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Heterooctanuclear Cluster Complex Formation with Phosphine Participation: Synthesis, Structure, and Magnetic Properties of $\mathrm{Co_6Ru_2(mp)_{10}(PBu^n{}_3)_6}$ ($\mathrm{H_2mp}$ = 2-Mercaptophenol, $\mathrm{PBu^n{}_3}$ = Tri-*n*-butylphosphine)

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The reaction of $\mathrm{CoCl_2}$, $\mathrm{RuCl_3}$, $\mathrm{Na_2(mp)}$, and $\mathrm{PBu^n{}_3}$ ($\mathrm{H_2mp}$ = 2-mercaptophenol, $\mathrm{PBu^n{}_3}$ = tri-*n*-butylphosphine) in ethanol in the molar ratio of 0.75:0.25:1:1 gave the complex $\mathrm{Co_6Ru_2(mp)_{10}(PBu^n{}_3)_6}$. The heterooctanuclear complex consists of six cobalt and two ruthenium ions chelated to as well as bridged by the 2-mercaptophenol ligands in a near-dimeric fashion with two μ_2-OR groups bridging the two $\mathrm{Co_3Ru(mp)_5(PBu^n{}_3)_3}$ fragments without a crystallographic center of symmetry. Each fragment is formed by binding two of the $\mathrm{Co(mp)_2(PBu^n{}_3)}$ structural units and one Co(mp) species to a central Ru(III) ion through the S donors of the five mp ligands, while the sixth coordination site of the octahedral Ru environment is completed by a phosphine ligand in the axial position. The $\mathrm{Co_6Ru_2}$ moiety exhibits a zigzag assembly constructed by the μ_2-O and μ_2-S bridges of the bidentate 2-mercaptophenol ligands in a highly asymmetric fashion. The Co atoms are square pyramidally coordinated with apices that are occupied by the phosphine ligands or an oxygen atom from a $\mathrm{mp^{2-}}$ ligand. Variable-temperature magnetic susceptibilities that were measured in the temperature range 300−1.6 K reveal that the spin cluster exhibits weak antiferromagnetic exchange interactions. A quantitative interpretation of the magnetic data was carried out by the irreducible tensor operator approach. Crystal data of the complex are as follows: triclinic space group $P\bar{1}$, a = 14.931(3) Å, b = 23.195(5) Å, c = 24.259(5) Å, α = 74.91(3)°, β = 74.83(3)°, γ = 78.80(3)°, and Z = 2.

Introduction

Although metal thiolato complexes are well-known to adopt various nuclearity and great structural complexity, those with mixed phosphine and thiolato ligands have attracted the attention of inorganic chemists only recently.[1−7] In attempts to investigate the synergetic effect between atoms or groups of atoms in a molecule and to design molecular materials with high-nuclearity spin clusters, we have studied the coordination chemistry as well as the reactivity of transition metal complexes with both thiolate and phosphine ligands.[8,9] It has been found that the involvement of phosphine not only can modify the bonding modes of the thiolato ligand but also will favor the formation of polynuclear species involving 1,2-bidentate thiolato ligands under the appropriate conditions.[2,3]

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Table 1. Crystallographic Data for the Title Complex

formula	$C_{132}H_{202}O_{10}P_6S_{10}Co_6Ru_2$
fw	3011.3
space group	$P\bar{1}$
a, Å	14.931(3)
b, Å	23.195(5)
c, Å	24.259(5)
α, deg	74.91(3)
β, deg	74.83(3)
γ, deg	78.80(3)
V, Å^3	7757(4)
Z	2
T, °C	21
λ(Mo Kα), Å	0.710 73
ρ_{calcd}, g·cm^{-3}	1.289
μ, cm^{-1}	10.72
$R(F_o^2)^a$	0.0914
$R_w(F_o^2)^b$	0.1006

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

Table 2. Positional Parameters ($\times 10^4$) and Equivalent Isotropic Temperature Factors (Å $^2 \times 10^3$) for the Title Complex

