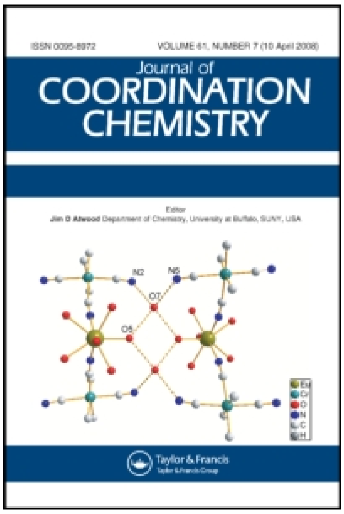

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SYNTHESIS, CRYSTAL STRUCTURE AND MAGNETIC PROPERTIES OF AN ASYMMETRIC, MIXED-VALENCE, TETRANUCLEAR $Co^{II}_3Co^{III}$ COMPLEX WITH 2-MERCAPTOPHENOL AND DIMETHYLPHENYLPHOSPHINE LIGANDS

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A neutral mixed-valence tetranuclear complex $[Co_4(mp)_4(Hmp)(PMe_2Ph)_3]$ (PMe_2Ph = dimethylphenylphosphine, H_2mp = 2-mercaptophenol) was isolated from the reaction of $CoCl_2$, H_2mp, NaOMe, and PMe_2Ph in 1:1:2:1 mol ratio in the presence of a limited amount of air with Co^{II} partially oxidized to Co^{III}. The molecule consists of a $Co^{II}_3Co^{III}$ core with a cyclic arrangement, and which is unsymmetrically bridged by μ_2-S and μ_2-O atoms from three mp^{2-} ions in O_bS_b-T and one in O_tS_b mode, while the monoanion Hmp^- is terminally chelated to the Co^{III} ion in HO_tS_t mode. The three Co^{II} centres are located in approximately square-based pyramidal environments, and the Co^{III} ion in distorted trigonal bipyramidal geometry. Variable-temperature magnetic susceptibility measurements showed that the complex exhibits weak antiferromagnetic exchange interactions due to the inefficiency of the μ_2-S and μ_2-O bridges in facilitating coupling between cobalt atoms with Co-Co distances of 2.6-3.4 Å. Least-squares fitting of the experimental data shows coupling constants in the range -0.3 to $-3.2\ cm^{-1}$.

Keywords: crystal structure; magnetic properties; tetranuclear cobalt complex; mixed-valence complex; 2-mercaptophenol; dimethylphenylphosphine; X-ray structure

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INTRODUCTION

Both thiolate and phosphine ligands play important roles in the design of polymetallic systems.[1,2] In recent years, we have studied the coordination chemistry of a series of transition metals with mixed phosphine and thiolato ligands.[3-5] It has been shown that the participation of phosphine not only can modify the bonding modes of the thiolato ligand, but also in suitable environments favours the ligation of bidentate thiolates to bridge metal centres in forming polynuclear species.[4-7] Most of the work to date has concentrated on cobalt[3-6,8-10] iron,[11] and nickel,[7,12,13] and a variety of species of different nuclearities and oxidation levels have been obtained.[14,15]

As a 1,2-bidentate thiolato ligand with both oxygen and sulfur donors, 2-mercaptophenol (H_2mp) has been found to be multifunctional and can chelate and/or bridge various metal ions to show versatile coordination modes.[5,6,14-17] It can form a monoanion Hmp^- $[(HOC_6H_4S)^-]$ or a dianion mp^{2-} $[(OC_6H_4S)^{2-}]$, chelating and/or bridging metal ions to exhibit four bonding modes HOS_t (**I**), HO_tS_t (**II**), HOS_b (**III**), HO_tS_b (**IV**) for Hmp^-, and five modes O_tS_t (**V**), O_tS_b (**VI**), O_bS_t (**VII**), O_bS_b-B (**VIII**), and O_bS_b-T (**IX**) (b stands for bridge, t for terminal, B for binuclear, and T for trinuclear) for mp^{2-}.[5,6,14-17] Moreover, it has been observed that transition metal complexes with mixed phosphine and H_2mp ligands exhibit very different molecular structures compared to those without phosphine participation.[14,15] For example, only a binuclear nickel(II) compound $(Et_4N)_2[Ni_2(mp)_2(Hmp)_2]$[16] was obtained in the absence of phosphine, in which the Ni^{II} ions are connected by μ_2-S with H_2mp displaying the bridging mode HOS_b (**III**). In contrast, three complexes $Ni_3(mp)_2(Hmp)_2(PBu^n{}_3)_2$, $Ni(mp)(PMe_2Ph)_2$, and $(HNEt_3)[Ni(mp)(Hmp)(PBu^n{}_3)]$ have been obtained when phosphine participates in the reaction,[17] where the chelating and bridging modes HO_tS_b (**IV**) and O_bS_t (**VII**) are involved. Dimeric $(Et_4N)_2[Co(mp)(Hmp)]_2$[16] was isolated when no phosphine was involved, while tri- or tetranuclear cobalt cluster complexes[5],[6] were obtained when both phosphine and H_2mp took part in coordination. By keeping a restricted amount of air in the reaction system, a mixed-valence tetracobalt complex, $Co_4(mp)_4(Hmp)(PMe_2Ph)_3$, was obtained in the presence of dimethylphenylphosphine. This paper reports its synthesis and crystal structure together with a description of its magnetic behavior.

