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Registry No. $(\eta^5\text{-}C_5H_5)(CO)\overline{Mo(\mu\text{-}(\eta^5{:}\eta^1\text{-}C_5H_4))Mn}(CO)_4$, 71411-08-0.

Supplementary Material Available: Figure 3 (unit cell of the title compound) and Table IV (structure factor amplitudes) (25 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) The present work has been taken in part from the dissertation of R. J. Hoxmeier, UCLA, 1972. This is part 15 of a series of papers on the metalation reactions. (b) Part 14: R. J. Hoxmeier, J. R. Blickensderfer, and H. D. Kaesz, *Inorg. Chem.*, preceding paper in this issue.

(2) A preliminary communication of this work was presented by R. Hoxmeier, B. Deubzer, and H. D. Kaesz, *J. Am. Chem. Soc.*, **93**, 536 (1971).

(3) "International Tables for X-ray Crystallography", Vol. I, Kynoch Press, Birmingham, England, 1965, p 99.

(4) The programs used in this work included the following: locally written data reduction programs (based on the program of E. N. Duesler and K. N. Raymond, *Inorg. Chem.*, **10**, 1486 (1971)); LATPAR, least-squares refinement of lattice parameters (R. Sparks); UCLAFOUR, Fourier program (P. Gantzel and H. Hope); UCLALS4, full-matrix least-squares refinement program ACA No. 317 (modified) (P. Gantzel, R. Sparks, R. Long, and K. N. Trueblood); SECEXT, secondary extinction (Christensen and H. Hope); ORTEP, figure plotting (C. K. Johnson); MGTL, least-squares planes and dihedral angles (P. Gantzel and K. N. Trueblood); ORFFE, distance, angle, and error computations (W. R. Busing, K. O. Martin, and H. A. Levy).

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Sulfur Ligand–Transition Metal Complexes. 4.[1] Dinuclear Mercapto Complexes of Iron(II) with the Tridentate Ligand Bis[2-(diphenylphosphino)ethyl]phenylphosphine: Synthesis and X-ray Crystal Structure

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Stable trimercapto dinuclear complexes of iron(II) are formed with the tris(tertiary phosphine) bis[2-(diphenylphosphino)ethyl]phenylphosphine (ppp). The X-ray structure determination of the compound $[Fe_2(\mu\text{-}SH)_3(ppp)_2]ClO_4{\cdot}CO(CH_3)_2$ (triclinic, $P1$, $a = 13.989$ (5) Å, $b = 13.270$ (4) Å, $c = 12.020$ (6) Å, $\alpha = 109.23$ (4)°, $\beta = 120.93$ (3)°, $\gamma = 63.93$ (2)°) has shown that the coordination geometry is confacial bioctahedral. Each metal atom is bonded to the three phosphorus atoms of one ppp molecule and to the three sulfur atoms of the bridging SH groups.

Introduction

In previous papers[1,2] we have shown that some poly(tertiary phosphines) such as tris[2-(diphenylphosphino)ethyl]amine, np_3, tris[2-(diphenylphosphino)ethyl]phosphine, pp_3, and bis[2-(diphenylphosphino)ethyl]phenylphosphine, ppp, form stable mercapto complexes of 3d metals. In this manner many complexes of cobalt and nickel were added to the scanty list of the thiol–metal complexes so far obtained.

In this paper we wish to report two iron–mercapto complexes obtained by reaction of a mixture of the ppp ligand and $[Fe(H_2O)_6]X_2$ salts ($X = BF_4$, ClO_4) with hydrogen sulfide. The compounds so obtained have the formula $[Fe_2(\mu\text{-}SH)_3(ppp)_2]X$. They have been characterized by means of the usual chemical and physical measurements. The structure of the perchlorate has been elucidated by means of a complete X-ray diffraction analysis.

Experimental Section

All solvents were of reagent quality. The ligand ppp was purchased from Strem Chemicals Inc., Danvers, Mass., and was used without further purification. All the reactions were carried out under nitrogen by using deoxygenated solvents.

