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Transition-Metal Complexes with Sulfur Atoms as Ligands. 5.[1] Synthesis and Structural Characterization of Doubly Sulfur-Bridged Binuclear Complexes of Cobalt with the Tris(tertiary phosphine) 1,1,1-Tris((diphenylphosphino)methyl)ethane

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By reaction of $HSCH_3$ and H_2S with the dinuclear dihydroxo-bridged complex $[(\text{triphos})Co(\mu\text{-}OH)_2Co(\text{triphos})]^{2+}$ (triphos = 1,1,1-tris((diphenylphosphino)methyl)ethane) and, in some cases, suitable redox agents, the dinuclear sulfur-bridged complexes $[(\text{triphos})Co(\mu\text{-}SCH_3)_2Co(\text{triphos})]^{2+}$ (**1**) and $[(\text{triphos})Co(\mu\text{-}S)_2Co(\text{triphos})]^{0,1+,2+}$ ($n = 0$ (**3**), $n = 1+$ (**2**), $n = 2+$ (**4**)) have been prepared. The structures of all these compounds have been elucidated through the X-ray structure determinations of **1**, **2**, and **3**. Crystal data: (**1**) $a = 26.139$ (6) Å, $b = 15.574$ (5) Å, $c = 15.069$ (5) Å, $\beta = 90.24$ (2)°, $Z = 2$, space group $P2_1/n$; (**2**) $a = 27.109$ (5) Å, $b = 26.887$ (5) Å, $c = 14.591$ (4) Å, $\beta = 110.19$ (3)°, $Z = 4$, space group $P2_1/a$; (**3**) $a = 12.700$ (4) Å, $b = 12.899$ (4) Å, $c = 14.218$ (5) Å, $\alpha = 68.99$ (2)°, $\beta = 65.29$ (2)°, $\gamma = 73.75$ (2)°, $Z = 1$, space group $P\bar{1}$. The structures were solved by Patterson syntheses and refined by least-squares methods to R values 0.088, 0.075, and 0.082 for **1**, **2**, and **3**, respectively. In these dinuclear complexes the two cobalt atoms of the two Co(triphos) fragments are bridged by two sulfur atoms. Common structural features of these complexes are the planarity of the inner Co_2S_2 ring as well as the large metal–metal distances (3.579 (2), 3.434 (8), and 3.598 (2) Å in **1**, **2**, and **3**, respectively). Significant variations of the metal–sulfur distances are observed in the structures of the three complexes. A simplified qualitative MO approach has been used to rationalize structural and spectromagnetic properties of the compounds.

Introduction

In the past few years many binuclear transition-metal complexes with S or SR (R = H, alkyl, phenyl) as bridging groups have been prepared and investigated.[1,3] Often these compounds show anomalous magnetic behavior which can be ascribed either to a superexchange effect through the bridging sulfur atoms or to the formation of a direct metal–metal bond. Some of these compounds can also undergo reversible redox reactions with a gain or loss of electrons and without change of the geometric framework. In many cases both the features and the properties of such compounds have been clarified through complete X-ray diffraction analyses.

Recent studies from our laboratory have shown that the tripod-like poly(tertiary phosphines) such as 1,1,1-tris((diphenylphosphino)methyl)ethane, triphos, tris(2-(diphenylphosphino)ethyl)amine, np_3, and tris(2-(diphenylphosphino)ethyl)phosphine, pp_3, can stabilize mercapto, methylthio, and thio complexes of 3d transition metals.[1,3m,4] Not only have many five-coordinate monomeric complexes with the general formula $[M(SR)L]BPh_4$ been obtained (where M = Fe, Co, Ni; R = H, CH_3; L = np_3, pp_3) but also dinuclear linearly singly S-bridged diamagnetic compounds with formulas $[(\text{triphos})Ni\text{–}S\text{–}Ni(\text{triphos})](BPh_4)_2$ and $[(np_3)Co\text{–}S\text{–}Co(np_3)]$.

Now we have found that, by reactions of $HSCH_3$ or H_2S with the dimeric complex$[(\text{triphos})_2Co_2(\mu\text{-}OH)_2](BPh_4)_2$,[5] sulfur-containing complexes with formulas $[(\text{triphos})_2Co_2(SCH_3)_2](BPh_4)_2\cdot 2C_3H_6O$ (**1**) (C_3H_6O = acetone) and $[(\text{triphos})_2Co_2S_2](BPh_4)\cdot 0.5C_3H_7NO$ (**2**) (C_3H_7NO = *N,N*-dimethylformamide) can be obtained. Reduction of the latter compound with sodium borohydride produces the uncharged species $[(\text{triphos})_2Co_2S_2]\cdot 1.4C_3H_7NO$ (**3**), while oxidation with nitrosyl fluoroborate yields the complex $[(\text{triphos})_2Co_2S_2](BPh_4)_2\cdot 4CH_2Cl_2$ (**4**).

All four complexes have been characterized by appropriate physical methods; the complete X-ray structural analysis of the complexes $[(\text{triphos})_2Co_2S_2](BPh_4)_n\cdot xC_3H_7NO$, $n = 0$ and 1, and $[(\text{triphos})_2Co_2(SCH_3)_2](BPh_4)_2\cdot 2C_3H_6O$ have been carried out. Owing to the very poor quality of the crystals the complex $[(\text{triphos})_2Co_2S_2](BPh_4)_2$ could not be structurally investigated.

Experimental Section

Reagents. All solvents were of reagent grade quality and were used without further purification. The ligand 1,1,1-tris((diphenylphosphino)methyl)ethane, triphos,[6] and the complex $[(\text{triphos})_2Co_2(\mu\text{-}OH)_2](BPh_4)_2\cdot 4C_3H_6O$[5] were prepared by methods previously described.

Preparation of the Complexes. All the reactions were carried out under dry nitrogen by using deoxygenated solvents. The solid complexes were collected on a sintered-glass frit and dried in a stream of dry nitrogen.

$[(\text{triphos})_2Co_2(SCH_3)_2](BPh_4)_2\cdot 2C_3H_6O$ (1). A 1-mmol sample of $[(\text{triphos})_2Co_2(\mu\text{-}OH)_2](BPh_4)_2\cdot 4C_3H_6O$ was dissolved in 30 mL of acetone, and methyl mercaptan was bubbled through the solution, at room temperature, until the color turned dark brown (about 5 min). A 10-mL sample of 1-butanol was added to the resulting solution and dark brown crystals slowly precipitated. They were washed with 1-butanol and with petroleum ether. Anal. Calcd for $C_{132}H_{124}B_2Co_2P_6\cdot 2C_3H_6O$: C, 74.79; H, 6.18; Co, 5.32; S, 2.89. Found: C, 74.21; H, 6.24; Co, 5.17; S, 3.04. μ_{eff}(293 K) for dimer: 1.80 μ_B.

$[(\text{triphos})_2Co_2S_2]BPh_4\cdot 0.5C_3H_7NO$ (2). A 1-mmol sample of $[(\text{triphos})_2Co_2(\mu\text{-}OH)_2](BPh_4)_2\cdot 4C_3H_6O$ was dissolved in 15 mL of *N,N*-dimethylformamide, and hydrogen sulfide was bubbled through the solution, at room temperature, until the color turned dark brown

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Table I. Crystal Data and Data Collection Details

	1	2	3
molecular formula	$Co_2C_{132}H_{124}P_6S_2B_2 \cdot 2C_3H_6O$	$Co_2C_{106}H_{98}P_6S_2B \cdot 0.5C_3NOH_7$	$Co_2C_{82}H_{78}P_6S_2 \cdot 1.4C_3NOH_7$
mol wt	2216.11	1797.97	1533.71
a,b, and *c*, Å	26.139 (6), 15.574 (5), 15.069 (5)	27.109 (5), 26.887 (5), 14.591 (4)	12.700 (4), 12.899 (4), 14.218 (5)
α,β, and γ, deg	90, 90.24 (2), 90	90, 110.19 (3), 90	68.99 (2), 65.29 (2), 73.75 (2)
d_{obsd}(by flot), g cm^{-3}	1.21	1.20	1.30
d_{calcd}, g cm^{-3}	1.200	1.203	1.304
V, Å^3	6134.37	9981.72	1951.87
Z	2	4	1
space group	$P2_1/n$	$P2_1/a$	$P\bar{1}$
abs coeff μ(MoKα), cm^{-1}	4.45	5.32	6.41
color	brown	brown	dark greenish
habit	prism	prism	prism
dimens, mm	0.1 × 0.1 × 0.16	0.05 × 0.06 × 0.12	0.1 × 0.1 × 0.05
λ(MoKα), Å	0.7107	0.7107	0.7107
monochromator	flat graphite crystal for all compounds		
attenuator	not used for all compounds		
takeoff angle, deg	3 for all compounds		
method	ω–2ϑ scan for all compounds		
scan speed	0.07°/s in a range of 0.9° across the peak	0.07°/s in a range of 0.9° across the peak	0.08°/s in a range of 0.9 across the peak
bkgd time	equal to half the scan time for all compounds		
std	3 every 100′	3 every 90′	3 every 90′
max dev of std	9%	12%	10%
2ϑ limits	5° ⩽ 2ϑ ⩽ 45°	6° ⩽ 2ϑ ⩽ 40°	6° ⩽ 2ϑ ⩽ 40°
no. of data	8729	4691	3530
no. of data used	4116 ($I \geq 3\sigma(I)$)	1750 ($I \geq 3\sigma(I)$)	2374 ($I \geq 3\sigma(I)$)

Table II. Atomic[a] Parameters for the Structure of $[(triphos)Co(\mu\text{-}SCH_3)_2Co(triphos)](BPh_4)_2 \cdot 2C_3H_6O$

atom	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co	547 (1)	425 (1)	4440 (1)	311 (8)	450 (10)	312 (8)	−38 (8)	51 (6)	2 (8)
S1	158 (1)	427 (2)	5778 (2)	451 (19)	568 (20)	394 (18)	−135 (18)	140 (15)	−91 (18)
P1	1329 (1)	764 (2)	5043 (2)	309 (17)	529 (21)	349 (18)	−30 (15)	33 (14)	0 (16)
P2	408 (1)	1828 (2)	3895 (2)	394 (20)	479 (21)	400 (19)	17 (16)	67 (15)	37 (17)
P3	968 (1)	38 (2)	3226 (2)	313 (17)	495 (19)	310 (17)	9 (16)	51 (14)	−14 (16)

[a] The form of the thermal ellipsoid is $\exp(-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + \ldots))$. *F* (relative scale factor) = 34.361.

