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Co(III) and Cr(III) complexes of diphosphadithia ligands and the crystal structure of $[CoCl_2(L^3)]PF_6 \cdot CH_2Cl_2$ $(L^3=Ph_2P(CH_2)_2S(o-C_6H_4)S(CH_2)_2PPh_2)$

Julie Connolly, Robin J. Forder, Geoffrey W. Goodban, Simon J.A. Pope, Martin Predel, Gillian Reid*

Department of Chemistry, University of Southampton, Highfield, Southampton SO17 1BJ, UK

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Abstract

 $[CrX_3(thf)_3]$ (X=Cl or Br) reacts with L (L=L¹-L³ or Ph₂[14]aneP₂S₂) (L¹=Ph₂P(CH₂)₂S(CH₂)₂S(CH₂)₂PPh₂, L²= Ph₂P(CH₂)₂S(CH₂)₂S(CH₂)₂PPh₂, L³=Ph₂P(CH₂)₂S(o-C₆H₄)S(CH₂)₂PPh₂, Ph₂[14]aneP₂S₂=4,8-diphenyl-1,11-dithia-4,8-diphosphacyclotetradecane) and TlPF₆ in MeNO₂ solution to yield the distorted octahedral complexes [CrX₂(L)]PF₆ as green coloured solids in high yield. UV/visible spectroscopy suggests that these are *cis*-dihalo species and they have also been characterised by IR spectroscopy, electrospray mass spectrometry and microanalyses. The Co(III) analogues $[CoX_2(L)]^+$ are readily prepared in a two-stage reaction, involving treatment of $CoX_2 \cdot 6H_2O$ with L (L=L¹-L³) and NH₄PF₆ in EtOH solution to give a green/brown solid, followed by halogen oxidation of this product in CH₂Cl₂ solution using X₂/CCl₄, to give the final products as brown coloured solids. A mixture of PF₆⁻ and $[CoX_4]^{2-}$ anions are present in the final Co(III) compounds in varying ratios. Crystal structures of $[CoCl_2(L^2)]_2[CoCl_4] \cdot 4H_2O$ and $[CoCl_2(L^3)]PF_6 \cdot CH_2Cl_2$ confirm tetradentate P₂S₂ coordination of L in each case, with mutually *cis* halogens completing the distorted octahedral geometry. In both cases the complex cation adopts the *cis*- α form in the solid state and this is also consistent with the solution ³¹P{¹H} NMR spectroscopic data. ⁵⁹Co NMR spectroscopy reveals a very broad single resonance at ≈3200 ppm for these species. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Mixed phosphathia ligands; Cr(III) and Co(III) complexes; Crystal structure

1. Introduction

Recently we have been interested in investigating the binding characteristics of mixed phosphathia ligands such as L^1-L^3 ($L^1=Ph_2P(CH_2)_2S(CH_2)_2S(CH_2)_2Ph_2$, $L^2=Ph_2P(CH_2)_2S(CH_2)_3S(CH_2)_2PPh_2$, $L^3=Ph_2P(CH_2)_2S(o-C_6H_4)S(CH_2)_2PPh_2$) and the macrocyclic analogue $Ph_2[14]$ ane P_2S_2 (4,8-diphenyl-1,11-dithia-4,8-diphosphacyclotetradecane) with a variety of transition metal centres. The majority of our work to-date has focused upon the platinum group metals, e.g., the square planar $[M(L)]^{2+}$ and octahedral $[PtX_2(L)]^{2+}$ (M=Pd, Pt; $L=L^1-L^3$ or $Ph_2[14]$ ane P_2S_2 ; X=Cl or Br), $[M'Cl_2(L)]^+$ (M'=Rh or Ir) and RuCl_2(L)], as well as complexes involving the group 11 elements, including for example tetrahedral

 $[Cu(L)]^+$ and the helical dinuclear species $[Au_2(L^1)_2]Cl_2$, which incorporates a Cl⁻ anion within the metallocyclic cavity [1-6]. However, complexes involving these and other phosphathia ligands with 3d metal ions such as Co(III) and Cr(III) are rather less common. The preparation of the Co(II) species [CoX{Ph₂P(CH₂)₃S(CH₂)₃- $S(CH_2)_2PPh_2$ BPh₄ (X=Cl, Br or I) [7] and Co(II) and Co(III) complexes involving the bidentate 0- $C_6H_4(PPh_2)(SMe)$ [8] have been reported. Also, Ciampolini and co-workers have reported the preparation of several Co(II) complexes involving the hexa-coordinated P_4S_2 -donor macrocycles [9–13]. A range of Cr(III) complexes involving coordinated phosphine or thioether ligands are known, including several macrocyclic thioether derivatives, several of which have also been structurally characterised [14-21].

