Syntheses, Structures and Properties of Tri-*n*-butylphosphine Cobalt Complexes containing *o*-Benzenedithiolate Ligands in Unusual Co-ordination Modes[†]

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The complex $[Co_3(bdt)_3(PBu^n{}_3)_3]$ **1** (H_2bdt = benzene-1,2-dithiol) was obtained by the reaction of $CoCl_2$, Na_2bdt and $PBu^n{}_3$ in 1:1:2 molar ratio in methanol. It crystallizes in triclinic space group $P\bar{1}$ with a = 13.694(4), b = 18.460(4), c = 13.656(4) Å, α = 100.69(2), β = 108.68(2), γ = 85.06(2)°, Z = 2, from 6366 reflections with $I > 3\sigma(I)$, final $R(R')$ = 0.059 (0.066). The Co_3 atoms form an isosceles triangle with rather short Co–Co bonds. The bdt ligands either bridge between two Co atoms or strongly chelate terminally to one Co atom and simultaneously bridge weakly to the others. Restricted air oxidation of **1** results in the isolation of $[PHBu^n{}_3][Co(bdt)_2(PBu^n{}_3)]$ **2**, which crystallizes in triclinic space group $P\bar{1}$ with a = 10.800(3), b = 13.533(4), c = 15.342(2) Å, α = 96.37(2), β = 108.57(2), γ = 97.02(2)°, Z = 2, from 3801 reflections with $I > 3\sigma(I)$, $R(R')$ = 0.086 (0.088). The Co atom is in a square-pyramidal co-ordination environment with P in the axial position. The $PBu^n{}_3$ group dissociates easily in dimethyl sulphoxide yielding paramagnetic $[Co(bdt)_2]^-$ **3** with square-planar cobalt co-ordination. Proton NMR data are discussed and cyclic voltammetry data reported.

Cobalt complexes with mixed phosphine and thiolate ligands have not been widely investigated except for a few early reports on the spectroscopic properties and reactivity of dithiolene complexes.[1–3] Balch[1,2] and Schrazuer *et al*[3] have studied the magnetic, electronic, and ligand-exchange properties of mononuclear complexes $[Co(S_2C_2R_2)_2L]^{z-}$ and $[Co(S_2C_2R_2)_2L_2]^-$ [R = CF_3 or Ph; L = PPh_3, $PBu^n{}_3$ or $P(OEt)_3$]. A new complex of this type, $[Co_2(dppe)(SPh)_4]$ [dppe = 1,2-bis(diphenylphosphino)ethane] containing asymmetrical cobalt ligations, has been obtained from bidentate phosphine and monodentate thiolate ligands.[4] The structure of $[Co(SPh)_3(PPh_3)]^-$ has recently been determined.[5] We have synthesised a trinuclear complex with simultaneous ligations of monodentate phosphine and bidentate thiolate from the reaction of the two reagents with cobalt chloride. The complex breaks down to mononuclear $[Co(bdt)_2(PBu^n{}_3)]^-$ (H_2bdt = benzene-1,2-dithiol) on oxidation. Here we report their syntheses, crystal structures, ^1H NMR and cyclic voltammetry (CV) studies.

Results and Discussion

Synthesis.—The complex $[Co_3(bdt)_3(PBu^n{}_3)_3]$ **1** was obtained from the reaction of $CoCl_2$, bdt^{2-} and $PBu^n{}_3$ in 1:1:2 molar ratio under anaerobic conditions. Reactant ratios of 1:1:1 or 1:2:1 did not give product **1**, while a ratio of 1:2:2 yielded only a small amount of **1**. These results show that a two-fold excess of $PBu^n{}_3$ relative to $CoCl_2$ is necessary to give **1** as the major product, yet an excess of bdt is disadvantageous. When a measured quantity of air is allowed to enter the reaction system or if the reaction solution is exposed to air for a suitable length of time, $[PHBu^n{}_3][Co(bdt)_2(PBu^n{}_3)]$ **2** is obtained which is very possibly the oxidation–decomposition product of **1**. Oxidation of cobalt(II) amine complexes to mononuclear cobalt(III) complexes by O_2 has been reported.[6]

If complex **1** is recrystallized from CH_2Cl_2 instead of obtained directly from the reaction solution of MeOH, a compound $\mathbf{1}\cdot n CH_2Cl_2$ of essentially the same molecular structure except for the presence of solvate molecules was obtained.