Table III. Atomic Parameters for the Structure of $[(triphos)Co(\mu\text{-}SCH_3)_2Co(triphos)](BPh_4)_2 \cdot 2C_3H_6O$ (all quantities × 10 000)

atom	*x*	*y*	*z*	*U*, Å^2
C	101 (4)	1455 (8)	6360 (8)	527 (33)
C1	1873 (4)	2227 (7)	2895 (8)	483 (33)
C2	1463 (4)	1672 (7)	3407 (7)	446 (31)
C3	1733 (4)	1274 (7)	4231 (7)	421 (30)
C4	1031 (4)	2298 (8)	3644 (8)	501 (34)
C5	1244 (4)	983 (7)	2745 (7)	418 (30)
C1[a]	951	4764	52	2000
C2[a]	982	5480	47	2000
C3[a]	693	4384	−719	2000
C4[a]	1030	4311	538	2000
C5[a]	5041	1058	3568	2000
C6[a]	5255	1531	3438	2000
C7[a]	5122	182	3216	2000
C8[a]	4664	1047	3918	2000
B	2555 (5)	25 (9)	−22 (9)	448 (35)

[a] Atoms belonging to the solvent molecules.

(about 5 min). By addition of 25 mL of 1-butanol dark brown crystals precipitated which were washed with ethanol and then with petroleum ether. Anal. Calcd for $C_{106}H_{98}BCo_2P_6S_2 \cdot 0.5C_3H_7NO$: C, 71.80; H, 5.69; N, 0.39; S, 3.57; Co, 6.55. Found: C, 71.55; H, 6.34; N, 0.64; S, 3.47; Co, 6.31. μ_{eff}(293 K) for dimer: 1.78 μ_B.

$[(triphos)_2Co_2S_2] \cdot 1.4C_3H_7NO$ (3). A 1.3-mmol sample of $NaBH_4$ in ethanol (10 mL) was added, at room temperature, to a solution of the complex **2** in *N,N*-dimethylformamide (15 mL). By addition of 25 mL of 1-butanol dark brown crystals precipitated slowly. These were washed with 1-butanol and petroleum ether. Anal. Calcd for $C_{82}H_{78}Co_2P_6S_2 \cdot 1.4C_3H_7NO$: C, 67.51; H, 5.77; N, 1.28; S, 4.18; Co, 7.69. Found: C, 67.89; H, 6.32; N, 0.89; S, 4.15; Co, 7.75.

$[(triphos)_2Co_2S_2](BPh_4)_2 \cdot 4CH_2Cl_2$ (4). A 1.2-mmol sample of $NOBF_4$ solid was added at room temperature to a solution of compound **2** in 15 mL of CH_2Cl_2. When the color turned to green (after ca. 5 min), the solution was filtered and 1 mmol of $NaBh_4$ in 10 mL of ethanol was added. The green crystals which precipitated were washed with ethanol and petroleum ether. Anal. Calcd for $C_{130}H_{112}B_2Co_2P_6S_2 \cdot 4CH_2Cl_2$: C, 66.79; H, 5.27; S, 2.66; Co, 4.89. Found: C, 65.57; H, 5.52; S, 3.02; Co, 4.90.

$[(triphos)Co(CO)(SCH_3)]BPh_4$. Carbon monoxide was bubbled at 0 °C through a solution of complex **1** in 50 mL of CH_2Cl_2. Butanol (20 mL) was added to the green resultant solution, and a brisk stream of nitrogen was passed through the solution until crystallization was initiated. The crystalline dark green product was filtered off and washed with ethanol and light petroleum ether. Anal. Calcd for $C_{67}H_{62}BCoOP_3S$: C, 74.64; H, 5.80. Found: C, 74.80; H, 6.12. μ_{eff}(293 K): 2.02 μ_B. ν_{CO}: 2020 cm^{-1}.

$[(triphos)Co(SCH_3)]$. Sodium borohydride (2 mmol) dissolved in ethanol (15 mL) was added dropwise to the solution of 1 mmol of complex **2** in 50 mL of CH_2Cl_2. A brisk current of nitrogen was passed through the solution and the methylene chloride evaporated until crystallization occurred. The crystalline yellow product was filtered off and washed with ethanol and light petroleum ether. Anal. Calcd for $C_{42}H_{42}CoP_3S$: C, 69.03; H, 5.79. Found: C, 69.29; H, 5.90. μ_{eff}(293 K): 3.06 μ_B.

Physical Measurements. IR spectra and magnetic susceptibilities were recorded by previously described methods.[7] The ESCA spectra have been recorded with Varian VIEE-15 spectrometer with Mg anode. The vacuum was about 10^{-6} torr. The substances were cooled with liquid nitrogen during the measurements. The charging effect has been taken into account by referencing of the spectra to CIS value of the contaminant layer. This value has been set equal to 285.0 eV. The reproducibility of the values in the Table XIV is about ±0.1–0.2 eV.

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Table IV. Final Least-Squares Parameters for [(triphos)Co(μ-SCH_3)$_2$Co(triphos)](BPh_4)$_2$·$2C_3H_6O$ Groups[a]

group	x'	y'	z'	ϑ	ϕ	ψ
1	0.1930 (2)	−0.0738 (4)	0.5819 (4)	2.679 (5)	1.811 (6)	2.808 (6)
2	0.1412 (2)	0.1868 (4)	0.6709 (4)	1.736 (8)	1.014 (6)	−1.377 (6)
3	−0.0120 (3)	0.3297 (4)	0.5076 (4)	0.855 (6)	−0.543 (7)	2.807 (9)
4	−0.0328 (3)	0.2088 (4)	0.2143 (4)	1.807 (6)	−0.075 (6)	2.583 (6)
5	0.1842 (2)	−0.1219 (4)	0.3468 (4)	0.511 (5)	0.242 (11)	0.532 (11)
6	0.0424 (2)	−0.0736 (4)	0.1593 (4)	0.997 (7)	−1.419 (8)	−2.533 (9)
7	0.1626 (2)	0.1225 (4)	0.0153 (3)	0.237 (6)	2.602 (14)	1.198 (15)
8	0.3125 (3)	0.0640 (4)	−0.1654 (5)	1.915 (10)	−2.112 (8)	3.020 (18)
9	0.3249 (2)	0.0167 (4)	0.1658 (4)	1.063 (7)	1.969 (7)	−2.405 (7)
10	0.2169 (2)	−0.1827 (4)	−0.0252 (4)	1.631 (6)	0.104 (6)	−1.210 (5)

[a] x', y', and z' (fractional coordinates) define the origin of the working system of the group. The Goldstein definition is used for Euler angles ϑ, ϕ, and ψ (radians): Goldstein, H. "Classical Mechanics"; Addison-Wesley: Reading, Mass., 1959.

Collection and Reduction of X-ray Intensity Data. The crystals of the compounds, very irregular prisms in shape, were mounted in an arbitrary orientation, and **2** and **3** were coated in paraffin to prevent crystal–air decomposition. Unit cell dimensions were determined by least-squares refinements of the setting angles of 20–25 carefully centered reflections by using a Philips PW 1100 diffractometer. Details of crystal data and data collection for the three compounds are given in Table I. After correction for the background, the intensities were assigned standard deviations calculated as described elsewhere,[8] by using the values of 0.05 for **1** and 0.04 for **2** and **3** for the instability factors. The intensities were corrected for Lorentz–polarization effects, while no absorption correction was applied in view of the small dimensions and shape of the crystals used and of the small values of the linear absorption coefficients.

Solution and Refinement of the Structures. All calculations were carried out by using the XRY72 crystallographic system, adapted to the University of Florence C.I.I. 10070 computer.[9] Atomic scattering factors were taken from ref 10 for Co, S, P, N, C, and B atoms and from ref 11 for hydrogen atoms. An anomalous dispersion correction (a real and an imaginary part) was applied in the F_c calculations for compounds **1** and **3**.[12] Full-matrix least-squares refinement was based on F, and the function minimized was $\sum w(|F_o| - |F_c|)^2$. The weights w were taken as $1/\sigma^2(F_o)$; the agreement factors are defined as $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$.

[(triphos)$_2$Co$_2$(SCH_3)$_2$](BPh_4)$_2$·$2C_3H_6O$ (1). A three-dimensional Patterson synthesis revealed the position of the cobalt and sulfur atoms. Successive Fourier maps showed all the other nonhydrogen atoms of the cation and of the tetraphenylborate anion. Several peaks, whose electron densities were about one-half to one-third that of the average electron density of a carbon atom, were attributed to the solvating acetone whose presence was already inferred from analytical and infrared data. On the basis of bond distances and angles, these peaks were considered derived from two acetone molecules differently oriented in the same region of the unit cell. Full-matrix least-squares refinements were then undertaken by using isotropic thermal parameters for all atoms. Anisotropic thermal parameters were introduced only for the atoms within the coordination sphere in the final stages. A few cycles of refinements reduced the conventional R factor to 0.102. An attempt to refine the acetone molecules was unsuccessful yielding poor bond distances and angles. The solvating molecules were introduced in the following calculation as a fixed contribution by using the parameters derived from the Fourier maps and population parameters of 0.5. The phenyl rings of the ligand and of the tetraphenylborate were treated as rigid groups of D_{6h} symmetry (d(C–C) = 1.392 Å). The hydrogen atoms were introduced in calculated positions (C–H = 0.95 Å) and were not refined. The refinement converged at R = 0.088 and R_w = 0.110.