We report herein the preparation and spectroscopic characterisation of a range of distorted octahedral Cr(III) and Co(III) complexes involving the phosphathia ligands L^1-L^3 and the macrocycle Ph₂[14]aneP₂S₂, of general

^{*}Corresponding author. Tel.: +44-170-359-5000; fax: +44-170-359-3781.

E-mail address: gr@soton.ac.uk (G. Reid)

formula $[MX_2(L)]PF_6$, including the crystal structures of $[CoCl_2(L^3)]PF_6$ ·CH₂Cl₂ and $[CoCl_2(L^2)]_2[CoCl_4]$ ·4H₂O.

2. Results and discussion

Reaction of $[CrX_3(thf)_3]$ (X=Cl or Br) with one molar equivalent of L (L= L^1 - L^3 or Ph₂[14]aneP₂S₂) in anhydrous MeNO₂ solution and in the presence of one molar equivalent of TIPF₆, gave a deep green or brown solution and a white precipitate (TIX). After removal of the TIX and concentration of the solution, dry Et₂O was added to afford green or brown powdered solids in high yield. These compounds are stable in the solid state as long as they are protected from a moist atmosphere. Similarly, they are quite stable in anhydrous solvents and are soluble in MeNO₂, MeCN and acetone. Their electrospray mass spectra (MeCN) show intense peaks, with the correct isotope pattern corresponding to $[CrX_2(L)]^+$. IR spectra were recorded as Nujol mulls and show peaks associated with the non-coordinating PF_6^- anion (840 and 558 cm⁻¹) as well as peaks associated with L and $\nu(Cr-X)/\nu(Cr-S/$ P) below 400 cm⁻¹. Together with microanalytical data, these results indicate the successful formation of the products [CrX₂(L)]PF₆, involving a distorted octahedral $P_2S_2X_2$ donor set at Cr(III). For an octahedral d³ metal ion, theory predicts three spin allowed d-d transitions although, in practice, usually only the two at lower energy $({}^{4}A_{2g} \rightarrow {}^{4}T_{2g} \text{ and } {}^{4}A_{2g} \rightarrow {}^{4}T_{1g}(F))$ are observed, the third $({}^{4}A_{2\sigma} \rightarrow {}^{4}T_{1\sigma}(P))$ being obscured by more intense charge transfer transitions [22]. For the Cr(III) compounds reported here we observe two d-d transitions and their energies are similar to those observed for other Cr(III) phosphine and thioether complexes and are consistent with the relatively soft $P_2S_2X_2$ donor set at Cr(III) [14-21]. Furthermore, since no splittings of these bands are observed, the compounds are assigned as cis isomers (trans isomers usually exhibit marked splittings). For octahedral complexes involving $L^1 - L^3$, three gross geometric isomers are possible, $cis - \alpha$, $cis - \beta$ and *trans*. The $cis \alpha$ arrangement has been observed for several other octahedral complexes involving L^1 , L^2 and L^3 , e.g., cis-[RhCl₂(L^1)]⁺, cis- $[\operatorname{RuCl}_2(L^1)]^2$, cis- $[\operatorname{CoCl}_2(L^2)]^+$ and $[\operatorname{CoCl}_2(L^3)]^+$ (see below), thus it seems likely that the Cr(III) complexes involving $L^1 - L^3$ ligation also adopt the *cis*- α form. Since these Cr(III) species are paramagnetic, NMR spectroscopy cannot be used to confirm which isomer is adopted, and attempts to obtain crystals of these rather unusual complexes involving coordination of the soft phosphathia ligands to hard Cr(III) ions were unsuccessful.