Structure.—The atomic coordinates of complexes **1** and **2** are listed in Tables 1 and 2, respectively. Tables 3 and 4 show selected atomic distances and bond angles. Neglecting the alkyl carbon atoms, atoms Co_3P_3 form a mirror plane in complex **1**. An ORTEP diagram of **1** is depicted in Fig. 1 while Fig. 2 is a side view along the Co_3P_3 plane, both with only the α-carbon atoms of the alkyl groups. The three Co atoms form an isosceles triangle with two long Co–Co bonds [2.546(1) and 2.5545(9) Å] and one short [2.4510(9) Å] to give a mean Co–Co distance of 2.517 Å, similar to that in the only other mixed monodentate phosphine and bidentate thiolate complex $[Co_3(CO)_6(PPh_3)S(S_2COMe)]$[7] (average 2.520 Å). Each Co atom is in a square-pyramidal co-ordination environment with atom P in the apical position and S_4 as the base which is perpendicular to the non-crystallographic symmetry plane. The distance of Co from the basal plane averages 0.50 Å toward P.

The ligand bdt 3 bridging Co(1) and Co(3) bisects and is perpendicular to the Co_3P_3 plane while bdt 1 and 2 are mirror images of each other. The bdt ligands showed unusual co-ordination modes. First bdt 3 bridges two Co atoms with mean Co–S 2.277 Å resulting in an exceptionally short Co(1)–Co(3) bond [2.4510(9) Å], previously observed in carbonyl or cyclopentadienyl complexes such as $[Co_2(CO)_4(dppm)(N_2C_6H_4Me\text{-}p)]^+$ (dppm = $Ph_2PCH_2PPh_2$),[8] [2.440(2) Å], $[Co_3H(CO)_6(PPh_3)_3]$[9] [2.473(3), 2.490(3), 2.453(3) Å], $[Co_3(\eta\text{-}C_5H_5)_3(CO)S]$[10] (average 2.452 Å) and $[Co_4(\eta\text{-}C_5H_5)_4S_2]$[11] [2.438(1) Å]. The Co–Co distance in the mixed bidentate phosphine and monodentate thiolate complex $[Co_2(dppe)(SPh_4)]$[4] [2.632(2) Å] is 0.18 Å longer. The second co-

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[†] *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Table 1 Atomic coordinates and estimated standard deviations for $[Co_3(bdt)_3(PBu^n{}_3)_3]$ **1**

Atom	x	y	z
Co(1)	0.326 6(1)	0.257 25(7)	0.271 69(9)
Co(2)	0.237 4(1)	0.135 50(7)	0.187 22(9)
Co(3)	0.147 73(9)	0.260 29(6)	0.157 01(9)
S(1)	0.313 8(2)	0.164 0(1)	0.359 2(2)
S(2)	0.083 1(2)	0.165 8(1)	0.205 7(2)
S(3)	0.389 8(2)	0.157 7(2)	0.177 4(2)
S(4)	0.157 9(2)	0.161 4(1)	0.027 7(2)
S(5)	0.200 9(2)	0.328 4(1)	0.321 2(2)
S(6)	0.273 5(2)	0.324 5(1)	0.138 9(2)
P(1)	0.471 4(2)	0.308 1(2)	0.374 9(2)
P(2)	0.247 0(3)	0.013 9(2)	0.163 6(2)
P(3)	0.005 0(2)	0.319 5(1)	0.080 7(2)
C(11)	0.209 2(8)	0.181 8(5)	0.410 7(7)
C(12)	0.107 7(8)	0.182 4(5)	0.342 8(7)
C(13)	0.024 0(9)	0.193 5(6)	0.385 2(8)
C(14)	0.046(1)	0.205 5(8)	0.491 9(8)
C(15)	0.146(1)	0.207 4(8)	0.559 5(9)
C(16)	0.229 4(9)	0.195 0(7)	0.519 7(7)
C(21)	0.362 3(8)	0.169 9(6)	0.045 8(7)
C(22)	0.261 1(8)	0.172 2(6)	0.020 0(7)
C(23)	0.240(1)	0.180 1(7)	−0.126 4(8)
C(24)	0.320(1)	0.184 5(8)	−0.164 2(8)
C(25)	0.423(1)	0.182 9(9)	−0.097 4(9)
C(26)	0.444 6(9)	0.174 6(8)	0.006 0(8)
C(31)	0.221 1(7)	0.414 8(5)	0.295 6(8)
C(32)	0.255 1(7)	0.413 2(5)	0.209 3(8)
C(33)	0.275 8(9)	0.479 3(7)	0.180(1)
C(34)	0.257(1)	0.547 1(6)	0.245(1)
C(35)	0.225(1)	0.546 4(7)	0.330(1)
C(36)	0.203 9(9)	0.482 6(5)	0.358 2(9)
C(111)	0.463 1(9)	0.377 8(6)	0.489 7(9)
C(112)	0.421(1)	0.347 0(8)	0.562 3(9)
C(113)	0.406(1)	0.411 2(9)	0.649(1)
C(114)	0.353(2)	0.393(1)	0.713(1)
C(121)	0.534 5(9)	0.364 8(7)	0.315(1)
C(122)	0.562(1)	0.321(1)	0.223(1)
C(123)	0.600(1)	0.370(1)	0.159(1)
C(124)	0.543(2)	0.397(1)	0.086(2)
C(131)	0.568 8(8)	0.237 1(6)	0.431 0(9)
C(132)	0.670 6(9)	0.264 6(7)	0.508(1)
C(133)	0.741(1)	0.200 7(8)	0.549(1)
C(134)	0.834(1)	0.231(1)	0.635(2)
C(211)	0.132(1)	−0.032 6(7)	0.162(1)
C(212)	0.114(1)	−0.021 5(7)	0.265(1)
C(213)	0.010(1)	−0.052(1)	0.256(1)
C(214)	−0.010(2)	−0.037(1)	0.357(1)
C(221)	0.351(1)	−0.029 4(7)	0.263(1)
C(222)	0.459(1)	0.007 2(7)	0.287(1)
C(223)	0.535(1)	−0.052 6(8)	0.366(1)
C(224)	0.640(1)	−0.022(1)	0.398(2)
C(231)	0.281(2)	0.031 3(9)	0.041(1)
C(232)	0.221(2)	−0.042(1)	−0.037(2)
C(233)	0.246(2)	−0.099(1)	−0.144(2)
C(234)	0.300(2)	−0.062(1)	−0.165(2)
C(311)	−0.101 4(7)	0.257 7(6)	0.000 2(8)
C(312)	−0.202 3(8)	0.296 5(6)	−0.060 3(9)
C(313)	−0.283 5(9)	0.239 1(7)	−0.124(1)
C(314)	−0.380 7(9)	0.276 4(8)	−0.188(1)
C(321)	−0.052 1(8)	0.386 1(6)	0.169 5(9)
C(322)	−0.078 2(9)	0.351 7(7)	0.248 8(9)
C(323)	−0.105(1)	0.413 2(9)	0.331(1)
C(324)	−0.123(2)	0.387(1)	0.412(1)
C(331)	0.015 6(9)	0.381 7(6)	−0.006 6(8)
C(332)	0.047(1)	0.342 0(7)	−0.099 0(9)
C(333)	0.064(1)	0.399 0(9)	−0.160(1)
C(334)	0.093(2)	0.379(1)	−0.237(2)

