR spectra and the molecular structures of *cis*-α-[$CoCl_2${*rac*(P)-L^1}]BF_4 and *trans*-[$CoCl_2${*meso*(P)-L^2}]BF_4 were determined by single-crystal X-ray diffraction. The last two complexes comprise a slightly distorted octahedron with bond distances Co−P 2.210(1), Co−S 2.254(1) and Co−Cl 2.281(1) and Co−P 2.227(3), Co−S 2.327(3) and Co−Cl 2.241(3) Å (all averages) respectively. The differences in Co−S and Co−Cl bond distances are attributable to the strong *trans* influence of the phosphino group. Acetylacetonate complexes of *rac*(P)-SPPS in organic solvents form equilibrium mixtures of the *cis*-α and *cis*-β isomers, the molar ratio in $MeNO_2$ solution at 60 °C being 2 : 1 for the L^1 complex and 3 : 2 for the L^2 complex.

Linear tetradentate tetraphosphine ligands exist as *racemic* (*RR*/*SS*) and *meso* (*RS*) diastereomers by virtue of the absolute configurations of the two internal phosphorus atoms in the skeletons.[1] Each of the diastereomers generates stereospecific co-ordination modes upon complexation.[2] We have prepared a large number of linear tetradentate phosphine(soft base)–amine(hard base) hybrid compounds where the phosphorus donor atoms are chiral, examined the complexation to cobalt(III) of a typical Lewis hard acid, and found that these complexes have quite different properties from those of analogous tetradentate tetramines.[3–6] In a previous paper[7] we extended the study to a tetradentate phosphorus–sulfur hybrid bearing only soft donor groups, 5,8-diphenyl-2,11-dithia-5,8-diphosphadodecane (L^1), and obtained $[Co(acac)_2L^1]^+$ (acac = pentane-2,4-dionate) in which L^1 acts only as a bidentate ligand through two phosphorus atoms. The purpose of this paper is to examine more thoroughly the complexation ability of L^1 and the related L^2 (5,9-diphenyl-2,12-dithia-5,9-diphosphatridecane) to cobalt(III) and clarify the correlations between the co-ordination modes and the absolute configurations of the chiral phosphorus atoms and/or the conformations (or size) of the central P−Co−P chelate rings.

Bosnich *et al.*[8,9] reported the preparation of a series of cobalt(III) complexes with the linear tetradentate tetraarsine $[Me_2As(CH_2)_3As(Ph)CH_2–]_2$, and clarified the optical stability of the chiral arsine atoms and topological stabilities of various geometrical isomers of the complexes. However, this arsine differs in the kind of donor atoms and the skeletal structure from our present phosphines: the number of methylene groups of the arsine is 3,2,3, while our phosphines have 2,2,2 and 2,3,2. Such differences often result in different topological preferences and stabilities upon complexation.

To our knowledge, only two papers have appeared on metal complexes of SPPS-type tetradentate ligands. Issleib and Gans[10] prepared $[MX(NH_3)(SCH_2CH_2PHCH_2CH_2PHCH_2CH_2S)]$ (M = Co, X = Br; M = Rh, X = Cl) and [M{SCH(R)$CH_2PHCH_2CH_2PHCH_2$CH(R)S}] (M = Ni, Pd or Pt; R = H or Me). However, the stereochemistry of the complexes was not well defined. Schmelzer and Schwarzenbach[11] reported the crystal structure of *racemic*(P) and *meso*(P) isomers of $[Ni(SCH_2CH_2PPhCH_2CH_2CH_2PPhCH_2CH_2S)]$, but experimental details and chemical properties were not described.

Experimental

The phosphines were handled under an atmosphere of nitrogen using Schlenk techniques until the cobalt(III) complexes were formed. All of the solvents used for the preparation of ligands and complexes were made oxygen-free by bubbling nitrogen for 20 min immediately before use. Absorption spectra were recorded on a Hitachi U3400 spectrophotometer and NMR spectra on Hitachi R-90H and Varian INOVA 500 spectrometers.

Preparation of phosphines

L^1. This compound was prepared from 1,2-bis(phenylphosphino)ethane and 2-chloroethyl methyl sulfide according to a previous method.[7]

L^2. A 15% hexane solution of butyllithium (30 cm^3, 48.6 mmol) was added dropwise with stirring to a tetrahydrofuran solution (400 cm^3) of 1,3-bis(phenylphosphino)propane (Strem Chem. Inc.) (5 g, 19.2 mmol). After stirring for 30 min, 2-chloroethyl methyl sulfide (4.25 g, 38.4 mmol) was added portionwise to the resulting yellow solution. The solution was stirred for 1 h at 50 °C, and then overnight at room temperature. Water (50 cm^3) was added dropwise with stirring. After a while the ethereal layer was separated, dried over $MgSO_4$ (5 g) overnight, filtered, and the filtrate evaporated to give a viscous syrup. The product could not be distilled because of the very high boiling point, and was used as such for the preparation of cobalt(III) complexes. Yield: 6.92 g (88%). It was found to be a mixture of *racemic* and *meso* isomers (*ca.* 1 : 1 according to the NMR spectra. ($CDCl_3$): $^{31}P-\{^1H\}$ (external 85% H_3PO_4), δ −25.64 and −25.69; $^{13}C-\{^1H\}$, δ 15.40 (s, SCH_3), 15.41 (s, SCH_3), 22.34 (t, J = 14.96, CH_2), 22.44 (t, J = 14.96, CH_2), 28.20 (d, J = 13.24, PCH_2), 28.31 (d, J = 14.39, PCH_2), 29.34 (t, J = 12.09, PCH_2), 29.41 (t, J = 12.09, PCH_2), 30.58 (d,

$J = 17.84$, SCH_2), 30.62 (d, $J = 17.84$, SCH_2), 128.42 (d, $J = 6.91$, *m*-C), 128.44 (d, $J = 7.48$, *m*-C), 129.01 (s, *p*-C), 132.33 (d, $J = 18.99$, *o*-C), 132.34 (d, $J = 18.99$, *o*-C), 137.19 (d, $J = 11.51$, *ipso*-C) and 137.31 (d, $J = 11.51$ Hz, *ipso*-C); ^{1}H, δ 1.45 (m, CH_2), 1.80 (m, PCH_2), 1.92 (m, PCH_2), 2.01 (s, SCH_3), 2.02 (s, SCH_3), 2.42 (m, SCH_2), 7.31 (m, C_6H_5) and 7.43 (m, C_6H_5).