atom	x	y	z	U_{eq}^a
Ru(1)	2785(1)	2783(1)	2600(1)	49(1)
Ru(2)	1890(1)	2341(1)	7227(1)	40(1)
Co(1)	1895(3)	3053(1)	1611(1)	74(1)
Co(2)	2183(2)	1805(1)	3522(1)	42(1)
Co(3)	1973(2)	2509(1)	4362(1)	44(1)
Co(4)	2403(2)	2737(1)	5457(1)	44(1)
Co(5)	2686(2)	3282(1)	6343(1)	49(1)
Co(6)	2884(2)	1790(1)	8181(1)	54(1)
S(11)	3311(6)	2604(3)	1620(2)	72(2)
S(21)	2166(6)	3729(2)	2002(2)	73(3)
S(31)	1441(4)	2214(2)	2801(2)	54(2)
S(41)	3527(4)	1757(2)	2895(2)	51(2)
S(51)	1999(4)	3225(2)	3464(2)	49(2)
S(61)	2344(3)	1983(2)	6311(2)	42(1)
S(71)	1464(4)	3427(2)	7006(3)	58(2)
S(81)	3442(4)	2694(2)	6978(2)	54(2)
S(91)	2291(4)	1319(2)	7725(2)	52(2)
S(01)	1605(4)	2413(3)	8220(2)	54(2)
P(1)	2027(11)	3470(3)	693(3)	131(6)
P(2)	4251(5)	3124(2)	2470(3)	67(2)
P(3)	2008(4)	865(2)	3692(2)	49(2)
P(4)	3278(7)	4093(3)	6191(3)	83(3)
P(5)	289(4)	2232(3)	7404(3)	64(2)
P(6)	2725(7)	1234(4)	9050(3)	88(3)
O(11)	1655(17)	2305(10)	1445(8)	91(10)
O(21)	594(14)	3311(8)	1753(16)	157(17)
O(31)	1131(9)	2066(6)	4064(6)	47(4)
O(41)	2868(10)	1789(8)	4096(7)	66(6)
O(51)	2623(12)	3081(7)	4581(6)	61(6)
O(61)	1626(8)	2258(5)	5221(5)	34(4)
O(71)	1952(12)	3496(6)	5733(7)	65(6)
O(81)	3566(11)	2944(6)	5682(7)	61(6)
O(91)	4121(13)	1409(10)	7900(10)	100(9)
O(01)	3453(13)	2319(7)	8396(6)	68(7)

^{a} Equivalent isotropic U_{eq} defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

As a multifunctional thiolato ligand with oxygen and sulfur donors, 2-mercaptophenol (H_2mp) can chelate to and/or bridge various metal ions to exhibit versatile coordination modes:[8] HO_tS_t, HOS_b, O_tS_t, O_bS_t, and O_bS_b-B (where b stands for bridge, t for terminal, and B for binuclear). When phosphine is involved in the reactions, nickel[10] and cobalt clusters[3a,b] have been obtained where four more coordination modes, i.e., HOS_t, HO_tS_b, O_tS_b, and O_bS_b-T (where T stands for trinuclear), have been observed. It has been shown that the mixed ligand metal complexes of 2-mercaptophenol and are highly complex and diverse.

Since 2-mercaptophenol contains oxygen and sulfur donors with different coordination behaviors, which may bridge different types of metal ions, it is possible to isolate heterometallic species. As confirmed by structural[3b] and fast atom bombardment mass spectroscopic data,[9] the Co^{III} ion is only loosely bonded in the mixed valence complex $Co^{II}_3Co^{III}$(mp)$_4$(Hmp)(PBu$^n_3$)$_3$. On this ground, the partially iron(III)-substituted form $Co^{II}_3Fe^{III}$(mp)$_4$(Hmp)(PBu$^n_3$)$_3$ has been obtained successfully,[11] which is very similar to Co_4(mp)$_4$(Hmp)(PBu$^n_3$)$_3$ in structure.[3b] In order to extend this investigation, we have engaged in the design of more heterometallic complexes of cobalt with various metal ions. This paper describes the synthesis, crystal structure, and magnetic behavior of a novel heterooctanuclear compound Co_6Ru_2(mp)$_{10}$(PBu$^n_3$)$_6$, which exhibits very different structural features from those previously reported for polynuclear cobalt complexes.[3a,b,11]

Experimental Section

All operations were carried out under a dinitrogen atmosphere with Schlenk-type apparatus unless otherwise stated. 2-Mercaptophenol (H_2mp), tri-*n*-butylphosphine (PBu$^n_3$), anhydrous $CoCl_2$, and $RuCl_3$ 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.

Preparation of Co_6Ru_2(mp)$_{10}$(PBu$^n_3$)$_6$. To 40 mL of absolute ethanol containing anhydrous $CoCl_2$ (0.75 mmol, 0.10 g), $RuCl_3$ (0.25 mmol, 0.05 g), and NaOMe (2.0 mmol, 0.11 g) were added, via syringes, 0.25 mL (1.0 mmol) of PBu$^n_3$ and then 0.10 mL (1.0 mmol) of H_2mp. After the solution was stirred for 10 min at room temperature, the solution was filtered and the filtrate was allowed to stand at 4 °C for several days to give well-shaped dark black crystals. Yield: 48%. IR (KBr cm^{-1}): 424 (m), 437 (w), 460 (w), 636 (m), 719 (s), 742 (s), 773 (m), 846 (m), 902 (s), 1049 (m), 1091 (s), 1119 (m), 1209 (m), 1265 (s), 1300 (s), 1377 (m), 1414 (m), 1437 (s), 1452 (s), 1574 (s), 2870 (s), 2929 (s), 2954 (s), 3053 (m). ^{31}P NMR: 50.3 ppm. Anal. Calcd. for $C_{132}H_{202}O_{10}P_6S_{10}Co_6Ru_2$: C, 52.59; H, 6.76; P, 6.18; S, 10.62; Co, 11.74. Found: C, 52.32; H, 6.94; P, 6.10; S, 10.23; Co, 11.98.