Preparation of the Complexes $[Fe_2(\mu\text{-}SH)_3(ppp)_2]X$ ($X = ClO_4$, BF_4). The ligand ppp (1 mmol) in 20 mL of acetone was added to a solution of $[Fe(H_2O)_6](ClO_4)_2$ (or $[Fe(H_2O)_6](BF_4)_2$) (1 mmol) in 15 mL of ethanol. When hydrogen sulfide was bubbled into the solution, at room temperature, a deep red color appeared. After bubbling of H_2S for a further 3 min, the resulting solution was concentrated in a stream of nitrogen. The deep red crystals that formed were filtered off and washed with ethanol and then with petroleum ether. Anal. Calcd for $[Fe_2(\mu\text{-}SH)_3(ppp)_2](ClO_4){\cdot}(CH_3)_2CO$, $C_{71}H_{75}ClFe_2O_5P_6S_3$: C, 59.32; H, 5.26; Fe, 7.77; S, 6.69. Found: C, 59.85; H, 5.51; Fe, 7.55; S, 6.36. Calcd for $[Fe_2(\mu\text{-}SH)_3(ppp)_2](BF_4){\cdot}(CH_3)_2CO$, $C_{71}H_{75}BF_4Fe_2OP_6S_3$: C, 59.84; H, 5.30; Fe, 7.84; P, 13.04; S, 6.75. Found: C, 60.44; H, 5.97; Fe, 7.45; P, 12.77; S, 6.53.

Physical Measurements. The physical measurements were executed by the previously described methods.[3]

X-ray Data Collection and Reduction. Crystals of the compound belong to the $P1$ space group of the triclinic system. Lattice constants, obtained by least-squares refinement of the setting angles of 24 reflections are $a = 13.989$ (5) Å, $b = 13.270$ (4) Å, $c = 12.020$ (6) Å, $\alpha = 109.23$ (4)°, $\beta = 120.93$ (3)°, and $\gamma = 63.93$ (2)°. The value of the density calculated for one $[Fe_2(\mu\text{-}SH)_3(ppp)_2]ClO_4{\cdot}CO(CH_3)_2$ unit in the cell, of 1.398 g cm^{-3}, agrees with the value measured by flotation, of 1.40 g cm^{-3}. A Philips PW 1100 automated diffractometer and monochromated Mo Kα radiation (λ = 0.7107 Å) were used for all operations. The crystal used for data collection was irregularly shaped and had approximate dimensions of 0.18 × 0.17 × 0.40 mm, along the a, b, and c directions, in that order. The intensity data were collected in the interval $4° \leq 2\vartheta \leq 55°$ by the ϑ–2ϑ scan technique, with a symmetric scan range of $(1.0 + 0.5 \tan \vartheta)°$ and a scan speed of 4.0°/min in 2ϑ. Stationary-background countings were taken at each end of the scan for a time equal to half the scan time. The intensities of three standard reflections, monitored every 100 min, showed small deviations from their average values (<2.0%) and an overall linear decrease of ca. 3%, probably due to a small amount of decomposition. Data sets were rescaled and processed by using a 0.04 value for p[4]. Of the 7780 independent reflections measured, 4997 having $I \geq 3\sigma(I)$ were considered observed and included in subsequent calculation. No correction for absorption was applied in view of the irregular shape of the crystal and of the limited spread of values (ca. 0.87–0.90) estimated for the transmission coefficients (μ = 7.39 cm^{-1} for Mo Kα radiation). The principal computer programs used have been listed previously.[2]