Table 2 Atomic coordinates and estimated standard deviations for $[PHBu^n{}_3][Co(bdt)_2(PBu^n{}_3)]$ **2**

Atom	x	y	z
Co	0.3035(1)	0.1417(1)	0.2309(1)
S(1)	0.4298(3)	0.2103(2)	0.1602(2)
S(2)	0.2060(3)	0.2741(2)	0.2268(2)
S(3)	0.1356(3)	0.0571(2)	0.2564(2)
S(4)	0.3693(3)	−0.0017(2)	0.2006(2)
P(1)	0.4301(3)	0.1876(2)	0.3712(2)
P(2)	0.2008(4)	−0.1152(3)	−0.0480(3)
C(11)	0.394(1)	0.3321(8)	0.1550(7)
C(12)	0.532(1)	0.601(1)	0.8847(9)
C(13)	0.566(1)	0.500(1)	0.887(1)
C(14)	0.663(1)	0.471(1)	0.856(1)
C(15)	0.738(1)	0.5407(9)	0.8196(9)
C(16)	0.296(1)	0.3607(8)	0.1821(7)
C(21)	0.715(1)	0.0891(8)	0.7519(7)
C(22)	0.178(1)	0.9376(8)	0.2701(8)
C(23)	0.102(1)	0.8692(9)	0.3074(8)
C(24)	0.856(2)	0.228(1)	0.6834(8)
C(25)	0.751(2)	0.253(1)	0.7076(9)
C(26)	0.323(1)	0.8154(9)	0.2568(9)
C(31)	0.483(1)	0.6832(8)	0.6065(8)
C(32)	0.616(1)	0.351(1)	0.496(1)
C(33)	0.703(2)	0.455(1)	0.496(1)
C(34)	0.190(2)	0.513(1)	0.430(2)
C(41)	0.442(1)	0.8904(9)	0.5846(9)
C(42)	0.332(1)	0.879(1)	0.626(1)
C(43)	0.237(1)	0.958(1)	0.585(1)
C(44)	0.871(2)	0.054(1)	0.383(1)
C(51)	0.354(1)	0.176(1)	0.4597(9)
C(52)	0.258(1)	0.248(1)	0.4671(9)
C(53)	0.269(3)	0.282(2)	0.622(2)
C(54)	0.816(2)	0.750(2)	0.452(1)
C(61)	0.068(1)	0.854(1)	−0.0071(8)
C(62)	0.945(1)	0.251(1)	0.9804(9)
C(63)	0.056(1)	0.270(1)	0.943(1)
C(64)	0.926(2)	0.625(1)	0.085(1)
C(71)	0.217(1)	0.0168(9)	0.9345(9)
C(72)	0.660(1)	0.944(1)	0.085(1)
C(73)	0.346(2)	0.168(1)	−0.101(1)
C(74)	0.380(3)	0.198(2)	0.851(1)
C(81)	0.824(1)	0.193(1)	0.162(1)
C(82)	0.180(2)	0.699(1)	0.842(1)
C(83)	0.834(2)	0.352(1)	0.257(1)
C(84)	0.845(2)	0.462(2)	0.255(2)

