There is good evidence available[29,32] to indicate the existence of a steric effect in the octahedral $Ni(DMA)_6^{2+}$ complex. The ease with which the octahedral cobalt complex is converted to the tetrahedral complex is probably partially due to the existence of steric effects in the six-coordinate complex. The attempted conversion of less sterically hindered $[Co(DMF)_6](ClO_4)_2$ to $[Co(DMF)_4](ClO_4)_2$ by the procedures described above was unsuccessful. This experiment offers some chemical evidence for the importance of the steric effect in the formation of $[Co(DMA)_4]^{2+}$. The large ratio of $\Delta(T_d)/\Delta(O_h)$ is thus partially due to a steric effect lowering Δ in the octahedral complex.

The Δ value for DMA toward nickel(II) in the absence of a steric effect is estimated to be 8700 cm^{-1} as an upper limit. This number is obtained by interpolation from the Δ's for $HC(O)NHCH_3$ (8380 cm^{-1}), $HC(O)N(CH_3)_2$ (8500 cm^{-1}), and CH_3CONH_2 (8240 cm^{-1}). The value 8700 cm^{-1} would give a $\Delta(T_d)$ to $\Delta(O_h^{cor})$ ratio of 0.56. In order to obtain the ratio 0.44, the Δ for DMA in the octahedral complex would have to have an unreasonably large value of 11,150 cm^{-1}. The lack of quantitative agreement between the adjusted experimentally determined ratio, 0.56, and the value predicted by crystal-field theory (0.44) requires that factors other than a steric effect contribute to the large ratio.

The larger Δ ratio is believed to be due in part to greater covalency in the tetrahedral compared to the octahedral complex. In addition to the evidence in the previous section to support this claim, Ballhausen and Liehr have shown semiquantitatively that electronic spectral intensities for d–d transitions are a direct function of the mixing of metal and ligand orbitals.[33] This conclusion has received support from the experimental observation that the measured oscillator strength for the d–d transition in tetrahedral Co(II) complexes is directly related to predicted metal–ligand covalency.[17] A portion of the large ratio of tetrahedral to octahedral Δ observed experimentally in the DMA complexes may be due to a larger covalent σ interaction in the tetrahedral complex. The partially filled σ d orbitals are raised in energy by mixing with the filled σ ligand orbitals. This process would tend to split the metal d orbitals further, and d–d transitions would thus occur at higher energy. It is reasonable that there should be more effective covalent bonding in the tetrahedral complex, for ligand–ligand repulsions are decreased and effective metal ion charge is enhanced for the tetrahedral complex relative to the octahedral case.

A more detailed description of these interesting complexes must await the results of a complete structural analysis.

Acknowledgment. The authors wish to thank the Chemistry Branch of the Atomic Energy Commission for their generous support of this research through Contract No. AT(11-1)758.

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[32] J. H. Bright, R. S. Drago, D. M. Hart, and S. K. Maden, *Inorg. Chem.*, 4, 18 (1965).

[33] C. J. Ballhausen and A. D. Liehr, *J. Mol. Spectry.*, 2, 34 (1958).

Coordination Compounds with Delocalized Ground States. Bisdithiodiketone Complexes of Iron and Cobalt[1]

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Contribution from the Institute of Inorganic Chemistry, The University, Munich, Germany, and, in part, Shell Development Company, Emeryville, California. *Received June 10, 1966*

Abstract: The preparation, properties and reactions of dithiodiketone complexes of iron and cobalt are reported. It is concluded that $FeS_4C_4(CF_3)_4$ as well as $FeS_4C_4Ph_4$ and $CoS_4C_4Ph_4$ are metal–sulfur bridged dimers $M_2S_8C_8R_8$ with structures analogous to that observed for $Co_2S_8C_8(CF_3)_8$. Thermal degradation of "$FeS_4C_4Ph_4$" affords a sulfur-bridged dimeric complex of composition $Fe_2S_2(S_2C_2Ph_2)_2$. The same compound is also formed from the reaction of metallic iron or iron carbonyls with sulfur and diphenylacetylene under conditions similar to the original preparation of $NiS_4C_4Ph_4$. Both "$FeS_4C_4Ph_4$" and "$CoS_4C_4Ph_4$" form stable five-coordinate 1:1 adducts with phosphines. A well-defined tributylphosphine adduct of $FeS_4C_4H_4$ is also reported. The phosphine adducts of the iron complexes may be regarded as isoelectronic with the neutral nickel compounds $NiS_4C_4R_4$, and the analogous compounds of cobalt as isoelectronic with $NiS_4C_4R_4^-$. The reaction of the Fe, Co, and Ni complexes $MS_4C_4R_4$ with $Fe(CO)_5$ affords the compounds $Fe_2(CO)_6C_2S_2R_2$, of which several derivatives, including $Fe_2(CO)_6S_2C_2H_2$, are also described. The bonding in the complexes is discussed and additional evidence in support of the proposed delocalized ground states of the compounds is presented.