[(triphos)$_2$Co$_2$S$_2$]BPh_4·$0.5C_3H_7NO$ (2). Patterson and Fourier syntheses allowed the detection of all the nonhydrogen atoms, with the exception of the DMF solvent atoms. Group refinement was used for phenyl groups; groups attached to phosphorus atoms were assigned

Table V. Thermal and Derived Positional Parameters of Group Atoms for [(triphos)Co(μ-SCH_3)$_2$Co(triphos)](BPh_4)$_2$·$2C_3H_6O$ (All Quantities × 10 000)

atom	group	x	y	z	U, Å^2
C1	1	1696 (3)	−168 (5)	5476 (6)	453 (31)
C2	1	1442 (3)	−903 (5)	5762 (6)	611 (38)
C3	1	1714 (3)	−1567 (5)	6162 (6)	747 (42)
C4	1	2241 (3)	−1497 (5)	6277 (6)	727 (43)
C5	1	2496 (3)	−763 (5)	5992 (6)	840 (48)
C6	1	2223 (3)	−99 (5)	5591 (6)	690 (41)
C1	2	1427 (3)	1450 (5)	6046 (4)	424 (29)
C2	2	1305 (3)	1062 (5)	6850 (4)	520 (34)
C3	2	1287 (3)	1549 (5)	7624 (4)	679 (42)
C4	2	1392 (3)	2425 (5)	7594 (4)	793 (46)
C5	2	1515 (3)	2813 (5)	6790 (4)	843 (48)
C6	2	1532 (3)	2326 (5)	6016 (4)	661 (39)
C1	3	130 (4)	2693 (5)	4551 (6)	505 (34)
C2	3	411 (4)	3319 (5)	4998 (6)	745 (43)
C3	3	161 (4)	3923 (5)	5523 (6)	1073 (59)
C4	3	−369 (4)	3900 (5)	5600 (6)	1000 (58)
C5	3	−650 (4)	3274 (5)	5153 (6)	870 (49)
C6	3	−400 (4)	2671 (5)	4629 (6)	729 (42)
C1	4	−3 (3)	1976 (6)	2867 (5)	486 (32)
C2	4	120 (3)	2567 (6)	2209 (5)	822 (47)
C3	4	−205 (3)	2679 (6)	1485 (5)	1108 (62)
C4	4	−653 (3)	2200 (6)	1418 (5)	934 (52)
C5	4	−776 (3)	1609 (6)	2077 (5)	892 (49)
C6	4	−451 (3)	1497 (6)	2801 (5)	640 (39)
C1	5	1508 (3)	−704 (5)	3375 (6)	411 (35)
C2	5	1995 (3)	−534 (5)	3049 (6)	488 (35)
C3	5	2385 (3)	−1135 (5)	3158 (6)	583 (39)
C4	5	2287 (3)	−1906 (5)	3591 (6)	688 (43)
C5	5	1800 (3)	−2077 (5)	3917 (6)	749 (45)
C6	5	1411 (3)	−1476 (5)	3809 (6)	674 (45)
C1	6	622 (3)	−465 (6)	2250 (5)	447 (32)
C2	6	155 (3)	−133 (6)	1968 (5)	576 (39)
C3	6	−76 (3)	−449 (6)	1201 (5)	739 (46)
C4	6	160 (3)	−1097 (6)	716 (5)	828 (51)
C5	6	628 (3)	−1428 (6)	998 (5)	1139 (67)
C6	6	859 (3)	−1112 (6)	1765 (5)	738 (46)
C1	7	2053 (3)	654 (5)	38 (5)	500 (36)
C2	7	1564 (3)	369 (5)	255 (5)	520 (38)
C3	7	1151 (3)	913 (5)	368 (5)	646 (42)
C4	7	1213 (3)	1775 (5)	265 (5)	719 (46)
C5	7	1682 (3)	2096 (5)	52 (5)	733 (46)
C6	7	2091 (3)	1540 (5)	−58 (5)	605 (41)
C1	8	2863 (4)	317 (6)	−885 (6)	545 (39)
C2	8	3391 (4)	436 (6)	−912 (6)	719 (46)
C3	8	3647 (4)	745 (6)	−1649 (6)	977 (54)
C4	8	3378 (4)	950 (6)	−2395 (6)	884 (54)
C5	8	2861 (4)	850 (6)	−2412 (6)	869 (50)
C6	8	2612 (4)	539 (6)	−1668 (6)	724 (45)
C1	9	2923 (3)	102 (6)	889 (5)	461 (35)
C2	9	3342 (3)	−433 (6)	1032 (5)	603 (38)
C3	9	3658 (3)	−375 (6)	1769 (5)	730 (46)
C4	9	3563 (3)	230 (6)	2399 (5)	855 (53)
C5	9	3159 (3)	773 (6)	2300 (5)	908 (52)
C6	9	2847 (3)	705 (6)	1557 (5)	619 (39)
C1	10	2359 (3)	−965 (4)	−153 (6)	483 (35)
C2	10	2297 (3)	−1362 (4)	−974 (6)	651 (43)
C3	10	2114 (3)	−2191 (4)	−1077 (6)	824 (52)
C4	10	1985	−2658 (4)	−348 (6)	786 (51)
C5	10	2036 (3)	−2307 (4)	476 (6)	758 (45)
C6	10	2220 (3)	−1477 (4)	564 (6)	701 (47)

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(10) Cromer, D. T.; Waber, J. T. *Acta Crystallogr.* **1965**, *18*, 104.

(11) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

(12) Cromer, D. T. *Acta Crystallogr.* **1965**, *18*, 17.

Table VI. Atomic[a] Parameters for the Structure of $[(\text{triphos})\text{Co}(\mu\text{-S})_2\text{Co}(\text{triphos})]\text{BPh}_4\cdot 0.5\text{C}_3\text{H}_7\text{NO}$

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co1	891 (2)	2931 (2)	5189 (4)	379 (44)	325 (44)	553 (53)	−19 (41)	132 (41)	−67 (42)
Co2	599 (2)	2118 (2)	3259 (4)	282 (40)	298 (43)	510 (52)	−73 (40)	184 (37)	−122 (43)
P1	1639 (4)	2954 (5)	6508 (8)	473 (87)	664 (99)	549 (101)	−136 (93)	353 (80)	24 (101)
P2	972 (4)	3741 (4)	4976 (9)	524 (98)	536 (98)	525 (114)	−72 (84)	124 (86)	209 (85)
P3	428 (4)	3063 (4)	6122 (8)	399 (83)	315 (94)	334 (92)	−8 (71)	−17 (73)	38 (72)
P4	130 (4)	2344 (4)	1743 (8)	345 (82)	280 (85)	543 (106)	86 (69)	168 (77)	58 (76)
P5	1158 (4)	1684 (4)	2713 (8)	366 (82)	493 (90)	505 (103)	−124 (83)	156 (78)	−77 (87)
P6	156 (4)	1417 (4)	3180 (9)	415 (85)	205 (86)	621 (110)	−29 (72)	207 (80)	−59 (78)
S2	294 (5)	2439 (5)	4298 (10)	652 (99)	1111 (125)	1302 (139)	−437 (95)	610 (99)	−683 (115)
S1	1181 (5)	2639 (6)	4086 (11)	880 (119)	2140 (200)	1729 (171)	−565 (125)	773 (120)	−1364 (157)

[a] The form of the thermal ellipsoid is $\exp(-2\pi^2(U_{11}h^2a^* + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + \ldots))$. F (relative scale factor) = 163 149.

Table VII. Atomic Parameters for the Structure of $[(\text{triphos})\text{Co}(\mu\text{-S})_2\text{Co}(\text{triphos})]\text{BPh}_4\cdot 0.5\text{C}_3\text{H}_7\text{NO}$ (All Quantities ×1000)

atom	x	y	z	U, Å^2
C1	169 (1)	351 (1)	725 (3)	41 (13)
C2	105 (1)	410 (1)	610 (3)	42 (13)
C3	72 (1)	351 (1)	716 (3)	56 (13)
C4	121 (2)	383 (1)	710 (3)	57 (14)
C5	130 (1)	425 (1)	787 (3)	55 (14)
C6	−8 (1)	179 (1)	90 (3)	41 (13)
C7	82 (1)	132 (1)	161 (2)	28 (11)
C8	3 (1)	106 (1)	207 (3)	34 (12)
C9	20 (1)	128 (1)	126 (3)	52 (13)
C10	2 (1)	94 (1)	35 (2)	42 (12)
B	328 (2)	462 (2)	906 (3)	42 (15)
C1[a]	229 (4)	483 (3)	152 (7)	59 (31)
C2[a]	269 (3)	509 (3)	213 (6)	87 (29)
C3[a]	128 (4)	499 (4)	21 (8)	137 (41)
C4[a]	177 (5)	470 (4)	99 (7)	110 (36)
C5[a]	195 (5)	523 (5)	117 (10)	182 (58)

[a] Atoms belonging to the solvent molecule.