EXPERIMENTAL

All operations were carried out under dinitrogen with Schlenk-type apparatus unless otherwise stated. 2-Mercaptophenol (H_2mp), dimethylphenylphosphine

(PMe_2Ph), and anhydrous cobaltous chloride were used as received. Absolute ethanol was flushed with pure dinitrogen for 5 min before use. Sodium methoxide was prepared by dissolving sodium metal in dry methanol and then evaporating the solvent and drying under reduced pressure. Elemental analyses were performed by the Chemical Analysis Division of Fujian Institute.

$Co_4(mp)_4(Hmp)(PMe_2Ph)_3$

To a solution of anhydrous $CoCl_2$ (1 mmol, 0.13 g) in 20 cm^3 of absolute ethanol was added an absolute ethanol solution (10 cm^3) containing H_2mp (1 mmol, 0.10 cm^3), PMe_2Ph (1 mmol, 0.14 cm^3), and NaOMe (2 mmol, 0.11g). The solution was filtered after stirring for 30 min, then 20 cm^3 of dry air was added *via* a syringe. Well-shaped, black crystals were obtained in 76% yield when the dark-brown filtrate was allowed to stand at 10°C for several days. Found: C, 50.7; H, 4.3; P, 7.2; S, 12.4; Co, 18.4. Calc. for $C_{54}H_{54}O_5P_3S_5Co_4$ (%): C, 50.9; H, 4.3; P, 7.3; S, 12.6; Co, 18.5%. ^{31}P NMR: 34.1 ppm.

Crystal structure determination

A single crystal with suitable dimensions was mounted on a glass fibre and data collection was performed on a Rigaku RAXIS[18] diffractometer using graphite-monochromated MoKα radiation ($\lambda = 0.71073$ Å). Crystallographic data, data collection and structure refinement parameters are summarized in Table I.

Coordinates of the metal atoms were determined by direct methods and the remaining non-hydrogen atoms were located from successive Fourier difference syntheses. The structure was refined by full-matrix least-squares techniques with anisotropic thermal parameters for the non-hydrogen atoms. Hydrogen atoms were added to the structure factor calculations but not refined. All calculations were performed on an IBM PC/486 computer with the Siemens SHELXTL-PC program package.[19] Atomic scattering factors were taken from ref. 20.

Physical measurements

^{31}P NMR spectra were recorded on a Bruker AM500 spectrometer with 85% H_3PO_4 as external standard. FAB mass spectra were obtained from a Finnigan MAT-8230 high resolution double focusing mass spectrometer in *m*-nitrobenzyl alcohol matrix. Ions were generated from impact on the target matrix derived from an Ar^+ ion beam at an accelerating potential of 8 KV. The FAB gun emission current was 1 mA. A reference spectrum of a CsI cluster was used for mass calibration. Variable-temperature magnetic susceptibilities in the temperature range 1.5-300 K were measured on a CF-1 superconducting magnetometer

TABLE I Crystal data, data collection and structure refinement parameters for the complex.

Formula	$C_{54}H_{54}O_5P_3S_5Co_4$
Formula weight	1271.9
Colour and habit	black grain
Crystal size, mm	0.20 × 0.30 × 0.40
Crystal system	monoclinic
Space group	$P2_1/c$
a, Å	12.143(1)
b, Å	21.620(1)
c, Å	21.040(1)
β, °	91.75(3)
V, Å^3	5521(3)
Z	4
T, K	293
D_{calc}, g cm^{-3}	1.530
μ (MoKα), cm^{-1}	15.03
F(000)	2604
No. of parameters refined	641
Observed reflections	10004
Independent reflections	4686 [$F_o > 8\sigma(F_o)$]
R[a]	0.045
R_w[b]	0.052
Goodness of fit	0.77
Largest and mean Δ/σ	0.042, 0.003
Residual extrema, e Å^{-3}	+0.46 to −0.54

[a] $R = (\Sigma||F_o| - |F_c||)/|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w=[6^2|Fo + 0.000001|Fo|^2]^{-1}$.

at a magnetic field of 1.0 T with powdered samples. Correction for diamagnetism was estimated from Pascal's constants to be -630×10^{-6} cm^3 mol^{-1}.