Crystal Structure Determination. Single crystals of the title compound with suitable dimensions were mounted on glass fibers, and data collections were performed on a MSC/Rigaku RAXIS II imaging plate diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). Determination of the crystal class, orientation matrix, and cell dimensions was performed according to the established procedures.[12] The crystallographic data are summarized in Table 1.

The coordinates of the metal atoms were determined by direct methods, and the remaining non-hydrogen atoms were located from successive difference Fourier syntheses. The structure was refined by full-matrix least-squares techniques with anisotropic thermal parameters for the Co, Ru, O, S, and P atoms. The C atoms in the phenyl groups were fixed as rigid bodies, with the C−C distances of 1.395 Å, and were refined isotropically. The hydrogen atoms were not included in the structure factor calculations. The difficulties associated with the refinements are reflected in the relatively high merging R value of 9.14%, due to the disorder of the C atoms in the *n*-butyl groups. All calculations were performed on an IBM PC/486 computer with the Siemens SHELXTL-PC program package.[13] Atomic scattering factors were taken from ref 14. Atomic coordinates of the Co, Ru, O, S, and P atoms are listed in Table 2. Selected atomic distances and bond

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Table 3. Selected Atomic Distances (Å) in the Title Complex

		M−M			
Ru(1)−Co(1)	2.910(4)	Ru(2)−Co(6)	2.952(3)	Ru(1)−Co(2)	2.839(3)
Ru(2)−Co(5)	2.830(3)	Co(2)−Co(3)	2.848(4)	Co(4)−Co(5)	2.914(5)
		Co−O			
Co(1)−O(11)	1.996(26)	Co(6)−O(01)	1.863(21)	Co(1)−O(21)	1.886(19)
Co(6)−O(91)	1.918(18)	Co(2)−O(31)	1.877(12)	Co(5)−O(81)	2.014(15)
Co(2)−O(41)	1.920(18)	Co(5)−O(71)	1.971(20)	Co(3)−O(31)	2.129(16)
Co(4)−O(81)	2.122(18)	Co(3)−O(41)	2.058(16)	Co(4)−O(71)	1.979(16)
Co(3)−O(51)	2.029(20)	Co(4)−O(61)	2.022(14)	Co(3)−O(61)	1.967(10)
Co(4)−O(51)	2.027(14)				
		Co−S			
Co(1)−S(11)	2.169(9)	Co(6)−S(01)	2.156(6)	Co(1)−S(21)	2.180(8)
Co(6)−S(91)	2.173(7)	Co(2)−S(31)	2.222(6)	Co(5)−S(81)	2.174(6)
Co(2)−S(41)	2.181(5)	Co(5)−S(71)	2.131(6)	Co(3)−S(51)	2.366(5)
Co(4)−S(61)	2.332(5)				
		Ru−S			
Ru(1)−S(11)	2.419(6)	Ru(2)−S(01)	2.378(6)	Ru(1)−S(21)	2.455(6)
Ru(2)−S(91)	2.404(5)	Ru(1)−S(31)	2.488(7)	Ru(2)−S(81)	2.480(6)
Ru(1)−S(41)	2.431(5)	Ru(2)−S(71)	2.427(5)	Ru(1)−S(51)	2.488(5)
Ru(2)−S(61)	2.457(5)				
		M−P			
Co(1)−P(1)	2.159(8)	Co(6)−P(6)	2.147(7)	Co(2)−P(3)	2.166(6)
Co(5)−P(4)	2.138(9)	Ru(1)−P(2)	2.387(8)	Ru(2)−P(5)	2.368(7)

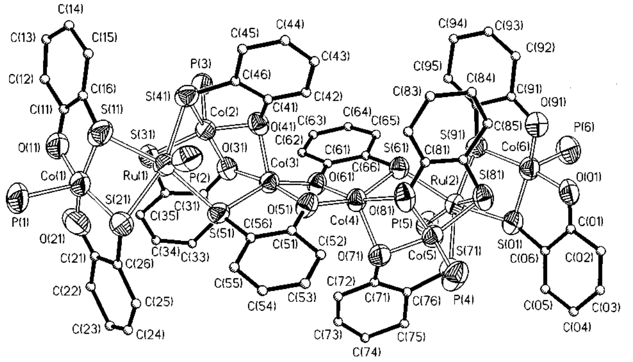

Figure 1. Thermal ellipsoid plot (50%) showing the atom-labeling scheme of $Co_6Ru_2(mp)_{10}(PBu^n{}_3)_6$. All of the carbon atoms of the phenyl rings are represented by arbitrary spheres, and the *n*-butyl groups are omitted for clarity.