ordination mode involves bdt 1 and 2 which chelate terminally to atom Co(2) with the shortest Co–S bond [average 2.220 Å] of the molecule and at the same time ligate to the other two Co atoms by weak bonds Co(1)–S(3), Co(3)–S(4) and Co(1)–S(1), Co(3)–S(2) (average 2.316 Å) on each side of the Co_3P_3 plane. Therefore the strength of the Co–S bonds decreases in the order Co(2)–S(1,2,3,4) > Co(1,3)–S(5,6) > Co(1)–S(1,3) and Co(3)–S(2,4). The average Co–S distance of 2.271 Å is similar to that in another trinuclear cobalt(II) complex $[Co_3S\{o\text{-}(SCH_2)_2\text{-}C_6H_4\}_3]^{2-}$ (average 2.288 Å)[12] but longer than that in dinuclear $[Co_2(S_2C_6H_4)_4]^{2-}$ (average 2.161 Å).[13] The planarity of bdt 3 is maintained but those of bdt 1 and 2 are slightly disturbed by chelation although they are still roughly perpendicular to the skeletal plane. The dihedral angle of the planes of bdt 1 or 2 to bdt 3 is 91.7° (average), again indicating perpendicularity.

Ligand bdt 3 of complex **1** has a particularly short bite distance of 2.95 Å and a small bite angle of 80.74(6)° as compared to bdt 1 or 2 [average 3.18 Å, 91.63(6)°], with the latter values reasonably more comparable to those for the

Table 3 Selected bond distances (Å) and angles (°) for complex **1**

Co(1)–Co(2)	2.546(1)	Co(2)–P(2)	2.207(2)
Co(1)–Co(3)	2.4510(9)	Co(3)–S(2)	2.312(2)
Co(2)–Co(3)	2.5545(9)	Co(3)–S(4)	2.321(2)
Co(1)–S(1)	2.318(2)	Co(3)–S(5)	2.282(1)
Co(1)–S(3)	2.313(2)	Co(3)–S(6)	2.274(2)
Co(1)–S(5)	2.274(2)	Co(3)–P(3)	2.202(2)
Co(1)–S(6)	2.279(2)	S(1)–C(11)	1.770(6)
Co(1)–P(1)	2.200(2)	S(2)–C(12)	1.765(6)
Co(2)–S(1)	2.225(1)	S(3)–C(21)	1.767(6)
Co(2)–S(2)	2.220(2)	S(4)–C(22)	1.774(6)
Co(2)–S(3)	2.212(2)	S(5)–C(31)	1.757(6)
Co(2)–S(4)	2.222(1)	S(6)–C(32)	1.779(6)
Co(2)–Co(1)–Co(3)	61.45(3)	S(3)–Co(2)–S(4)	91.73(6)
Co(1)–Co(2)–Co(3)	57.44(3)	S(3)–Co(2)–P(2)	99.55(7)
Co(1)–Co(3)–Co(2)	61.10(3)	S(4)–Co(2)–P(2)	104.16(6)
Co(3)–Co(1)–S(1)	98.51(5)	Co(1)–Co(3)–S(2)	99.72(4)
Co(3)–Co(1)–S(3)	99.25(4)	Co(1)–Co(3)–S(4)	98.91(5)
Co(3)–Co(1)–S(5)	57.61(5)	Co(1)–Co(3)–S(5)	57.29(4)
Co(3)–Co(1)–S(6)	57.32(4)	Co(1)–Co(3)–S(6)	57.54(4)
Co(3)–Co(1)–P(1)	153.92(6)	Co(1)–Co(3)–P(3)	152.11(5)
S(1)–Co(1)–S(3)	79.64(6)	S(2)–Co(3)–S(4)	77.86(5)
S(1)–Co(1)–S(5)	93.18(6)	S(2)–Co(3)–S(5)	95.46(6)
S(1)–Co(1)–S(6)	154.48(6)	S(2)–Co(3)–S(6)	155.21(6)
S(1)–Co(1)–P(1)	101.58(6)	S(2)–Co(3)–P(3)	101.46(6)
S(3)–Co(1)–S(5)	154.78(6)	S(4)–Co(3)–S(5)	154.24(6)
S(3)–Co(1)–S(6)	95.30(6)	S(4)–Co(3)–S(6)	94.93(7)
S(3)–Co(1)–P(1)	100.61(6)	S(4)–Co(3)–P(3)	103.12(6)
S(5)–Co(1)–S(6)	80.76(6)	S(5)–Co(3)–S(6)	80.72(6)
S(5)–Co(1)–P(1)	104.53(6)	S(5)–Co(3)–P(3)	102.59(6)
S(6)–Co(1)–P(1)	103.94(6)	S(6)–Co(3)–P(3)	103.28(7)
S(1)–Co(2)–S(2)	91.53(6)	Co(1)–S(1)–Co(2)	68.14(4)
S(1)–Co(2)–S(3)	83.89(6)	Co(2)–S(2)–Co(3)	68.61(5)
S(1)–Co(2)–S(4)	154.35(6)	Co(1)–S(3)–Co(2)	68.46(5)
S(1)–Co(2)–P(2)	101.49(6)	Co(2)–S(4)–Co(3)	68.39(4)
S(2)–Co(2)–S(3)	155.16(7)	Co(1)–S(5)–Co(3)	65.10(4)
S(2)–Co(2)–S(4)	81.88(6)	Co(1)–S(6)–Co(3)	65.14(5)
S(2)–Co(2)–P(2)	105.29(7)		

