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Phosphine-Participated Cluster Formation: Syntheses, Structures, and Magnetic Properties of Tri- and Tetracobalt Phosphine Complexes of *o*-Mercaptophenol (H_2mp), $Co_3(mp)_2(Hmp)_2(PEt_3)_3$ and $Co_4(mp)_4(PBu^n_3)_3Cl(MeOH)$

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Neutral tri- and tetracobalt complexes $Co_3(mp)_2(Hmp)_2(PEt_3)_3$ (**1**) and $Co_4(mp)_4(PBu^n_3)_3Cl(MeOH)$ (**2**) with mixed trialkylphosphine and *o*-mercaptophenolate (mp^{2-}) ligands were obtained by the reactions of cobaltous salts with mp^{2-} in the presence of phosphine in alcoholic solutions. Complex **1** crystallizes in the triclinic space group $P\bar{1}$, with fw = 1029.95, $a = 13.668(5)$ Å, $b = 16.988(6)$ Å, $c = 11.237(3)$ Å, $\alpha = 100.36(2)°$, $\beta = 103.90(3)°$, $\gamma = 81.41(3)°$, $V = 2476.0$ Å^3, $Z = 2$, $R = 0.055$, and $R_w = 0.057$. Complex **2** crystallizes also in the triclinic space group $P\bar{1}$, with fw = 1406.85, $a = 13.316(6)$ Å, $b = 24.721(7)$ Å, $c = 11.946(4)$ Å, $\alpha = 91.20(3)°$, $\beta = 111.83(3)°$, $\gamma = 75.17(3)°$, $V = 3516.9$ Å^3, $Z = 2$, $R = 0.066$, and $R_w = 0.067$. Structural analyses revealed that both complexes are unsymmetrical due to the different bonding characters of the sulfur and oxygen donor atoms of the *o*-mercaptophenol ligand. Possible reactive fragments are proposed for the formation of these complexes. Variable-temperature magnetic susceptibility measurements revealed the antiferromagnetic interaction in **1** and **2**.

Introduction

The coordination chemistry of transition metal complexes with mixed phosphine and thiolato ligands has attracted the attention of inorganic chemists as early as the sixties,[1-3] yet systematic studies and investigations of the coordination behavior are still frugal. For the complexes containing both phosphine and thiolato ligands, they can be classified into four categories, those with either both ligands monodentate or both bidentate and those with either the phosphine ligand monodentate and the thiolato ligand bidentate or vice versa. Since the synthesis of the first dinuclear cobalt complex with bidentate dppe[4] and monodentate thiophenlate,[5,6] a series of such mixed-ligated cobalt complexes has been reported.[7-13] However, it is surprising to note that before the successful isolation and characterization of the tricobalt complex $Co_3(bdt)_3(PBu^n_3)_3$,[4,10] polynuclear cobalt complexes with mixed monodentate phosphine and 1,2-bidentate thiolate ligations were unknown.

We are engaged in the investigation of the structural chemistry of this latter type of cobalt complex and have reported the cluster complex $Co_4(mp)_4(Hmp)(PBu^n_3)_3$.[4,13] By variation of the molar ratio of the reactants and changing of the reaction conditions such as the amount of air, two new cluster complexes $Co_3(mp)_2(Hmp)_2(PEt_3)_3$ (**1**)[12] and $Co_4(mp)_4(PBu^n_3)_3Cl(MeOH)$ (**2**) were obtained and are presented in this paper. Also included are the crystal structures and variable-temperature magnetic susceptibility measurements.

Experimental Section

All operations were carried out under a dinitrogen atmosphere with Schlenk type apparatus unless otherwise stated. *o*-Mercaptophenol (H_2mp), tri-*n*-butylphosphine (PBu^n_3), and triethylphosphine (PEt_3) purchased from Merck-Schuchardt and anhydrous cobaltous chloride or cobaltous acetate were used as received. Absolute ethanol was flushed with pure dinitrogen for 2–3 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 this Institute.

Preparation of Compounds. $Co_3(mp)_2(Hmp)_2(PEt_3)_3$ (1). To a solution containing 0.21 g (1.62 mmol) of $CoCl_2$ and 0.33 g (6.11 mmol) of NaOMe in 30 mL of absolute EtOH was added 0.24 mL (1.63 mmol) of PEt_3 ($d = 0.81$ g·cm^{-3}) via a syringe. After the mixture was stirred for a while, 0.16 mL of H_2mp (1.55 mmol) was added. The solution was filtered immediately after the quick mixing. The dark brown filtrate was kept at 5 °C for several days to give 0.36 g (65% yield based on Co) of very hygroscopic and air-sensitive black cubic crystals of **1**. It was observed that single crystals suitable for X-ray diffraction analysis can be obtained with the presence of an excess of NaOMe. IR (KBr; cm^{-1}): 419 (m), 465 (w), 625 (m), 717 (s), 749 (s), 757 (sh), 848 (m), 1001 (m), 1032 (s), 1122 (m), 1149 (w), 1233 (s), 1266 (s), 1300 (s), 1379 (m), 1438 (sh), 1452 (s), 1560 (m), 1573 (m), 2876 (m), 2910 (m), 2934 (m), 2964 (m), 3054 (w). ^{31}P NMR: 54.4 ppm (broad, $\Delta\delta = 30$ ppm). Anal. Calcd for $C_{42}H_{63}Co_3O_4P_3S_4$: C, 48.98; H, 6.17; Co, 17.17; P, 9.02. Found: C, 50.81; H, 7.33; Co, 16.82; P, 9.04.

$Co_4(mp)_4(PBu^n_3)_3Cl(MeOH)$ (2). To the solution of 0.10 g (0.77 mmol) of $CoCl_2$ in 30 mL of MeOH was added first 0.4 mL (1.61 mmol) of PBu^n_3 with stirring and then 0.01 mL (0.097 mmol) of H_2mp at room temperature. After filtration, the reddish brown filtrate gave 0.022 g (8% yield based on Co) of dark block-shaped crystals of product **2**. The addition of NaOMe did not change the product. IR (KBr; cm^{-1}): 720 (s), 742 (s), 774 (m), 848 (m), 901 (s), 1049 (m), 1090 (m), 1119 (w), 1208 (w), 1234 (w), 1269 (m), 1304 (m), 1411 (w), 1437 (s), 1450 (s), 1573 (m), 2868 (s), 2929 (s), 2954 (s), 3050 (w). Anal. Calcd for

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(4) Abbreviations: bdt = 1,2-benzenedithiolate; mp = *o*-mercaptophenolate; Hmp = *o*-hydroxybenzenethiolate; dppe = (diphenylphosphino)ethane; mpo = 2-mercaptopyridine *N*-oxide.