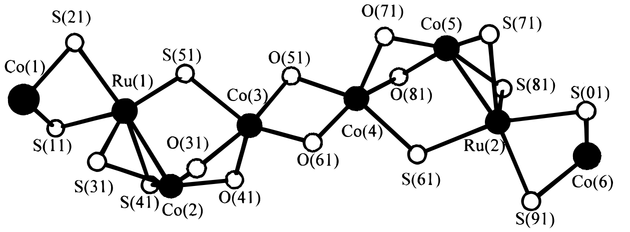

Figure 2. Simplified diagram of the bridging skeleton in $Co_6Ru_2(mp)_{10}$-$(PBu^n{}_3)_6$.

angles are presented in Tables 3 and 4, respectively. Complete crystallographic data, atomic coordinaties, thermal parameters, and bond distances and angles are gathered in the Supporting Information.

Physical Measurements. IR spectra were obtained from a Perkin-Elmer 577 spectrophotometer. ^{31}P NMR spectra were recorded on a Bruker AM500 spectrometer with 85% H_3PO_4 as the external standard. Variable-temperature magnetic susceptibilities in the temperature range 1.6−300 K were measured 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 was raised gradually from 1.6 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 maintained between collection of dat points, and each measurement took 10 s.

Results and Discussion

The rich coordination chemistry of 2-mercaptophenol, which behaves either as monoanionic Hmp^- ($(HOC_6H_4S)^-$) and/or as dianionic mp^{2-} [$(OC_6H_4S)^{2-}$], affords four coordination modes HOS_t, HO_tS_t, HOS_b, and HO_tS_b, for Hmp^- and five modes O_tS_t, O_bS_t, O_tS_b, O_bS_b-B, and O_bS_b-T, for mp^{2-}. The dimer $(NEt_4)_2$-$[Co(mp)(Hmp)]_2$[15] with two $[Co(mp)(Hmp)]^-$ fragments simply connected by two strong hydrogen bonds was the only product obtained when no phosphine was present in the system, where the mercaptophenol ligands exhibit the chelating modes HO_tS_t and O_tS_t without bridging the metal ions. Once phosphine takes part in the coordination, a variety of products are isolated, depending upon the reaction conditions. When the reaction of $CoCl_2$, H_2mp, NaOMe, and PR_3 was carried out in the molar ratio of 1:1:2:1 under strictly anaerobic circumstances, the cyclic trinuclear compound $Co_3(mp)_2(Hmp)_2(PR_3)_3$[3a] was obtained, which can be viewed as the combination of two $Co(mp)(PR_3)$ fragments and one $Co(Hmp)_2(PR_3)$ fragment, despite the fact that an attempt to isolate the mononuclear species was unsuccessful due to the strong tendency of their further construction by bridging through the O and S donors to give the neutral trinuclear species. When a restricted amount of air entered the reaction system, a more stable assembly having the cyclic tetranuclear skeleton[3a,b] was formed, owing to the partial oxidization of the bivalent cobalt ions. Accordingly, the asymmetric mixed valent tetranuclear complexes $Co_4(mp)_4$-$(Hmp)(PR_3)_3$ ($R_3 = Bu^n{}_3$,[3b] Me_2Ph[11]) were isolated, which were considered to be constructed by two $Co(mp)_2(PR_3)^{2-}$ anions to which one $Co(PR_3)^+$ cation and one $Co(Hmp)^{2+}$ cation are bridged.[8] Considering $Co(mp)_2(PR_3)^{2-}$ as a basic building block for the construction of Co−(mp)−phosphine cluster complexes, the novel heterooctanuclear compound $Co_6Ru_2(mp)_{10}(PBu^n{}_3)_6$ is obtained by addition of $RuCl_3$ into the reaction mixture, where partial oxidation of Co(II) might have occurred, as before,[3b,11] due to prolonged standing of the reaction solution, and thus, a certain amount of air might have leaked into the Schlenk tube.

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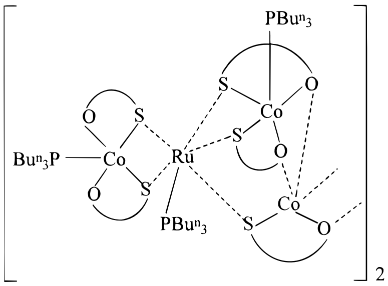
Table 4. Selected Bond Angles (deg) in the Title Complex