RESULTS AND DISCUSSION

Synthesis

When the reaction of $CoCl_2$ with H_2mp was carried out in the absence of phosphine, the product isolated was a dimer, $(Et_4N)_2[Co(mp)(Hmp)]_2$,[16] constructed by two fragments $Co(mp)(Hmp)^-$ connected by H-bonds, where the Hmp^- and mp^{2-} ligands exhibit the chelating modes HO_tS_t (**II**) and O_tS_t (**V**). With phosphine taking part in the reaction, the variety of products isolated is determined not only by the mol ratio of the reactants, but also by whether or not air is present. Under strictly anaerobic circumstances, the cyclic trinuclear complexes $[Co_3(mp)_2(Hmp)_2(PR_3)_3]$ (R = Et[6] and Bu^n[15]) were obtained; these can be viewed as the combination of two $Co(mp)(PR_3)$ and $Co(Hmp)_2(PR_3)$. Attempts to isolate the mononuclear species were unsuccessful due to the strong

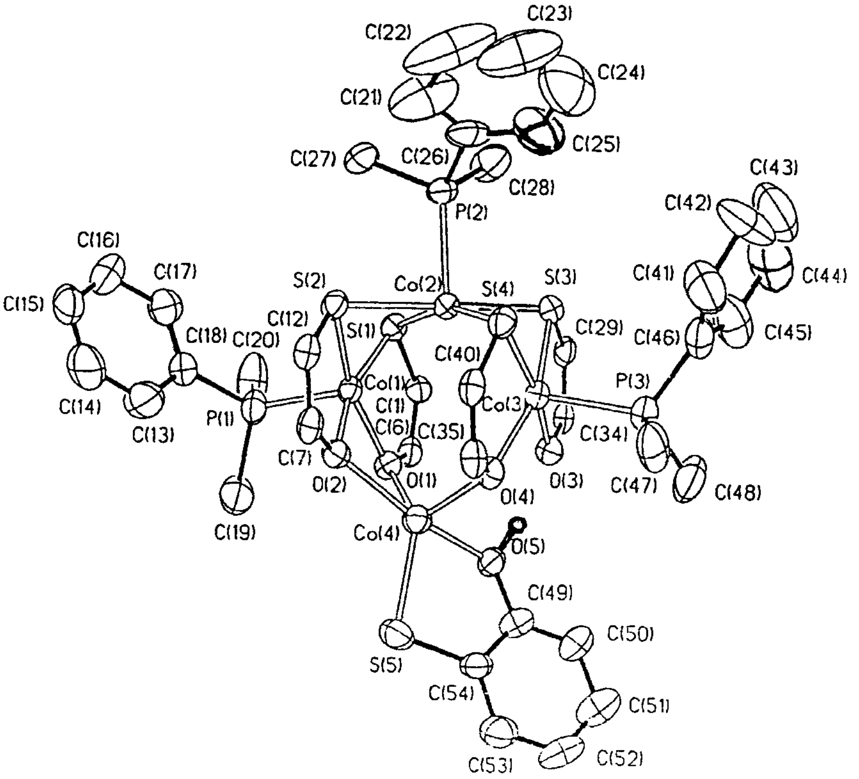

FIGURE 1 Structure of $Co_4(mp)_4(Hmp)(PMe_2Ph)_3$ with the atom labelling scheme. Four carbon atoms of each phenyl ring of the mp^{2-} ligands have been omitted for clarity.

tendency to form the neutral trinuclear species. If a restricted amount of air was introduced into the reaction system, the mixed-valence tetranuclear complex $[Co_4(mp)_4(Hmp)(PR_3)_3]$ was isolated. This displays a more stable assembly with a cyclic Co_4 skeleton, in which one Co atom is in oxidation state III. When Fe^{III} was used to substitute Co^{III}, the partially Fe^{III}-substituted heterotetranuclear complex $[Co_3Fe(mp)_4(Hmp)(PBu^n{}_3)_3]$ was isolated.[21] If Ru^{III} was employed instead, the product obtained was a novel heterooctanuclear complex $[Co_6Ru_2(mp)_{10}(PBu^n{}_3)_6]$ with a zigzag metal arrangement.[22]

Crystal structure

The structure of the title complex with the atom numbering schemes is depicted in Figure 1. Atomic coordinates are listed in Table II. Selected atomic distances

TABLE II Atomic coordinates and isotropic temperature factors ($Å^2 \times 10^3$) for the complex.