The Co(III) complexes were prepared in a two-step procedure from CoX_2 . Thus, equimolar quantities of CoX_2 (X=Cl or Br) and NH_4PF_6 were dissolved in degassed EtOH. One molar equivalent of L (L=L¹, L² or L³) was then added. After work-up, a dark green solid was ob-

tained. A solution of this species in CH₂Cl₂ was then treated with excess X_2 (X=Cl or Br) in CCl₄ to give a brown solution, which yielded a brown solid upon addition of Et₂O. The electrospray mass spectra for these final products each show peaks with the correct isotopic distribution for $[CoX_2(L)]^+$. IR spectroscopy shows peaks due to the coordinated L, and in some cases only weak absorptions due to PF_6^- counter anion (840 and 558 cm⁻¹). This suggests that while PF_6^- acts as the counterion in some cases, in others an alternative anion is present, probably $[CoX_4]^{2-}$. The presence of this anion is clearly identified in the crystal structure of $[CoCl_2(L^2)]_2[CoCl_4]$. $4H_2O$ (see below). This type of partial decomposition to produce some $[CoX_4]^{2-}$ counterion has been observed previously for other Co(III) complexes¹⁵ and, consequently, severely hinders attempts to obtain meaningful microanalytical data for these compounds.

³¹P{¹H} NMR spectra were also recorded for the Co(III) compounds (Table 1). In each case a singlet is observed due to the coordinated ligand L (L=L¹-L³) and the large, positive coordination shift ($\delta_{complex} - \delta_{ligand}$) is indicative of the P donor atoms being part of a five-membered chelate ring, thus confirming tetradentate P₂S₂ coordination in solution [24]. The presence of a single resonance precludes the existence of the *cis*-β isomer for these species, although it does not distinguish between the *trans* and *cis*-α forms. In some cases a septet at approximately -145 ppm is also observed due to PF₆⁻. Although, for the reasons discussed above, the relative integrals of the L:PF₆⁻ resonances does not indicate a stoichiometric PF₆⁻ anion.

⁵⁹Co NMR spectroscopy (I=7/2, 100%) has previously been shown to be a useful technique for the characterisation of cobalt(III) dihalogeno complexes of group 15 and 16 donor ligands, although the relatively high quadrupole moment results in significant broadening of the resonances [23,25-27]. For the complexes prepared in this work we observe a very broad resonance at \approx 3200 ppm, $w_{1/2} \approx$ 10 000-20 000 Hz. These chemical shifts compare with shifts in the range 7062-7384 ppm for $[CoX_2([14]aneS_4)]^+$ $([14]aneS_4 = 1, 4, 8, 11$ -tetrathiacyclotetradecane) [25] and 8436-9590 ppm for [CoX2- $([16]aneSe_4)]^+$ (X=Cl, Br or I; [16]aneSe_4=1,5,9,13tetraselenacyclohexadecane) [26]. The previously reported phosphathia ligand complexes trans-[CoCl₂{o-

Table 1 ${}^{31}P{}^{1}H$ and ${}^{59}Co$ NMR spectroscopic data^a

	$\delta({}^{31}P{}^{1}H)/ppm$	$\delta(^{59}\text{Co})/\text{ppm}$	$w_{1/2}/\mathrm{Hz}$
$[CoCl_2(L^1)]^+$	40.7	3410	10 500
$[\text{CoBr}_2(\text{L}^1)]^+$	40.7	3420	10 000
$[\text{CoCl}_2(\text{L}^2)]^+$	45.5	3390	20 000
$[\text{CoBr}_2(\text{L}^2)]^+$	46.5	3290	20 000
$[\text{CoCl}_2(\text{L}^3)]^+$	53.6	3210	20 000
$[\text{CoBr}_2(\text{L}^3)]^+$	56.5	3180	17 000

 a Spectra recorded in MeCN/CDCl $_3$ at 145.8 and 85.6 MHz, respectively, for $^{31}\text{P}[^1\text{H}]$ and $^{59}\text{Co.}$

 $C_6H_4(PPh_2)(SMe)$]BF₄ show $\delta(^{59}Co)=3475$ (X=Cl) and 3430 (X=Br) ppm [28] and the line widths for these species are comparable with the $w_{1/2}$ values found for $[CoX_2(L)]^+$. These are considerably larger than those observed for the thioether and selenoether macrocyclic complexes, reflecting the high dependence of the linewidths upon subtle changes in the electric field gradient at the metal centre. Cobalt-59 NMR data have been obtained for a range of Co(III) phosphine complexes [27], e.g., $[Co(Me_2PCH_2CH_2PMe_2)_3]^{3+} \delta(^{59}Co) -2530 (w_{1/2} 10\,000 \text{ Hz})$ and *trans*- $[CoCl_2(Me_2PCH_2CH_2PMe_2)_2]^+ \delta(^{59}Co) + 1660 (14\,000)$.