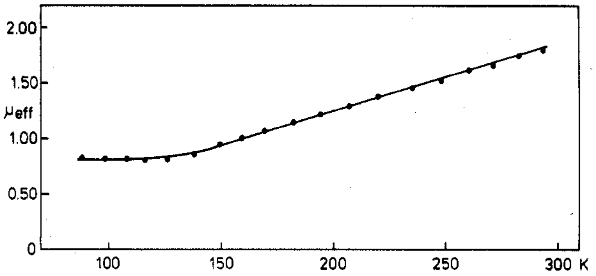
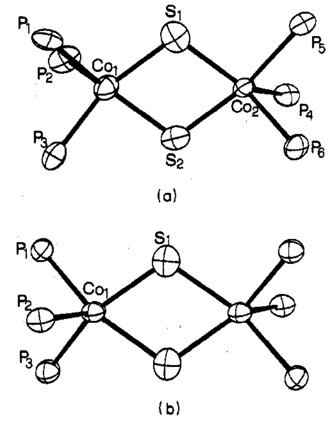


Figure 1. Variation of the magnetic moment μ_{eff} of $[(\text{triphos})\text{Co}(\mu\text{-SCH}_3)_2\text{Co}(\text{triphos})](\text{BPh}_4)_2\cdot 2\text{C}_3\text{H}_6\text{O}$ with temperature.

a D_{6h} symmetry, while a slightly distorted geometry was assigned to the phenyl groups attached to boron atoms, as suggested elsewhere.[13] Fully isotropic block diagonal least-squares cycles followed by mixed-mode cycles, where only Co, P, and S atoms were treated anisotropically, lowered R and R_w to 0.101 and 0.115, respectively. Atoms belonging to a highly distorted DMF molecule were detected at this stage by means of ΔF synthesis. According to the results of the elemental analysis, these atoms were allotted a population parameter of 0.5 which was not varied. At this point also hydrogen atoms were introduced in the structure at calculated positions. A final full-matrix least-squares cycle in which 347 variables were simultaneously varied gave final discrepancy factors R and R_w equal to 0.075 and 0.099, respectively. At the end of refinement the model obtained for the solvent is still highly disordered. Nevertheless this model was considered adequate for deriving the desired chemical information from the structure.

$[(\text{triphos})_2\text{Co}_2\text{S}_2]\cdot 1.4\text{C}_3\text{H}_7\text{NO}$ (3). A three-dimensional Patterson synthesis revealed the cobalt, sulfur, and phosphorus atoms positions. A Fourier map calculated from the atomic positions of these atoms led to location of several carbon atoms. A successive Fourier map detected all nonhydrogen atoms and some disordered positive peaks belonging to a solvent molecule. The complete trial structure was refined by full-matrix least-squares procedure. Through the refinement the phenyl rings were treated as rigid groups of D_{6h} symmetry. Some isotropic cycles on all nonhydrogen atoms were followed by mixed cycles, with anisotropic thermal parameters associated to cobalt, phosphorus, and sulfur atoms. At this stage of refinement the hydrogen atoms were included in idealized positions with temperature factors equal to those of the carbon atoms to which they are attached. The refinement had converged to a final fit of R and R_w of 0.082 and 0.099, respectively. At the end of this refinement the solvent atoms, whose population parameters refined to ca. 0.7, were still highly disordered in spite of much effort to find a definite solution, and in this case also it was decided to waste no more computing time in attempting to get better crystallographic agreement.



(a)

(b)

Figure 2. Perspective view of the skeleton of (a) $[(\text{triphos})\text{Co}(\mu\text{-S})_2\text{Co}(\text{triphos})]\text{BPh}_4$ and (b) $[(\text{triphos})\text{Co}(\mu\text{-S})_2\text{Co}(\text{triphos})]$ (ORTEP drawing with 30% ellipsoid probability).

Tables II–XIII report final atomic and group parameters for all the compounds. Listings of F_o and F_c are available as supplementary material.

Results and Discussion

The dinuclear complex $[(\text{triphos})\text{Co}(\mu\text{-OH})_2\text{Co}(\text{triphos})](\text{BPh}_4)_2$ in ethanol/acetone or ethanol/DMF solution rapidly reacts with CH_3SH or H_2S to form crystalline complexes having the formula $[(\text{triphos})\text{Co}(\mu\text{-SCH}_3)_2\text{Co}(\text{triphos})](\text{BPh}_4)_2\cdot 2\text{C}_3\text{H}_6\text{O}$ (**1**) and $[(\text{triphos})\text{Co}(\mu\text{-S})_2\text{Co}(\text{triphos})]\text{BPh}_4\cdot 0.5\text{C}_3\text{H}_7\text{NO}$ (**2**), respectively. Compound **2** can be reduced with NaBH_4 in methylene chloride–ethanol to produce $[(\text{triphos})\text{Co}(\mu\text{-S})_2\text{Co}(\text{triphos})]\cdot 1.4\text{C}_3\text{H}_7\text{NO}$ (**3**) and can be oxidized with NOBF_4 in methylene chloride to produce $[(\text{triphos})\text{Co}(\mu\text{-S})_2\text{Co}(\text{triphos})](\text{BPh}_4)_2\cdot 4\text{CH}_2\text{Cl}_2$ (**4**). All four complexes (**1**–**4**) are fairly stable in air in the solid state but decompose rapidly in solution. Complexes **1** and **2** are moderately soluble in polar solvents such as acetone, DMF, 1,2-dichloroethane, methylene chloride, and nitroethane. The

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[13] (a) Domenicano, A.; Vaciago, A. *Acta Crystallogr., Sect. B* **1975**, *31*, 2553. (b) Domenicano, A.; Vaciago, A.; Coulson, C. A. *Ibid.* **1975**, *31*, 221. (c) Domenicano, A.; Vaciago, A.; Coulson, C. A. *Ibid.* **1975**, *31*, 1630.

Table VIII. Final Least-Squares Parameters for [(triphos)Co(μ-S)$_2$Co(triphos)]BPh$_4$·0.5C$_3$H$_7$NO Groups[a]

group	x'	y'	z'	ϑ	ϕ	ψ
1	0.1786 (6)	0.2085 (8)	0.7883 (14)	1.127 (26)	0.708 (30)	1.298 (22)
2	0.2705 (7)	0.2911 (6)	0.6382 (14)	1.573 (18)	−0.029 (24)	0.106 (16)
3	0.1875 (7)	0.4036 (6)	0.4327 (15)	1.314 (16)	0.321 (27)	2.827 (18)
4	0.0098 (8)	0.4262 (8)	0.3445 (15)	0.870 (19)	1.983 (35)	−1.473 (14)
5	0.0171 (5)	0.2195 (7)	0.7228 (11)	0.704 (17)	0.851 (29)	1.375 (19)
6	0.0712 (7)	0.3382 (7)	0.5043 (11)	2.584 (13)	1.127 (23)	1.394 (16)
7	−0.0935 (7)	0.2907 (5)	0.1084 (13)	1.882 (15)	−2.348 (23)	−2.727 (18)
8	0.0682 (6)	0.3027 (7)	0.0813 (12)	0.802 (14)	0.515 (29)	2.018 (17)
9	−0.0926 (7)	0.1511 (5)	0.3402 (14)	1.511 (14)	3.071 (22)	0.127 (14)
10	0.0661 (6)	0.0677 (7)	0.4764 (14)	2.014 (24)	−2.216 (26)	1.718 (19)
11	0.2090 (6)	0.2189 (8)	0.2155 (9)	2.644 (17)	2.482 (27)	−0.733 (17)
12	0.1830 (6)	0.0955 (7)	0.4187 (13)	1.009 (19)	2.173 (24)	−1.475 (15)
13	0.2944 (6)	0.3599 (7)	0.9657 (10)	0.318 (14)	1.429 (43)	0.510 (44)
14	0.3948 (7)	0.4475 (6)	0.7851 (13)	2.149 (17)	2.411 (25)	−0.255 (21)
15	0.3864 (5)	0.5150 (6)	1.1037 (14)	1.665 (19)	−1.030 (24)	1.804 (15)
16	0.2271 (7)	0.5276 (6)	0.8026 (14)	1.684 (16)	−0.479 (25)	−2.505 (15)

[a] x', y', and z' (fractional coordinates) define the origin of the working system of the group. The Goldstein definition is used for Euler angles ϑ, ϕ, and ψ (radians): Goldstein, H. "Classical Mechanics"; Addison-Wesley: Reading, Mass., 1959.