atom	*x/g*	*y/b*	*z/c*	$U_{eq}{}^{a}$
Co(1)	0.45869(9)	0.11333(6)	0.70036(4)	36.5(3)
Co(2)	0.33385(9)	0.19559(4)	0.75070(5)	37.9(3)
Co(3)	0.21012(9)	0.11904(4)	0.81187(4)	37.8(3)
Co(4)	0.33763(10)	0.00107(5)	0.73751(5)	42.0(3)
S(1)	0.5176(2)	0.1792(1)	0.7701(1)	40(1)
S(2)	0.3858(2)	0.1868(1)	0.6458(1)	43(1)
S(3)	0.2763(2)	0.2024(1)	0.8528(1)	43(1)
S(4)	0.1496(2)	0.1779(1)	0.7352(1)	46(1)
S(5)	0.3074(2)	−0.0999(1)	0.7113(1)	59(1)
O(1)	0.4797(4)	0.0473(2)	0.7600(2)	41(1)
O(2)	0.3702(4)	0.0535(2)	0.6544(2)	42(2)
O(3)	0.2959(4)	0.0715(2)	0.8742(2)	42(1)
O(4)	0.1952(4)	0.0469(2)	0.7558(2)	42(1)
O(5)	0.3392(2)	−0.0327(2)	0.8325(2)	46(1)
P(1)	0.6103(2)	0.0919(1)	0.6507(1)	53(1)
P(2)	0.3538(2)	0.2997(1)	0.7439(1)	45(1)
P(3)	0.0534(2)	0.1077(1)	0.8624(1)	51(1)
C(1)	0.5651(6)	0.1233(3)	0.8266(3)	41(1)
C(2)	0.6350(6)	0.1385(4)	0.8769(3)	53(1)
C(3)	0.6821(6)	0.0927(4)	0.9140(3)	55(1)
C(4)	0.6617(7)	0.0317(4)	0.9008(3)	55(1)
C(5)	0.5906(6)	0.0158(4)	0.8512(3)	50(1)
C(6)	0.5413(6)	0.0617(3)	0.8119(3)	43(1)
C(7)	0.3166(6)	0.0761(4)	0.6021(3)	45(1)
C(8)	0.2688(6)	0.0360(4)	0.5576(3)	57(1)
C(9)	0.2199(7)	0.0601(5)	0.5028(4)	75(1)
C(10)	0.2171(7)	0.1229(5)	0.4912(4)	77(1)
C(11)	0.2619(6)	0.1625(4)	0.5349(4)	61(1)
C(12)	0.3119(6)	0.1391(3)	0.5910(3)	44(1)
C(13)	0.5770(8)	0.0900(4)	0.5189(4)	80(1)
C(14)	0.5806(8)	0.1155(5)	0.4588(4)	95(1)
C(15)	0.6269(8)	0.1707(5)	0.4492(4)	87(1)
C(16)	0.6664(8)	0.2035(5)	0.4988(4)	87(1)
C(17)	0.6619(8)	0.1796(4)	0.5601(4)	76(1)
C(18)	0.6185(6)	0.1222(4)	0.5707(3)	49(1)
C(19)	0.6288(9)	0.0093(4)	0.6448(5)	113(1)
C(20)	0.7335(8)	0.1181(6)	0.6912(5)	108(1)
C(21)	0.2181(9)	0.3640(6)	0.6571(7)	137(1)
C(22)	0.1127(10)	0.3954(7)	0.6357(8)	214(1)
C(23)	0.0464(10)	0.3966(7)	0.6834(8)	186(1)
C(24)	0.0538(10)	0.3778(7)	0.7425(9)	179(1)
C(25)	0.1458(9)	0.3469(6)	0.7592(8)	140(1)
C(26)	0.2328(7)	0.3416(4)	0.7158(5)	75(1)
C(27)	0.4611(7)	0.3265(4)	0.6936(5)	72(1)
C(28)	0.3926(8)	0.3367(4)	0.8181(4)	91(1)
C(29)	0.3567(6)	0.1682(3)	0.9143(3)	45(1)
C(30)	0.4149(6)	0.2034(4)	0.9602(3)	53(1)