Solution and Refinement of the Structure. The structure was solved by standard heavy-atom procedures. A series of Fourier syntheses yielded the positions of all atoms, except for those of the solvent molecule and for the hydrogen atoms. Full-matrix least-squares refinement minimized the function $\sum w(|F_o| - |F_c|)^2$ with weights $w = 1/\sigma^2(F_o)$. The position of one heavy atom was not allowed to change during the least-squares cycles as the position of the origin of the coordinate system is undefined in the $P1$ space group. In the final cycles anisotropic thermal parameters were used for all atoms heavier than carbon. The positions of the hydrogen atoms attached to the phenyl and methylene carbons showed up clearly (with heights 0.2–0.5 e Å^{-3}) in a ΔF Fourier calculated at R = 0.064. However such atoms were introduced in calculated positions (C–H = 1.00 Å) as fixed contributions, each with a temperature factor ca. 15% larger than that of the respective carbon atoms. The difference Fourier showed in addition an extended region of electron density with four prominent peaks having heights of 0.6–1.0 e Å^{-3}, approximately arranged as the atoms in the molecule of acetone. Presence of the solvent in the structure was also indicated by the infrared spectrum (see below). One molecule of solvent per cell was assumed, on the basis of the density and elemental analysis data. The molecule, with idealized geometry,[5] was assigned the orientation that fitted best the distribution of residual density in the ΔF map and was treated as a rigid group with an overall thermal factor in the least-squares cycles. Refinement converged at R = 0.050 and R_w = 0.059 (R_w is defined as $[\sum w(|F_o| - |F_c|)^2/\sum w F_o^2]^{1/2}$). No shift was higher than 0.2σ in the last cycle of refinement. The error in an observation of unit weight was 1.39. The atomic scattering factors used in the calculations were those of Cromer and Waber[6] for all nonhydrogen atoms and those of Stewart et al.[7] for neutral hydrogens. Anomalous dispersion terms for Fe, Cl, S, and P were included in F_c.[8] A final difference synthesis revealed maximum residuals (<0.5 e Å^{-3}) in the proximity of the solvent molecule and of the perchlorate anion. Low positive residual density was also present near the positions of the sulfur atoms, but the positions of the hydrogen atoms of the SH groups could not be detected unambiguously. Refinement on the enantiomer of the first model chosen did not produce significant differences either in the R and R_w values or in those of bond distances and angles.[9] The final positional and thermal parameters appear in Table I. A listing of the observed and calculated structure amplitudes is available.[10]

Results and Discussion

The two compounds, which decompose slowly in air, are sparingly soluble in common organic solvents like acetone, 1,2-dichloroethane, and nitroethane, in which they behave as 1:1 electrolytes. They are diamagnetic. Their solution spectra are essentially identical with each other, exhibiting two strong bands at 18 700 and 25 000 cm^{-1}. In addition, two much weaker bands are observed at 9500 and 13 700 cm^{-1}, whose intensity changes slightly with time. Since only the two high-energy bands are present in the reflectance spectra of the compounds, it is likely that the low-energy features appearing only in the solution spectra are due to species originating from decomposition of the complexes. In fact, mild heating was required in order to reach concentrations sufficiently high to record the spectra. The infrared spectra of both complexes show a strong band at 1720 cm^{-1} that may be attributed to the CO stretching vibration of acetone.

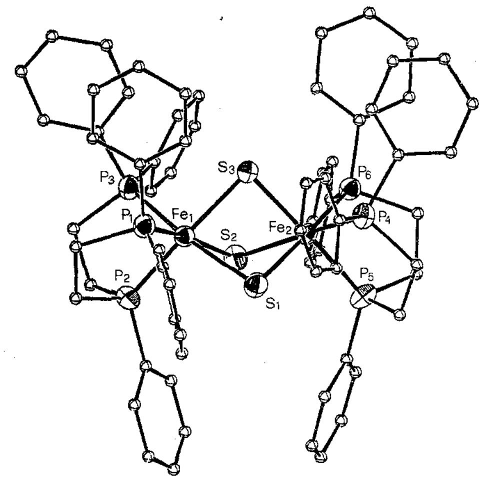

Figure 1. Perspective view of the $[(ppp)Fe(\mu\text{-}SH)_3Fe(ppp)]^+$ cation.

The structure of the compound $[(ppp)Fe(\mu\text{-}SH)_3Fe(ppp)]ClO_4{\cdot}CO(CH_3)_2$ consists of discrete cations, perchlorate anions, and acetone molecules. Each metal atom in the dinuclear cation is bonded to the three phosphorus atoms of one ppp ligand and to the three sulfur atoms of the bridging SH groups, in a distorted octahedral arrangement. The overall geometry of coordination is confacial bioctahedral. The Fe⋯Fe distance, equal to 3.191 (1) Å, excludes any direct metal–metal interaction. Values of important bond distances and angles in the cation are reported in Table II. Figure 1 shows a perspective view of the cation.