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Table 1. Crystallographic Data for Complexes **1** and **2**

	1	**2**
formula	$C_{42}H_{63}Co_3O_4P_3S_4$	$C_{61}H_{101}ClCo_4O_5P_3S_4$
fw	1029.95	1406.85
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a, Å	13.668(5)	13.316(6)
b, Å	16.988(6)	24.721(7)
c, Å	11.237(3)	11.946(4)
α, deg	100.36(2)	91.20(3)
β, deg	103.90(3)	111.83(3)
γ, deg	81.41(3)	75.17(3)
V, Å^3	2476.0	3516.9
Z	2	2
T, °C	23	23
D_{calcd}, g·cm^{-3}	1.38	1.33
μ, cm^{-1}	12.9	11.9
transm coeff	0.890–0.999	0.872–0.997
R^a	0.055	0.066
$R_w{}^b$	0.057	0.067

[a] $R = (\sum||F_o| - |F_c||)/\sum|F_o|$. [b] $R_w = \{[\sum w(|F_o| - |F_c|)^2]/\sum w|F_o|^2\}^{1/2}$.

$C_{61}H_{101}ClCo_4O_5P_3S_4$: Co, 16.76; Cl, 2.52; P, 6.60; S, 91.2. Found: Co, 15.98; Cl, 2.30; P, 6.42; S, 8.12.

Structure Determination. Single crystals of compounds **1** and **2** of suitable dimensions were sealed inside glass capillaries under nitrogen. Diffraction data were collected on a Rigaku AFC-5R diffractometer in the ω–2θ scan mode with Mo Kα radiation (λ = 0.710 69 Å) and a graphite monochromator. The parameters utilized in intensity collections and refinements together with the crystallographic data are summarized in the supplementary material. All calculations were performed on a VAX 11/785 computer using the SDP/VAX program package.

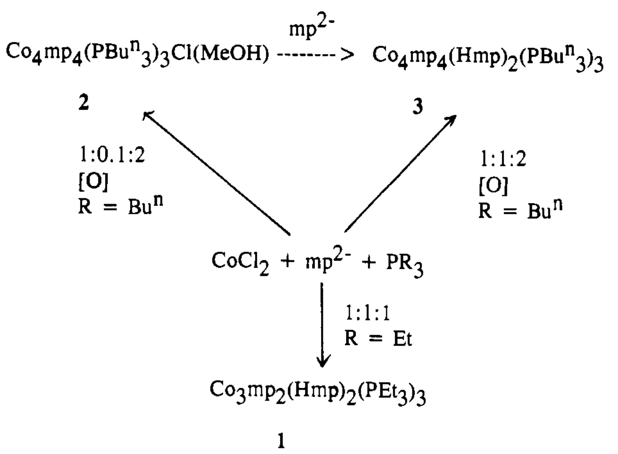
The intensity data collected were corrected for Lp factors and empirical absorptions. The structures were solved by direct methods and difference Fourier syntheses and refined by full-matrix least-squares techniques with anisotropic thermal parameters for all the non-hydrogen atoms. The hydrogen atoms except H_b of **1** were added only to the structure factor calculations, but their positions were not refined. The position of H_b of **1** was refined isotropically. The crystallographic data for complexes **1** and **2** are listed in Table 1.

Physical Measurements. Infrared spectra (KBr pellet) were recorded on a Digilab FTS-40 spectrophotometer. ^{31}P NMR spectra were obtained from a Bruker AM500 NMR spectrometer, with 85% H_3PO_4 as external standard. The ^{31}P chemical shift of free ligand PEt_3 appears at −20.1 ppm.[14] Chemical shifts are quoted on the δ scale (downfield shifts are positive). Variable-temperature magnetic susceptibility of compound **1** was measured on a Shimadzu MB-2 magnetic balance at a magnetic field of 1.2 T with the temperature of the sample raised gradually from 70 to 300 K, while that of compound **2** was performed on a Model CF-1 superconducting extracting sample magnetometer at a magnetic field of 5.0 T with the powdered samples kept in capsules for weighing. The temperature of the latter was raised gradually from 1.5 to 300 K. Data were recorded at an applied field gradient $H(dH/dX)$ of 1.4 × 10^7 Oe × Oe/cm. An interval of 30 s was kept between data collection, and each measurement took 10 s. Values of g, J, and TIP are obtained by a QCP230 program.[15] Calculations were done on the VAX 11/785 computer with the VAX/VMS operating system.

Results and Discussion

Synthesis and Structure. In the presence of phosphine, the products of the reaction of Co(II) salt with o-mercaptophenolate in protic solvents (MeOH or EtOH) vary not only with the molar ratio of the reactants but also with whether or not air is strictly excluded. When 1:1:1 ratio of Co^{2+}:H_2mp:PR_3 was employed in the presence of excess of NaOMe, the tricobalt complexed $Co_3(mp)_2(Hmp)_2(PEt_3)_3$ (**1**) was obtained anaerobically overnight, which has been preliminarily communicated.[12] When the reaction solution of 1:1:2 molar ratio of reagents was left in an icebox for a long period of time (1 month), a certain amount of air might have leaked into the Schlenk tube and the product identified was $Co_4(mp)_4(Hmp)(PBu^n{}_3)_3$ (**3**)[13] in which one Co atom is in the oxidized form. If a molar ratio of 1:0.1:2 of the starting reagents was used, only the product $Co_4(mp)_4(PBu^n{}_3)_3Cl(MeOH)$ (**2**) was isolated in low yield (based on Co) due to insufficient amount of the ligand mp. Complex **2** cannot be isolated if the reaction is strictly anaerobic but can be formed when a trace of air was passed into the reaction solution, again indicating the coordination of Co(III) because of air oxidation. The reactions can be summarized in the Scheme 1.