In the course of our work on dithiodiketone complexes of transition metals, the bisdithiobenzil complexes of iron and cobalt so far have been mentioned only briefly.[3] *Neutral* complexes of iron and cobalt were reported by Davison, *et al.*,[4] with $S_2C_2(CF_3)_2$ as ligands. The iron compound was initially

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[1] (a) Paper XI of the series: The Chemistry of Coordination Compounds. (b) Paper X: G. N. Schrauzer, and V. P. Mayweg, *J. Am. Chem. Soc.*, 88, 3235 (1966).

[2] Department of Chemistry, The University of California at San Diego, La Jolla, Calif.

[3] G. N. Schrauzer, V. P. Mayweg, H. W. Finck, U. Müller-Westerhoff, and W. Heinrich, *Angew. Chem.*, 76, 345 (1964); *Angew. Chem. Intern. Ed. Engl.*, 3, 381 (1964).

[4] A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *Inorg. Chem.*, 3, 814 (1964).

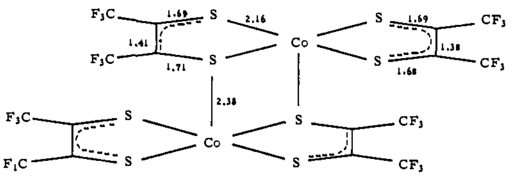
described as a tris complex, $FeS_6C_6(CF_3)_6$.[4] We have found that is is actually $FeS_4C_4(CF_3)_4$.[1b] The compound is quite reactive in solution and readily forms the anion $FeS_4C_4(CF_3)_4^-$ of which salts were isolated.[4] With MNT (maleonitriledithiolate) and TDT (toluenedithiolate) as ligands so far only the anionic species $Fe(MNT)_2^{-,2-}$, $Fe(MNT)_3^{3-}$, and $Fe(TDT)_2^-$ were described.[1b,5–7] The cobalt complex $CoS_4C_4(CF_3)_4$ (I) was shown to have a dimeric structure.[8] The dimerization occurs through Co–S linkages of 2.38 A in length and is shown in Figure 1. We have recently found that the iron complex $FeS_4C_4(CF_3)_4$ is isomorphous with the cobalt compound.[1b] Various salts of the respective mono- and dianions of cobalt complexes with MNT, TDT, and $S_2C_2(CF_3)_2$ and several five- and six-coordinated cobalt complex anions have also been described.[9–11] In the present paper we report a part of our work on *neutral* iron and cobalt complexes of α-dithiodiketones.

Preparation and Properties

Iron Complexes. Bis(dithiobenzil)iron, $FeS_4C_4Ph_4$ (II), is readily obtained by the benzoin–P_4S_{10} method.[3,12a] The black, crystalline compound is only sparingly soluble in common organic solvents and stable to dilute acids and bases; it is cleaved by aqueous cyanide and reduced to metallic iron in warm hydrazine solution (the corresponding nickel complex is stable to cyanide and in hydrazine is only reduced to $NiS_4C_4Ph_4^{2-}$ under similar conditions). The solid complex remains unchanged up to about 290°. However, heating a toluene suspension of II in a closed tube to 190–200° causes a partial degradation which leads to a new complex of composition $Fe_2S_2(S_2C_2Ph_2)_2$ (III), together with organic products (eq 1).

$$\underset{\text{II}}{2\text{FeS}_4\text{C}_4\text{Ph}_4} \longrightarrow \underset{\text{III}}{\text{Fe}_2\text{S}_2(\text{S}_2\text{C}_2\text{Ph}_2)_2} + \begin{cases}\text{tetraphenylthiophene}\\ \text{2-phenylthionaphthene}\end{cases} \qquad (1)$$