Table 4 Selected bond distances (Å) and angles (°) for complex **2**

Co–S(1)	2.183(2)	S(2)–C(16)	1.763(8)
Co–S(2)	2.186(2)	S(3)–C(22)	1.753(8)
Co–S(3)	2.190(2)	S(4)–C(21)	1.769(9)
Co–S(4)	2.203(2)	P(1)–C(31)	1.824(7)
Co–P(1)	2.124(2)	P(1)–C(41)	1.842(8)
S(1)–C(11)	1.746(9)	P(1)–C(51)	1.811(9)
S(1)–Co(1)–S(2)	89.93(9)	S(3)–Co(1)–S(4)	88.92(9)
S(1)–Co(1)–S(3)	161.9(2)	S(3)–Co(1)–P(1)	98.6(1)
S(1)–Co(1)–S(4)	87.90(9)	S(4)–Co(1)–P(1)	99.28(9)
S(1)–Co(1)–P(1)	99.49(9)	C(31)–P(1)–C(41)	106.5(4)
S(2)–Co(1)–S(3)	88.97(9)	C(31)–P(1)–C(51)	106.8(4)
S(2)–Co(1)–S(4)	166.3(1)	C(41)–P(1)–C(51)	96.6(5)
S(2)–Co(1)–P(1)	94.39(9)		

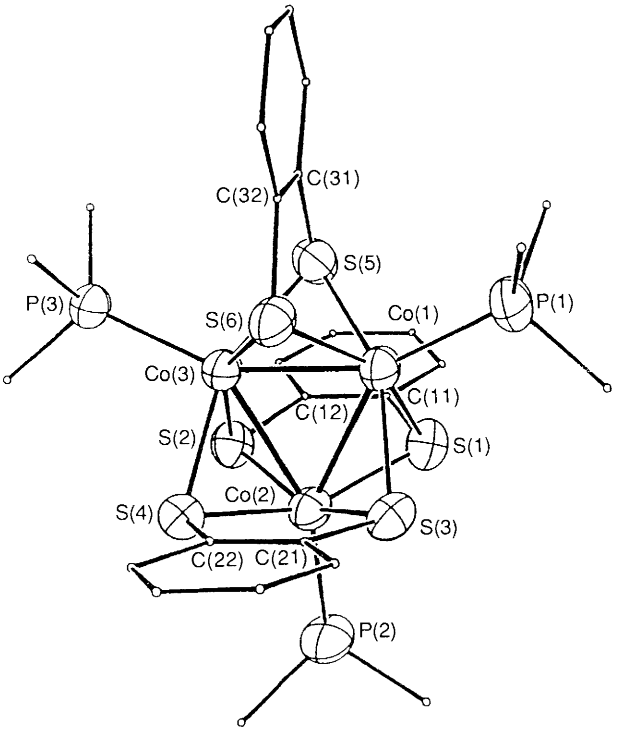

Fig. 1 An ORTEP diagram of $[Co_3(bdt)_3(PBu^n{}_3)_3]$ with the phenyl and the α-carbon atoms of the alkyl groups as spheres of arbitrary size for clarity

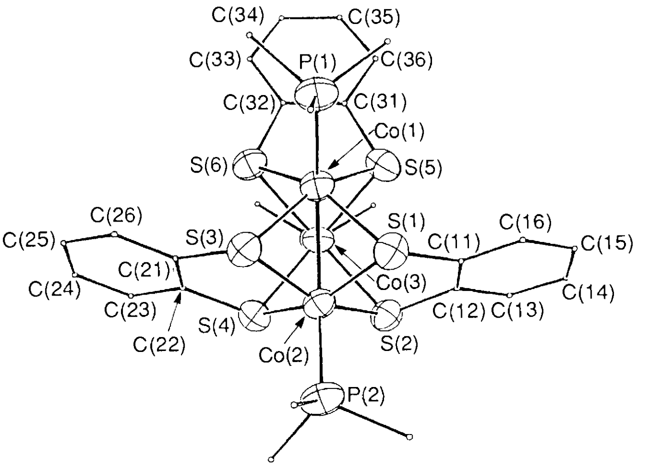

Fig. 2 Side view along the Co_3P_3 plane of $[Co_3(bdt)_3(PBu^n{}_3)_3]$ with the phenyl and the α-carbon atoms of the alkyl groups as spheres of arbitrary size for clarity