Preparation of complexes

***trans*-[CoCl$_2${*meso*(P)-L^1}$_2$]BF$_4$ 1 and *cis*-α-[CoCl$_2${*rac*(P)-L^1}]BF$_4$ 2.** A methanol solution (120 cm^3) containing *trans*-[CoCl$_2$(py)$_4$]Cl·6H$_2$O[12] (py = pyridine) (2.45 g, 4.13 mmol) and L^1 (1.63 g, 4.13 mmol) was stirred overnight at room temperature, and then concentrated to a small volume. The concentrate was chromatographed with a column (3 × 35 cm) of Toyopearl HW-40 and methanol as eluent. Two large green and red bands were obtained separately, the former being eluted faster. Each eluate was evaporated to dryness under reduced pressure, and the residue mixed with a small amount of methanol to extract the complex. On addition of an excess of $LiBF_4$ the methanol extract gave a green or a red precipitate, which was filtered off and recrystallized from acetonitrile and diethyl ether to afford green (**1**) and red (**2**) *crystals*, respectively. Yield: 0.48 (12) for **1** and 0.79 g (31%) for **2** (Found: C, 47.5; H, 5.5. Calc. for $C_{40}H_{56}BCl_2CoF_4P_4S_4$ **1**: C, 47.75; H, 5.6. Found: C, 39.5; H, 4.8. Calc. for $C_{20}H_{28}BCl_2CoF_4P_2S_2$ **2**: C, 39.3; H, 4.6%). Both complexes **1** and **2** are soluble in nitromethane, acetonitrile, acetone, chloroform, or dichloromethane, but insoluble in water or diethyl ether; **1** is slightly soluble in methanol or ethanol.

***cis*-β-[Co(acac){*rac*(P)-L^1}][SbF$_6$]$_2$ 3 and *cis*-α-[Co(acac){*rac*-(P)-L^1}][SbF$_6$]$_2$ 4.** A methanol solution (50 cm^3) of Li(acac) (0.087 g, 0.82 mmol) was added to an acetonitrile solution (60 cm^3) of *cis*-α-[CoCl$_2${*rac*(P)-L^1}]BF$_4$ (0.50 g, 0.82 mmol). The solution was stirred overnight at room temperature, then diluted ten times with water, and applied to a column (3 × 130 cm) of SP-Sephadex C-25. By elution with an aqueous 0.15 mol dm^{-3} NaCl solution a small dark red band of [Co(acac)$_2${*rac*(P)-L^1}]$^+$ [7] and then two large red-orange and red bands were eluted separately. Each eluate of the two large bands was evaporated to dryness under reduced pressure at 20 °C. The residue was mixed with a small amount of ethanol to extract the complex, and the extract evaporated again to dryness under reduced pressure at 20 °C. The residue was dissolved in a small amount of water. On addition of an excess of $NaSbF_6$ the solution yielded a red-orange (**3**) or red (**4**) precipitate, which was filtered off and recrystallized from methanol and diethyl ether to afford the *crystals*, respectively. Yields: 0.084 (10) for **3** and 0.352 g (42%) for **4** (Found: C, 29.55; H, 3.2 for **3**. C, 29.2; H, 3.45 for **4**. Calc. for $C_{25}H_{35}CoF_{12}O_2P_2S_2Sb_2$: C, 29.3; H, 3.45%). Both complexes **3** and **4** are soluble in nitromethane, acetonitrile, acetone, methanol or ethanol, slightly soluble in chloroform, dichloromethane or water, but insoluble in diethyl ether.

[Co(acac){*meso*(P)-L^1}$_2$][SbF$_6$]$_2$·3H$_2$O 5. A methanol solution (30 cm^3) of Li(acac) (0.023 g, 0.22 mmol) was added to an acetonitrile solution (50 cm^3) of *trans*-[CoCl$_2${*meso*(P)-L^1}$_2$]BF$_4$ (0.217 g, 0.22 mmol). The solution was stirred for 5 h at room temperature, diluted ten times with water, and filtered. The filtrate was applied to a column (3 × 60 cm) of SP-Sephadex C-25, and the adsorbed products were eluted with an aqueous 0.15 mol dm^{-3} NaCl solution to give two large dark red and red-orange bands. The eluate of the second red-orange band was evaporated to dryness under reduced pressure, and the complex extracted with ethanol from the residue. The extract was evaporated again to dryness under reduced pressure, and the residue was dissolved in a small amount of water. On addition of an excess of $NaSbF_6$ a red-orange precipitate was obtained, filtered off and recrystallized from nitromethane and diethyl ether to afford the *crystals*. Yield: 0.042 g (14%) (Found: C, 36.5; H, 4.2. Calc. for $C_{45}H_{69}CoF_{12}O_5P_4S_4Sb_2$: C, 36.7; H, 4.7%). The complex is soluble in nitromethane, acetonitrile, acetone, chloroform, dichloromethane, methanol or ethanol, slightly soluble in water, but insoluble in diethyl ether.

From the eluate of the first dark red band, [Co(acac)$_2${*meso*-(P)-L^1}]SbF$_6$ [7] was obtained in 15% yield by the same method as that for complex **5**.