Table IX. Thermal and Derived Positional Parameters of Group Atoms for [(triphos)Co(μ-S)$_2$Co(triphos)]BPh$_4$·0.5C$_3$H$_7$NO (All Quantities × 1000)

atom	group	x	y	z	U, Å^2	atom	group	x	y	z	U, Å^2
C1	1	172 (1)	244 (1)	737 (3)	63 (14)	C1	9	−50 (1)	146 (1)	334 (3)	35 (12)
C2	1	165 (1)	247 (1)	828 (3)	58 (14)	C2	9	−94 (1)	152 (1)	250 (3)	61 (14)
C3	1	173 (1)	206 (1)	887 (3)	88 (16)	C3	9	−144 (1)	158 (1)	257 (3)	61 (14)
C4	1	188 (1)	161 (1)	856 (3)	104 (18)	C4	9	−149 (1)	158 (1)	349 (3)	90 (16)
C5	1	194 (1)	158 (1)	766 (3)	115 (19)	C5	9	−105 (1)	152 (1)	433 (3)	80 (15)
C6	1	186 (1)	200 (1)	706 (3)	80 (16)	C6	9	−56 (1)	146 (1)	425 (3)	101 (16)
C1	2	227 (1)	296 (1)	641 (3)	48 (12)	C1	10	43 (1)	96 (1)	414 (2)	53 (15)
C2	2	235 (1)	293 (1)	551 (3)	63 (14)	C2	10	31 (1)	46 (1)	402 (2)	49 (14)
C3	2	285 (1)	288 (1)	548 (3)	129 (19)	C3	10	58 (1)	13 (1)	476 (2)	57 (14)
C4	2	328 (1)	285 (1)	635 (3)	80 (14)	C4	10	96 (1)	30 (1)	560 (2)	91 (16)
C5	2	321 (1)	288 (1)	724 (3)	112 (18)	C5	10	109 (1)	80 (1)	571 (2)	110 (18)
C6	2	270 (1)	293 (1)	727 (3)	96 (16)	C6	10	82 (1)	113 (1)	498 (2)	76 (16)
C1	3	152 (1)	394 (1)	459 (3)	59 (14)	C1	11	169 (1)	198 (1)	242 (2)	69 (15)
C2	3	147 (1)	385 (1)	363 (3)	110 (17)	C2	11	203 (1)	168 (1)	217 (2)	95 (16)
C3	3	189 (1)	396 (1)	332 (3)	101 (18)	C3	11	243 (1)	188 (1)	190 (2)	118 (19)
C4	3	235 (1)	416 (1)	397 (3)	99 (17)	C4	11	249 (1)	240 (1)	189 (2)	84 (15)
C5	3	239 (1)	426 (1)	494 (3)	86 (17)	C5	11	215 (1)	270 (1)	215 (2)	105 (17)
C6	3	198 (1)	414 (1)	525 (3)	64 (14)	C6	11	175 (1)	250 (1)	241 (2)	64 (15)
C1	4	45 (1)	406 (2)	405 (2)	66 (16)	C1	12	155 (1)	122 (1)	358 (2)	46 (13)
C2	4	45 (1)	457 (2)	397 (2)	129 (20)	C2	12	147 (1)	71 (1)	351 (2)	59 (15)
C3	4	4 (1)	481 (2)	326 (2)	119 (20)	C3	12	179 (1)	40 (1)	422 (2)	78 (15)
C4	4	−37 (1)	453 (2)	263 (2)	132 (20)	C4	12	221 (1)	60 (1)	500 (2)	83 (15)
C5	4	−37 (1)	402 (2)	272 (2)	107 (17)	C5	12	229 (1)	111 (1)	506 (2)	101 (17)
C6	4	4 (1)	378 (2)	343 (2)	68 (15)	C6	12	196 (1)	142 (1)	436 (2)	65 (14)
C1	5	28 (1)	253 (1)	680 (2)	60 (13)	C1	13	306 (1)	407 (1)	933 (2)	47 (13)
C2	5	0 (1)	262 (1)	743 (2)	72 (15)	C2	13	261 (1)	398 (1)	954 (2)	64 (14)
C3	5	−13 (1)	223 (1)	792 (2)	88 (16)	C3	13	249 (1)	353 (1)	985 (2)	80 (15)
C4	5	2 (1)	175 (1)	779 (2)	82 (15)	C4	13	283 (1)	314 (1)	997 (2)	84 (17)
C5	5	30 (1)	166 (1)	717 (2)	103 (18)	C5	13	328 (1)	321 (1)	978 (2)	79 (16)
C6	5	43 (1)	205 (1)	667 (2)	58 (13)	C6	13	339 (1)	367 (1)	947 (2)	78 (14)
C1	6	−27 (1)	325 (1)	546 (2)	55 (13)	C1	14	363 (1)	456 (1)	844 (2)	46 (13)
C2	6	−40 (1)	376 (1)	542 (2)	71 (14)	C2	14	413 (1)	476 (1)	866 (2)	70 (14)
C3	6	−92 (1)	391 (1)	493 (2)	100 (16)	C3	14	444 (1)	468 (1)	810 (2)	63 (15)
C4	6	−130 (1)	355 (1)	449 (2)	57 (13)	C4	14	426 (1)	439 (1)	728 (2)	82 (16)
C5	6	−117 (1)	305 (1)	453 (2)	69 (14)	C5	14	377 (1)	419 (1)	703 (2)	74 (14)
C6	6	−65 (1)	290 (1)	502 (2)	67 (13)	C6	14	346 (1)	427 (1)	760 (2)	86 (16)
C1	7	−72 (1)	287 (1)	49 (2)	59 (13)	C1	15	359 (1)	489 (1)	1014 (2)	50 (12)
C2	7	−121 (1)	311 (1)	25 (2)	87 (17)	C2	15	375 (1)	466 (1)	1105 (2)	58 (13)
C3	7	−145 (1)	316 (1)	94 (2)	54 (14)	C3	15	401 (1)	491 (1)	1192 (2)	73 (15)
C4	7	−122 (1)	296 (1)	187 (2)	64 (13)	C4	15	413 (1)	540 (1)	1190 (2)	98 (15)
C5	7	−73 (1)	271 (1)	211 (2)	82 (16)	C5	15	398 (1)	565 (1)	1104 (2)	72 (14)
C6	7	−49 (1)	267 (1)	142 (2)	33 (12)	C6	15	372 (1)	540 (1)	1018 (2)	57 (13)
C1	8	44 (1)	274 (1)	112 (2)	42 (13)	C1	16	272 (1)	497 (1)	851 (3)	54 (14)
C2	8	63 (1)	259(1)	39 (2)	61 (13)	C2	16	244 (1)	522 (1)	901 (3)	70 (16)
C3	8	91 (1)	292 (1)	3 (2)	85 (15)	C3	16	200 (1)	551 (1)	855 (3)	86 (16)
C4	8	100 (1)	340 (1)	40 (2)	79 (15)	C4	16	183 (1)	557 (1)	756 (3)	68 (14)
C5	8	82 (1)	356 (1)	113 (2)	88 (17)	C5	16	210 (1)	534 (1)	703 (3)	100 (17)
C6	8	54 (1)	322 (1)	149 (2)	52 (13)	C6	16	253 (1)	505 (1)	750 (3)	51 (13)

other two complexes are practically insoluble in these solvents. Conductivity measurements in nitroethane solution show that **1** and **2** behave as 1:2 and 1:1 electrolytes, respectively.

The IR spectra of complexes **2**, **3**, and **4** are very similar in the region 4000–250 cm^{-1}, except for those bands which are attributable to the anions and to solvent molecules of crystallization; in no case were bands observed attributable to S–H vibrations. Moreover the IR spectrum of a sample of complex **2** obtained by using deuterated reagents and solvents did not show any differences.

Table X. Atomic[a] Parameters for the Structure of $[(\text{triphos})\text{Co}(\mu\text{-S})_2\text{Co}(\text{triphos})]\cdot 1.4\text{C}_3\text{H}_7\text{NO}$

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co	125 (1)	−881 (1)	1268 (1)	435 (10)	349 (9)	406 (10)	−60 (7)	−185 (8)	−131 (7)
P1	474 (3)	−2719 (2)	1664 (2)	501 (20)	372 (18)	438 (20)	−60 (15)	−195 (17)	−159 (15)
P2	−1344 (3)	−887 (2)	2808 (2)	413 (20)	406 (19)	473 (21)	−68 (15)	−160 (16)	−158 (16)
P3	1374 (3)	−875 (2)	1955 (2)	466 (20)	381 (18)	383 (19)	−72 (15)	−184 (16)	−124 (15)
S1	−440 (4)	−766 (3)	−61 (3)	1570 (42)	778 (28)	920 (31)	−487 (27)	−828 (32)	85 (23)

[a] The form of the thermal ellipsoid is $\exp(-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + \ldots))$. F (relative scale factor) = 21 061.

Table XI. Atomic Parameters for the Structure of $[(\text{triphos})\text{Co}(\mu\text{-S})_2\text{Co}(\text{triphos})]\cdot 1.4\text{C}_3\text{H}_7\text{NO}$ (All Quantities × 1000)

atom	x	y	z	U, Å^2
C1	285 (10)	−3383 (9)	4846 (9)	551 (33)
C2	225 (9)	−2627 (8)	3740 (8)	440 (30)
C3	665 (9)	−3399 (8)	2987 (8)	422 (29)
C4	−1058 (9)	−2087 (9)	3926 (8)	483 (30)
C5	1065 (9)	−1781 (9)	3367 (8)	498 (31)
C1[a]	3657 (25)	3385 (25)	3495 (23)	1294 (96)
C2[a]	3704 (30)	4208 (32)	3740 (27)	1892 (116)
C3[a]	4026 (34)	4721 (37)	4026 (31)	1991 (131)
C4[a]	4913 (41)	4624 (43)	4848 (39)	2540 (189)
C5[a]	4333 (42)	5392 (43)	4152 (38)	2299 (190)

[a] Atoms belonging to the solvent molecule.

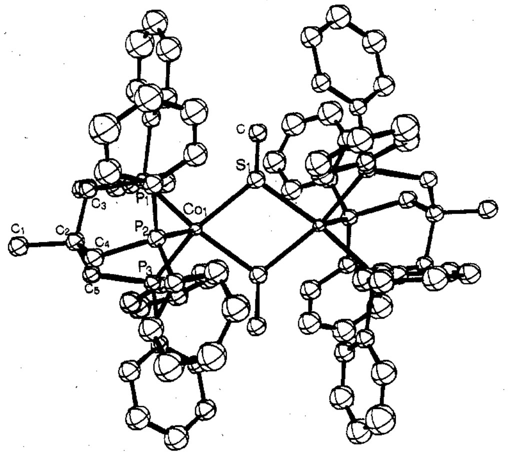

Figure 3. Perspective view of the complex cation of $[(\text{triphos})\text{Co}(\mu\text{-SCH}_3)_2\text{Co}(\text{triphos})]^{2+}$.