The Fe–S distances ranging from 2.32 to 2.36 Å are considerably longer than those found in two dinuclear iron compounds containing two bridging SR groups (2.217–2.219 Å in $[Fe(SC_2H_5)(S_2CSC_2H_5)_2]_2$[11] and 2.233–2.235 Å in $[Fe(\eta^5\text{-}C_5H_5)(CO)(SCH_3)]_2{}^+$[12]). Such a difference is probably due to the larger number of bridging groups in the present complex, compared to the other two. The mean value of the Fe–P distances, 2.231 Å, is quite close to that of 2.221 Å found in the confacial bioctahedral hydrido complex $[Fe_2H_3(p_3)_2]PF_6$[13] (p_3 = 1,1,1-tris[(diphenylphosphino)methyl]ethane) and to that of 2.236 Å existing in the five-coordinate complex $[Fe(pppp)Br]BPh_4$,[14] formed by the tetradentate linear ligand hexaphenyl-1,4,7,10-tetraphosphadecane, pppp. The values of the bond distances and angles in the anion show large deviations from their mean values (Cl–O, 1.26–1.41 Å; O–Cl–O, 92–124°), probably due to the effects of high thermal motion affecting the anion position. There are a number of short contact distances within the dimer, between the sulfur atoms and carbon atoms of the phenyl groups, the shortest one being S1⋯C20 of 3.25 Å. There are no contact distances below 3.20 Å, formed by the anion or by the solvent molecule with the rest of the structure.

The spectral and magnetic properties of the compounds are consistent with the existence of the low-spin d^6 configuration for the two independent metal centers in the cation. The bands at 18 800 and 25 000 cm^{-1} in the electronic spectrum may be assigned to the two spin-allowed transitions ($^1A_{1g} \rightarrow {}^1T_{1g}, {}^1T_{2g}$) expected for such configuration in O_h effective symmetry,[15] although the higher energy band could also be of charge-transfer type. With the use of standard expressions[15] the above assignment yields reasonable values of $10Dq$ (ca. 20 000 cm^{-1}) and B (ca. 450 cm^{-1}) on the assumption that $C = 4B$. It is readily verified that the assignment of the two weak bands in

Table I. Atomic Parameters for the Structure of $[Fe_2(\mu\text{-}SH)_3(ppp)_2]ClO_4 \cdot CO(CH_3)_2$[a]

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{33}
Fe1	0.2996	0.5057	0.3993	0.0336 (6)	0.0284 (6)	0.0306 (6)	−0.0093 (5)	0.0138 (5)	0.0044 (5)
Fe2	0.4491 (1)	0.2782 (1)	0.5310 (2)	0.0358 (6)	0.0304 (6)	0.0284 (6)	−0.0142 (5)	0.0131 (5)	0.0034 (5)
Cl	0.8484 (4)	0.8751 (4)	−0.0549 (5)	0.086 (3)	0.109 (3)	0.129 (3)	−0.004 (2)	0.057 (3)	0.071 (3)
S1	0.3781 (2)	0.4679 (2)	0.6141 (3)	0.054 (1)	0.036 (1)	0.035 (1)	−0.013 (1)	0.021 (1)	0.002 (1)
S2	0.2540 (2)	0.3479 (2)	0.3774 (3)	0.036 (1)	0.037 (1)	0.045 (1)	−0.015 (1)	0.014 (1)	0.007 (1)
S3	0.4767 (2)	0.3618 (2)	0.4122 (3)	0.040 (1)	0.033 (1)	0.043 (1)	−0.007 (1)	0.021 (1)	0.011 (1)
P1	0.3514 (2)	0.6588 (2)	0.4574 (3)	0.044 (1)	0.030 (1)	0.039 (1)	−0.012 (1)	0.018 (1)	0.005 (1)
P2	0.1246 (2)	0.6285 (2)	0.3796 (3)	0.035 (1)	0.035 (1)	0.046 (1)	−0.008 (1)	0.018 (1)	0.006 (1)
P3	0.2242 (2)	0.5016 (2)	0.1834 (3)	0.038 (1)	0.036 (1)	0.032 (1)	−0.010 (1)	0.011 (1)	0.007 (1)
P4	0.6322 (2)	0.2556 (2)	0.6958 (3)	0.040 (1)	0.036 (1)	0.032 (1)	−0.017 (1)	0.010 (1)	0.005 (1)
P5	0.4220 (3)	0.2104 (2)	0.6557 (3)	0.055 (2)	0.047 (1)	0.032 (1)	−0.028 (1)	0.019 (1)	0.002 (1)
P6	0.4878 (2)	0.0997 (2)	0.4319 (3)	0.039 (1)	0.032 (1)	0.033 (1)	−0.013 (1)	0.016 (1)	0.004 (1)
O1	0.748 (1)	0.954 (1)	−0.069 (2)	0.17 (1)	0.17 (1)	0.34 (2)	0.06 (1)	0.11 (1)	0.20 (1)
O2	0.921 (2)	0.882 (2)	0.082 (2)	0.29 (2)	0.28 (2)	0.18 (2)	−0.02 (2)	0.14 (2)	0.04 (2)
O3	0.841 (1)	0.781 (2)	−0.061 (2)	0.14 (1)	0.22 (2)	0.52 (4)	−0.06 (1)	0.01 (2)	0.26 (2)
O4	0.919 (2)	0.877 (2)	−0.090 (2)	0.37 (3)	0.38 (3)	0.23 (2)	−0.21 (2)	0.22 (2)	−0.02 (2)