Scheme 1



The reaction might have proceeded through the substitution of mp^{2-} onto the initially formed $(PR_3)_2CoCl_2$ giving the metastable intermediates $(mp)_xCo(PR_3)_y{}^{n-}$ (x = 1, y = 1, 2, n = 0; x = 2, y = 1, 2, n = 2). These latter intermediates are too reactive to be isolated and interact rapidly with other species such as $Co(mp)_2{}^{2-}$ or/and $Co(PR_3)_2Cl_2$ in solution to give the various products. Species such as $L_2Co(PBu_3)^{n-}$ (L = mpo,[4] n = 0;[11] L = bdt,[4], n = 1[10]) with Co(II) or Co(III) in a square pyramidal environment are stable and have been identified structurally. The reactive fragments with L = mp may assemble under suitable conditions to form various types of multinuclear complexes whose isolation depends on the basicity of the solution and the solvents. In the cases of **1**–**3**, protic solvents favor the formation of intramolecular hydrogen bonds and stabilize the molecules.

The atomic coordinates and their standard deviations and thermal parameters of the non-hydrogen atoms of complexes **1** and **2** are listed in Tables 2 and 3, respectively. Selected atomic distances and bond angles of **1** and **2** are listed in Tables 4 and 5, respectively.

Figure 1 depicts the structure of **1**. The molecule is highly unsymmetrical due to the presence of two intramolecular hydrogen bonds. The three Co atoms form a nonequilateral triangle with varied Co–Co distances which are significantly shorter than those in another tricobalt–thiolato complex $[Co_3S(o\text{-}(SCH_2)_2C_6H_4)_3]^{2-}$ (average 2.780(6) Å),[16] in which all the Co atoms are tetrahedrally coordinated by sulfur atoms and bridged by a μ_3-S, although the tetrahedral S-coordinated Co complex $[Co_8S_6(SC_6H_5)_8]^{4-}$ [17] was found to have short Co–Co distances (2.662(16) Å). The S and O donor atoms from four o-mercaptophenol ligands bridge the three Co atoms, while a PEt_3 group is terminally coordinated to each Co atom, resulting in two coordination geometries for the metal environments: 4-coordinated trigonal pyramidal Co(1)-S_2OP with O(4) in the apex and 5-coordinate square pyramidal Co(2 or 3)S_3OP with P in the apex.

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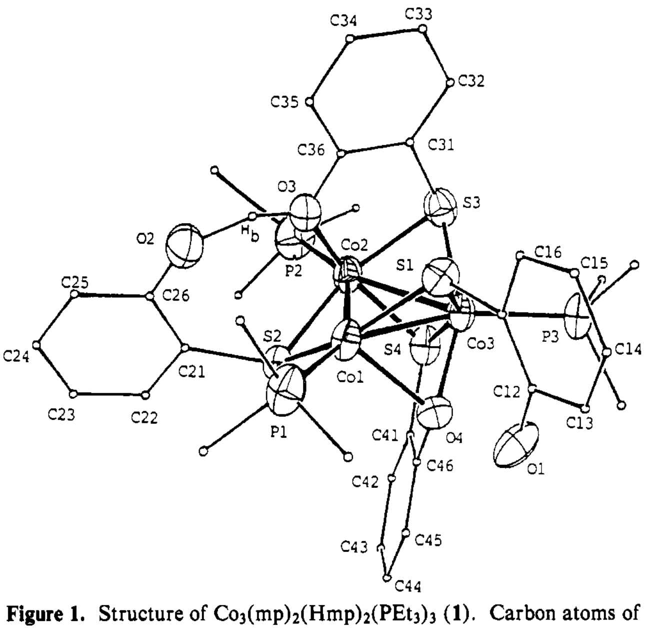


Figure 1. Structure of $Co_3(mp)_2(Hmp)_2(PEt_3)_3$ (**1**). Carbon atoms of the phenyl rings and of the ethyl groups of the phosphine are represented by spheres of arbitrary size for clarity.

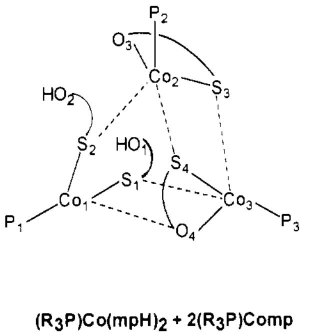
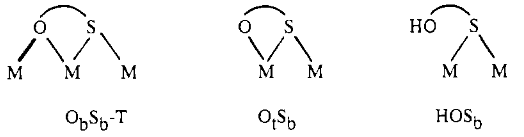


Figure 2. Schematic view of complex $Co_3(mp)_2(Hmp)_2(PEt_3)_3$ (**1**) with atomic labeling.

The four *o*-mercaptophenolate ligands coordinate to the Co atoms in three different modes O_bS_b-T, O_tS_b, and HOS_b:



Here b stands for bridge, t for terminal, and T for trinuclear. The chelating modes O_bS_b-T and O_tS_b have been observed in $Co_4(mp)_4(Hmp)(PBu^n{}_3)_3$ (**3**)[10] and mode HOS_b in $[Ni_2(mp)_2(Hmp)_2]^{2-}$;[18] the latter complex was also stabilized by intramolecular hydrogen bonds.

On close examination of the Co–S and Co–O distances, it is found that they are obviously shorter within a five-membered chelate ring than outside in both complexes **1** and **2**, which is generally true for most 1,2-bidentate chelations, as compared in Table 6 together with complex **3**.

In complex **1**, bidentate thiolate mp3 (with donor atoms O(3) and S(3)) and mp4 (O(4) and S(4)) can be considered terminally chelated to Co(2) and Co(3), respectively, since Co(3)–S(3)$_{out}$ (2.242(3) Å), Co(2)–S(4)$_{out}$ (2.240(2) Å), and Co(1)–O(4)$_{out}$ (2.222(6) Å) are longer than the respective bonds Co(2)–S(3)$_{in}$ (2.212(3) Å), Co(3)–S(4)$_{in}$ (2.201(2) Å), and Co(3)–O(4)$_{in}$ (1.995(5) Å) of the same chelate ring. In the meantime, Hmp2 (donor atom S(2)) and Hmp1 (S(1)) can be considered monodentately ligated to Co(1) through the sulfur atoms as Co(1)–S(2) and Co(1)–S(1) are slightly (0.01–0.03 Å) but evidently shorter than Co(2)–S(2) and Co(3)–S(1), respectively. In this way, the molecule can be envisaged as the combination of one $R_3PCo(Hmp)_2$ (**a**) and two $R_3PCo(mp)$ (**b**) groups as shown in Figure 2. Since we have not been able to isolate binuclear species like $(R_3P)_2Co_2(mp)_y$ (y = 1–3, n = 2+, 0, or 2–), the construction process of a molecule of **1**—whether by spontaneous assembly of mononuclear species **a** and **b** or by stepwise reaction through a binuclear species—cannot be determined for the time being.