Originally, complex III was obtained by the reaction of metallic iron, $Fe(CO)_5$, or $Fe_3(CO)_{12}$ with sulfur and diphenylacetylene, under conditions analogous to the synthesis of $NiS_4C_4Ph_4$.[12b] The initial organic product of the thermal degradation of III must be the highly reactive fragment Ph—C=C(S)—Ph which is responsible for the formation of the 2-phenylthionaphthene and tetraphenylthiophene in eq 1. Reduction of complex II may be achieved; *e.g.*, with hydrazine or sodium borohydride, salts of the $FeS_4C_4Ph_4^-$ ion have been isolated. Polarographic reduction of complex III indicates the existence of ions $Fe_2S_2(S_2C_2Ph_2)_2^{n-}$ (n = 1, 2, 3, 4) and a well-defined salt of the dianion was also prepared. With $Ni(CO)_4$ II reacts forming a black material of approximate composition $NiFeS_4C_4Ph_4$ which, in acid, decomposes into Fe^{2+} and $NiS_4C_4Ph_4$. With $Fe(CO)_5$ both II and $NiS_4C_4Ph_4$ form the complex $Fe_2(CO)_6S_2C_2Ph_2$ (IV). It is of interest that reaction of IV with sulfur produces III, whereas the thermal degradation yields FeS, CO, and diphenylacetylene. The preparation of several substituted complexes is also reported. The basic unsubstituted iron complex, $FeS_4C_4H_4$, could not be isolated in pure form. However, addition of tributylphosphine to the reaction mixture afforded a soluble, crystalline 1:1 adduct, $FeS_4C_4H_4\cdot P(n\text{-}C_4H_9)_3$. The substituted iron complexes $FeS_4C_4R_4$ behave similarly. Several of the very unusual five-coordinate species $FeS_4C_4R_4\cdot PR_3'$ are described in the Experimental Section. According to polarographic measurements, the phosphine adducts of the iron complexes are reduced in two one-electron steps. Since only the first wave is reversible, it is concluded that the phosphine does not remain attached to the metal atom upon addition of the second electron. No reaction was observed with triphenylarsine or -stibine, respectively. With NO, however, a variety of complexes are formed, among them $Fe(NO)S_4C_4Ph_4$.[13] These complexes will not be discussed in the present paper, however. The X-ray powder patterns of $FeS_4C_4Ph_4$ and $FeS_4C_4(CF_3)_4$ are definitely similar and show coincident lines. The two compounds are therefore probably isostructural.



I

Figure 1. Structure of $[CoS_4C_4(CF_3)_4]_2$[8] (observed bond distances in A).

Cobalt Complexes. Bis(dithiobenzil)cobalt, $CoS_4C_4Ph_4$ (complex V), was obtained by the benzoin–P_4S_{10} method. It is a sparingly soluble, black, diamagnetic substance whose X-ray powder pattern is similar to that of $FeS_4C_4Ph_4$. We have actually obtained samples of $FeS_4C_4Ph_4$ and $CoS_4C_4Ph_4$ which were isomorphous, a result which later could not be reproduced. Above 360° $CoS_4C_4Ph_4$ starts to decompose into cobalt sulfide, and, largely, 2-phenylthionaphthene; the formation of a bridged dimer analogous to III was not observed. However, paramagnetic addition compounds of V with phosphines are obtained under essentially the same conditions as the iron complexes. The compound $CoS_4C_4Ph_4\cdot PPh_3$ (VI), for example, forms almost black, but microscopicially deeply red, air-stable crystals which are soluble in nonpolar organic solvents. With hydrazine, V is reduced and salts of the monoanion $CoS_4C_4Ph_4^-$ can be isolated; there is also evidence for a dianion, although the isolation of salts of this species proved more difficult.[14] The phosphine adducts VI

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(5) J. F. Weiher, L. R. Melby, and R. E. Benson, *J. Am. Chem. Soc.*, **86**, 4329 (1964).

(6) R. Williams, E. Billig, J. H. Waters, and H. B. Gray, *ibid.*, **88**, 43 (1966).

(7) M. Gerloch, S. F. A. Kettle, J. Locke, and J. A. McCleverty, *Chem. Commun.*, 29 (1966).

(8) J. H. Enemark and W. N. Lipscomb, *Inorg. Chem.*, **4**, 1729 (1965).

(9) H. B. Gray and E. Billig, *J. Am. Chem. Soc.*, **85**, 2019 (1963).

(10) E. Billig, H. B. Gray, S. I. Shupack, J. H. Waters, and R. Williams, *Proc. Chem. Soc.*, 110 (1964).