In order to confirm the stereochemistry at Co(III), the ligand conformation and the bond length and angle distributions, single crystal X-ray structure analyses were undertaken on two samples, $[CoCl_2(L^3)]PF_6 \cdot CH_2Cl_2$ and $[CoCl_2(L^2)]_2[CoCl_4] \cdot 4H_2O$. Crystals were grown by diffusion of Et₂O into a solution of the appropriate complex in CH₂Cl₂. The structure of the former shows (Fig. 1, Table 2) the Co(III) ion coordinated to a distorted octahedral $P_2S_2Cl_2$ donor set. The complex cation adopts the *cis*- α form, with the P-donor atoms *trans* to one another and the S-donor atoms trans to the Cl ligands, consistent with the solution spectroscopic data. A PF₆⁻ anion maintains electroneutrality. The bond lengths around the Co ion reveal that $d(\text{Co}-\text{S}) \le d(\text{Co}-\text{Cl}) \le d(\text{Co}-\text{P})$, a similar trend is observed in $cis-\alpha$ -[RhCl₂(L¹)]⁺ and in $cis-\alpha$ -[RuCl₂(L¹)]² and is attributed to the greater trans influence of S(thioether) over Cl in these species. The angles involved in the five-membered chelate rings are only marginally smaller than the ideal 90°, indicating that the ligand is well suited to the ionic radius of Co(III).



Fig. 1. View of the structure of $[CoCl_2(L^3)]^+$ with the numbering scheme adopted. Ellipsoids are drawn at the 40% probability level.

Table 2 Selected bond lengths and angles for $[CoCl_2(L^3)]^+$

Bond lengths (Å)			
Co(1)-Cl(1)	2.269(3)	Co(1)-Cl(2)	2.252(2)
Co(1) - S(1)	2.202(3)	Co(1) - S(2)	2.207(3)
Co(1) - P(1)	2.281(3)	Co(1)–P(2)	2.269(3)
Bond angles (°)			
Cl(1)-Co(1)-Cl(2)	97.3(1)	Cl(1)-Co(1)-S(1)	176.5(1)
Cl(1)-Co(1)-S(2)	86.5(1)	Cl(1)-Co(1)-P(1)	87.7(1)
Cl(1)-Co(1)-P(2)	89.8(1)	Cl(2)-Co(1)-S(1)	84.2(1)
Cl(2)-Co(1)-S(2)	175.4(1)	Cl(2)-Co(1)-P(1)	92.2(1)
Cl(2)-Co(1)-P(2)	90.7(1)	S(1)-Co(1)-S(2)	92.2(1)
S(1)-Co(1)-P(1)	89.0(1)	S(1)-Co(1)-P(2)	93.4(1)
S(1)-Co(1)-P(1)	90.6(1)	S(2)-Co(1)-P(2)	86.6(1)
P(1)-Co(1)-P(2)	176.4(1)		

The crystals of $[CoCl_2(L^2)]_2[CoCl_4] \cdot 4H_2O$ were rather poor quality and hence the data were weak and the final residuals higher than normal. However, the analysis¹ was sufficient to establish unambiguously the coordination geometry at Co(III) and the nature of the anion present. The structure shows (Fig. 2) a very similar coordination geometry to that above, with the Co(III) centre coordinated to a distorted octahedral $P_2S_2Cl_2$ donor set with the ligand in the *cis*- α form. A tetrahedral $[CoCl_4]^{2-}$ anion on a two-fold site maintains electroneutrality in this case, despite the addition of PF_6^- during the reaction (see above). The bond lengths around the metal ion in the Co(III) cations are similar to those in $cis-\alpha-[CoCl_2(L^3)]^+$ above, with $d(Co-S) \le d(Co-P)$, however, more detailed comparisons of the geometric parameters are not justified for this rather poor quality crystal.