In addition to the bridging effect of the S and O atoms of the mercaptophenol ligands, the molecule of **1** is stabilized further by two strong intramolecular H-bonds between O(3)···O(2) (2.499 Å) and O(1)···O(4) (2.535 Å).

The molecular structure of complex **2** as depicted in Figure 3 is very similar to that reported for $Co_4(mp)_4(Hmp)(PBu^n{}_3)_3$ (**3**)[13] except for the ligation of Co(4), where the bidentate *o*-mercaptophenolate group has been substituted by a Cl ion and a MeOH molecule. On comparison (Table 6), we can see that all the important structural parameters are nearly the same for the complexes **2** and **3**. The ligation of Cl to Co(4) changes electronically but only slightly the geometry of the molecule. The Co(4)–Cl distance of 2.284(6) Å is rather long compared to other Co(III)–Cl distances either in 5-coordinate $Co(PEt_3)_2Cl_3$ (2.196(2) Å)[19] or in 6-coordinate *trans*-$[Co\{o\text{-}(Me_2P)_2C_6H_4\}_2Cl_2]^+$ (2.253 Å)[20] and implies a rather weak binding and can be easily substituted by other coordinating groups like an excess of H_2mp. The ligation of MeOH stabilizes the molecule in two ways; it not only completes the coordination sphere of the Co(4) atom but also provides a very strong hydrogen bond intramolecularly (O···O(4) = 2.360 Å).

The bond length differences in complex **2** of the bridging Co–S and Co–O bonds inside and outside the five-membered chelate rings $\overline{\text{S–C–C–O–Co}}$ lead to the assumption of the presence of fragment $Bu_3PCo(mp)_2{}^{2-}$, two of which on coordination by species $(Bu_3P)_2CoCl_2$ and $Co^{III}Cl_4{}^-$ present in solution gave the tetranuclear product **2** as schematically depicted in Figure 4.

As only 0.01 mL (0.1 mmol) of H_2mp was added in the preparative process of **2**, being one-eighth the amount needed for **3**, the yield of **2** was very low. However, the trace amount of air present in the reaction system was just enough to oxidize some of the Co(II) into Co(III) for coordination. When the amounts of starting materials were increased 5-fold, no product **2** could be isolated without the deliberate addition of dry air. If more mp^{2-} was added, **2** was rapidly transformed into **3** (identified by single-crystal unit cell parameters). It is worthwhile to note that the production of complex **2** is not affected by the basicity of the reaction. On the other hand, the complexes **1** and **3** are obtained only under basic conditions.

Magnetic Properties. The magnetic properties of a polynuclear complex are extremely sensitive to structural modifications. On the basis of variable-temperature magnetic susceptibility measurements, the magnetic properties of **1** and **2** can be derived in terms of antiferromagnetic interactions and relation is drawn between magnetic behavior and the molecular structures.

The temperature-dependent behaviors of the effective magnetic moments of the two complexes are similar. They rise quickly in

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Table 2. Positional Parameters and Their Estimated Standard Deviations for the Tricobalt Complex **1**

atom	x	y	z	B^a (Å^2)	atom	x	y	z	B^a (Å^2)
Co(1)	0.2416(1)	0.21294(9)	0.8944(1)	3.39(4)	C(34)	0.1727(9)	0.5405(7)	0.998(1)	6.1(4)
Co(2)	0.1460(1)	0.27066(9)	0.6891(1)	3.42(4)	C(35)	0.1321(9)	0.4687(7)	0.967(1)	6.0(4)
Co(3)	0.3358(1)	0.24716(8)	0.7424(1)	3.16(4)	C(36)	0.1546(8)	0.4125(6)	0.867(1)	4.7(3)
S(1)	0.3600(2)	0.2953(2)	0.9426(2)	3.74(7)	C(41)	0.2643(6)	0.0920(6)	0.5951(8)	2.9(3)
S(2)	0.1094(2)	0.1669(2)	0.7602(2)	3.32(7)	C(42)	0.2275(7)	0.0305(6)	0.5080(8)	4.0(3)
S(3)	0.2457(2)	0.3590(2)	0.6775(2)	4.05(8)	C(43)	0.2481(7)	–0.0478(6)	0.5327(9)	4.1(3)
S(4)	0.2418(2)	0.1931(2)	0.5675(2)	3.58(7)	C(44)	0.3049(8)	–0.0642(6)	0.6480(9)	4.5(3)
P(1)	0.2429(2)	0.1669(2)	1.0654(3)	4.80(9)	C(45)	0.3411(7)	–0.0010(6)	0.7380(9)	3.8(3)
P(2)	0.0050(2)	0.3009(2)	0.5512(3)	5.8(1)	C(46)	0.3209(7)	0.0754(6)	0.7099(8)	3.2(3)
P(3)	0.4816(2)	0.2569(2)	0.6934(3)	4.08(8)	C(111)	0.3652(8)	0.1136(8)	1.129(1)	6.9(4)
O(1)	0.5215(5)	0.1316(4)	0.9515(6)	4.9(2)	C(112)	0.370(1)	0.071(1)	1.242(1)	9.3(6)
O(2)	0.0146(6)	0.2972(4)	0.9626(7)	5.6(2)	C(121)	0.209(1)	0.2412(9)	1.191(1)	8.5(5)
O(3)	0.1166(5)	0.3424(4)	0.8355(7)	4.9(2)	C(122)	0.264(1)	0.3143(9)	1.224(1)	9.8(6)
O(4)	0.3538(5)	0.1388(4)	0.7946(5)	3.2(2)	C(131)	0.1543(8)	0.919(8)	1.053(1)	6.5(4)
C(11)	0.4833(7)	0.2706(6)	1.0393(8)	3.8(3)	C(132)	0.172(1)	0.0153(9)	0.964(1)	8.7(5)
C(12)	0.5448(7)	0.1984(7)	1.0313(9)	4.3(3)	C(211)	0.032(1)	0.3364(9)	0.419(1)	8.9(5)
C(13)	0.6391(8)	0.1952(8)	1.113(1)	5.7(4)	C(212)	–0.053(1)	0.353(1)	0.314(2)	14.4(8)
C(14)	0.6700(8)	0.2580(8)	1.198(1)	6.3(4)	C(221)	–0.0770(9)	0.2206(9)	0.488(1)	8.3(5)
C(15)	0.6090(9)	0.3303(7)	1.209(1)	6.0(4)	C(222)	–0.028(1)	0.149(1)	0.417(1)	10.6(6)
C(16)	0.5135(8)	0.3371(7)	1.1266(9)	4.7(3)	C(231)	–0.088(1)	0.376(1)	0.611(2)	13.1(7)
C(21)	–0.0063(7)	0.1758(5)	0.8108(8)	2.9(3)	C(232)	–0.135(3)	0.389(3)	0.669(4)	16(2)
C(22)	–0.0654(8)	0.1144(6)	0.7610(9)	4.3(3)	C(232′)	0.061(3)	0.554(2)	0.360(3)	12(1)
C(23)	–0.1506(8)	0.1087(7)	0.800(1)	5.5(4)	C(311)	0.5661(8)	0.3249(7)	0.798(1)	5.4(4)
C(24)	–0.1790(8)	0.1640(7)	0.891(1)	4.8(3)	C(312)	0.520(1)	0.4117(7)	0.822(1)	7.1(4)
C(25)	–0.1250(8)	0.2275(6)	0.941(1)	4.5(3)	C(321)	0.5674(8)	0.1651(7)	0.679(1)	5.0(3)
C(26)	–0.0370(7)	0.2341(6)	0.9037(9)	3.8(3)	C(322)	0.5268(9)	0.0990(8)	0.578(1)	6.9(4)
C(31)	0.2192(7)	0.4315(6)	0.799(1)	4.2(3)	C(331)	0.4588(9)	0.2918(8)	0.543(1)	6.7(4)
C(32)	0.2593(8)	0.5045(6)	0.830(1)	4.8(3)	C(332)	0.556(1)	0.297(1)	0.498(1)	11.0(7)
C(33)	0.2375(9)	0.5592(7)	0.930(1)	6.1(4)	Hb	0.064(8)	0.329(6)	0.921(9)	6(3)*