(11) C. H. Langford, E. Billig, S. I. Shupack, and H. B. Gray, *J. Am. Chem. Soc.*, **86**, 2958 (1964).

(12) (a) G. N. Schrauzer, V. P. Mayweg, and W. Heinrich, *Inorg. Chem.*, **4**, 1615 (1965); (b) G. N. Schrauzer and V. P. Mayweg, *J. Am. Chem. Soc.*, **84**, 3221 (1962).

(13) Reaction of $FeS_4C_4Ph_4$ with NO in benzene afforded a red, crystalline, paramagnetic $FeS_4C_4Ph_4\cdot NO$, dec pt ~140°. *Anal.* Calcd for $C_{28}H_{20}NOS_4Fe$: C, 58.95; H, 3.51; N, 2.36. Found: C, 58.75; H, 3.42; N, 2.11. Several additional NO-containing complexes are formed; *e.g.*, on chromatography on silica gel using a 1:1 benzene–cyclohexane mixture violet crystals of a complex tentatively described as $(C_{14}H_{10}S_2Fe)_3\cdot 2NO$ were isolated, dec pt 100°. *Anal.* Calcd for $C_{42}H_{30}S_6Fe_3N_2O_2\cdot C_6H_6\cdot C_6H_{12}$: C, 58.6; H, 4.4; S, 17.4; N, 2.5; Fe, 15.1; mol wt, 1106. Found: C, 58.8; H, 4.4; S, 17.9; N, 2.4; Fe, 15.2; mol wt, 1040.

(14) An extremely air-sensitive, red $(Na^+(diglyme)_2)_2CoS_4C_4CoS_4C_4Ph_4^{2-}$ was obtained on reducing V with $NaBH_4$ in diglyme, but has not yet been investigated in detail.

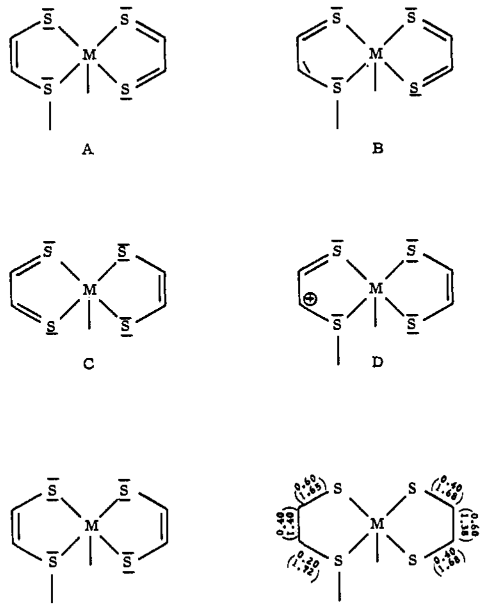


Figure 2. A–E, mainly contributing valence bond structures in a dimer of the type observed in $[CoS_4C_4(CF_3)_4]_2$; F, calculated double bond characters and distances (A). Structures containing M=S bonds are not included.

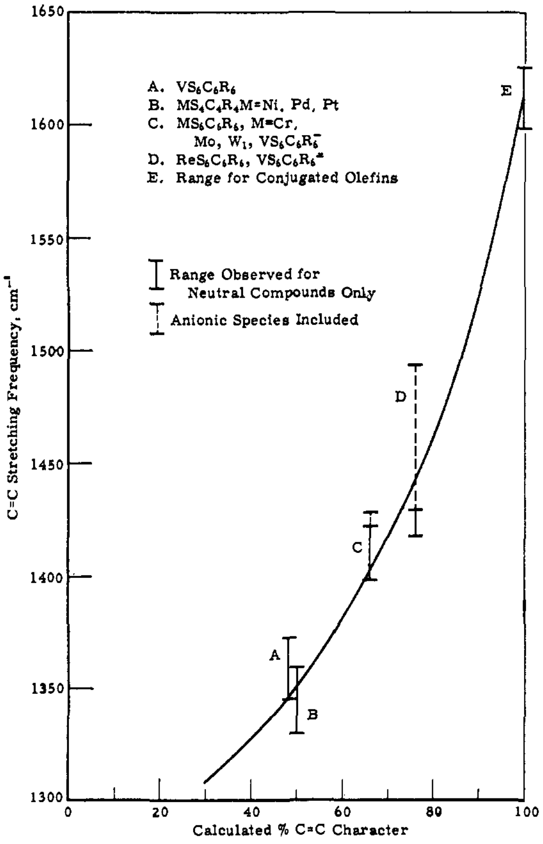


Figure 3. Relation between the C=C stretching frequencies.

may also be reduced to mono- and dianions; as with the iron complexes, only the first reduction wave is reversible. Reaction of V with $Fe(CO)_5$ also afforded IV. Several derivatives of V with substituents other than phenyl and the relevant phosphine adducts have been prepared and are described in the Experimental Section.