terminal co-ordination mode in **2** [3.08 Å, 89.43(9)°], $[Cu(bdt)_2]^-$ [3.13 Å, 90.0(1)°][14] or $[Fe_2(bdt)_4]^{2-}$ [3.13 Å, 88.85(3)°],[15] although atoms S(1,2,3,4) are bridged. This result agrees also with the short terminal S(1,2,3,4)–Co(2) bond. It is worth noting that the rather short S(1) ··· S(3) or S(2) ··· S(4) distances (average 2.94 Å) between bdt 1 and 2 indicate possible interaction of adjacent sulphur atoms.

The three Co–P bonds (average 2.203 Å) are nearly equivalent and comparable to other bonds to five-co-ordinate Co^{II} such as those in $[Co_2(dppe)(SPh)_4]$ (average 2.210 Å)[4] and $[\{Co[CH_3C(CH_2PPh_2)_3](\mu\text{-}N_3)\}_2][BPh_4]_2\cdot 2Me_2CO$ (average basal Co–P 2.215 Å).[16]

Complex **2** has Co^{III} co-ordinated in square-pyramidal geometry with the sulphur atoms from two bdt ligands forming the basal plane and the P atom in the axial position as depicted in Fig. 3. The Co atom is 0.3 Å above the plane toward the P atom with a Co–P distance of 2.124(2) Å which is shorter than that in **1** where strong Co–Co interactions might have weakened the Co–P bonds. The two bdt ligands form a dihedral angle of 171.44° and are mirror images of each other with the non-crystallographic pseudo-symmetry plane passing along bond Co–P and through the midpoints of S(2) ··· S(3) and S(1) ··· S(4), if the alkyl groups of the phosphine ligands are omitted. The mean Co–S distance of 2.191 Å is in the range for terminally co-ordinated bdt in **1** (see above).

Properties.—Computer simulation[17] of the ^1H NMR spectrum of complex **1** in CD_2Cl_2 confirmed the integrity of the molecule in solution. The protons in the bdt groups appear at δ 6.35–6.70 and 6.75–7.28 as one and two multiplets in ratio of 1 : 2 for bdt 3 and bdt 1 + bdt 2, respectively, while those in ligands $PBu^n{}_3$ appear upfield in the region δ 0.70–2.14. The latter peaks

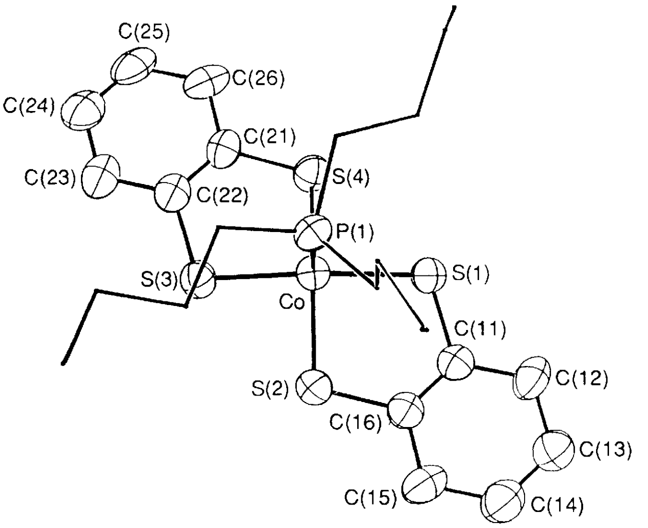

Fig. 3 An ORTEP diagram of the anion $[Co(bdt)_2(PBu^n{}_3)]^-$

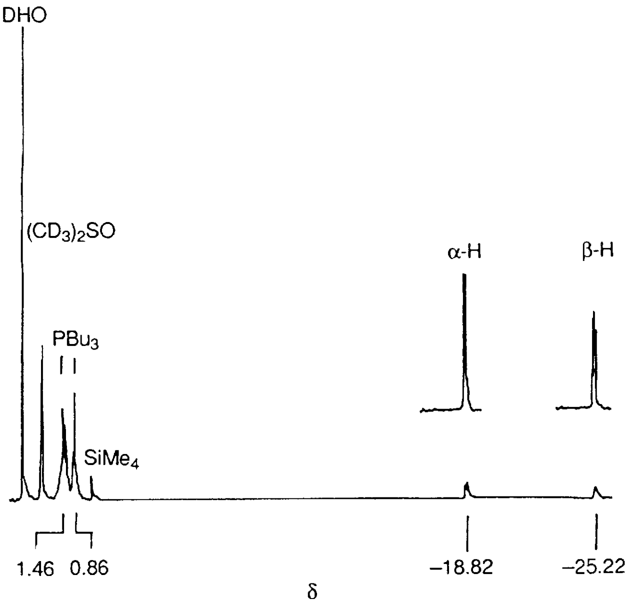

Fig. 4 The ^1H NMR spectrum of a solution of $[PHBu^n{}_3][Co(bdt)_2(PBu^n{}_3)]$ in $(CD_3)_2SO$ which turned blue on prolonged standing at ambient temperature