atom	x	y	z	U, Å^2	atom	x	y	z	U, Å^2
C1	0.218 (1)	0.773 (1)	0.374 (1)	0.045 (2)	C37	0.263 (1)	0.632 (1)	−0.056 (1)	0.065 (3)
C2	0.115 (1)	0.775 (1)	0.389 (1)	0.052 (2)	C38	0.213 (1)	0.613 (1)	0.009 (1)	0.054 (2)
C3	0.015 (1)	0.604 (1)	0.210 (1)	0.052 (2)	C39	0.764 (1)	0.160 (1)	0.672 (1)	0.042 (2)
C4	0.066 (1)	0.592 (1)	0.120 (1)	0.050 (2)	C40	0.773 (1)	0.158 (1)	0.562 (1)	0.053 (2)
C5	0.647 (1)	0.205 (1)	0.832 (1)	0.051 (2)	C41	0.875 (1)	0.098 (1)	0.547 (1)	0.061 (3)
C6	0.525 (1)	0.240 (1)	0.828 (1)	0.051 (2)	C42	0.971 (1)	0.032 (1)	0.640 (1)	0.066 (3)
C7	0.473 (1)	0.053 (1)	0.630 (1)	0.057 (2)	C43	0.964 (1)	0.029 (1)	0.748 (1)	0.072 (3)
C8	0.552 (1)	0.005 (1)	0.555 (1)	0.049 (2)	C44	0.863 (1)	0.091 (1)	0.768 (1)	0.057 (2)
C9	0.464 (1)	0.660 (1)	0.425 (1)	0.041 (2)	C45	0.678 (1)	0.382 (1)	0.780 (1)	0.043 (2)
C10	0.579 (1)	0.589 (1)	0.485 (1)	0.057 (2)	C46	0.746 (1)	0.409 (1)	0.752 (1)	0.059 (3)
C11	0.667 (1)	0.583 (1)	0.463 (1)	0.073 (3)	C47	0.778 (1)	0.506 (1)	0.815 (1)	0.075 (3)
C12	0.645 (1)	0.648 (1)	0.379 (1)	0.071 (3)	C48	0.738 (1)	0.577 (1)	0.904 (1)	0.072 (3)
C13	0.534 (1)	0.718 (1)	0.319 (1)	0.063 (3)	C49	0.675 (1)	0.553 (1)	0.938 (1)	0.086 (3)
C14	0.443 (1)	0.727 (1)	0.341 (1)	0.046 (2)	C50	0.642 (1)	0.453 (1)	0.875 (1)	0.073 (3)
C15	0.397 (1)	0.730 (1)	0.628 (1)	0.046 (2)	C51	0.285 (1)	0.251 (1)	0.669 (1)	0.054 (2)
C16	0.477 (1)	0.785 (1)	0.686 (1)	0.058 (3)	C52	0.246 (1)	0.352 (1)	0.736 (1)	0.061 (2)
C17	0.499 (1)	0.846 (1)	0.813 (1)	0.075 (3)	C53	0.143 (1)	0.385 (1)	0.748 (1)	0.078 (3)
C18	0.439 (1)	0.854 (1)	0.876 (1)	0.079 (3)	C54	0.075 (1)	0.315 (1)	0.690 (1)	0.082 (3)