***trans*-[CoCl$_2${*meso*(P)-L^2}]BF$_4$ 6 and *cis*-α-[CoCl$_2${*rac*(P)-L^2}]BF$_4$ 7.** Complexes **6** (green) and **7** (red) were obtained by methods similar to those for the corresponding L^1 complexes **1** and **2**, respectively, using L^2.Yields: 36% for **6** and 40% for **7** (Found: C, 40.3; H, 4.9 for **6**. C, 40.4; H, 4.9 for **7**. Calc. for $C_{21}H_{30}BCl_2CoF_4P_2S_2$: C, 40.35; H, 4.85%). Both complexes are soluble in nitromethane, acetonitrile, acetone, chloroform or dichloromethane, less soluble in methanol or ethanol, but insoluble in diethyl ether.

***cis*-β-[Co(acac){*rac*(P)-L^2}][SbF$_6$]$_2$ 8 and *cis*-α-[Co(acac)-{*rac*(P)-L^2}][SbF$_6$]$_2$ 9.** Complexes **8** (red-orange) and **9** (red) were prepared from *cis*-α-[CoCl$_2${*rac*(P)-L^2}]BF$_4$ and Li(acac) by methods similar to those for the corresponding L^1 complexes **3** and **4**, respectively. In contrast to the case of L^1, [Co(acac)$_2${*rac*(P)-L^2}]$^+$ was not formed. Yields: 24% for **8** and 48% for **9** (Found: C, 29.8; H, 3.6 for **8**. C, 29,3; H, 3.45 for **9**. Calc. for $C_{26}H_{37}CoF_{12}O_2P_2S_2Sb_2$: C, 30.1; H, 3.6%). The solubilities of **8** and **9** are similar to those of **3** and **4**.

***cis*-β-[Co(acac){*meso*(P)-L^2}][SbF$_6$]$_2$ 10.** To an acetonitrile solution (20 cm^3) of *trans*-[CoCl$_2${*meso*(P)-L^2}]BF$_4$ (0.20 g, 0.32 mmol) were added a methanol solution (40 cm^3) of Li(acac) (0.034 g, 0.32 mmol) and active charcoal (0.05 g). The mixture was stirred for 24 h at room temperature, and then filtered to remove charcoal. The filtrate was diluted ten times with water, and applied to a column (3 × 60 cm) of SP-Sephadex C-25. By elution with an aqueous 0.15 mol dm^{-3} NaCl solution, a red-orange band was developed. The eluate of the band was evaporated to dryness under reduced pressure, and the residue mixed with a small amount of ethanol to extract the complex. The extract was evaporated again to dryness under reduced pressure, and the residue dissolved in a small amount of water. On addition of an excess of $NaSbF_6$ the solution gave a red precipitate, which was filtered off and recrystallized from methanol and diisopropyl ether to afford the *crystals*. Yield: 0.05 g (15%) (Found: C, 30.1; H, 3.55. Calc. for $C_{26}H_{37}CoF_{12}O_2P_2S_2Sb_2$: C, 30.1; H, 3.6%). The solubility of the complex is similar to those of **8** and **9**.

[Co(acac)$_2${*meso*(P)-L^2}]SbF$_6$ 11 and Δ(*RR*)/Λ(*SS*)-[Co-(acac)$_2${*rac*(P)-L^2}]SbF$_6$ 12. A mixture of [Co(acac)$_3$][13] (0.44 g, 1.22 mmol), L^2 (0.50 g, 1.22 mmol), and active charcoal (0.05 g) in methanol (50 cm^3) was stirred for 15 h at room temperature, and then filtered to remove charcoal. The filtrate was diluted ten times with water, and applied to a column (3 × 20 cm) of SP-Sephadex C-25. By elution with an aqueous 0.05 mol dm^{-3} NaCl solution, two large dark red bands of complexes **11** and **12** appeared, the former being eluted faster. Each eluate of these bands was evaporated to dryness under reduced pressure, and the complex extracted from the residue with dichloromethane. The extract was evaporated again to dryness under reduced pressure, and the residue dissolved in a small amount of water. On addition of an excess of $NaSbF_6$ the solution yielded orange-brown *crystals*, which were filtered off and recrystallized from hot methanol. Yields: 0.22 (20) for **11** and 0.18 g (16%) for **12** (Found: C, 41.3; H, 4.9 for **11**. C, 41.2; H, 4.9 for **12**. Calc. for $C_{31}H_{44}CoF_6O_4P_2S_2Sb$: C, 41.3; H, 4.9%). The complexes are soluble in methanol, ethanol, chloroform or acetone, and slightly soluble in water or diethyl ether.

Complex **11** was also prepared by the following method. To an acetonitrile solution (20 cm^3) of *trans*-[$CoCl_2${*meso*(P)-L^2}]BF_4 (0.15 g, 0.24 mmol) were added a methanol solution (30 cm^3) of Li(acac) (0.077 g, 0.72 mmol) and active charcoal (0.03 g). The mixture was stirred for 24 h at room temperature, and then filtered to remove charcoal. The filtrate was diluted ten times with water, applied to a column (3 × 60 cm) of SP-Sephadex C-25, and the adsorbed products were eluted with an aqueous 0.05 mol dm^{-3} NaCl solution. A large orange band appeared, and the eluate was treated as described above to give orange *crystals* of **11**. Yield: 0.11 g (49%).

[Co(acac)$_2${*meso*(P)-L^1}]SbF_6 13 and Δ(*RR*)/Λ(*SS*)-[Co(acac)$_2${*rac*(P)-L^1}]SbF_6 14. These complexes were prepared by a previous method.[7]

Crystallography

Single crystals of complexes **2** (0.25 × 0.25 × 0.40 mm) and **6** (0.20 × 0.30 × 0.40 mm) were fixed on the end of a glass fibre with epoxy resin. They were mounted on a Rigaku AFC-5 diffractometer individually, and the diffraction data collected at 298 K with graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å) using the ω–2θ scan mode for **2** and the ω scan mode for **6**. Cell dimensions were determined by least-squares refinement of the angular positions of 25 independent reflections in the range $25 < 2\theta < 30°$ for each sample. Crystallographic data and experimental details are listed in Table 1. The position of the cobalt was determined by direct methods (SHELXS 86[14]) for each complex and the remaining non-hydrogen atoms were located by subsequent Fourier syntheses. The structure was refined on *F* by full-matrix least-squares techniques with anisotropic thermal parameters for non-hydrogen atoms. The disordered tetrafluoroborate anions of **6** were refined with isotropic thermal parameters. All the hydrogen atoms were placed at calculated positions with isotropic displacement parameters of their parent carbon atoms. The calculations were carried out with the XTAL 3.2[15] software, and the refinement of positional and thermal parameters finally converged to $R = 0.047$ ($R' = 0.055$) for **2** and $R = 0.058$ ($R' = 0.059$) for **6**.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/289.