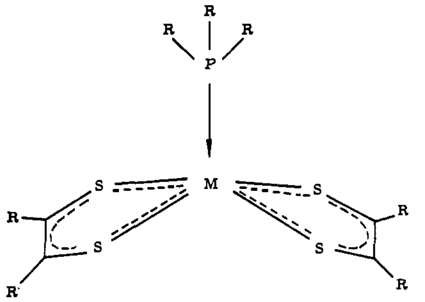
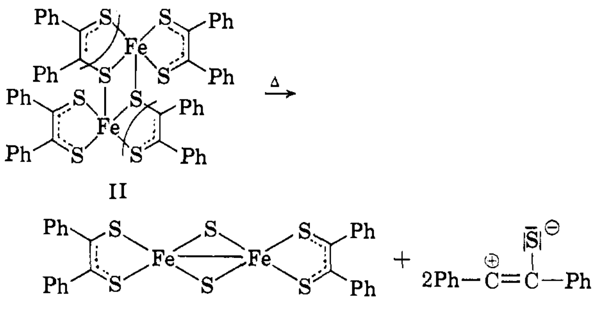


Figure 4. Proposed structure of the phosphine adducts of complexes $MS_4C_4R_4$ (M = Fe, Co).

Discussion

The observed isomorphism relationships indicate that the iron complexes have structures similar to $Co_2S_8C_8(CF_3)_8$. In the latter the cobalt atom has the coordination number 5 and is 0.37 A out of the plane of the S_4 group.[8] The C–C and C–S distances observed indicate that the resonance of the vertical π-electron systems in the monomers is disturbed by the perpendicular M–S interactions. In the cobalt complex in addition, spin pairing must occur, probably *via* metal d-orbital interactions. With this structure the high yield conversion of $FeS_4C_4Ph_4$ into III may also be understood (eq 2)



(2)

It is apparent from the observed bond distances in I that the ligands are extensively delocalized. In the dimeric complexes the five limiting structures shown in Figure 2 must be the mainly contributing ones.[15] Assuming equal weights, the bond distances calculated from the double bond characters agree reasonably well with the experimental values. The double bond characters calculated similarly for systems $M(S_2C_2R_2)_n^{z-}$ (n = 2, 3; z = 0, 1, 2) also correlate with the C=C stretching frequencies (Figure 3). For the C=S bands the situation is more complicated due to the proximity of the metal and effects of charge and substituents. For both $FeS_4C_4Ph_4$ and $CoS_4C_4Ph_4$ the frequency of the observed intense C=C stretch suggests about 50% double bond character, in agreement with the assumed structure.[16] The C=S stretching bands are usually quite intense in the monomeric dithione complexes but are weak in both the iron and cobalt complex and split into at least two bands, as one would expect from the nonequality of the C=S groups in the molecule. In the phosphine adducts of $FeS_4C_4Ph_4$ the C=C stretch appears at about the same energy as in the free com-

(15) For previous applications of VB formalisms to complexes of this type see ref 1b.

(16) In principle, a second C=C stretch should be observable at lower frequency which would correspond to that of the $S_2C_2Ph_2$ group participating in the dimer formation. This band, whose intensity may be quite weak, so far could not be detected, however.

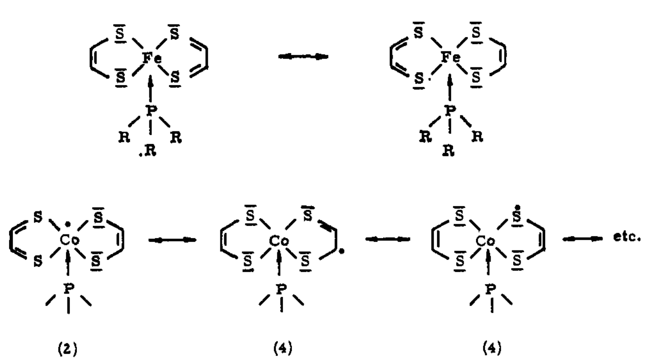


Figure 5. Mainly contributing limiting structures in phosphine adducts of complexes $MS_4C_4R_4$ (M = Fe, Co).