also showed a ratio of 1:2 for $PBu^n{}_3$ ligated to Co(2) [δ 0.70 (3 H), 1.24 (4 H) and 1.80 (2 H)] and those to Co(1) and Co(3) [δ 0.93 (6 H), 1.44 (8 H) and 2.14 (4 H)]. Complex **1** with three low-spin Co^{II} (d^7, $S = \frac{1}{2}$) atoms showed an effective magnetic moment μ_{eff} of 2.6 μ_B at ambient temperature, indicating antiferromagnetic coupling among the Co atoms as anticipated from the short Co–Co distances.

Complex **2** is diamagnetic ($\chi_M = -438.92 \times 10^{-9}\ m^3 kg^{-1} s^{-1}$), where Co^{III} (d^6) must be in the low-spin state ($S = 0$) although the compound $[NBu_4][Co(bdt)_2]$ is paramagnetic ($\mu = 3.27\ \mu_B$).[18] Its ^1H NMR spectrum in $(CD_3)_2SO$ showed two broad peaks for bdt protons at δ 6.69 (α-H) and 7.32 (β-H) in ratio of 1:1, substantiating a certain degree of electron delocalization in solution. The $PBu^n{}_3$ protons are differentiated from those in the ligand [δ, 0.68 (δ-H) and 1.21 (α,β,γ-H)] and those in the cation (δ 0.88, 1.45) with the latter values close to the chemical shifts of the free ligand (δ 0.90, 1.0–1.9). The cationic proton may have exchanged with the deuteriated solvent and was not observable.

It is interesting that a small amount of air changed the dark brown dimethyl sulphoxide (dmso) solution of **2** into a blue solution possibly of the complex $[PHBu^n{}_3][Co(bdt)_2]$ **3** with the dissociation of $PBu^n{}_3$ according to equation (1). The ^1H

$$\underset{\mathbf{2}}{[PHBu^n{}_3][Co(bdt)_2(PBu^n{}_3)]} \xrightarrow{dmso} \underset{\mathbf{3}}{[PHBu^n{}_3][Co(bdt)_2]} + PBu^n{}_3 \quad (1)$$

NMR spectrum for a dmso solution of **2** on prolonged standing in the NMR tube (Fig. 4) showed sharp peaks at δ −18.82 (α-H) and −25.22 (β-H) for the bdt protons, substantiating the presence of a paramagnetic species which is reasonably expressed by **3**. The dissociated $PBu^n{}_3$ of **2** was indistinguishable from that in the cation. The change in co-ordination geometry of Co^{III} from square pyramidal in **2** to square planar[19] in **3** is caused by a change of electronic arrangement[20] from $(d_{yz},d_{xz})^4(d_{xy})^2$ to $(d_{yz},d_{xz})^4(d_{xy})^1(d_{z^2})^1$ and complex **3** is paramagnetic with $S = 1$.[19]

Complex **1** displays one reversible reduction wave at −0.53 V ($E_{\frac{1}{2}} = -0.49$ V, $i_{p,a}/i_{p,c} \approx 1$) and one reversible oxidation wave at 1.08 V ($E_{\frac{1}{2}} = 1.04$ V, $i_{p,a}/i_{p,c} \approx 1$) in CH_2Cl_2 solution in the range of −1.02 to 1.50 V at room temperature, corresponding to the one-electron redox reactions (2).

$$[Co_3(bdt)_3(PBu^n{}_3)_3]^+ \underset{-e}{\overset{+e}{\rightleftharpoons}} [Co_3(bdt)_3(PBu^n{}_3)_2] \underset{-e}{\overset{+e}{\rightleftharpoons}} [Co_3(bdt)_3(PBu^n{}_3)_3]^- \quad (2)$$

Experimental

Reactions unless specified otherwise were carried out under an atmosphere of dinitrogen in Schlenk-type apparatus. All solvents were dried over molecular sieves, distilled in the presence of N_2, and degassed before use. The reagents $CoCl_2$ and $PBu^n{}_3$ (Merck-Schuchardt) and H_2bdt (Fluka) are commercially available. Elemental analyses were carried out by Mr. Enshui Lin and his associates of this Institute.