M−M−M			
Co(1)−Ru(1)−Co(2)	115.5(1)	Co(5)−Ru(2)−Co(6)	116.6(1)
Ru(1)−Co(2)−Co(3)	90.5(1)	Ru(2)−Co(5)−Co(4)	89.5(1)
S−Ru−S			
S(11)−Ru(1)−S(21)	77.5(2)	S(01)−Ru(2)−S(91)	77.0(2)
S(21)−Ru(1)−S(51)	86.6(2)	S(91)−Ru(2)−S(61)	87.5(2)
S(51)−Ru(1)−S(41)	111.3(2)	S(61)−Ru(2)−S(71)	109.3(2)
S(41)−Ru(1)−S(11)	84.5(2)	S(71)−Ru(2)−S(01)	86.2(2)
S(31)−Ru(1)−S(11)	91.1(2)	S(81)−Ru(2)−S(01)	92.8(2)
S(31)−Ru(1)−S(21)	98.9(2)	S(81)−Ru(2)−S(91)	99.5(2)
S(31)−Ru(1)−S(41)	79.2(2)	S(81)−Ru(2)−S(71)	78.4(2)
S(31)−Ru(1)−S(51)	89.2(2)	S(81)−Ru(2)−S(61)	88.4(2)
P−Co−X			
P(1)−Co(1)−O(11)	88.6(6)	P(6)−Co(6)−O(01)	90.3(5)
P(1)−Co(1)−O(21)	90.3(12)	P(6)−Co(6)−O(91)	94.9(7)
P(1)−Co(1)−S(11)	101.1(4)	P(6)−Co(6)−S(01)	103.7(3)
P(1)−Co(1)−S(21)	105.3(3)	P(6)−Co(6)−S(91)	103.5(3)
P(3)−Co(2)−O(31)	99.5(4)	P(4)−Co(5)−O(71)	101.1(5)
P(3)−Co(2)−O(41)	101.4(5)	P(4)−Co(5)−O(81)	97.8(5)
P(3)−Co(2)−S(31)	101.8(3)	P(4)−Co(5)−S(71)	101.1(3)
P(3)−Co(2)−S(41)	97.0(2)	P(4)−Co(5)−S(81)	100.2(3)
P−Ru−X			
P(2)−Ru(1)−S(11)	88.0(3)	P(5)−Ru(2)−S(61)	94.9(2)
P(2)−Ru(1)−S(21)	92.7(2)	P(5)−Ru(2)−S(71)	89.1(2)
P(2)−Ru(1)−S(31)	167.9(2)	P(5)−Ru(2)−S(81)	167.4(2)
P(2)−Ru(1)−S(41)	88.6(2)	P(5)−Ru(2)−S(91)	92.8(2)
P(2)−Ru(1)−S(51)	95.0(2)	P(5)−Ru(2)−S(01)	87.3(2)
O−Co−X (S,O)			
O(31)−Co(3)−O(51)	168.8(5)	O(61)−Co(4)−O(81)	158.8(5)
O(61)−Co(3)−S(51)	153.1(3)	O(51)−Co(4)−S(61)	156.2(5)
O(31)−Co(3)−S(51)	85.6(4)	O(81)−Co(4)−S(61)	84.4(4)
O(51)−Co(3)−O(61)	80.1(6)	O(51)−Co(4)−O(61)	78.9(6)
O(31)−Co(3)−O(61)	104.4(5)	O(51)−Co(4)−O(81)	103.1(7)
O(41)−Co(3)−O(31)	75.6(6)	O(71)−Co(4)−O(81)	74.6(7)
O(41)−Co(3)−S(51)	101.9(4)	O(71)−Co(4)−S(61)	104.6(5)
O(41)−Co(3)−O(51)	113.5(7)	O(71)−Co(4)−O(61)	126.3(6)
O(41)−Co(3)−O(61)	104.8(5)	O(71)−Co(4)−O(51)	99.1(6)
Bridging Co−X−M (M = Ru, Co)			
Co(1)−S(11)−Ru(1)	78.5(2)	Co(6)−S(01)−Ru(2)	81.1(2)
Co(1)−S(21)−Ru(1)	77.5(2)	Co(6)−S(91)−Ru(2)	80.2(2)
Co(2)−S(31)−Ru(1)	73.9(2)	Co(5)−S(81)−Ru(2)	74.6(2)
Co(2)−S(41)−Ru(1)	75.8(2)	Co(5)−S(71)−Ru(2)	76.5(2)
Co(2)−O(31)−Co(3)	90.4(6)	Co(4)−O(81)−Co(5)	89.6(6)
Co(2)−O(41)−Co(3)	91.3(6)	Co(4)−O(71)−Co(5)	95.1(6)
Co(3)−S(51)−Ru(1)	112.6(2)	Co(4)−S(61)−Ru(2)	115.3(2)
Co(3)−O(51)−Co(4)	98.9(7)	Co(3)−O(61)−Co(4)	101.2(5)
X−Co−X (S, O)			
S(11)−Co(1)−S(21)	89.0(3)	S(31)−Co(2)−S(41)	90.9(2)
S(71)−Co(5)−S(81)	92.2(2)	S(91)−Co(6)−S(01)	86.9(3)
O(11)−Co(1)−O(21)	88.7(11)	O(31)−Co(2)−O(41)	85.0(6)
O(71)−Co(5)−O(81)	77.2(7)	O(91)−Co(6)−O(01)	87.0(9)
O−Co−S			
O(11)−Co(1)−S(11)	86.3(7)	O(01)−Co(6)−S(01)	90.5(6)
O(21)−Co(1)−S(21)	93.1(10)	O(91)−Co(6)−S(91)	91.1(8)
O(31)−Co(2)−S(31)	90.2(5)	O(81)−Co(5)−S(81)	91.7(5)
O(41)−Co(2)−S(41)	87.3(4)	O(71)−Co(5)−S(71)	91.9(5)
O(51)−Co(3)−S(51)	86.0(4)	O(61)−Co(4)−S(61)	86.2(3)