C19	0.354 (1)	0.803 (1)	0.818 (1)	0.071 (3)	C55	0.109 (1)	0.215 (1)	0.618 (1)	0.094 (4)
C20	0.335 (1)	0.738 (1)	0.696 (1)	0.063 (3)	C56	0.216 (1)	0.181 (1)	0.610 (1)	0.080 (3)
C21	0.052 (1)	0.639 (1)	0.475 (1)	0.046 (2)	C57	0.360 (1)	0.053 (1)	0.304 (1)	0.040 (2)
C22	0.032 (1)	0.730 (1)	0.567 (1)	0.064 (3)	C58	0.363 (1)	−0.025 (1)	0.196 (1)	0.052 (2)
C23	−0.025 (1)	0.734 (1)	0.637 (1)	0.076 (3)	C59	0.269 (1)	−0.067 (1)	0.110 (1)	0.065 (3)
C24	−0.060 (1)	0.649 (1)	0.616 (1)	0.069 (3)	C60	0.177 (1)	−0.033 (1)	0.133 (1)	0.066 (3)
C25	−0.041 (1)	0.557 (1)	0.525 (1)	0.069 (3)	C61	0.166 (1)	0.046 (1)	0.240 (1)	0.063 (3)
C26	0.014 (1)	0.553 (1)	0.455 (1)	0.061 (3)	C62	0.260 (1)	0.090 (1)	0.326 (1)	0.052 (2)
C27	0.215 (1)	0.365 (1)	0.082 (1)	0.040 (3)	C63	0.588 (1)	0.032 (1)	0.355 (1)	0.042 (2)
C28	0.116 (1)	0.334 (1)	0.039 (1)	0.063 (3)	C64	0.568 (1)	0.079 (1)	0.255 (1)	0.055 (2)
C29	0.108 (1)	0.231 (1)	−0.034 (1)	0.072 (3)	C65	0.637 (1)	0.023 (1)	0.185 (1)	0.073 (3)
C30	0.201 (1)	0.157 (1)	−0.062 (1)	0.071 (3)	C66	0.725 (1)	−0.074 (1)	0.219 (1)	0.078 (3)
C31	0.298 (1)	0.182 (1)	−0.023 (1)	0.069 (3)	C67	0.747 (1)	−0.123 (1)	0.316 (1)	0.079 (3)
C32	0.305 (1)	0.288 (1)	0.052 (1)	0.055 (2)	C68	0.680 (1)	−0.072 (1)	0.385 (1)	0.063 (3)
C33	0.284 (1)	0.541 (1)	0.110 (1)	0.041 (2)	C69[b]	0.847 (3)	0.292 (3)	0.214 (3)	0.380 (8)
C34	0.406 (1)	0.495 (1)	0.144 (1)	0.046 (2)	C70[b]	0.838 (3)	0.188 (3)	0.235 (3)	0.380 (8)
C35	0.455 (1)	0.514 (1)	0.080 (1)	0.060 (3)	C71[b]	0.947 (3)	0.278 (3)	0.183 (3)	0.380 (8)
C36	0.378 (1)	0.585 (1)	−0.020 (1)	0.069 (3)	O5[b]	0.774 (3)	0.387 (3)	0.223 (3)	0.380 (8)