Preparations.—$[Co_3(bdt)_3(PBu^n{}_3)_3]$ **1**. To a solution (50 cm^3) of MeOH containing sodium metal (0.29 g, 12.64 mmol) was added H_2bdt (1.0 g, 7.04 mmol) and $PBu^n{}_3$ (3 cm^3, 12.64 mmol) with vigorous stirring. The resulting solution turned purplish red immediately when anhydrous $CoCl_2$ (0.82 g, 6.32 mmol) was added during stirring. After 20 h the solution was filtered and allowed to stand at 5 °C overnight to give 0.6 g of dark brown crystals of complex **1**. After 1 month, nice square plate crystals suitable for X-ray analysis were obtained (1.0 g, total yield 63%). The two batches of product had the same IR spectra (KBr): 455, 440, 390 and 340 cm^{-1} (Found: C, 53.95; H, 7.70; Co, 13.70; P, 7.45; S, 15.40. $C_{54}H_{93}Co_3P_3S_6$ requires C, 53.90; H, 7.75; Co, 14.70; P, 7.75; S, 15.95%).

If CH_2Cl_2 (25 cm^3) was used to recrystallize the crude product, the solvated complex $\mathbf{1}\cdot nCH_2Cl_2$ was obtained as rod-like crystals and identified by IR and X-ray diffraction analyses.

$[PHBu^n{}_3][Co(bdt)_2(PBu^n{}_3)]$ **2**. To a solution of sodium metal (0.29 g, 12.64 mmol) and H_2bdt (1.0 g, 7.04 mmol) in MeOH (50 cm^3) was added first $PBu^n{}_3$ (3 cm^3, 12.64 mmol) and then anhydrous $CoCl_2$ (0.829 g, 6.32 mmol) with stirring at room temperature. The mixture turned purple immediately. Dry air (5 cm^3) was added by a syringe and the mixture was stirred for 20 h and then filtered. Brown square crystals of complex **2** (0.7 g, 15%) separated from the purplish filtrate after standing at 5 °C for 4 d. IR (KBr): 455, 430 and 355 cm^{-1} (Found: Co, 7.95; P, 7.90; S, 17.10. $C_{36}H_{63}CoP_2S_4$ requires Co, 7.90; P, 8.35; S, 17.20%).

Physicochemical Measurements.—Infrared spectra were obtained on a Perkin-Elmer 577 spectrophotometer, ^1H NMR spectra on a Varian FT-80A spectrometer in appropriate deuteriated solvents with $SiMe_4$ as internal standard at ambient temperature. Magnetic susceptibility data were obtained by the Faraday method on a Guoy–Faraday magnetic balance. Cyclic

Table 5 Crystallographic data for complexes **1** and **2**[a]

	1	**2**
Formula	$C_{54}H_{93}Co_3P_3S_6$	$C_{36}H_{63}CoP_2S_4$
M_r	1204.45	745.04
Dimensions/mm	0.20 × 0.20 × 0.35	0.15 × 0.20 × 0.35
a/Å	13.694(4)	10.800(3)
b/Å	18.460(4)	13.533(4)
c/Å	13.656(4)	15.342(2)
α/°	100.69(2)	96.37(2)
β/°	108.68(2)	108.57(2)
γ/°	85.06(2)	97.02(2)
U/Å^3	3212.2	2085.6
Diffractometer	Rigaku AFC/5R	Enraf–Nonius CAD-4
D_c/g cm^{-3}	1.25	1.19
$F(000)$	1278	800
μ/cm^{-1}	10.6	7.0
Unique reflections [$I > 3\sigma(I)$]	6366	3801
Variables	595	388
DIFABS correction	*b*	0.84–1.76
R	0.059	0.086
R' [c]	0.066	0.088

[a] Details in common: triclinic, space group $P\bar{1}$; $Z = 2$; 2θ range 2–50. [b] Not performed, the decay correction is 0.99–1.00. [c] $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{\frac{1}{2}}$, $w = 1$.

voltammetry measurements were performed on a DHZ-1 electrochemical apparatus equipped with an X–Y recorder in a three-electrode cell with platinum working and auxiliary electrodes and a saturated calomel electrode (SCE) as reference electrode. The supporting electrolyte was $NBu^n_4BF_4$ (0.1 mol dm^{-3}) and scan rate 100 mV s^{-1}.

Crystal Structure Determinations.—The crystallographic data for the compounds are summarized in Table 5. Single crystals were either sealed in capillary tubes under nitrogen or coated with epoxy resin. After data reduction (including correction for Lorentz and polarizarion effects), the remaining unique reflections with $I > 3\sigma(I)$ were used for subsequent structure solution and refinement. The structures were solved by direct methods and the non-hydrogen atoms except carbon atoms were located from the E map. A Fourier map phased by the metal atoms contained most of the remaining non-hydrogen atoms. Full-matrix least-squares refinement with anisotropic thermal parameters for all non-hydrogen atoms led to convergence.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

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