TABLE II *Continued*

atom	*x/g*	*y/b*	*z/c*	U_{eq}[a]
C(31)	0.4695(7)	0.1730(4)	1.0104(3)	59(1)
C(32)	0.4648(7)	0.1095(4)	1.0154(4)	61(1)
C(33)	0.4068(7)	0.0741(4)	0.9700(3)	51(1)
C(34)	0.3537(6)	0.1042(3)	0.9186(3)	43(1)
C(35)	0.1273(6)	0.0572(4)	0.7034(3)	45(1)
C(36)	0.0806(6)	0.0083(4)	0.6689(3)	55(1)
C(37)	0.0148(7)	0.0194(5)	0.6171(4)	73(1)
C(38)	−0.0105(7)	0.0786(5)	0.5971(4)	75(1)
C(39)	0.0345(6)	0.1278(4)	0.6309(4)	56(1)
C(40)	0.1044(6)	0.1169(4)	0.6850(3)	45(1)
C(41)	−0.0654(9)	0.2178(6)	0.8599(6)	110(1)
C(42)	−0.0983(10)	0.2757(6)	0.8838(8)	174(1)
C(43)	−0.0644(10)	0.2913(7)	0.9405(8)	167(1)
C(44)	0.0038(9)	0.2560(6)	0.9790(6)	136(1)
C(45)	0.0356(8)	0.1991(6)	0.9547(6)	108(1)
C(46)	0.0024(7)	0.1785(4)	0.8962(4)	66(1)
C(47)	−0.0618(7)	0.0775(5)	0.8142(5)	79(1)
C(48)	0.0631(8)	0.0538(5)	0.9287(5)	93(1)
C(49)	0.2821(7)	−0.0856(3)	0.8422(4)	51(1)
C(50)	0.2490(7)	−0.1022(4)	0.9012(4)	63(1)
C(51)	0.1971(8)	−0.1582(5)	0.9094(5)	89(1)
C(52)	0.1779(8)	−0.1974(4)	0.8580(5)	84(1)
C(53)	0.2149(7)	−0.1803(4)	0.7979(5)	72(1)
C(54)	0.2655(7)	−0.1241(3)	0.7885(4)	55(1)

[a] *U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.*

and bond angles are presented in Table III. The tetranuclear molecule can be viewed as being composed of two building blocks, Co^{II}(mp)$_2$(PMe$_2$Ph)$^{2-}$, linked through bridging sulfur and oxygen atoms to Co^{II}(PMe$_2$Ph)$^{2+}$ and Co^{III}(Hmp)$^{2+}$ moieties. The complex exhibits a cyclic skeleton, Co$^{II}_3$Co^{III}S$_4$O$_3$, with two double μ_2-S bridges, one double μ_2-O bridge, and one single μ_2-O bridge. The four mp^{2-} ligands display two coordination modes, O$_b$S$_b$-T and O$_t$S$_b$, while the monoanion Hmp$^-$ is terminally chelated to the Co^{III} ion in HO$_t$S$_t$ fashion, where the atom H(5B) on O(5) has been unambiguously located from the crystallographic data. The shorter distances Co(1)-Co(2) and Co(2)-Co(3) (average 2.593 Å) compared with Co(1)-Co(4) (2.956 Å) and Co(3)-Co(4) (3.391 Å) reveal strong interactions of Co(2) with Co(1) and Co(3), whereas Co(4) is only loosely bonded to Co(1) and Co(3). However, the Co-Co distances in this complex are slightly shorter than those in Co$_4$(mp)$_4$(Hmp)(PBu$^n_3$)$_3$,[6] probably due to the presence of the phenyl group in PMe$_2$Ph. The cyclic Co$_4$ framework results in Co···Co···Co angles 98.9(1), 96.9(1), 88.4(2), and 75.1(1)° for

TABLE III Selected atomic distances (Å) and bond angles (°) for the complex.