These results confirm that the acyclic phosphathia ligands L^1-L^3 and $Ph_2[14]aneP_2S_2$ coordinate readily to the 3d metal ions Cr(III) and Co(III) via both the P- and S-donor atoms, giving tetradentate binding. The resultant distorted octahedral complexes probably all exist as *cis* isomers, with those involving L^1-L^3 adopting the *cis*- α form and involving a $P_2S_2X_2$ donor set. The new compounds are relatively stable both in solution and in the solid state.

 $^{{}^{1}}C_{62}H_{76}Co_{3}Cl_{8}O_{6}P_{4}S_{4}$ – blue-green crystal (0.25×0.15×0.10 mm), M =1597.8, monoclinic, space group $C_{2/c}$, a=31.495(3), b=15.197(5), c=1.448 g cm⁻³, $\mu = 12.07$ cm⁻¹, F(000) = 3284, T = 150 K. Rigaku AFC7S four-circle diffractometer, graphite monochromated Mo Ka radiation, 6271 unique data. The structure was solved by heavy atom Patterson methods [29] and expanded using Fourier techniques [30] to reveal one $[CoCl_{2}(L^{2})]^{+}$ cation occupying a general position, one half $[CoCl_{4}]^{2}$ anion occupying a two-fold site and two solvent H₂O molecules. At isotropic convergence the data were corrected for absorption using DIFABS [31]. All non-H atoms refined anisotropically, H atoms included in fixed, calculated positions [d(C-H)=0.96 Å] (the H atoms associated with the H2O solvent molecules were not located and therefore were omitted from the final structure factor calculation), 1740 observed reflections with $(I \ge 2.0\sigma(I))$, 219 variables, R = 0.097, $R_w = 0.105$, $w^{-1} =$ $\sigma^2(F).$



Fig. 2. View of the structure of $[CoCl_2(L^2)]^+$ with the numbering scheme adopted. Ellipsoids are drawn at the 40% probability level. Co-Cl(1)=2.25(1), Co-Cl(2)=2.257(9), Co-S(1)=2.22(1), Co-S(2)=2.27(1), Co-P(1)=2.28(1), Co-P(2)=2.26(1) Å.

3. Experimental

Infrared spectra were measured as KBr or CsI discs or as Nujol mulls between CsI plates using a Perkin-Elmer 983G spectrometer over the range $200-4000 \text{ cm}^{-1}$. Mass spectra were run by fast atom bombardment (FAB) using a VG Analytical 70-250-SE normal-geometry double-focusing spectrometer or by positive electrospray using a VG Biotech Platform. ¹H NMR spectra were recorded using a Bruker AM300 spectrometer operating at 300 MHz. ³¹P{¹H} and ⁵⁹Co NMR spectra were recorded in 10 mm O.D. tubes containing $\approx 10\%$ deuterated solvent, using a Bruker AM360 spectrometer operating at 145.8 and 85.6 MHz and are referenced to external 85% H_3PO_4 [δ (³¹P)= 0] and external aqueous $[Co(CN)_6]^{3-}$ respectively. Microanalyses were performed by the University of Strathclyde microanalytical service, although, as discussed in the text, facile rearrangement of the Co(III) complexes resulted in some $[CoX_4]^{2-}$ acting as counterion, and precluded satisfactory microanalytical data. This behaviour is well known in cobalt coordination chemistry.¹⁵ L¹-L³ and $Ph_2[14]aneP_2S_2$ were prepared by the literature procedures.

4.1. Preparations

4.1.1. $[CrCl_2(L^1)]PF_6$

To a stirring solution of $[CrCl_3(thf)_3]$ (0.09 g, 0.24 mmol) in dry, degassed MeNO₂ (20 cm³) was added

TIPF₆ (0.085 g, 0.24 mmol) and L¹ (0.12 g, 0.24 mmol). Stirring for ≈ 2 h gave a white precipitate (TICl) which was removed by filtration, leaving a green solution. After concentrating this solution in vacuo, Et₂O was added to afford a dark green solid (Yield 0.10 g, 54%). Required for [C₃₀H₃₂Cl₂CrF₆P₃S₂] C, 45.8; H, 4.1; found: C, 45.4; H, 4.0%. Electrospray mass spectrum (MeCN): found m/z =640; calculated for [⁵²Cr³⁵Cl₂(L¹)]⁺ m/z = 640. IR spectrum (nujol): 834 s, 556 s, 353 br,w (cm⁻¹). UV-visible spectrum (BaSO₄/cm⁻¹): 16 950, 21 370.