[a] Starred B values are for atoms that were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Table 3. Positional Parameters and Their Estimated Standard Deviations for the Tetracobalt Complex **2**

atom	x	y	z	B^a (Å^2)	atom	x	y	z	B^a (Å^2)
Co(1)	0.8203(2)	0.26257(8)	0.4876(2)	3.44(5)	C(44)	0.938(1)	0.4221(7)	0.740(2)	6.5(6)
Co(2)	0.6354(2)	0.26908(9)	0.5234(2)	3.48(5)	C(45)	0.974(1)	0.3666(7)	0.725(1)	5.3(5)
Co(3)	0.7294(2)	0.20098(8)	0.7224(2)	3.69(6)	C(46)	0.897(1)	0.3403(6)	0.647(1)	4.0(4)
Co(4)	0.9591(2)	0.1599(1)	0.7211(3)	8.6(1)	C(111)	0.802(1)	0.2978(7)	0.202(1)	5.0(5)
Cl	1.0918(6)	0.0764(3)	0.7951(6)	10.7(2)	C(112)	0.711(1)	0.3541(9)	0.175(2)	8.4(7)
S(1)	0.6831(3)	0.2330(2)	0.3660(4)	3.7(1)	C(113)	0.619(2)	0.364(1)	0.059(2)	8.6(7)
S(2)	0.5794(3)	0.1966(2)	0.5771(4)	4.3(1)	C(114)	0.560(2)	0.4249(9)	0.023(2)	11.7(9)
S(3)	0.6572(3)	0.2897(2)	0.7190(4)	3.9(1)	C(121)	1.011(1)	0.2250(7)	0.349(1)	6.0(5)
S(4)	0.6977(3)	0.3405(2)	0.4761(4)	3.6(1)	C(122)	1.116(1)	0.2104(8)	0.466(2)	6.8(6)
P(1)	0.8950(3)	0.2821(2)	0.3596(4)	4.3(1)	C(123)	1.199(2)	0.1545(8)	0.461(2)	8.5(7)
P(2)	0.4519(3)	0.3156(2)	0.4138(4)	4.4(1)	C(124)	1.303(2)	0.142(1)	0.574(2)	12(1)
P(3)	0.7041(4)	0.1681(2)	0.8784(4)	5.4(1)	C(131)	0.949(1)	0.3419(6)	0.403(1)	4.9(5)
O	1.059(1)	0.2077(6)	0.750(1)	13.0(6)	C(132)	1.005(1)	0.3606(8)	0.321(2)	6.7(6)
O(1)	0.9108(7)	0.1842(4)	0.5402(8)	4.3(3)	C(133)	1.037(2)	0.4178(8)	0.356(2)	10.3(7)
O(2)	0.8051(7)	0.1300(4)	0.6867(8)	4.1(3)	C(134)	0.946(2)	0.463(1)	0.339(3)	18(1)
O(3)	0.8789(7)	0.2100(4)	0.8093(8)	4.0(3)	C(211)	0.427(1)	0.3627(6)	0.285(1)	4.7(5)
O(4)	0.9276(7)	0.2867(4)	0.6227(8)	3.9(3)	C(212)	0.303(1)	0.3912(8)	0.205(2)	7.5(7)
C	1.159(2)	0.1913(8)	0.792(2)	7.7(7)	C(213)	0.291(2)	0.431(1)	0.103(2)	12(1)
C(11)	0.760(1)	0.1624(5)	0.378(1)	3.5(4)	C(214)	0.171(2)	0.457(1)	0.025(3)	16(1)
C(12)	0.718(1)	0.1245(6)	0.297(1)	4.2(5)	C(221)	0.355(1)	0.2722(6)	0.344(1)	4.7(5)
C(13)	0.789(1)	0.0719(7)	0.298(1)	6.1(6)	C(222)	0.385(1)	0.2338(7)	0.254(2)	7.0(6)
C(14)	0.898(1)	0.0572(7)	0.382(1)	6.1(6)	C(223)	0.299(2)	0.2029(8)	0.193(2)	8.9(8)
C(15)	0.940(1)	0.0935(6)	0.462(1)	4.4(5)	C(224)	0.333(2)	0.1620(9)	0.108(2)	13(1)
C(16)	0.870(1)	0.1467(5)	0.462(1)	3.4(4)	C(231)	0.380(1)	0.3602(8)	0.500(1)	6.3(6)
C(21)	0.629(1)	0.1267(6)	0.543(1)	4.5(5)	C(232)	0.430(2)	0.4092(8)	0.549(2)	7.7(7)
C(22)	0.557(1)	0.0960(7)	0.466(1)	5.9(5)	C(233)	0.385(2)	0.4374(9)	0.645(2)	14(1)
C(23)	0.607(2)	0.0401(7)	0.458(2)	8.3(7)	C(234)	0.433(3)	0.486(1)	0.688(2)	19(2)
C(24)	0.719(2)	0.0163(7)	0.519(2)	7.4(6)	C(311)	0.653(2)	0.1047(7)	0.847(1)	7.2(6)
C(25)	0.788(1)	0.0445(6)	0.596(1)	5.2(5)	C(312)	0.641(2)	0.0790(8)	0.954(2)	10.2(6)
C(26)	0.740(1)	0.1012(6)	0.609(1)	4.1(4)	C(313)	0.611(2)	0.019(1)	0.921(3)	17(1)
C(31)	0.784(1)	0.3043(6)	0.819(1)	3.7(4)	C(314)	0.508(3)	0.032(2)	0.841(3)	25(2)
C(32)	0.785(1)	0.3562(7)	0.870(1)	5.2(5)	C(321)	0.833(1)	0.1518(8)	1.016(1)	5.8(5)
C(33)	0.884(1)	0.3614(6)	0.957(1)	5.4(5)	C(322)	0.921(2)	0.1000(9)	1.015(2)	9.5(8)
C(34)	0.975(1)	0.3179(7)	0.995(1)	5.5(5)	C(323)	1.036(2)	0.102(1)	1.133(2)	15(1)
C(35)	0.978(1)	0.2661(7)	0.944(1)	5.0(5)	C(324)	1.115(3)	0.055(2)	1.133(3)	20(2)
C(36)	0.879(1)	0.2588(6)	0.855(1)	3.3(4)	C(331)	0.603(1)	0.2159(8)	0.926(2)	6.4(6)
C(41)	0.785(1)	0.3726(6)	0.587(1)	4.2(4)	C(332)	0.484(2)	0.2322(9)	0.838(2)	8.9(7)
C(42)	0.753(1)	0.4296(6)	0.605(2)	6.0(6)	C(333)	0.411(2)	0.280(1)	0.874(3)	16(1)
C(43)	0.829(2)	0.4544(8)	0.686(2)	7.3(6)	C(334)	0.303(2)	0.299(1)	0.798(4)	22(2)