Co(1)-Co(2)	2.584(2)	Co(2)-Co(3)	2.602(2)
Co(1)-Co(4)	2.956(2)	Co(1)-P(1)	2.194(3)
Co(1)-S(1)	2.152(2)	Co(1)-S(2)	2.135(2)
Co(1)-O(1)	1.913(5)	Co(1)-O(2)	1.924(5)
Co(2)-S(1)	2.283(2)	Co(2)-S(2)	2.322(2)
Co(2)-S(3)	2.284(2)	Co(2)-S(4)	2.283(2)
Co(2)-P(2)	2.268(2)	Co(3)-S(3)	2.142(2)
Co(3)-S(4)	2.166(2)	Co(3)-O(3)	1.944(5)
Co(3)-O(4)	1.961(5)	Co(3)-P(3)	2.222(3)
Co(4)-S(5)	2.278(2)	Co(4)-O(1)	2.037(5)
Co(4)-O(2)	2.131(5)	Co(4)-O(4)	2.040(5)
Co(4)-O(5)	2.128(5)	Co(3)-Co(4)	3.391(2)
Co(2)-Co(1)-Co(4)	98.9(1)	Co(1)-Co(2)-Co(3)	96.9(1)
S(1)-Co(1)-S(2)	89.9(1)	S(1)-Co(1)-O(2)	163.1(2)
S(1)-Co(1)-O(1)	90.7(1)	S(2)-Co(1)-O(1)	162.3(2)
S(2)-Co(1)-O(2)	90.8(2)	O(1)-Co(1)-O(2)	83.6(2)
S(1)-Co(1)-P(1)	101.5(1)	S(2)-Co(1)-P(1)	104.0(1)
O(1)-Co(1)-P(1)	93.3(2)	O(2)-Co(1)-P(1)	94.7(2)
S(1)-Co(2)-S(2)	82.2(1)	S(1)-Co(2)-S(3)	99.6(1)
S(2)-Co(2)-S(3)	177.7(1)	S(1)-Co(2)-S(4)	161.3(1)
S(2)-Co(2)-S(4)	98.3(1)	S(3)-Co(2)-S(4)	79.5(1)
S(1)-Co(2)-P(2)	93.4(1)	S(2)-Co(2)-P(2)	89.4(1)
S(3)-Co(2)-P(2)	91.8(1)	S(4)-Co(2)-P(2)	105.2(1)
S(3)-Co(3)-S(4)	85.4(1)	S(3)-Co(3)-O(3)	89.2(2)
S(4)-Co(3)-O(3)	167.4(2)	S(3)-Co(3)-O(4)	159.6(2)
S(4)-Co(3)-O(4)	89.8(1)	O(3)-Co(3)-O(4)	91.3(2)
S(3)-Co(3)-P(3)	102.5(1)	S(4)-Co(3)-P(3)	98.3(1)
O(3)-Co(3)-P(3)	93.9(2)	O(4)-Co(3)-P(3)	97.8(2)
S(5)-Co(4)-O(1)	130.9(2)	S(5)-Co(4)-O(2)	110.1(1)
O(1)-Co(4)-O(2)	75.7(2)	O(1)-Co(4)-O(4)	115.8(2)
S(5)-Co(4)-O(4)	112.3(2)	O(2)-Co(4)-O(4)	94.4(2)
S(5)-Co(4)-O(5)	84.0(1)	O(1)-Co(4)-O(5)	88.1(2)
O(2)-Co(4)-O(5)	163.1(2)	O(4)-Co(4)-O(5)	88.4(2)
Co(1)-S(1)-Co(2)	71.2(1)	Co(1)-S(2)-Co(2)	70.7(1)
Co(2)-S(3)-Co(3)	71.9(1)	Co(2)-S(4)-Co(3)	71.5(1)
Co(1)-O(1)-Co(4)	96.9(2)	Co(1)-O(2)-Co(4)	93.5(2)
Co(3)-O(4)-Co(4)	115.9(2)		

Co(2)···Co(1)···Co(4), Co(1)···Co(2)···Co(3), Co(2)···Co(3)···Co(4), and Co(3)···Co(4)···Co(1), respectively.

The Co^{II} atoms are five-coordinate with $Co(1)S_2O_2P$, $Co(2)S_4P$, and $Co(3)S_2O_2P$ in distorted square-based pyramidal geometries. The basal planes are composed of S_2O_2 or S_4 atoms while the pyramidal apices occupied by terminal bonding P atoms. The $Co(2)S_4$ plane is nearly perpendicular to the $Co(1)S_2O_2$ and $Co(3)S_2O_2$ planes with dihedral angles of 89.1 and 81.7°, respectively. The $Co(4)^{III}$ atom is in a distorted trigonal bipyramidal environment with atoms O(1), O(4), and S(5) in the equatorial plane, and O(2) and O(5) in axial positions. Although four of the mp^{2-} ligands in the molecule are chelated to Co(1) and Co(3), only three of them bound to Co(4) through μ_2-O bridges in O_bS_b-T mode, while the fourth is in O_tS_b mode without bonding to Co(4). Accordingly, the severe asymmetry of the molecule may result from the non-bonding feature between Co(4) and O(3) atoms (Co(4)···O(3) 3.307 Å) and the formation of a strong H-bond between O(3) and O(5) with O(3)···O(5) being 2.480 Å.