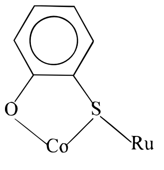
Noteworthily, the reaction of nickel(II) ion with mixed H_2-mp and phosphine ligands favors the formation of the trinuclear species $Ni_3(mp)_2(Hmp)_2(PR_3)_2$[10] with Ni_3 atoms in a quasi-linear array. On the other hand, the tri- and tetracobalt complexes[3a,b] afford cyclic skeletons, owing to the formation of a square-based pyramidal and/or a trigonal bipyramidal geometry for the cobalt ions. Since Ru^{3+} has a strong affinity for S and P donors to afford an octahedral coordination, the combination of $Co(mp)_2(PBu^n{}_3)^{2-}$ and $Co(mp)^+$ with $Ru(PBu^n{}_3)^{3+}$ through the S donors makes the structure of the Co_6Ru_2 assembly more complicated, with the final skeleton in a zigzag arrangement.

The structure of $Co_6Ru_2(mp)_{10}(PBu^n{}_3)_6$ with the atom-labeling scheme is depicted in Figure 1. The zigzag metal skeleton Co_6-Ru_2 with only the μ_2-S and μ_2-O bridging atoms is shown in the simplified diagram in Figure 2, with the neighboring Co−Ru separations in the range 2.830− 4.060 Å and the Co−Co distances in the range 2.848−3.069 Å, the latter being significantly longer than those (2.57−2.63 Å) observed in the cyclic tri- or tetracobalt complexes,[3a,b] implying the weak Co−Co interactions in the title compound. The compound can be envisaged as a dimer of $Co_3Ru(mp)_5(PBu^n{}_3)_3$ fragments linked by two μ_2-OR bridges, since the two structural units are nearly identical in formal charges and respective structural parameters (see Tables 3 and 4), in spite of the absence of a crystallographic center of inversion in the molecule due to the floatation of the long carbon chains of the *n*-butyl groups. Thus, the discussion of the structural characteristics will only be on the monomer for clarity. Each $Co_3Ru(mp)_5(PBu^n{}_3)_3$ monomer is constructed from two $Co(mp)_2(PBu^n{}_3)^{2-}$ building blocks (**B₁**),[3a,8] one Co(mp)$^+$ species (**B₂**, which may be present in solution as $Co(mp)Cl_2^-$), and one $Ru(PBu^n{}_3)^{3+}$ species (**B₃**) by bridging **B₁** and **B₂** to **B₃** through the five μ_2-S donors; furthermore, one of the **B₁** building blocks is additionally attached to **B₂** via the μ_2-O atoms in the fashion shown below:

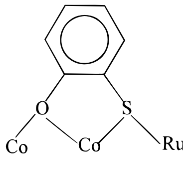


The cobalt atoms are five-coordinate with the CoO_2S_2P or CoO_4S moiety better described as distorted square-based pyramids, where the basal planes are composed of O_2S_2 or O_3S atoms and the apical sites are occupied by the P atoms and either O(41) or O(71), respectively. For the Co(3) (or Co(4)) atom, the trigonal bipyramidal description would place the O(41), O(61), and S(51) (or O(51), O(71), and S(61)) atoms in the equatorial positions and the O(31) and O(51) (or O(61) and O(81)) atoms in the axial positions with the *trans*-angle O(31)−Co(3)−O(51) (or O(61)−Co(4)−O(81)) being 168.8° (or 158.8°). Although the Co(3) and Co(4) atoms deviate by only 0.050 and 0.028 Å, respectively, from the trigonal planes, the angles in the planes depart significantly from the theoretical value 120°. The two six-coordinate ruthenium ions are in distorted octahedral environments with the equatorial planes defined by the S_4 atoms, whereas the axial sites are occupied by the S and P atoms.

The 2-mercaptophenolate ligands chelate and bridge the metal atoms in only two (O_tS_b and O_bS_b-T) of the nine possible coordination modes. However, this is the first example of the O_tS_b and O_bS_b-T modes to bridge heterometals in the fashion:



O_tS_b



O_bS_b-T

The average Co−S (2.208 Å) and Co−O (1.972 Å) distances within the CoSCCO chelate rings are slightly longer than those in the Co_4 complexes (average distance of 2.148 and 1.93 Å, respectively).[3a,b,8] However, the Co−O_t bond (average distance of 1.916 Å) in the O_tS_b mode, chelated mp^{2-} group on Co(1) (or Co(6)), is obviously shorter than the corresponding bond in $Co_4(mp)_4(Hmp)(PBu^n{}_3)_3$ (2.012 Å).[3b] This provides evidence for the dianionic ligation of mp^{2-} rather than Hmp^-. The Co−