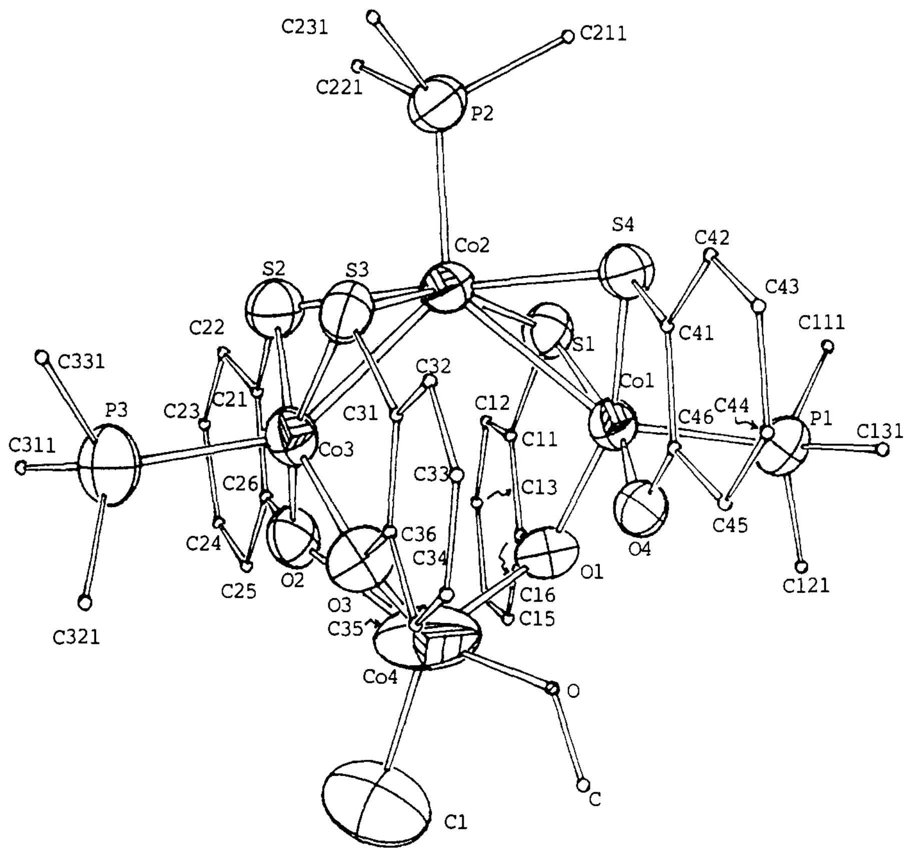

Figure 3. Structure of $Co_4(mp)_4(PBu^n_3)_3Cl(MeOH)$ (**2**). Carbon atoms of the phenyl rings and of the butyl groups of the phosphine are represented by spheres of arbitrary size for clarity. The oxygen atom of MeOH on Co(4) is also represented by an arbitrary sphere.

Table 4. Selected Atomic Distances (Å) and Bond Angles (deg) for the Tricobalt Complex **1**

Co(1)–Co(2)	2.641(1)	Co(2)–O(3)	1.950(7)
Co(1)–Co(3)	2.559(1)	Co(3)–O(4)	1.995(5)
Co(2)–Co(3)	2.505(1)	Co(1)–P(1)	2.197(3)
Co(1)–S(1)	2.203(3)	Co(2)–P(2)	2.221(3)
Co(1)–S(2)	2.200(2)	Co(3)–P(3)	2.227(2)
Co(2)–S(2)	2.226(2)	S(1)–C(11)	1.809(8)
Co(2)–S(3)	2.212(3)	S(2)–C(21)	1.783(8)
Co(2)–S(4)	2.240(2)	S(3)–C(31)	1.732(9)
Co(3)–S(1)	2.214(2)	S(4)–C(41)	1.768(8)
Co(3)–S(3)	2.242(3)	O(1)–C(12)	1.34(2)
Co(3)–S(4)	2.201(2)	O(2)–C(26)	1.35(1)
Co(1)–O(4)	2.222(6)	O(3)–C(36)	1.33(2)
Co(1)–Co(2)–Co(3)	59.57(5)	Co(2)–O(3)–C(36)	118.7(6)
Co(2)–Co(3)–Co(1)	62.86(4)	Co(3)–O(4)–C(46)	119.1(5)
Co(3)–Co(1)–Co(2)	57.57(5)	O(3)–Co(2)–S(3)	86.6(2)
Co(2)–S(3)–C(31)	98.3(3)	O(4)–Co(3)–S(4)	86.3(2)
Co(3)–S(4)–C(41)	98.1(3)		

the range 1.5–60 K and then keep almost constant in the range 60–300 K implying weak antiferromagnetic coupling of the complexes. The value of complex **2** is larger than that of **1**, which implies a larger effective spin of the former.