In the bridging groups Co-S_b-Co and Co-O_b-Co, the Co-S_b and Co-O_b distances inside the five-membered chelate rings are significantly shorter than those outside, as often observed in complexes of H_2mp[5],[16],[17] (except for the Ni-S_b bond in $Ni_3(mp)_2(Hmp)_2(PBu^n{}_3)_2$,[17] where the bond is abnormally long due to its location on the axis of the elongated octahedron). The bridging Co-S-Co angles (average 71.3°) are much smaller than Co-O-Co (average 102.1°). Co-S-C angles (average 96.4°) are smaller than Co-O-C (average 115.1°) due to the employment of different orbitals for bonding S and O atoms.[16]

FAB mass spectra

The molecular ion $[Co_4(mp)_4(Hmp)(PMe_2Ph)_3]^-$ (*m/z* 1271) and fragment ions $[Co_4(mp)_4(Hmp)(PMe_2Ph)]^-$ (*m/z* 995), $[Co_4(mp)_4(Hmp)]^-$ (*m/z* 857), $[Co_4(mp)_4]^-$ (*m/z* 732), $[Co_3(mp)_4]^-$ (*m/z* 673), $[Co_3(mp)_3]^-$ (*m/z* 549), $[Co_2(mp)_3]^-$ (*m/z* 490), and $[Co(mp)]^-$ (*m/z* 183) were observed in the FAB mass spectra. Obviously, the dissociation of the fragments follows the order PMe_2Ph first, then the mp ligands, conforming to the structural data in which the Co-P bonds located in the pyramidal apical sites are relatively weak. In the meantime, the dissociation of Co(Hmp) is quite easy, followed by Co(mp) and $Co(mp)_2$, in agreement with the fact that Co(Hmp) is only loosely linked by three OR bridges as shown by the structural data as well as the isolation of the partially Fe^{III}-substituted complex $Co_3Fe(mp)_4(Hmp)(PBu^n{}_3)_3$.[21]

Magnetic properties

The magnetic behaviour of the title complex is presented in Figure 2 in the form of χ_M *versus* T and μ_{eff} *versus* T, where χ_M and μ_{eff} denote the molar susceptibility and the effective magnetic moment per molecule, respectively. The molar susceptibilities increase continuously with decreasing temperature. However, deviation from Curie-like behaviour is obvious from using Curie-Weiss equations to fit the magnetic data in the range 300-30 K. Curie-Weiss parameters are $C = 2.53$ cm^3 K mol^{-1} ($C = 17Ng^2\beta^2/12k$) and θ = -4.8 K. The values give a g factor of 2.2.

In the temperature range 300-80 K, μ_{eff}/molecule values remain almost constant, then decrease gradually with decreasing temperature, indicating that there is appreciable intramolecular magnetic exchange. At temperature below 16 K, μ_{eff} values drop rapidly; this may be caused by intermolecular antiferromagnetic coupling or single-ion zero-field splitting of Co^{III}. This effect was neglected in the following magnetic analysis.

The Co^{II} centres may possess one or three unpaired electrons according to whether it in low ($S = 1/2$) or high ($S = 3/2$) spin state and the Co(III) ion can afford $S = 0$, 1 or 2 in different circumstances. Obviously, by fitting the experimental data, the title complex can best be described by assuming that the distorted square-pyramidally coordinated Co^{II} ions have low spin state with $S = 1/2$,[5],[23],[24] whereas the Co^{III} ion in trigonal-bipyramidal geometry has medium ground state spin of $S = 1$.[5] At 300 K, the measured μ_{eff} of 4.27 μ_B per Co$_4$ corresponds quite well to the spin-only value (4.12 μ_B for g = 2.0) expected for