4.1.2. $[CrBr_2(L^1)]PF_6$

Yield 51%. Required for $[C_{30}H_{32}Br_2CrF_6P_3S_2]$ C, 41.1; H, 3.7; found: C, 41.6; H, 3.9%. Electrospray mass spectrum (MeCN): found m/z=730; calculated for $[{}^{52}Cr^{79}Br_2(L^1)]^+ m/z=728$. IR spectrum (nujol): 836 s, 556 s, 320 w (cm⁻¹). UV-visible spectrum (BaSO₄/ cm⁻¹): 16 470, 20 370.

4.1.3. $[CrCl_2(L^2)]PF_6$

Yield 45%. Required for $[C_{31}H_{34}Cl_2CrF_6P_3S_2]$ C, 48.1; H, 4.5; found: C, 49.1; H, 4.8%. Electrospray mass spectrum (MeCN): found m/z=654; calculated for $[{}^{52}Cr^{35}Cl_2(L^2)]^+ m/z=654$. IR spectrum (nujol): 840 s, 557 s, 348 br, w (cm⁻¹). UV–visible spectrum (BaSO₄/ cm⁻¹): 15 360, 20 880.

4.1.4. $[CrBr_2(L^2)]PF_6$

Yield 62%. Required for $[C_{31}H_{34}Br_2CrF_6P_3S_2]$ C, 43.2; H, 4.0; found: C, 43.0; H, 4.0%. Electrospray mass spectrum (MeCN): found m/z = 744; calculated for $[{}^{52}Cr^{79}Br_2(L^2)]^+ m/z = 742$. IR spectrum (nujol): 837 s, 557 s, 283 br, w (cm⁻¹). UV–visible spectrum (BaSO₄/ cm⁻¹): 14 470, 19 120.

4.1.5. $[CrCl_2(L^3)]PF_6$

Yield 60%. Required for $[C_{34}H_{32}Cl_2CrF_6P_3S_2]$ C, 48.9; H, 3.8; found: C, 48.9; H, 3.8%. Electrospray mass spectrum (MeCN): found m/z = 688; calculated for $[{}^{52}Cr^{35}Cl_2(L^3)]^+ m/z = 688$. IR spectrum (nujol): 836 s, 556 s, 368 w, 348 w (cm⁻¹). UV/visible spectrum (BaSO₄/cm⁻¹): 16 720, 21 280.

4.1.6. $[CrBr_2(L^3)]PF_6$

Yield 40%. Required for $[C_{34}H_{32}Br_2CrF_6P_3S_2]$ C, 44.2; H, 3.5; found: C, 44.5; H, 3.6%. Electrospray mass spectrum (MeCN): found m/z = 778; calculated for $[{}^{52}Cr^{79}Br_2(L^3)]^+ m/z = 776$. IR spectrum (nujol): 835 s, 556 s, 319 w (cm⁻¹). UV–visible spectrum (BaSO₄/ cm⁻¹): 16 260, 20 410.

4.1.7. [CrCl₂(Ph₂[14]aneP₂S₂)]PF₆

Yield 71%. Required for $[C_{22}H_{30}Cl_2CrF_6P_3S_2]$ C, 38.4; H, 4.4; found: C, 38.5; H, 4.2%. Electrospray mass spectrum (MeCN): found m/z = 542, 421; calculated for $[{}^{52}Cr^{35}Cl_2(Ph_2[14]aneP_2S_2)]^+ m/z = 542$, $[Ph_2[14]ane-$ P_2S_2]⁺ m/z=420. IR spectrum (nujol): 840 s, 557 s, 348 br,w (cm⁻¹). UV-visible spectrum (BaSO₄/cm⁻¹): 16 750, 23 100.