[a] Standard deviations on the last significant digits are in parentheses. Isotropic temperature factors are of the form $\exp[-8\pi^2 U(\sin^2 \vartheta)/\lambda^2]$ and anisotropic temperature factors are of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{12}hka^*b^* + \ldots)]$. [b] Atoms of acetone molecule.

the solution spectrum as spin-forbidden $^1A_{1g} \rightarrow {}^3T_{1g}, {}^3T_{2g}$ is inconsistent with that made above for the intense bands in the spectrum. This confirms that the former bands should be due to decomposition products, rather than to the compound investigated.

The SH proton signals could not be identified in the NMR spectra of the compounds, due to difficulties posed by their low solubility and slow decomposition in solution. No band has been observed in the infrared spectra that could be unambiguously assigned to the SH stretching vibration.[16]

The results of the present and of the previous investigations[1,2] provide some insight into the nature of the factors that favor the formation of SR derivatives of the 3d metals. Important factors have been found to be (a) the presence of polydentate ligands with donor sets predominantly composed of soft donor atoms, capable of forming strong covalent bonds to the metal, and (b) the presence of bulky substituents on the ligand atoms, which oppose the growth of the network of metal–sulfur linkages. The ppp ligand essentially fulfills such requirements; however, being quite flexible, it may not provide sufficient shielding with its phenyl groups. Actually, it does not form complexes of the above type as easily as the tripod-like phosphine ligands have been found to do. The other SR complexes previously obtained with this ligand, having the formula $[Ni(ppp)SR]BPh_4$, certainly gain part of their stability from that of the low-spin d^8 electronic configuration in a square-planar environment.[1] Similarly, the stability of the low-spin d^6 configuration in a ligand field of octahedral symmetry should be of importance in the present case. Finally, the fact that a dinuclear complex is formed may be understood by inspection of the structure: the phenyl groups of the two ligands in the cation are arranged in such a way that they completely shield

Table II. Bond Lengths (Å) and Angles (deg) within the Coordination Polyhedron of $[Fe_2(\mu\text{-}SH)_3(ppp)_2]ClO_4 \cdot CO(CH_3)_2$[a]

	Distances		
Fe1–P1	2.232 (4)	Fe2–P4	2.253 (3)
Fe1–P2	2.204 (4)	Fe2–P5	2.230 (5)
Fe1–P3	2.234 (4)	Fe2–P6	2.236 (3)
Fe1–S1	2.362 (4)	Fe2–S1	2.343 (3)
Fe1–S2	2.345 (5)	Fe2–S2	2.332 (3)
Fe1–S3	2.334 (3)	Fe2–S3	2.324 (5)
	Angles		
P1–Fe1–P2	84.6 (1)	P4–Fe2–P5	84.8 (1)
P1–Fe1–P3	96.4 (2)	P4–Fe2–P6	96.3 (1)
P2–Fe1–P3	85.3 (1)	P5–Fe2–P6	84.3 (2)
P1–Fe1–S1	96.2 (1)	P4–Fe2–S1	92.2 (1)
P1–Fe1–S2	169.9 (2)	P4–Fe2–S2	166.1 (1)
P1–Fe1–S3	100.9 (2)	P4–Fe2–S3	93.9 (2)
P2–Fe1–S1	99.2 (2)	P5–Fe2–S1	94.4 (2)
P2–Fe1–S2	94.7 (2)	P5–Fe2–S2	100.0 (2)
P2–Fe1–S3	174.4 (3)	P5–Fe2–S3	175.6 (2)
P3–Fe1–S1	167.0 (2)	P6–Fe2–S1	171.2 (2)
P3–Fe1–S2	93.6 (1)	P6–Fe2–S2	97.1 (1)
P3–Fe1–S3	93.6 (1)	P6–Fe2–S3	100.0 (2)
S1–Fe1–S2	73.9 (1)	S1–Fe2–S2	74.5 (1)
S1–Fe1–S3	80.8 (1)	S1–Fe2–S3	81.4 (1)
S2–Fe1–S3	79.9 (1)	S2–Fe2–S3	80.4 (1)
Fe1–S1–Fe2	85.4 (1)	Fe1–S3–Fe2	84.5 (2)
Fe1–S2–Fe2	86.1 (1)		

[a] Estimated standard deviations are in parentheses.

the cluster of the metal and donor atoms, preventing its further growth.