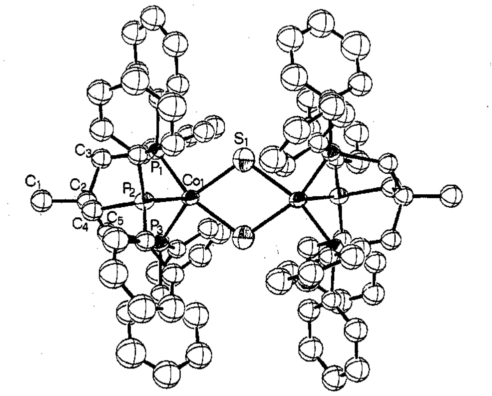

Figure 4. Perspective view of the complex molecule of $[(\text{triphos})\text{Co}(\mu\text{-S})_2\text{Co}(\text{triphos})]$.

Compound **1** has a μ_{eff} of 1.80 μ_{B} at 293 K. Susceptibility measurements at low temperature showed that μ_{eff} decreases with the temperature to the value of 0.8 μ_{B} at 130 K and remains constant to 87 K (Figure 1). This behavior can be attributed to an antiferromagnetic exchange taking place between the two cobalt atoms through the bridging SCH_3 groups. The limiting μ_{eff} value of 0.8 μ_{B} may be attributed to a contribution from partial occupation of the higher triplet state.

The magnetic moment of compound **2** is 1.78 μ_{B} for dimeric unit at 293 K. This is normal for first-row transition-metal complexes containing one unpaired electron. Compound **3** is diamagnetic. The magnetic susceptibility of compound **4** has been found to decrease with increasing field strength up to a very large negative value at infinite field. Thus the slight ferromagnetism detected can be attributed to impurities, the compound **4** being substantially diamagnetic.

Since the IR measurements and the crystallographic methods (absence of hydrogen attributable peaks in the final ΔF Fourier syntheses) do not definitely exclude the presence of SH groups in these complexes, ESCA spectra of the compounds have been recorded. Table XIV shows the values of the S 2p binding energies measured for complexes **2** and **3** and for some reference compounds which contain the fragments M–S–M (compounds a and b), M–SCH_3 (f, g, h), and M–SH–M (i, j, k). The ESCA spectra are known to be sensitive to the oxidation state of the sulfur atom and to the nature of the atoms which form chemical bonds with it.[14] Since bonds between sulfur and transition-metal atoms are less covalent than S–CH_3 and S–H bonds, the S 2p values for M–S–M fragments must be smaller than the values for fragments of the type M–SCH_3, M–SCH_3–M, M–SH–M, or M–SH. The S 2p energy values found for compounds c and d are almost equal to those of compounds a and b so that the existence of Co–S–Co fragments in c and d is confirmed. The energy values found for compound e, containing the bridging SCH_3 group, is larger than the values reported for compounds f, g, and h which contain terminal SCH_3 groups. This may be characteristic of bridging SCH_3 compared to terminal, but the suggestion that such a relationship exists should be considered to be tentative.

The molecular structures of **1**, **2**, and **3** consist of discrete dimeric complexes, with tetraphenylborate anions for **1** and **2**. In all of the structures nonstoichiometric amounts of DMF and acetone solvent molecules are present in the lattice. Figure 2 shows a perspective view of the inner coordination sphere of the complexes **2** and **3**. In Figures 3 and 4 are reported the perspective views of the complex cations of **1** and **3**, respectively. Table XV reports selected bond lengths and angles for all three complexes.

In these dinuclear complexes each of the two cobalt atoms is coordinated to three phosphorus atoms of the triphos ligand and to two bridging sulfur atoms which are equally shared between the two metal atoms. Thus each cobalt is five-coordinate and presents a distorted square-pyramidal geometry, with two bridging sulfur atoms and two phosphorus atoms from the triphos ligand forming the basal plane of each pyramid. Another common feature of the three dimeric complexes is the planarity of the Co_2S_2 rings. For compounds **1** and **3** this is geometrically imposed by the presence of an inversion center.

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(14) Lindberg, B. J.; Hamrin, K.; Johansson, G.; Gelins, U.; Fahlman, A.; Nordling, C.; Siegbahn, K. *Phys. Scr.* **1970**, *1*, 286.

Table XII. Final Least-Squares Parameters for [(triphos)Co(μ-S)$_2$Co(triphos)]·1.4C$_3$H$_7$NO Groups[a]

group	x'	y'	z'	ϑ	ϕ	ψ
1	0.2709 (5)	−0.3797 (4)	0.0236 (4)	0.996 (6)	2.385 (5)	1.301 (6)
2	−0.1281 (5)	−0.3918 (4)	0.1690 (5)	1.641 (5)	0.026 (5)	−0.478 (5)
3	−0.3759 (5)	−0.1234 (4)	0.3207 (4)	2.037 (5)	2.931 (5)	−0.236 (6)
4	−0.1940 (4)	0.1209 (4)	0.3522 (4)	0.981 (5)	−2.868 (6)	−1.570 (6)
5	0.1640 (4)	0.1192 (4)	0.2324 (4)	0.380 (5)	−2.546 (11)	−1.677 (9)
6	0.3933 (4)	−0.1609 (4)	0.0733 (4)	0.780 (5)	−0.863 (5)	1.208 (5)

[a] x', y', and z' (fractional coordinates) define the origin of the working system of the group. The Goldstein definition is used for Euler angles ϑ, ϕ, and ψ (radians): Goldstein, H. "Classical Mechanics"; Addison-Wesley: Reading, Mass., 1959.

Table XIII. Thermal and Derived Positional Parameters of Group Atoms for [(triphos)Co(μ-S)$_2$Co(triphos)]·1.4C$_3$H$_7$NO (All Quantities ×10000)

atom	group	x	y	z	U, Å^2
C1	1	1811 (6)	−3378 (6)	790 (6)	457 (28)
C2	1	2131 (6)	−4540 (6)	1059 (6)	691 (37)
C3	1	3178 (6)	−5030 (6)	413 (6)	732 (38)
C4	1	3907 (6)	−4356 (6)	−503 (6)	822 (40)
C5	1	3587 (6)	−3194 (6)	−773 (6)	761 (39)
C6	1	2539 (6)	−2703 (6)	−126 (6)	603 (33)
C1	2	−583 (6)	−3481 (6)	1714 (7)	458 (29)
C2	2	−557 (6)	−3496 (6)	731 (7)	741 (38)
C3	2	−1371 (6)	−4006 (6)	702 (7)	847 (42)
C4	2	−2211 (6)	−4502 (6)	1657 (7)	906 (44)
C5	2	−2237 (6)	−4486 (6)	2640 (7)	1016 (48)
C6	2	−1423 (6)	−3975 (6)	2669 (7)	754 (38)
C1	3	−2814 (5)	−1050 (6)	3028 (6)	461 (29)
C2	3	−3001 (5)	−1376 (6)	2284 (6)	620 (33)
C3	3	−4104 (5)	−1591 (6)	2493 (6)	822 (41)
C4	3	−5020 (5)	−1480 (6)	3446 (6)	840 (42)
C5	3	−4832 (5)	−1154 (6)	4190 (6)	888 (43)
C6	3	−3730 (5)	−940 (6)	3982 (6)	719 (37)
C1	4	−1702 (6)	350 (5)	3287 (6)	431 (28)
C2	4	−1557 (6)	362 (5)	4201 (6)	594 (33)
C3	4	−1835 (6)	1365 (5)	4474 (6)	718 (37)
C4	4	−2257 (6)	2355 (5)	3834 (6)	795 (40)
C5	4	−2401 (6)	2342 (5)	2921 (6)	838 (41)
C6	4	−2124 (6)	1340 (5)	2647 (6)	628 (34)
C1	5	1557 (5)	405 (5)	2120 (6)	504 (30)
C2	5	2404 (5)	315 (5)	2538 (6)	572 (33)
C3	5	2501 (5)	1233 (5)	2776 (6)	727 (37)
C4	5	1750 (5)	2242 (5)	2596 (6)	713 (37)
C5	5	903 (5)	2332 (5)	2179 (6)	748 (38)
C6	5	807 (5)	1414 (5)	1941 (6)	588 (33)
C1	6	2930 (6)	−1355 (6)	1246 (6)	458 (28)
C2	6	3456 (6)	−657 (6)	232 (6)	616 (34)
C3	6	4628 (6)	−953 (6)	−367 (6)	810 (41)
C4	6	5271 (6)	−1947 (6)	49 (6)	659 (35)
C5	6	4745 (6)	−2645 (6)	1064 (6)	648 (34)
C6	6	3573 (6)	−2349 (6)	1662 (6)	553 (31)

Table XIV. S 2p Binding Energy (eV)

	compd	energy	ref
(a)	[(triphos)Ni(μ-S)Ni(triphos)](BPh$_4$)$_2$	161.5	3m
(b)	[(np$_3$)Co(μ-S)Co(np$_3$)]	161.5	3m
(c)	[(triphos)Co(μ-S)$_2$Co(triphos)]·1.4C$_3$H$_7$NO	161.5	this paper
(d)	[(triphos)Co(μ-S)$_2$Co(triphos)](BPh$_4$)·0.5C$_3$H$_7$NO	161.6	this paper
(e)	[(triphos)Co(μ-SCH$_3$)$_2$Co(triphos)](BPh$_4$)$_2$·2C$_3$H$_6$O	162.9	this paper
(f)	[Co(triphos)SCH$_3$]	162.3	4
(g)	[Co(pp$_3$)SCH$_3$]BPh$_4$	162.3	4
(h)	[Co(np$_3$)SCH$_3$]BPh$_4$	162.4	4
(i)	[Ni(np$_3$)SH]BPh$_4$	162.8	4
(j)	[Ni(pp$_3$)SH]BPh$_4$	162.6	4
(k)	[(ppp)Fe(μ-SH)$_3$Fe(ppp)][a]	162.4	1

[a] ppp = bis[2-(diphenylphosphino)ethyl] phenylphosphine.