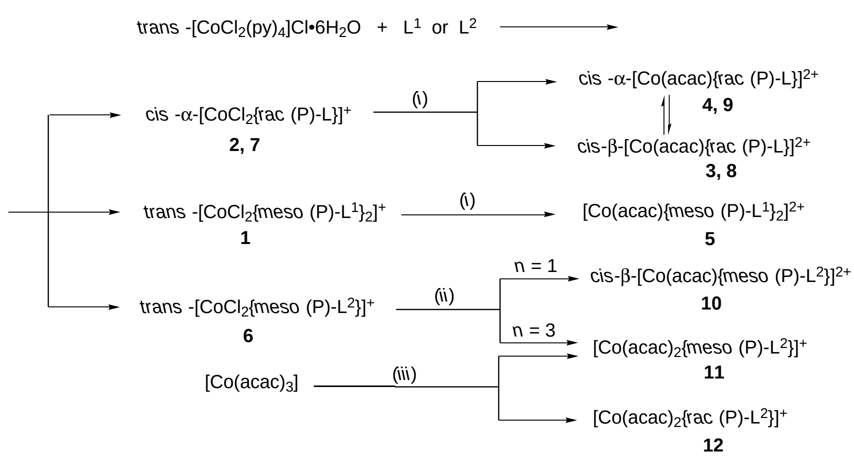
Results and Discussion

The synthetic routes for twelve new complexes are shown in Scheme 1.

Dichloro complexes

For L^1 and L^2 green and red dichlorocobalt(III) complexes were obtained by the reaction of [$CoCl_2(py)_4$]Cl·6H_2O in a molar ratio of 1:1 in methanol (green **1** and **6**, and red **2** and **7**). Elemental analyses of these complexes show that **1** involves two L^1 ligands, while **2**, **6** and **7** have a tetradentate L^1 or L^2 ligand. The structures of **2** and **6** were determined by X-ray diffraction. Perspective views of the complex cations are shown in Figs. 1 and 2, respectively, and selected bond distances and angles in Tables 2 and 3. The complex cations form an octahedron with two chloride ions and *rac*(P)-L^1 in a *cis*-α configuration for **2**, and with two chloride ions and *meso*(P)-L^2 in a *trans* one for **6**. Compound **2** crystallizes with molecular C_2 symmetry. The cation lies with Co and the centre of the C(10)–C(10′) bond on the two-fold axis along *a* while the boron atom of the anion lies on the two-fold axis along *c*. The Co–P bond distance of 2.210(1) Å in **2** is relatively short compared with those found in related cobalt(III) phosphine complexes (2.194–2.353 Å).[16] The Co–Cl bond distance 2.281(1) Å is appreciably longer than those not only in **6** [2.243(3) and 2.239(3) Å] but also the related dichlorocobalt(III) complexes *trans*(Cl,Cl)*cis*(P,P)-[$CoCl_2(NH_2CH_2CH_2PPh_2)_2$]·0.5[$CoCl_4$] [average 2.240(3) Å],[17] *trans*(Cl,Cl)*cis*(P,P)-[$CoCl_2(NH_2CH_2CH_2PBuPh)_2$]$ClO_4$ [average 2.238(3) Å][17] and *trans*(Cl,Cl)*cis*(P,P)-[$CoCl_2(NH_2CH_2CH_2PMe_2)_2$]$PF_6$·0.5MeOH [average 2.242(3) Å].[18] The elongation of the Co–Cl bond in **2** may be attributed to the stronger *trans* influence of the phosphine donor group relative to that of the chlorine atom in **6**. On the other hand, the Co–S bond distances of **6** [2.325(3) and 2.329(3) Å] are longer than that [2.252(1) Å] of **2**. The elongation in **6** is also interpreted by the stronger *trans* influence of the phosphine group than that of the thioether group in **2**. Several examples of Co–S bond distances in cobalt(III)–thioether complexes are [Co{(*R*)-$NH_2CH(CO_2)CH_2SMe$}$_2$]ClO_4·H_2O [average 2.272(2) Å],[19] [Co($NH_2CH_2CH_2SMe$)($NH_2CH_2CH_2NH_2$)$_2$][Fe(CN)$_6$]·4H_2O [2.268(10) Å][20] and [Co{(*R*)-[$MeSCH_2CH(CO_2)NHCH_2$–]$_2$}]ClO_4 [average 2.261(4) Å].[21]

The chelate angles of L^1 [86.79(4), 87.18(4)°] in complex **2** are typical for a five-membered chelate ring.[17,18,21] No large deviation from an octahedral angle was observed at the Co atom. The complex ion in Fig. 1 has a Λ configuration. In this configuration both the P and S donor atoms take an *S* configuration, and the P–P chelate ring a λ *gauche* conformation, while the two P–S chelate rings take an envelope one. The ^1H and ^{13}C NMR spectra of this complex in CD_3NO_2 at 30 °C show a singlet signal for the SMe group at δ 2.35 and 20.1, respectively (Table 4),which is retained even at −80 °C in $(CD_3)_2CO$. The singlet indicates a rapid configurational inversion or a preferential configuration of the (*S*)-sulfur atom in the Λ isomer as shown in Fig. 1. Although we have no evidence for either, molecular models indicate that the methyl group on the sulfur