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Registry No. $[Fe_2(\mu\text{-}SH)_3(ppp)_2](ClO_4) \cdot (CH_3)_2CO$, 71393-26-5; $[Fe_2(\mu\text{-}SH)_3(ppp)_2](BF_4)$, 71425-17-7.

Supplementary Material Available: A listing of structure factor amplitudes (22 pages). Ordering information is given on any current masthead page.

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(16) After this work had been submitted for publication, ESCA measurements were performed on the compound $[Fe_2(\mu\text{-}SH)_3(ppp)_2]ClO_4$ by Professor V. I. Nefedov at the Kurnakov Institute of General and Inorganic Chemistry of the Academy of Science of the USSR, in Moscow. The results indicate unambiguously that the compound contains SH groups and that there are no bridging unsubstituted sulfur atoms. The alternative formulation of the compound, as $[Fe_2(\mu\text{-}SH)(\mu\text{-}S)_2]ClO_4$, according to which spin pairing would be attained through strong antiferromagnetic coupling, may be therefore ruled out.

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Bifunctional Model Complexes Active in Carbon Dioxide Fixation: Synthesis and X-ray Structure of Bimetallic Cobalt(I)–Alkali Cation–Schiff Base Complexes

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Reduction of (*N,N'*-ethylenebis(salicylideniminato))cobalt(II), Co(salen), with lithium and sodium metals in tetrahydrofuran, THF, affords the bimetallic systems, which are active in carbon dioxide fixation, [(Co(salen))NaTHF] and $[(Co(salen))Li(THF)_{1.5}]$. The structures of these complexes have been solved by single-crystal X-ray diffraction methods. Both of them contain a diamagnetic cobalt(I) in a slightly distorted square-planar coordination geometry due to a salen ligand which coordinates the alkali cation through the oxygen atoms. [(Co(salen))NaTHF] crystallizes in the orthorhombic space group $P2_12_12$ with lattice parameters $a = 7.416$ (2) Å, $b = 21.848$ (9) Å, $c = 11.639$ (5) Å, and $Z = 4$. The structure has been solved by using 1579 observed reflections and refined to $R = 0.030$. The crystal structure consists of infinite chains, whose monomeric unit is $[(Co(salen))_2Na_2(THF)_2]$. They can be described by distorted octahedra around Na^+ sharing the opposite faces. Both THF and Co(salen) act, through the oxygen atoms, as bridging ligands between two adjacent sodium cations. $[(Co(salen))Li(THF)_{1.5}]$ is triclinic, space group $P\bar{1}$, with lattice parameters $a = 16.892$ (3) Å, $b = 14.310$ (3) Å, $c = 10.899$ (3) Å, $\alpha = 94.6$ (2)°, $\beta = 99.5$ (2)°, $\gamma = 122.3$ (2)°, and $Z = 2$. The structure has been solved by direct methods and refined by least-squares methods to $R = 0.089$, for 2680 reflections. In the structure of $[(Co(salen))Li(THF)_{1.5}]$ there are two different molecular complexes, $[(Co(salen))Li(THF)_2]$ and $[(Co(salen))_2Li_2(THF)_2]$, in a 2:1 ratio. In both complexes, Li^+ is in a distorted tetrahedral coordination. In the first complex, the four oxygens for the lithium coordination are provided by Co(salen), acting as a bidentate chelating ligand, and two THF molecules. In the centrosymmetric tetranuclear complex $[(Co(salen))_2Li_2(THF)_2]$ one of the THF oxygens of $[(Co(salen))Li(THF)_2]$ is replaced by a Co(salen) oxygen atom which bridges two lithium cations.

Introduction

Metal basicity has proved valuable in rationalizing reactivity patterns in organometallic and coordination compounds, especially in terms of the binding and activation of small gas molecules.[1] Particularly effective have been the d^8 and d^{10} metal complexes with tertiary phosphine type ligands,[1] but a second type includes macrocyclic ligand systems with harder N and O donors in which the metal has been reduced to a low

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