Although no inversion center is present in **2**, the largest deviation of any atom from the least-squares plane is only 0.029 Å.

In spite of these similarities the conformations of the molecules are somewhat different. Due to the presence of a center of symmetry halfway between the cobalt atoms the two Co(triphos) fragments are mutually staggered in complexes **1** and **3**; conversely the two moieties are rotated almost halfway between a staggered and an eclipsed conformation in **2**.

This marked difference in the primary geometry of complexes **1** and **3** with respect to complex **2** is accompanied by other important differences in some bond lengths and angles. Most evident is the Co–Co separation which in the monocationic derivative (**2**) is about 0.16 Å shorter than in the other two complexes (3.434 (8) Å vs. 3.579 (2) and 3.598 (2) Å in **1** and **3**, respectively). At the same time the Co–S distance is shorter in complex **2** than in the complexes **1** and **3**, being 2.157 (av) Å vs. 2.277(av) and 2.223(av) Å, respectively. These differences in bond lengths are very dependent upon the molecular orbital electronic configurations of the respective molecules; this matter will be discussed below in detail.

The Co–P bond distances and P–Co–P angles are all in the range usually found for structures containing the triphos ligand.[5,15] Most complexes containing bridging sulfur atoms have M–S–M angles of about 75° and substantial metal–metal bonding. However, in the present cases these angles are 103.6 (1), 106.0(av), and 108.0 (2)° in **1**, **2**, and **3**, respectively, and thus these complexes may be best described as sulfane derivatives.[3h]

Recently some detailed MO approaches to the structure of complexes of the type [L$_3$M(μ-A)$_2$ML$_3$] (L$_3$ = (CO)$_3$, Cp; A = Pr$_2$, SR, etc.) have appeared.[16] According to such treatments when two ML$_3$ fragments are combined, a nest of six "t$_{2g}$" levels and six high-lying MO's are formed. Within the latter group one orbital is too high in energy to enter into bonding; the remaining five orbitals may interact with four suitable hybrid orbitals formed by s and p atomic orbitals of the bridging ligands. This interaction destabilizes three of the five upper orbitals, leaving only "a$_1$" and "b$_2$" at accessible energies. These become the frontier orbitals and are available for electrons above the d^6–d^6 count. The a$_1$ orbital is predominantly metal–metal bonding in character but also has some metal-bridging ligand antibonding character. The b$_2$ is antibonding for both metal–metal and metal-bridging ligand interactions. The inner-ring puckering, if any, affects the energies of these two orbitals. For dimers with 14 d electrons (34 valence electrons), the theory predicts a large amount of puckering and a short metal–metal separation. These predictions are verified, for example, in the [Cp$_2$Co$_2$(PPh$_2$)$_2$][3a] complex (Co···Co = 2.56 (1) Å) but not in the present com-

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(15) Ghilardi, C. A.; Midollini, S.; Orlandini, A.; Sacconi, L. *Inorg. Chem.* **1980**, *19*, 301.

(16) (a) Teo, B. K.; Hall, M. B.; Fenske, R. F.; Dahl, L. F. *Inorg. Chem.* **1975**, *14*, 3103. (b) Burdett, J. K. *J. Chem. Soc., Dalton Trans.* **1977**, 423. (c) Pinhas, A. R.; Hoffmann, R. *Inorg. Chem.* **1979**, *18*, 654.

Table XV. Selected Bond Lengths (Å) and Angles (Deg) with Estimated Standard Deviations

	1	2	3
	Bond Lengths		
Co(1)···Co(2)[a]	3.579 (2)	3.434 (8)	3.598 (2)
Co(1)–P(1)	2.295 (3)	2.263 (11)	2.190 (3)
Co(1)–P(2)	2.362 (4)	2.222 (13)	2.204 (3)
Co(1)–P(3)	2.223 (3)	2.176 (14)	2.186 (4)
Co(2)–P(4)		2.222 (11)	
Co(2)–P(5)		2.265 (14)	
Co(2)–P(6)		2.217 (12)	
Co(1)–S(1)	2.261 (3)	2.166 (19)	2.231 (6)
Co(1)–S(2)[a]	2.293 (3)	2.149 (13)	2.215 (4)
Co(2)–S(1)		2.142 (15)	
Co(2)–S(2)		2.142 (17)	
S(1)–C	1.83 (1)		
S(1)···S(2)	2.817 (4)	2.584 (21)	2.613 (8)
P(1)–C(3)	1.80 (1)	1.82 (4)	1.85 (1)
P(1)–C(1,1)	1.86 (1)	1.83 (4)	1.83 (1)
P(1)–C(1,2)	1.87 (1)	1.77 (9)	1.84 (1)
P(2)–C(4)	1.83 (1)	1.85 (4)	1.86 (1)
P(2)–C(1,3)	1.82 (1)	1.83 (4)	1.82 (1)
P(2)–C(1,4)	1.89 (1)	1.79 (4)	1.82 (1)
P(3)–C(5)	1.79 (1)	1.89 (4)	1.86 (1)
P(3)–C(1,5)	1.84 (1)	1.86 (4)	1.84 (1)
P(3)–C(1,6)	1.89 (1)	1.87 (4)	1.84 (1)
P(4)–C(8)		1.89 (4)	
P(4)–C(1,7)		1.80 (4)	
P(4)–C(1,8)		1.79 (4)	
P(5)–C(9)		1.84 (3)	
P(5)–C(1,9)		1.82 (3)	
P(5)–C(1,10)		1.82 (3)	
P(6)–C(10)		1.81 (4)	
P(6)–C(1,11)		1.88 (4)	
P(6)–C(1,12)		1.81 (4)	
C(1)–C(2)	1.58 (2)	1.52 (5)	1.54 (1)
C(2)–C(3)	1.56 (1)	1.55 (6)	1.55 (2)
C(2)–C(4)	1.53 (2)	1.59 (9)	1.53 (1)
C(2)–C(5)	1.57 (1)	1.55 (6)	1.54 (2)
C(6)–C(7)		1.58 (5)	
C(7)–C(8)		1.58 (5)	
C(7)–C(9)		1.53 (6)	
C(7)–C(10)		1.54 (5)	
B–C(1,7)	1.64 (1)		
B–C(1,8)	1.60 (1)		
B–C(1,9)	1.68 (1)		
B–C(1,10)	1.64 (1)		
B–C(1,13)		1.68 (4)	
B–C(1,14)		1.52 (5)	
B–C(1,15)		1.67 (4)	
B–C(1,16)		1.73 (4)	
	Bond Angles		
P(1)–Co(1)–P(2)	93.5 (1)	89.4 (5)	92.8 (1)
P(1)–Co(1)–P(3)	86.8 (1)	90.2 (5)	91.1 (1)
P(2)–Co(1)–P(3)	92.3 (1)	91.9 (5)	91.6 (1)
P(4)–Co(2)–P(5)		90.7 (5)	
P(4)–Co(2)–P(6)		93.8 (4)	
P(5)–Co(2)–P(6)		87.7 (5)	
P(1)–Co(1)–S(1)	92.9 (1)	101.2 (5)	91.5 (2)
P(1)–Co(1)–S(2)	154.7 (1)	143.0 (5)	149.1 (2)
P(2)–Co(1)–S(1)	103.9 (1)	100.0 (6)	113.2 (2)
P(2)–Co(1)–S(2)	111.3 (1)	127.5 (5)	117.5 (1)
P(3)–Co(1)–S(1)	163.8 (1)	163.5 (5)	154.9 (1)
P(3)–Co(1)–S(2)	97.2 (1)	90.1 (5)	93.7 (2)
S(1)–Co(1)–S(2)	76.4 (1)	73.6 (6)	72.0 (2)
P(4)–Co(2)–S(1)		116.1 (6)	
P(4)–Co(2)–S(2)		111.5 (5)	
P(5)–Co(2)–S(1)		94.8 (6)	
P(5)–Co(2)–S(2)		157.7 (5)	
P(6)–Co(2)–S(1)		149.9 (6)	
P(6)–Co(2)–S(2)		92.5 (5)	
S(1)–Co(2)–S(2)		74.2 (6)	
Co(1)–S(1)–Co(2)	103.6 (1)	105.7 (7)	108.0 (2)
Co(1)–S(2)–Co(2)		106.3 (6)	
Co(1)–S(1)–C	117.8 (4)		
Co(2)–S(1)–C	120.5 (4)		

[a] For the homogeneity of labeling in the table the cobalt and sulfur atoms, symmetry related in structures 1 and 3 to Co(1) and S(1), are labeled Co(2) and S(2), respectively.

pounds $[(\text{triphos})\text{Co}(\mu\text{-SCH}_3)_2\text{Co}(\text{triphos})]^{2+}$ and $[(\text{triphos})\text{Co}(\mu\text{-S})_2\text{Co}(\text{triphos})]$, which also have 14 d electrons. In fact the structures of the latter two complexes are significantly different from that of the former, in respect both to the absence of any puckering and to the Co···Co separation which is 1.03 Å longer.