Scheme 1 (*i*) Li(acac); (*ii*) *n* Li(acac), activated charcoal; (*iii*) L^2, activated charcoal

Table 1 Crystallographic data for *cis*-α-$[CoCl_2\{rac(P)\text{-}L^1\}]BF_4$ **2** and *trans*-$[CoCl_2\{meso(P)\text{-}L^2\}]BF_4$ **6** *

	2	**6**
Formula	$C_{20}H_{28}BCl_2CoF_4P_2S_2$	$C_{21}H_{30}BCl_2CoF_4P_2S_2$
M	611.16	625.19
Space group	*Pnna* (no. 52)	$Pbc2_1$ (no. 29)
a/Å	12.392(1)	9.914(2)
b/Å	18.808(4)	29.945(4)
c/Å	10.900(1)	8.946(1)
U/Å^3	2540.4(7)	2655.8(9)
μ(Mo-Kα)/cm^{-1}	12.06	11.55
Crystal colour	Red	Green
D_c/g cm^{-3}	1.60	1.56
D_m/g cm^{-3}	1.59	—
Scan range/°	1.15 + 0.50 tan θ	0.735 + 0.50 tan θ
Reflections measured	$0 \leqslant h \leqslant 17, 0 \leqslant k \leqslant 26, 0 \leqslant l \leqslant 15$	$0 \leqslant h \leqslant 13, 0 \leqslant k \leqslant 42, 0 \leqslant l \leqslant 12$
No. reflections measured	3812	4203
No. reflections observed $[\lvert F_o\rvert > 3\sigma(\lvert F_o\rvert)]$	2297	2161
R	0.047	0.058
R′	0.055	0.059
S	1.72	1.61
Largest difference peak, hole/e Å^{-3}	0.93, −0.82	0.85, −0.78

* Details in common: orthorhombic; $Z = 4$; prismatic; scan speed 8° min^{-1}; $2\theta_{max}$ 60°; $R = \Sigma\,\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\Sigma\,\lvert F_o\rvert$, $R' = (\Sigma\,w\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert^2/\Sigma\,w\lvert F_o\rvert^2)^{\frac{1}{2}}$, $w = [\sigma^2(F_o) + (0.015F_o)^2]^{-1}$.

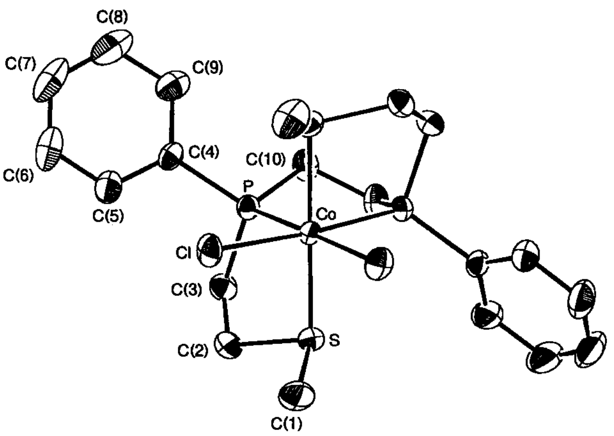


Fig. 1 Perspective view of *cis*-α-$[CoCl_2\{rac(P)\text{-}L^1\}]^+$, which crystallizes with molecular C_2 symmetry

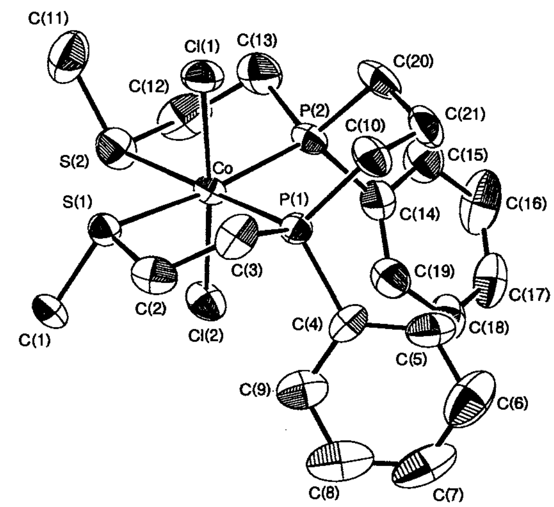


Fig. 2 Perspective view of *trans*-$[CoCl_2\{meso(P)\text{-}L^2\}]^+$

atom in the *R* configuration points to the phenyl group to form a crowded structure, suggesting the preferential co-ordination of the *S* (or *R*)-sulfur atom in the Λ (or Δ) isomer.

For complex **6** the five- and six-membered chelate rings of the *meso*(P)-L^2 ligand take a *gauche* and a chair conformation, respectively. The chelate angles of L^2 are almost 90° and no large deviation from an octahedron was observed at the Co atom.

Table 2 Selected bond distances (Å) and angles (°) for complex **2**

Co–Cl	2.281(1)	Co–P	2.210(1)
Co–S	2.254(1)		
Cl–Co–S	91.88(4)	Co–S–C(1)	109.6(2)
Cl–Co–P	89.72(3)	Co–S–C(2)	102.3(1)
Cl–Co–Cl′	93.93(4)	C(1)–S–C(2)	100.7(2)
Cl–Co–S′	89.82(4)	Co–P–C(3)	107.0(1)
Cl–Co–P′	175.35(4)	Co–P–C(4)	119.4(1)
S–Co–S′	177.51(5)	Co–P–C(10)	108.3(1)
S–Co–P	87.18(4)	C(3)–P–C(4)	107.7(2)
S–Co–P′	91.01(4)	C(3)–P–C(10)	105.5(2)
P–Co–P′	86.79(4)	C(4)–P–C(10)	108.1(2)