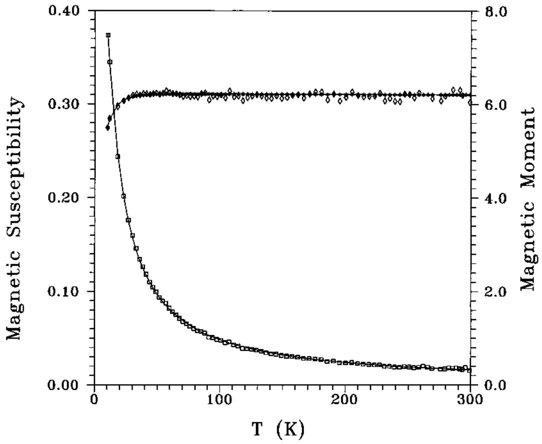


Figure 3. Plots of the temperature dependencies of the molar susceptibilities χ_M and of the effective magnetic moments μ_{eff} for the complex $Co_6Ru_2(mp)_{10}(PBu^n{}_3)_6$. The solid lines represent the best calculated curves.

O_{out} distances, average 2.047 Å, outside the chelate $\overline{CoSCCO}$ ring are longer than those Co−O_{in} inside (average 1.934 Å), as usual.[3,8,15] The chelate angles Co−S−C and Co−O−C and the bite angle O−Co−S are all within the range for mercaptophenolate-coordinated complexes,[8] without much deviations, showing the rigidity of the chelate rings.

The measured molar magnetic susceptibilities of $Co_6Ru_2(mp)_{10}(PBu^n{}_3)_6$ (χ_M) and the effective magnetic moments (μ_{eff}) are plotted in Figure 3 as a function of temperature. The molar susceptibility (0.015 $cm^3 \cdot mol^{-1}$ at 300 K) increases steadily with decreasing temperature (reaching 0.489 $cm^3 \cdot mol^{-1}$ at 1.6 K), while the value of μ_{eff} remains almost constant from 300 to 40 K, then decreases gradually in the range 40−8 K, showing the presence of intramolecular antiferromagnetic exchange interactions. The effective magnetic moment of 6.15 μ_B at 300 K is close to the spin-only value, 5.85 μ_B, assuming six magnetic centers of $S = {}^1/_2$ and two of $S = 1$ without magnetic interactions. The metal atoms in the $PO_2S_2Co^{II}$ (1, 2, 5, 6) and PS_5Ru^{III} moieties of square-based pyramidal and octahedral environments, respectively, are generally considered to be in low-spin states with $S = {}^1/_2$, as reported,[3a,16−19] whereas the Co atom in the O_4SCo^{III} (3, 4) unit is in an intermediate environment that is between a trigonal bipyramidal and square pyramidal geometry and might have spin states with $S = 1$.[3a] Therefore, the formal oxidation states of the metals in the title compound could be given as $Co^{II}{}_4Co^{III}{}_2Ru^{III}{}_2$. This assumption agrees with the room temperature magnetic susceptibility data.

The exchange pathways in the title complex with the $Co^{II}{}_4Co^{III}{}_2Ru^{III}{}_2$ metal skeleton can be schematized as shown in Figure 4. The spin−spin coupling Hamiltonian describing the isotropic exchange interactions for such an asymmetric octanuclear system can be written as

$$\boldsymbol{H} = -2(J_{12}\boldsymbol{S}_1 \cdot \boldsymbol{S}_2 + J_{23}\boldsymbol{S}_2 \cdot \boldsymbol{S}_3 + J_{24}\boldsymbol{S}_2 \cdot \boldsymbol{S}_4 + J_{34}\boldsymbol{S}_3 \cdot \boldsymbol{S}_4 + J_{45}\boldsymbol{S}_4 \cdot \boldsymbol{S}_5 + J_{56}\boldsymbol{S}_5 \cdot \boldsymbol{S}_6 + J_{57}\boldsymbol{S}_5 \cdot \boldsymbol{S}_7 + J_{67}\boldsymbol{S}_6 \cdot \boldsymbol{S}_7 + J_{78}\boldsymbol{S}_7 \cdot \boldsymbol{S}_8) \quad (1)$$

in which nine independent coupling constants are involved in various exchange pathways. Operating on the spin wavefunctions $\Psi_k = |S_1, M_{S_1}; S_2, M_{S_2}; S_3, M_{S_3}; S_4, M_{S_4}; S_5, M_{S_5}; S_6, M_{S_6}; S_7, M_{S_7}; S_8, M_{S_8}|$ with $-S_i \le M_{Si} \le S_i$, the Hamitonian matrix expressed by eq 1 is in the dimensions of 576 × 576. Obviously, quantitative interpretation of the magnetic properties of such a large metal ion cluster is hampered by the difficulties that are associated with the calculations of the thermally accessible energy levels in the system which is too large to use the simple approaches that are employed in the interpretation of di- and trinuclear clusters. Accordingly, even if a full-matrix diagonalization approach is employed,[20] it is difficult to diagonalize such a large matrix with the dimensions of 576 × 576 on a general computer. Fortunately, a fast and efficient procedure for the calculation of the spin levels of high-nuclearity spin clusters has been developed by the use of irreducible tensor operators (ITO),[21] which made the attempts of interpreting, quantitatively, the magnetic properties of large spin clusters possible. The most favorable aspect of this approach is the fact that the large matrix that is requiring diagonalization can be reduced dramatically.