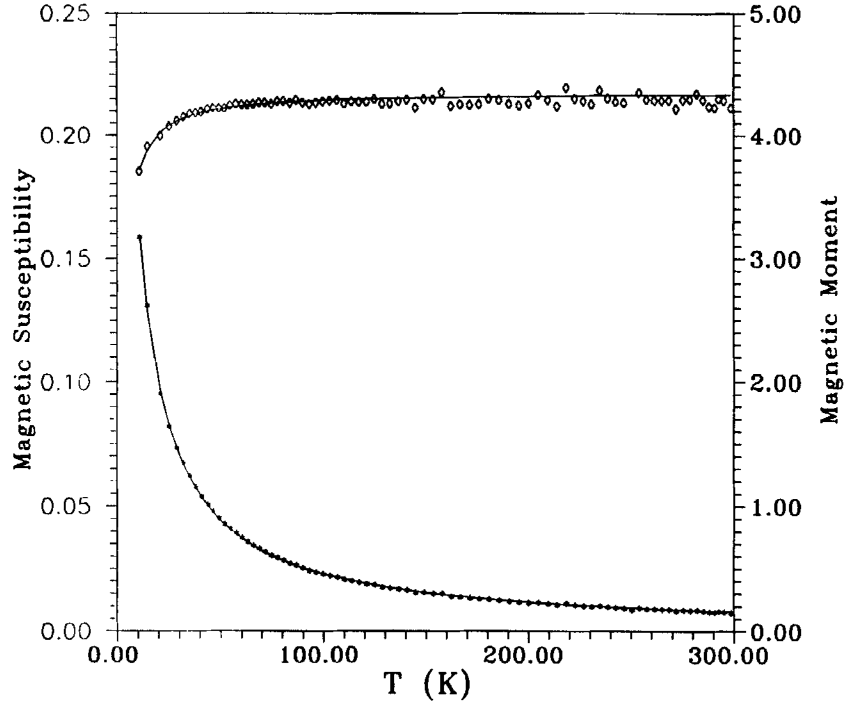

FIGURE 2 Plot of temperature dependences of the molar susceptibilities χ_M (*, cm^3/mol^{-1}) and the effective magnetic moments μ_{eff} (◇, μ_B) for Co$_4$(mp)$_4$(Hmp)(PMe$_2$Ph)$_3$. The solid lines represent the best calculated values.

three Co^{II} with $S = 1/2$ and one Co^{III} with $S = 1$, assuming no magnetic exchange interaction in the molecule.

The general spin Hamiltonian describing isotropic exchange interactions for a cyclic tetranuclear complex is given by (*1*), irrespective of the exchange interactions J_{13} and J_{24} which are negligible since the bridging pathways across the diamond shaped cyclic skeletal ring are too long. On the basis of the isotropic Heisenberg model, the molar susceptibility can be expressed as in (2), where N and k are Avogadro's and Boltzmann's constants, respectively, β is the Bohr magneton, $S_T = \Sigma S_i$, the total electronic spin of the magnetic centre concerned,

$$H = -2(J_{12}S_1 \cdot S_2 + J_{23}S_2 \cdot S_3 + J_{34}S_3 \cdot S_4 + J_{41}S_4 \cdot S_1) \qquad (1)$$

$$\chi_M = \frac{Ng^2\beta^2}{3kT} \frac{\sum_{ST} S_T(S_T + 1)(2S_T + 1)e^{-E(S_T)/kT}}{\sum_{ST} (2S_T + 1)e^{-E(S_T)/kT}} \qquad (2)$$

and $E(S_T)$ is the eigenvalue of the exchange interaction presented by (*1*). In the case of $S_1 = S_2 = S_3 = 1/2$ and $S_4 = 1$, if Kambe's theory is used,[24] then (*3*) results.

$$E(S_T) = -J_4S_T(S_T + 1) - S_{12}(S_{12} + 1)[J_1 - J_4] + S_{13}(S_{13} + 1)J_4 + S_{24}(S_{24} + 1)J_4 - S_{34}(S_{34} + 1)[J_3 - J_4] + S_1(S_1 + 1)(J_1 - J_4) + S_2(S_2 + 1)(J_1 + J_2 - 2J_4) + S_3(S_3 + 1)(J_1 + J_3 - 2J_4) + S_4(S_4 + 1)(-J_4 + J_3) \qquad (3)$$

In actual situations, suitable simplifications of the problem can often be made from symmetry considerations in order to reduce (*3*) to an unambiguous and simple expression, from which the energy values are available and hence the magnetic susceptibilities are readily obtained. However, for the cyclic tetranuclear coupling system with cobalt paramagnetic centres exhibiting different spin states, it is preferable to give the spin-spin interaction matrix rather than the expressions of the eigenvalues, and then the eigenvalues for the possible spin states can be obtained in numerical form from a full-matrix diagonalization of the Hamiltonian in (*1*).[25] With this method, the best fit parameters are $g = 2.1$, $J_{12} = -3.1$, $J_{23} = -3.2$, $J_{34} = -0.3$, and $J_{41} = -1.9\ cm^{-1}$. The best fit curve with this set of parameters is depicted in Figure 2.

Considering the fact that the Co(1,3)$^-$Co(4) distance is much longer than Co(1,3)$^-$Co(2), and thus the magnetic interactions of the former can be neglected, $Co^{III}(4)$ can be viewed as an isolated paramagnetic centre. Assuming the molecule to exhibit C_{2v} symmetry, and the interaction between Co(1) and Co(2) is equivalent to that between Co(2) and Co(3) with $J_{12} = J_{23} = J$, and Co^{II} and Co^{III} exhibit different g factors, a simplified model can be employed to carry out quantitative calculation according to (*4*), where $x = \exp(J/kT)$. A least-squares fit of the experimental data gave $g_1 = 2.10$, $g_2 = 2.25$, and $J = -4.1\ cm^{-1}$

which are quite close to those values for the complex $Co_4(mp)_4(PBu^n{}_3)_3(Cl)(MeOH)$[5] obtained by the same simplified method.1

$$\chi_M = \frac{Ng1^2\beta^2}{4kT}\,\frac{10x + x^{-2} + 1}{2x + x^{-2} + 1} + \frac{2Ng2^2\beta^2}{3kT} \qquad (4)$$

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