4.1.8. $[CrBr_2(Ph_2[14]aneP_2S_2)]PF_6$

Yield 62%. Required for $[C_{33}H_{40}Br_2CrF_6P_3S_2]$ C, 34.0; H, 3.9; found: C, 33.5; H, 3.5%. IR spectrum (nujol): 835 s, 557 s, 315 br, w (cm⁻¹). UV–visible spectrum (BaSO₄/cm⁻¹): 16 290, 22 730.

4.1.9. $[CoCl_2(L^1)]^+$

 $CoCl_2 \cdot 6H_2O$ (0.046 g, 0.19 mmol) and NH_4PF_6 (0.063 g, 0.39 mmol) were dissolved in degassed EtOH (10 cm^3). L^{1} (0.100 g, 0.19 mmol) was added and the resulting mixture was stirred for 3 h to give a green solution. Concentration of the solution in vacuo, followed by addition of Et₂O gave a green solid. This compound was then dissolved in CH_2Cl_2 (4 cm³) and excess Cl_2 in CCl_4 was added. The mixture was stirred for 1 h, yielding a brown solid which was filtered, washed with Et₂O and dried in vacuo. FAB mass spectrum (3-NOBA): found m/z = 647, 612, 577; calculated for $[Co^{35}Cl_2(L^1)]^+ m/z =$ 647, $[\text{Co}^{35}\text{Cl}(\text{L}^{1})]^{+} m/z = 612$, $[\text{Co}(\text{L}^{1})]^{+} m/z = 577$. ¹H NMR: δ 7.0–8.0 (*m*, Ph, 20H), 2.0–3.5 (*m*, CH₂, 12H). IR spectrum (CsI disk): 3060 w, 2980 w, 2930 w, 1481 m, 1432 s, 1408 w, 1093 s, 998 w, 840 vs, 743 s, 697 s, 558 s, 521 s, 490 w, 312 w, 298 w (cm $^{-1}$).

4.1.10. $[CoBr_2(L^1)]^+$

FAB mass spectrum (3-NOBA): found m/z = 737, 658, 577; calculated for $[\text{Co}^{79}\text{Br}_2(\text{L}^1)]^+ m/z = 735$, $[\text{Co}^{79}\text{Br}(\text{L}^1)]^+ m/z = 656$, $[\text{Co}(\text{L}^1)]^+ m/z = 577$. ¹H NMR: δ 7.1–8.1 (*m*, Ph, 20H), 2.1–3.6 (*m*, CH₂, 12H). IR spectrum (CsI disk): 3050 w, 2980 w, 2920 w, 1481 m, 1431 s, 1093 m, 998 w, 840 vs, 744 s, 703 s, 558 s, 520 s, 490 w, 298 w (cm⁻¹).

4.1.11. $[CoCl_2(L^2)]^+$

Electrospray mass spectrum (MeCN): found m/z = 661, 626; calculated for $[\text{Co}^{35}\text{Cl}_2(\text{L}^2)]^+ m/z = 661$, $[\text{Co}^{35}\text{Cl}(\text{L}^2)]^+ m/z = 626$. ¹H NMR: δ 7.1–8.0 (m, Ph, 20H), 2.0–3.3 (br m, CH₂, 14H). IR spectrum (CsI disk): 3057 w, 2970 w, 2926 w, 1568 w, 1482 m, 1432 s, 1162 s, 1095 s, 1040 m, 998 w, 920 w, 894 w, 851 w, 820 m, 745 s, 690 s, 525 s, 483 w, 422 w, 406 w, 366 w, 336 w, 306 w, 297 w (cm⁻¹).

4.1.12. $[CoBr_2(L^2)]^+$

Electrospray mass spectrum (MeCN): found m/z=751, 698; calculated for $[\text{Co}^{79}\text{Br}_2(\text{L}^2)]^+$ m/z=749, $[\text{Co}^{79}\text{Br}(\text{L}^2)]^+$ m/z=695. ¹H NMR: δ 7.0–7.8 (br m, Ph, 20H), 1.8–3.2 (br m, CH₂, 14H). IR spectrum (CsI disk): 3054 w, 2970 w, 298 w, 1481 m, 1431 s, 1408 s, 1261 w, 1092 s, 998 w, 907 w, 814 m, 743 s, 693 s, 522 s, 485 w, 297 w (cm⁻¹).