The basic theory for the description of an exchange-coupled system is the Heisenberg model, where the Hamiltonian appropriate for magnetic exchange interaction is presented as

$$H = -2\sum_{i>j} J_{ij} S_i \cdot S_j \tag{1}$$

where S_i and S_j are the spins of magnetic centers i and j, respectively. J_{ij} is the isotropic coupling constant between magnetic centers i and j and characterizes the exchange interaction, which is antiferromagnetic when $J < 0$ and ferromagnetic when $J > 0$. On the basis of the isotropic Heisenberg model, the molar susceptibility can be expressed as

$$\chi_M = \frac{Ng^2{\mu_B}^2}{3kT}\,\frac{\sum_{S_T} S_T(S_T + 1)(2S_T + 1)\exp(-E(S_T)/kT)}{\sum_{S_T} (2S_T + 1)\exp(-E(S_T)/kT} \tag{2}$$

where N and k are Avogadro's and Plank's constants, respectively, μ_B is the Bohr magneton, $S_T = \sum S_i$, the total electronic spin of the part concerned, and $E(S_T)$ is the eigenvalue of the exchange interaction presented by eq 1. Equation 2 is known from Kambe's theory.[20] On the basis of this equation, theories for the temperature dependence of the molar magnetic susceptibility of complexes **1** and **2** were deduced, which will be published elsewhere. Calculations were performed by the nonlinear fitting program QCP230; the results obtained were shown in Table 7. The experimental data and the theoretical fitting results of the molar magnetic susceptibility (χ_M) versus temperature (T) are shown in Figures 5 and 6 for **1** and **2**, respectively, together with the plots of $\chi_M T$ versus T shown as inserts of the respective figures.

Assuming the distorted tetrahedrally coordinated Co(1) atom in complex **1** is in a medium spin state of $S = {}^3/_2$ as usually the case for phosphine-substituted Co(II) complexes with tetrahedral structures[21,22] and the two square pyramidal Co(2,3) atoms are in a low spin state $S = {}^1/_2$, the calculated g value and the antiferromagnetic coupling constants J_1, J_2, and J_3 between Co(1)–Co(2), Co(1)–Co(3), and Co(2)–Co(3) are 1.86, −8.7, −11.9, and −22.9 cm^{-1}, respectively. The results indicates that the strongest coupling occurs between the two 5-coordinated Co atoms

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(22) Cotton, F. A.; Faut, O. D.; Goodgame, M. D. L.; Holm, R. H. *J. Am. Chem. Soc.* **1961**, *83*, 1780.

Table 5. Selected Atomic Distances (Å) and Bond Angles (deg) for the Tetracobalt Complex **2**

Co(1)–Co(2)	2.617(3)	Co(4)–O(3)	1.97(2)
Co(2)–Co(3)	2.633(3)	Co(4)–O	1.94(2)
Co(1)–S(1)	2.156(4)	Co(4)–Cl	2.284(6)
Co(1)–S(4)	2.152(4)	Co(1)–P(1)	2.230(7)
Co(2)–S(1)	2.294(5)	Co(2)–P(2)	2.292(4)
Co(2)–S(2)	2.294(5)	Co(3)–P(3)	2.218(6)
Co(2)–S(3)	2.309(5)	S(1)–C(11)	1.77(1)
Co(2)–S(4)	2.294(5)	S(2)–C(21)	1.78(2)
Co(3)–S(2)	2.130(4)	S(3)–C(31)	1.80(1)
Co(3)–S(3)	2.152(4)	S(4)–C(41)	1.73(1)
Co(1)–O(1)	1.973(9)	O(1)–C(16)	1.37(2)
Co(1)–O(4)	1.920(9)	O(2)–C(26)	1.35(2)
Co(3)–O(2)	1.913(9)	O(3)–C(36)	1.31(2)
Co(3)–O(3)	1.942(9)	O(4)–C(46)	1.35(2)
Co(4)–O(1)	2.07(2)	O–C	1.19(2)
Co(4)–O(2)	2.25(1)		
Co(1)–Co(2)–Co(3)	96.32(9)	Co(3)–O(2)–C(26)	116.7(8)
Co(1)–S(1)–C(11)	96.4(5)	Co(3)–O(3)–C(36)	113.6(8)
Co(1)–S(4)–C(41)	97.8(4)	O(1)–Co(1)–S(1)	89.9(3)
Co(3)–S(2)–C(21)	97.4(4)	O(2)–Co(3)–S(2)	89.2(3)
Co(3)–S(3)–C(31)	95.6(4)	O(3)–Co(3)–S(3)	90.7(3)
Co(1)–O(4)–C(46)	116.3(7)	O(4)–Co(1)–S(4)	89.5(3)
Co(1)–O(1)–C(16)	113.0(6)		

Table 6. Comparison of Structural Parameters[a] for the Cobalt Cluster Complexes with Mixed Trialkylphosphine and *o*-Mercaptophenolate

	complex		
param	**1**	**2**	**3**
	Co and P		
Co–Co	2.641(1)	2.617(3)	2.627(1)
	2.559(1)	2.633(3)	2.636(1)
	2.505(1)		
Co–P	2.215(16)	2.247(42)	2.247(40)
	Chelate Ring		
Co–S_{in}[b]	2.207(8)	2.148(12)	2.150(14)
Co–S_{out}[b]	2.241(1)	2.298(8)	2.302(18)
Co–O_{in}[b]	1.973(33)	1.827(27)	1.936(18)
Co–O_{out}[b]	2.222(6)	2.10(14)	2.072(56)
Co–S–C	98.2(1)	96.8(10)	96.3(10)
Co–O–C	118.9(3)	114.9(19)	114.8(27)
S–Co–O	86.5(2)	89.8(7)	90.1(10)

[a] Esd's for average interatomic distances and angles were computed as follows: $\sigma = [\sum (x_i - x)^2/(N-1)]^{1/2}$. [b] In indicates inside the chelate ring; out indicates outside the ring.