Table 3 Selected bond distances (Å) and angles (°) for complex **6**

Co–Cl(1)	2.243(3)	Co–S(2)	2.329(3)
Co–Cl(2)	2.239(3)	Co–P(1)	2.223(3)
Co–S(1)	2.325(3)	Co–P(2)	2.230(3)
Cl(1)–Co–Cl(2)	174.5(1)	C(1)–S(1)–C(2)	101.7(6)
Cl(1)–Co–S(1)	84.6(1)	Co–S(2)–C(11)	115.0(5)
Cl(1)–Co–S(2)	92.1(1)	Co–S(2)–C(12)	100.6(5)
Cl(1)–Co–P(1)	86.3(1)	C(11)–S(2)–C(12)	99.9(6)
Cl(1)–Co–P(2)	87.9(1)	Co–P(1)–C(3)	105.2(4)
Cl(2)–Co–S(1)	93.7(1)	Co–P(1)–C(4)	120.8(4)
Cl(2)–Co–S(2)	82.7(1)	Co–P(1)–C(10)	114.3(4)
Cl(2)–Co–P(1)	98.8(1)	C(3)–P(1)–C(4)	104.5(5)
Cl(2)–Co–P(2)	93.9(1)	C(3)–P(1)–C(10)	104.2(5)
S(1)–Co–S(2)	90.7(1)	C(4)–P(1)–C(10)	106.3(5)
S(1)–Co–P(1)	88.3(1)	Co–P(2)–C(13)	104.2(4)
S(1)–Co–P(2)	172.5(1)	Co–P(2)–C(14)	121.7(4)
S(2)–Co–P(1)	178.2(1)	Co–P(2)–C(20)	114.1(4)
S(2)–Co–P(2)	90.0(1)	C(13)–P(2)–C(14)	105.9(5)
P(1)–Co–P(2)	90.8(1)	C(13)–P(2)–C(20)	108.4(6)
Co–S(1)–C(1)	111.1(4)	C(14)–P(2)–C(20)	101.8(5)
Co–S(1)–C(2)	104.9(4)		

Complex **7** exhibits a singlet SMe signal in the ^{1}H and ^{13}C NMR spectra at δ 2.28 and 18.6, respectively, indicating a *trans* or a *cis*-α configuration. The complex shows an absorption spectral pattern very similar to that of **2** [Fig. 3(*a*)], and is assigned to *cis*-α-$[CoCl_2\{rac(P)\text{-}L^2\}]^+$. The *meso*(P)-SPPS ligand cannot form a *cis*-α isomer since the two terminal P–S chelate arms point to the same apical site with respect to the P–Co–P plane.

Table 4 Absorption and ^{1}H NMR spectral data

Complex	Absorption [a]	^{1}H NMR (δ) [b] CH$_3$	=CH−
1 *trans*-$[CoCl_2\{meso(P)\text{-}L^1\}_2]^+$	16.4 (2.15)	1.92	
6 *trans*-$[CoCl_2\{meso(P)\text{-}L^2\}]^+$	16.1 (2.25)	2.37	
2 *cis*-α-$[CoCl_2\{rac(P)\text{-}L^1\}]^+$	20.0 (3.19)	2.35	
7 *cis*-α-$[CoCl_2\{rac(P)\text{-}L^2\}]^+$	19.4 (2.91)	2.28	
3 *cis*-β-$[Co(acac)\{rac(P)\text{-}L^1\}]^{2+}$	20.5 (3.12)	1.76, 1.89	4.97
		2.00, 2.07	
4 *cis*-α-$[Co(acac)\{rac(P)\text{-}L^1\}]^{2+}$	19.5 (3.04)	1.95, 2.29	5.84
5 $[Co(acac)\{meso(P)\text{-}L^1\}_2]^{2+}$	20.2 (3.28)	0.96, 1.72, 1.80	4.68
		1.89, 2.06, 2.21	
8 *cis*-β-$[Co(acac)\{rac(P)\text{-}L^2\}]^{2+}$	19 (sh) (3.0)	1.79, 2.11	5.24
	20.7 (3.14)	2.56, 2.60	
9 *cis*-α-$[Co(acac)\{rac(P)\text{-}L^2\}]^{2+}$	18.9 (2.86)	1.73, 2.20	5.69
10 *cis*-β-$[Co(acac)\{meso(P)\text{-}L^2\}]^{2+}$	19 (sh) (2.8)	1.07, 1.75	4.96
	21.3 (2.98)	2.08, 2.41	
11 $[Co(acac)_2\{meso(P)\text{-}L^2\}]^+$	19 (sh) (2.7)	1.52, 1.64, 1.67	4.72
	21.6 (2.87)	1.90, 2.07, 2.11	5.34
12 $[Co(acac)_2\{rac(P)\text{-}L^2\}]^+$	19 (sh) (2.6)	1.64, 1.78	5.06
	21.6 (2.82)	1.97	
13 $[Co(acac)_2\{meso(P)\text{-}L^1\}]^+$	21.3 (2.98)	0.96, 1.58, 1.94	4.74
		2.03, 2.06, 2.16	5.51
14 $[Co(acac)_2\{rac(P)\text{-}L^1\}]^+$	21.2 (3.07)	1.34, 1.98, 2.04	4.86

[a] First absorption bands: $\nu/10^3$ cm^{-1} (log ε), solvent MeCN, sh = shoulder. [b] Solvents: CD_3NO_2 for complexes **1**–**10** and $CDCl_3$ for **11**–**14**.