In the absence of specific MO calculations for complexes **1**–**4**, we shall assume that on substituting the ligand triphos for Cp and SCH_3 or S for PR_2, the *frontier* orbitals are still a_1 and b_2, respectively. However, the large Co···Co distances of about 3.6 Å in complexes **1** and **3** suggest that the a_1 orbital has now lost a great part of its metal–metal bonding character. Also a Co···Co nonbonding distance of 3.43 Å in complex **2** (13 d electrons), where only one electron resides in a_1, strongly supports this hypothesis. Conversely the metal–ligand antibonding character of a_1 is magnified, as shown by an inspection of the lengths of the M–S bonds. The M–S distance shortens from 2.223 (av) Å (complex **3**) to 2.157 (av) Å (complex **2**) as a result of taking an electron out of the a_1 orbital. The even longer Co–S distance (2.277(av) Å) in complex **1**, where the a_1 orbital is again fully populated, must be referred to the presence of the CH_3 groups linked to the sulfur atoms. Their effect would be just opposite to that of the strongly electron-withdrawing CF_3 substituents which are known to shorten the metal–ligand distances. The absence of any puckering in these dimers can be attributed both to the rigidity of the M(triphos) fragment which forces the directions of the remaining orbitals on each metal as well as to the bulkiness of the six terminal phenyl groups in each triphos molecule. This bulkiness, however, does not prevent rotation of the two Co(triphos) units with respect to each other. We believe that a plot of the *frontier* orbital energies vs. the conformational angle along the Co–Co vector would be valuable. Moreover knowledge of the structural parameters of the $[(\text{triphos})_2\text{Co}_2\text{S}_2]^{2+}$ dication would be very useful for indicating whether an empty a_1 orbital favors an overall eclipsed conformation of the dimer.

Both the above MO picture and simple superexchange concepts can be used to qualitatively rationalize the magnetic behavior of these compounds.

While the paramagnetism of complex **2** (33 valence electrons) can be attributed to the existence of one unpaired electron in the a_1 orbital, the diamagnetism of complex **4** (32 valence electrons) must be attributed to the removal of the single a_1 electron upon oxidation.

Concerning complexes **1** and **3**, both having 34 valence electrons, one can assume that in complex **3**, which is diamagnetic, the unsubstituted bridging sulfur atoms are capable of producing a splitting of the levels a_1 and b_2 sufficiently large to allow spin pairing in the a_1 orbital even at room temperature. In complex **1** the presence of bridging SCH_3 groups does not induce the same amount of splitting between a_1 and b_2 orbitals; this can account for the fact that the complex **1** is still partially paramagnetic at temperatures where complex **3** has become diamagnetic. On the other hand, on the basis of simple electronegativity arguments,[17] the exchange coupling constant is predicted to be lower for bridging SCH_3^- than for unsubstituted S^{2-}. The hypothesis of the existence of a singlet–triplet equilibrium with consequent antiferromagnetic behavior of the dimer **1** is thus admissible.

The different chemical reactivities of the compounds $[(\text{triphos})\text{Co}(\mu\text{-SCH}_3)_2\text{Co}(\text{triphos})]^{2+}$ and $[(\text{triphos})\text{Co}(\mu\text{-S})_2\text{Co}(\text{triphos})]^+$ attest to the different nature of the inner rings of these complex cations. On reaction of complex **1** with carbon monoxide or with redox agents, the dimeric framework of this complex is broken and monomeric compounds are formed. Complex **2**, on the contrary, never loses its dimeric framework, neither by reduction and oxidation reactions nor

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[17] Martin, R. L. *New Pathways Inorg. Chem.* **1968**, 175–227.

by action of π ligands, which are without effect on it.

The reactions are summarized as follows:

$$[(\text{triphos})\text{Co}(\mu\text{-SCH}_3)_2\text{Co}(\text{triphos})]^{2+} \begin{cases} \xrightarrow{\text{CO}} 2[(\text{triphos})\text{Co}(\text{CO})(\text{SCH}_3)]^+ \\ \xrightarrow{\text{NaBH}_4} 2[(\text{triphos})\text{Co}(\text{SCH}_3)] \\ \xrightarrow{\text{NOBF}_4} \text{decomposition} \end{cases}$$

$$[(\text{triphos})\text{Co}(\mu\text{-S})_2\text{Co}(\text{triphos})]^{+} \begin{cases} \xrightarrow{\text{CO}} \text{no reaction} \\ \xrightarrow{\text{NaBH}_4} [(\text{triphos})\text{Co}(\mu\text{-S})_2\text{Co}(\text{triphos})] \\ \xrightarrow{\text{NOBF}_4} [(\text{triphos})\text{Co}(\mu\text{-S})_2\text{Co}(\text{triphos})]^{2+} \end{cases}$$

The complexes [(triphos)Co(SCH_3)] and [(triphos)Co(CO)(SCH_3)]BPh_4 are isostructural with both the pseudotetrahedral complexes[18] [(triphos)CoX] (X = Cl, Br, I) and the five-coordinated complexes[19] [(triphos)Co(CO)X]BPh_4 (X = Cl, Br), respectively. The latter five-coordinate complexes are obtained from $[(\text{triphos})_2\text{Co}_2\text{X}_2]^{2+}$ (X = Cl, Br) by reactions analogous to the above ones.

Acknowledgment. Thanks are expressed to Mr. F. Cecconi for technical assistance and to Mr. F. Nuzzi and Mr. G. Vignozzi for microanalyses.

Registry No. **1**, 73496-93-2; **2**, 73697-77-5; **3**, 73496-94-3; $[(\text{triphos})_2\text{Co}_2\text{S}_2](\text{BPh}_4)_2$, 73496-96-5; [(triphos)Co(CO)(SCH_3)]BPh_4, 73496-98-7; (triphos)Co(SCH_3), 73496-99-8; $[(\text{triphos})_2\text{Co}_2(\mu\text{-OH})_2](\text{BPh}_4)_2$, 56172-82-8.

Supplementary Material Available: Listings of structure factor amplitudes for compounds **1**–**3** (45 pages). Ordering information is given on any current masthead page.

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[18] (a) Sacconi, L.; Midollini, S. *J. Chem. Soc., Dalton Trans.* **1972**, 1213. (b) Dapporto, P.; Fallani, G.; Midollini, S.; Sacconi, L. *J. Chem. Soc., Chem. Commun.* **1972**, 1161.

[19] Ghilardi, C. A.; Midollini, S.; Sacconi, L. *J. Organomet. Chem.* **1980**, *186*, 279.

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Crystal Structure Analyses of $Rh_2(bridge)_4(BPh_4)_2{\cdot}CH_3CN$ and $Rh_2(TM4\text{-}bridge)_4(PF_6)_2{\cdot}2CH_3CN$. Further Electronic Spectral Studies of Binuclear Rhodium(I) Isocyanide Complexes

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We have performed X-ray crystal structure analyses of $Rh_2(bridge)_4(BPh_4)_2{\cdot}CH_3CN$ (bridge = 1,3-diisocyanopropane) (space group $P2_1/m$; C_{2h}^2; No. 11; $Z = 2$; $a = 17.359$ (6), $b = 12.573$ (4), $c = 15.666$ (8) Å; $\beta = 113.08$ (3)°; d(calcd) = 0.332 (1), d(obsd) = 1.31 (1) g/cm^3) and $Rh_2(TM4\text{-}bridge)_4(PF_6)_2{\cdot}2CH_3CN$ (TM4-bridge = 2,5-dimethyl-2,5-diisocyanohexane) (space group $P4_2/mbc$; No. 135; $Z = 4$; $a = b = 14.690$ (1), $c = 29.370$ (1) Å; d(calcd) = 1.294 (1), d(obsd) = 1.29 (1) g/cm^3). $Rh_2(bridge)_4(BPh_4)_2{\cdot}CH_3CN$ contains ligand-bridged binuclear cations. The ligands are rigorously eclipsed in $Rh_2(bridge)_4^{2+}$, and the coordination geometry about the Rh atoms is essentially square planar, with a Rh–Rh distance of 3.242 (1) Å. $Rh_2(TM4\text{-}bridge)_4(PF_6)_2{\cdot}2CH_3CN$ also contains discrete ligand-bridged binuclear cations. Although each Rh unit again exhibits approximately square-planar geometry, the rotameric ligand conformation is partially staggered (an angle of about 30° from eclipsed). The Rh–Rh distance is 3.262 (1) Å, which is slightly longer than that in $Rh_2(bridge)_4^{2+}$. The absorption and emission spectra of several binuclear rhodium(I) isocyanide complexes have been measured in acetonitrile solution at room temperature. All the complexes exhibit an intense low-energy absorption spectral band between 400 and 600 nm that is attributable to the fully allowed ${}^1A_{1g} \rightarrow {}^1A_{2u}$ transition. Relatively strong emission attributable to ${}^1A_{2u} \rightarrow {}^1A_{1g}$ is also observed in the 600–700-nm region; the Stokes shift of the emission band is a function of the rotameric conformation of the CNR groups in the binuclear Rh(I) complexes, the order being $CNPhCH_3$ (staggered) > TM4-bridge (partially staggered) > bridge (eclipsed).

The work reported in this paper grew out of studies of the spectroscopic properties of rhodium(I) isocyanides, which we initiated in 1973. One discovery we made early in these studies was that $Rh(CNR)_4^+$ complexes aggregate in solution, yielding discrete binuclear, trinuclear, and even higher oligomers.[1,2] We became intrigued with the spectroscopic properties of these oligomeric Rh(I) species and decided to prepare a particular binuclear complex, $Rh_2(bridge)_4^{2+}$ (bridge = 1,3-diisocyanopropane), for detailed study.[3] The spectroscopic properties, the thermal redox chemistry, and particularly the photoredox chemistry of $Rh_2(bridge)_4^{2+}$ and its derivatives turned out to be interesting,[3-8] and we are continuing our investigations of this system.

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