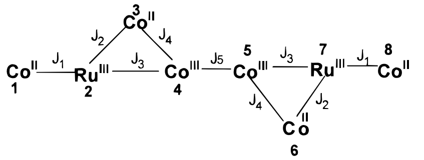


Figure 4. Scheme of the exchange pathways for the spin cluster $Co^{II}{}_4Co^{III}{}_2Ru^{III}{}_2$ with the numbered coupling constants.

For an octanuclear spin-coupling system $Co^{II}{}_4Co^{III}{}_2Ru^{III}{}_2$, the possible total spin values are S_t = 5, 4, 3, 2, 1, 0 and the corresponding n_{st} are 1, 7, 22, 40, 43, and 19, respectively, where n_{st} is the number of nondegenerate spin states for a given S_t. Accordingly, taking advantage of the irreducible tensor operators, the Hamiltonian matrix, thus, was simplified into the dimensions of 43 × 43, which can easily be diagonalized on a PC.

The magnetic analysis of the title complex was performed by employing five independent coupling constants with $J_{12} = J_{78} = J_1$, $J_{23} = J_{67} = J_2$, $J_{24} = J_{57} = J_3$, $J_{34} = J_{56} = J_4$, and $J_{45} = J_5$ under the assumption that the molecule is a dimer of the $Co_3Ru(mp)_5(PBu^n{}_3)_3$ fragment. Considering only a weak magnetic exchange interaction in the cluster, a set of trial coupling parameters with $|J_i| < 10$ cm^{-1} (i = 1−5) is given. By means of the ITO approach, the best fitting parameters are $J_1 = -4.00$, $J_2 = -1.75$, $J_3 = -0.34$, $J_4 = 6.50$, $J_5 = -1.85$ cm^{-1}, and $g = 2.13$. The fitting curve with this set of parameters is fairly well depicted from room temperature down to 10 K, as shown in Figure 3. It is obvious that only weak exchange interactions are present in the octanuclear spin cluster, although it affords several magnetic-coupling pathways by singly or doubly μ_2-O and/or μ_2-S bridging groups. This may be attributable to the lack of efficient overlap of the magnetic orbitals due to the non-coplanarity[22,23] of the neighboring coordination planes of the magnetic centers as well as the severe asymmetry of the μ_2-O and μ_2-S bridging systems, which are unfavorable for transmitting electronic and magnetic effects.

Interestingly, the doubly μ_2-O bridges of Co···Co pairs transmit two different types of exchange interactions, a weak ferromagnetic exchange between Co(2) and Co(3) ($J_4 = 6.50$ cm^{-1}) and a weak antiferromagnetic exchange between Co(3) and Co(4) ($J_5 = -1.85$ cm^{-1}). As shown experimentally and

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discussed theoretically,[24] the bridging angles of a M−O−M system seem to play a significant role in determining the sign of the exchange coupling constants in metal dimers with μ_2-OR bridges. The Co(2)−O(31)−Co(3) (90.4°) and Co(2)−O(41)−Co(3) (91.3°) angles are close to 90°, which may cause the magnetic orbitals to lie orthogonal to each other, resulting in ferromagnetic interactions, while the Co(3)−O(51)−Co(4) (98.9°) and Co(3)−O(61)−Co(4) (101.2°) angles have nearly a 10° deviation from 90° and results in antiferromagnetic couplings, although small. More structural and magnetic data of μ_2-OR-bridged cobalt complexes must be studied to confirm the dependence of the exchange coupling constants on the bridging angles.

Conclusions

The heterooctanuclear cluster complex $Co_6Ru_2(mp)_{10}(PBu^n_3)_6$ exhibits a zigzag array of metal atoms due to the strong tendency of ruthenium(III) to ligate to the S and P donors. The thiolato ligand 2-mercaptophenol chelates the cobalt ions with the involvment of tri-*n*-butylphosphine to form the building blocks $Co(mp)_2(PBu^n_3)^{2-}$ and possibly $Co(mp)Cl_2^-$, which combine with each other via the μ_2-O bridges as well as connect to the $Ru(PBu^n_3)$ species through the μ_2-S atoms to give the title complex. Such results indicate that the designed synthesis of heteronuclear cluster complexes is possible by selecting the proper construction units or building blocks, and the 1,2-bidentate thiolato ligand mixed with phosphine seems to be a good choice for the ligands as their coordinations give relatively stable but still reactive species.

Only weak magnetic exchange interactions are transmitted by the highly asymmetric μ_2-S and μ_2-O bridges in the cluster. The irreducible tensor operator method is applicable to give semiquantitative interpretation of the magnetic data.

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Supporting Information Available: Details of the X-ray structural analyses of the title compound including complete tables of crystallographic data, atomic coordinates and isotropic thermal parameters, bond distances and angles, and anisotropic thermal parameters (10 pages). Ordering information is given on any current masthead page.

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