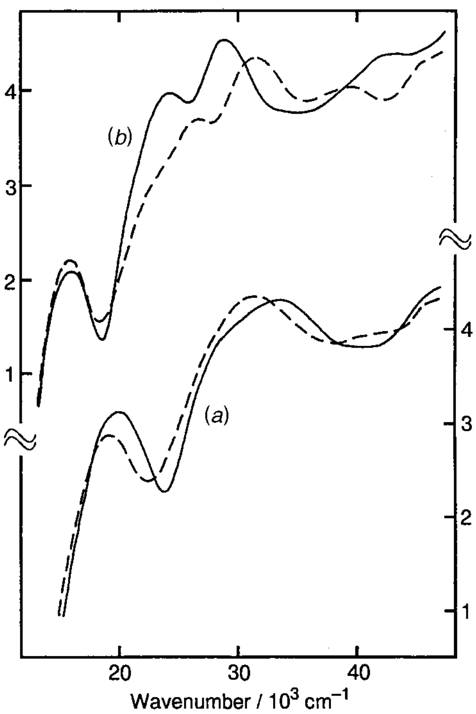


Fig. 3 Absorption spectra of (*a*) *cis*-α-$[CoCl_2\{rac(P)\text{-}L^1\}]^+$ (——) and *cis*-α-$[CoCl_2\{rac(P)\text{-}L^2\}]^+$ (– – – – –), (*b*) *trans*-$[CoCl_2\{meso(P)\text{-}L^1\}_2]^+$ (——) and *trans*-$[CoCl_2\{meso(P)\text{-}L^2\}]^+$ (– – – –) in MeCN

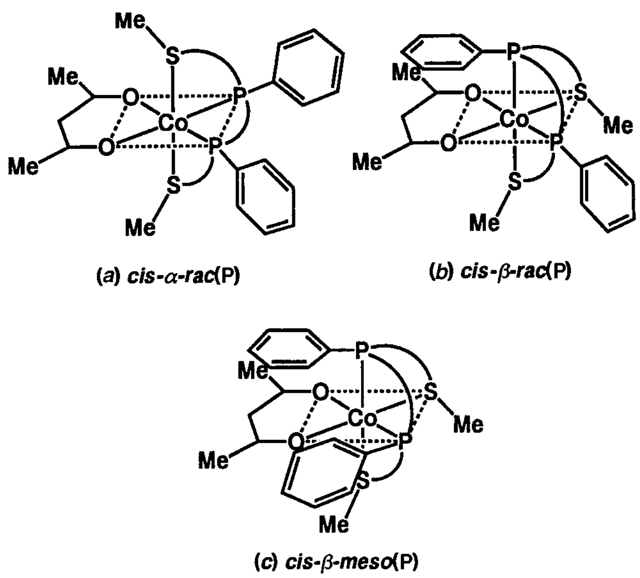


Fig. 4 Three possible isomers of *cis*-$[Co(acac)L]^{2+}$

Complex **1** which has the composition $[CoCl_2L^1{}_2]^+$ was obtained by the reaction of $[CoCl_2(py)_4]^+$ and L^1 in a molar ratio of 1 : 1. It shows a singlet signal for the SMe group in the ^{1}H and ^{13}C NMR spectra, and the absorption spectral pattern is similar to those of **6** [Fig. 3(*b*)] and *trans*-$[CoCl_2(Bu_2PCH_2CH_2PBu_2)_2]^+$ (first absorption peak: 16 610 cm^{-1} with log ε = 2.05).[22] Thus complex **1** is a *trans*-dichloro isomer with two didentate L^1 ligands chelated through two phosphorus atoms. The reaction of **1** with Li(acac) yielded only $[Co(acac)_2\{meso(P)\text{-}L^1\}]^+$ **13** and no *rac*(P)-L^1 complex was observed. Thus **1** is *trans*-$[CoCl_2\{meso(P)\text{-}L^1\}_2]^+$, although no assignment can be made for two diastereomers, *trans*[P(*R*)P(*R*) or P(*S*)P(*S*)] and *trans*[P(*R*)P(*S*)]. When *meso*(P)-L^1 acts as a tetradentate ligand to form a *trans* isomer the central five-membered P−Co−P chelate ring is forced to take an envelope conformation, and the complex will be unstable.

Acetylacetonato complexes

By the reaction with an equimolar amount of Li(acac), *cis*-α-$[CoCl_2\{rac(P)\text{-}L\}]^+$ (L = L^1 or L^2) yielded both *cis*-α and *cis*-β-$[Co(acac)\{rac(P)\text{-}L\}]^{2+}$. Since the *cis*-α and *cis*-β complexes have C_2 and C_1 symmetry, respectively (Fig. 4), the structures can be assigned easily from the ^{1}H NMR spectra (Table 4). The *cis*-β-$[Co(acac)\{meso(P)\text{-}L^2\}]^{2+}$ complex was prepared from *trans*-$[CoCl_2\{meso(P)\text{-}L^2\}]^+$ by a similar method. However, neither *cis*-β-$[Co(acac)\{meso(P)\text{-}L^1\}]^{2+}$ nor related complexes in which *meso*(P)-L^1 acts as a tetradentate ligand were obtained. The reaction of *trans*-$[CoCl_2\{meso(P)\text{-}L^1\}_2]^+$ with an equimolar amount of Li(acac) afforded $[Co(acac)\{meso(P)\text{-}L^1\}_2]^{2+}$ and $[Co(acac)_2\{meso(P)\text{-}L^1\}]^+$ in similar yields. When the tetradentate *meso*(P)-L^1 forms a *cis*-β structure the remaining two co-ordination sites are surrounded by the two bulky phenyl groups of L^1, and seem to hinder the co-ordination of a six-membered