4.1.13. $[CoCl_2(L^3)]^+$

Electrospray mass spectrum (MeCN): found m/z=695; calculated for $[\text{Co}^{35}\text{Cl}_2(\text{L}^3)]^+ m/z=695$. ¹H NMR: δ 7.1– 8.1 (br, *m*, aromatic CH, 24H), 2.4–3.5 (*m*, CH₂, 8H). IR spectrum (KBr disk): 3056 w, 2968 w, 2920 w, 2852 w, 1486 m, 1459 m, 1435 s, 1410 sh, 1359 s, 1263 w, 1194 w, 1094 m, 998 w, 839 s, 753 w, 742 m, 695 m, 668 m, 614 w, 558 m, 526 m, 497 w, 403 w (cm⁻¹).

4.1.14. $[CoBr_2(L^3)]^+$

Electrospray mass spectrum (MeCN): found m/z = 785; calculated for $[\text{Co}^{79}\text{Br}_2(\text{L}^3)]^+ m/z = 783$. ¹H NMR: δ 7.2–8.2 (br, *m*, aromatic CH, 24H), 2.6–3.5 (br *m*, CH₂, 8H). IR spectrum (KBr disk): 3056 w, 2964 w, 2924 w, 1569 w, 1433 m, 1404 m, 1359 s, 1264 w, 1092 m, 992 w, 850 m, 833 m, 808 m, 752 w, 745 m, 712 w, 695 m, 668 w, 613 w, 546 w, 524 m, 486 w (cm⁻¹).

4.2. X-ray crystallography

Details of the crystallographic data collection and refinement parameters are given in Table 3. Crystals of $[CoCl_2(L^3)]PF_6 \cdot CH_2Cl_2$ were grown by vapour diffusion of diethyl ether into solutions of the complexes in CH₂Cl₂. Data collection used a Rigaku AFC7S four-circle diffractometer operating at 150 K, using graphite monochromated

Table 3 Crystallographic data collection and refinement parameters

	$[CoCl_2(L^3)]PF_6 \cdot CH_2Cl_2$
Formula	$C_{35}H_{34}Cl_4CoF_6P_3S_2$
Μ	926.43
Colour, morphology	Deep red, column
Crystal dimensions (mm)	$0.55 \times 0.20 \times 0.10$
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	16.263(3)
<i>b</i> (Å)	12.632(3)
<i>c</i> (Å)	19.198(3)
β (°)	103.39(1)
$U(\text{\AA}^3)$	3836(1)
Ζ	4
F(000)	1880
$D_{c} (g \ cm^{-3})$	1.604
μ (Mo K α , cm ⁻¹)	10.16
$2\theta_{\rm max}$ (°)	50
Unique obs. reflections	7103
$R_{\rm int}$ (based on F^2)	0.074
Obs. reflections	3109
with $[I_0 > 2\sigma(I_0)]$	
No. of parameters	455
Goodness of fit	2.14
R ^a	0.057
R _w ^b	0.061
Final $\Delta(\sigma)$	0.01
Max. residual peak ($e \text{ Å}^{-3}$)	2.25
Max, residual trough (e $Å^{-3}$)	-0.67

^a $R = \Sigma(|F_{\text{obs}}|_i - |F_{\text{calc}}|_i) / \Sigma |F_{\text{obs}}|_i$

^b $R_w = \sqrt{[\Sigma w_i (|F_{obs}|_i - |F_{calc}|_i)^2 / \Sigma w_i |F_{obs}|_i^2]}.$

Mo K α X-radiation (λ =0.71073 Å). No significant crystal decay or movement was observed. The structure was solved by heavy atom Patterson methods [29] and developed by iterative cycles of full-matrix least-squares refinement and difference Fourier syntheses which located all non-H atoms [30]. A CH₂Cl₂ solvent molecule was also identified in the asymmetric unit. All non-H atoms (except the C atom in the CH₂Cl₂ molecule) were refined anisotropically. H-atoms were placed in fixed, calculated positions with d(C-H)=0.96 Å. The weighting scheme $w^{-1} = \sigma^2(F)$ gave satisfactory agreement analyses. Selected bond lengths and angles are presented in Table 2.

Supplementary data

Supplementary data are available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK on request, quoting the deposition number 132712.

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