Table 7. Magnetic Properties of Complexes **1** and **2**

complex	spin state	J, cm^{-1}	g	TIP,[a] cgsu
1	$^3/_2, {}^1/_2, {}^1/_2$	−8.7	1.86	−0.002
		−11.9		
		−22.9		
2	$^1/_2, {}^1/_2, {}^1/_2$	−5.2	2.09	0.0003
	1		2.03	

[a] TIP is the temperature-independent paramagnetism.

with two arenethiolate bridges and that the couplings of the 4-coordinate Co(1) with Co(3) and Co(2) are weaker, which is in agreement with the trend in M–M distances (2.641(1), 2.559(1), and 2.505(1) Å, respectively).

In the case of complex **2**, atom Co(4) in oxidation state III should have spin state $S = 1$ and the other atoms in oxidation level II should have spin state $S = {}^1/_2$. Since the distance of Co(4) to either Co(1) or Co(3) is larger than 3 Å, and Co(4) is ligated to Co(1,3) only through the rather weak aryloxy bridges, no interaction either electronic or magnetic is assumed and atom Co(4) is considered as an isolated magnetic center. If the interaction between Co(1) and Co(3) is negligible, and that between Co(1) and Co(2) is equivalent to that between Co(2) and Co(3) (due to the same environment of Co(1) and Co(3)) with a coupling constant J, the calculated value is −5.2 cm^{-1}, which agrees with the long average Co–Co distance of 2.625(11) Å.

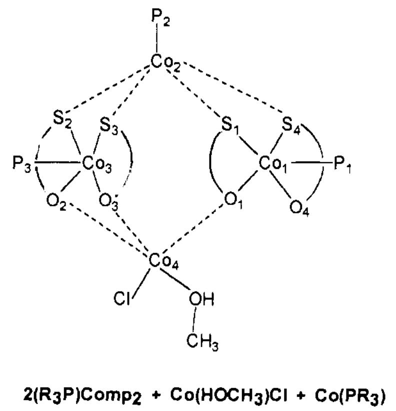

Figure 4. Schematic view of complex $Co_4(mp)_4(PBu^n{}_3)_3Cl(MeOH)$ (**2**) with atomic labeling.

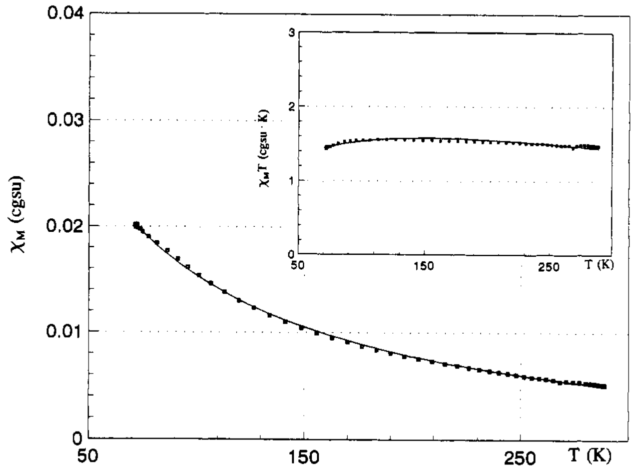

Figure 5. Experimental and calculated (—) temperature dependence of χ_M (cgsu) for compound $Co_3(mp)_2(Hmp)_2(PEt_3)_3$ (**1**). The relationship of $\chi_M T$ (cgsu·K) vs T (K) is shown in the insert.

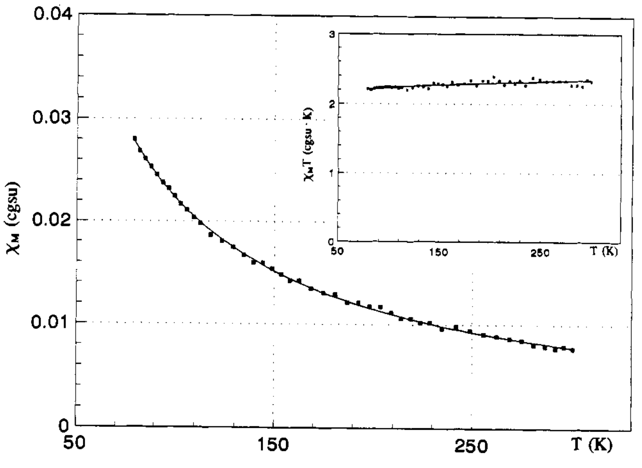

Figure 6. Experimental and calculated (—) temperature dependence of χ_M (cgsu) for compound $Co_4(mp)_4(PBu^n{}_3)_3Cl(MeOH)$ (**2**). The relationship of $\chi_M T$ (cgsu·K) vs T (K) is shown in the insert.

The residual error (Er) of fitting expressed by eq 3 can be applied to examine the accuracy of the exchange parameters J

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(23) Hendrichson, D. N.; Christou, G.; Schmitt, E. A.; Libby, E.; Bashkin, J. S.; Wang, S. Y.; Tsai, H. L.; Vincent, J. B.; Boyd, P. D. W.; Huffman, J. C.; Folting, K.; Li, Q.-Y.; Streib, W. E. *J. Am. Chem. Soc.* **1992**, *114*, 2455.

obtained:[23]

$$\mathrm{Er} = \frac{\sum_i [\chi_i(\exp) - \chi_i(\mathrm{calc})]}{\sum_i \chi_i(\exp)} \quad (3)$$

The behavior of Er as a function of J_1, J_2, and J_3 for complex **1**, and of J for complex **2**, is calculated according to this equation. There is a sharp minimum in Er versus J_1, J_2, and J, which means that these three parameters are well determined. The Er values are less sensitive to variation in J_3 and the minimum in Er versus J_3 is not so well defined, which results in relatively low accuracy of J_3. Plots of Er versus J_1, J_2, J_3, and J are included in the supplementary material.

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Supplementary Material Available: Complete tables of atomic distances and bond angles, general displacement parameters (*U*'s), and crystallographic data and data collection parameters and figures showing error vs *J* calculations of complexes **1** and **2** (13 pages). Ordering information is given on any current masthead page.