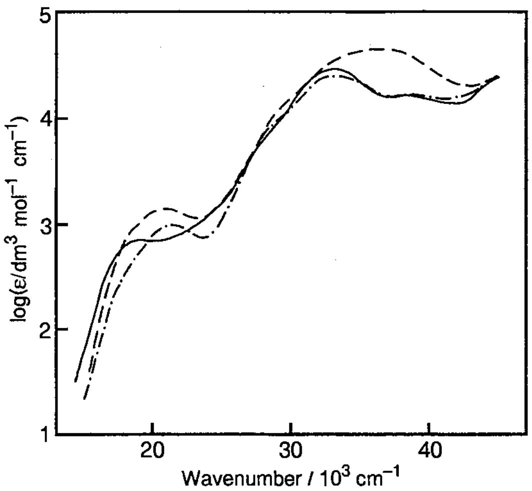


Fig. 5 Absorption spectra of *cis*-α-[Co(acac){*rac*(P)-L^2}]$^{2+}$ (——), *cis*-β-[Co(acac){*rac*(P)-L^2}]$^{2+}$ (– – – –), and *cis*-β-[Co(acac){*meso*(P)-L^2}]$^{2+}$ (–·–·–·–) in MeCN

acac chelate ring. An analogous ligand *meso*(P)-$NH_2CH_2CH_2PPhCH_2CH_2PPhCH_2CH_2NH_2$(L^3) yielded a *cis*-β isomer with acac in small yield, but the complex decomposed slowly in water.[4]

The ^{1}H NMR spectra of the acac ligand in *cis*-α and *cis*-β-[Co(acac){*rac*(P)- or *meso*(P)-L}]$^{2+}$ (L = L^1 or L^2) reflect the structures of three geometrical isomers shown in Fig. 4. The resonance peaks of the methine proton of *cis*-β-[Co(acac){*rac*(P)-L^1}]$^{2+}$ and the methine and one methyl group protons of *cis*-β-[Co(acac){*meso*(P)-L^2}]$^{2+}$ are observed at a fairly high field compared with those of the corresponding protons of other isomers (Table 4). The high-field shifts of these methine and methyl proton signals are attributed to the shielding effect of the phenyl group located near these protons. The complex [Co(acac){*meso*(P)-L^1}$_2$]$^{2+}$ **5** shows six singlet methyl proton signals, one of which and the methine proton signal of acac are shifted to high field. This spectral pattern is consistent only with the molecular model of the *trans*[P(*R*)P(*S*)] isomer.

Fig. 5 shows the absorption spectra of *cis*-α- and *cis*-β-[Co(acac){*rac*(P)-L^2}]$^{2+}$ and *cis*-β-[Co(acac){*meso*(P)-L^2}]$^{2+}$. These are similar to those of the corresponding isomers of [Co(acac)L^4]$^{2+}$ (L^4 = $NH_2CH_2CH_2PPhCH_2CH_2CH_2PPhCH_2CH_2NH_2$); the first d–d bands of the *cis*-β isomers are broader than that of the *cis*-α isomer and have a shoulder to lower energy.[4] The similarity in spectra between the L^2 and the L^4 complexes indicates that the ligand-field strength of SMe is similar to that of NH_2.[23] The spectra of the L^1 complexes are quite similar to those of the corresponding L^2 complexes.

Both *cis*-α and *cis*-β isomers of [Co(acac){*rac*(P)-L}]$^{2+}$ (L = L^1 or L^2) change in absorption spectra in organic solvents at elevated temperatures with isosbestic points, the final spectra being the same for both isomers. These results indicate that these two isomers isomerize to each other in solution to give an equilibrium mixture. The isomerization reactions were also monitored by the ^{1}H NMR spectral changes with time, and the molar ratios of the isomers at equilibrium in $MeNO_2$ solutions were obtained; *cis*-α : *cis*-β = 2 : 1 for the L^1 complex and 3 : 2 for the L^2 one. Such an isomerization reaction was not observed for the corresponding NPPN complexes.[4]

The reaction of L^2 [a mixture of *meso*(P) and *rac*(P) isomers] with [Co(acac)$_3$] in methanol in the presence of active charcoal afforded [Co(acac)$_2${*meso*(P)-L^2}]$^+$ and Δ(*RR*)/Λ(*SS*)-[Co(acac)$_2${*rac*(P)-L^2}]$^+$, and no Δ(*SS*)/Λ(*RR*) isomer of the *rac*(P)-L^2 complex was formed. The same reaction with L^1 did not yield the Δ(*SS*)/Λ(*RR*) isomer.[7] However, reactions of *cis*-α-[$CoCl_2${*rac*(P)-L}]$^+$ (L = L^1 or L^2) with Li(acac) in a molar ratio of 1 : 3 in the absence of active charcoal yielded a mixture of Δ(*RR*)/Λ(*SS*)- and Δ(*SS*)/Λ(*RR*)-[Co(acac)$_2${*rac*(P)-L}]$^+$. Although the two isomers were not separated by column chromatography, their molar ratio was estimated to be Δ(*RR*)Λ(*SS*) : Δ(*SS*)/Λ(*RR*) = 2 : 1 for both the L^1 and L^2 complexes from the intensity ratio of the methine proton of acac in the ^{1}H NMR spectra. Thus, [Co(acac)$_2${*rac*(P)-L}]$^+$ seems to be more stable in the Δ(*RR*)/Λ(*SS*) than the Δ(*SS*)/Λ(*RR*) isomer. In the Δ(*RR*)Λ(*SS*) isomer the phenyl group of the SPPS ligand is located over the acac chelate ring as indicated by the high-field shift of the methine proton of acac. This structure may be more stable than that of the other Δ(*SS*)/Λ(*RR*) isomer where the CH_2CH_2SMe group is located over the acac chelate ring.

Conclusion

This study has revealed that L^1 and L^2 bearing only soft donor groups can function as a tetradentate ligand to a hard cobalt(III) ion to afford complexes of various geometrical isomers (*trans*, *cis*-α, and *cis*-β). The co-ordination modes are governed specifically by the absolute configurations of the inner chiral phosphorus atoms and the conformations of the P–Co–P chelate rings. Several complexes in which the SPPS compounds co-ordinate as didentate ligands through two phosphorus atoms were obtained (complexes **1**, **5**, **11** and **12**), such co-ordination modes not being observed for the corresponding NPPN compounds. The isomerization equilibrium between the *cis*-α and *cis*-β isomers of acac complexes was observed also only for the SPPS-type ligands and not the NPPN-type ones. These differences in behaviour may be caused by the weaker co-ordination ability of thioether than amino groups to a cobalt(III) ion.

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