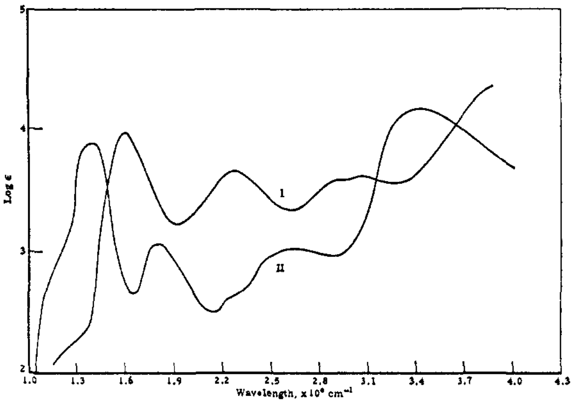


Figure 6. Electronic spectra of $FeS_4C_4H_4 \cdot P(n\text{-}C_4H_9)_3$ (I) and of $NiS_4C_4H_4$ (II), both in CH_2Cl_2. Additional weak bands in (I) below 12,000 cm^{-1} ($\epsilon \sim 10^2$) are not shown.

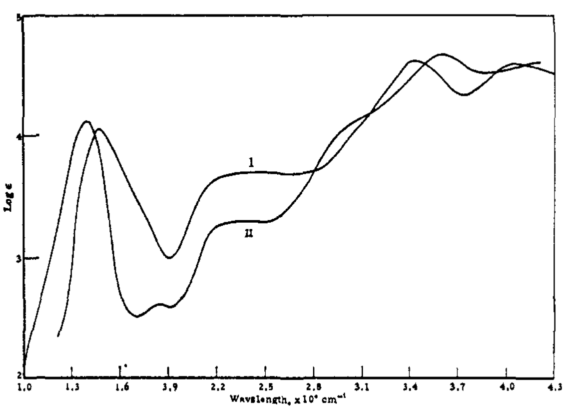


Figure 7. Electronic spectra of $CoS_4C_4Ph_4 \cdot PPh_3$ (I), in CH_2Cl_2, and of $NiS_4C_4Ph_4^-$ (II), in CH_3CN. Additional weak bands ($\epsilon \sim 10^2$) below 10,000 cm^{-1} are not shown.

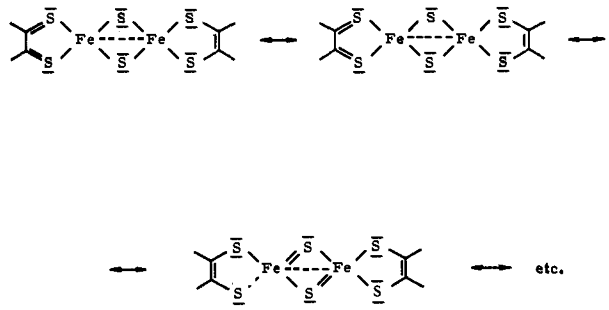


Figure 8. Mainly contributing limiting structures in complex III.

pound, but the C═S bands are no longer split and again quite intense. It is assumed that the $MS_4C_4R_4$ systems in these adducts are no loner planar but rather pyramidal as shown in Figure 4. The mainly contributing limiting structures in the iron complexes must be those shown in Figure 5, and, for all practical purposes, the complexes may be regarded as isoelectronic with the neutral nickel complexes. All properties are in agreement with this proposal; particularly the electronic spectra of $FeS_4C_4H_4 \cdot P(n\text{-}Bu_3)$ and $NiS_4C_4H_4$ are remarkably similar (Figure 6). Additional evidence for the assumed delocalization of the ground state in the former may also be obtained by nmr measurements. The signal of the dithioglyoxal protons appears at τ −0.1 ppm, thus in the same region as in $NiS_4C_4H_4$. The situation is somewhat different in the phosphine adducts of the cobalt complexes. Here the addition of the ligand in the fifth coordination position causes an increase of the C═C stretch from 1370 to 1403 (triphenylphosphine) and 1415 cm^{-1} (tributylphosphine), respectively, and the adducts are purple rather than green. This behavior is analogous to that of the nickel complex $NiS_4C_4Ph_4$ on reduction to the monoanion where the C═C stretch increases from 1359 to 1428 cm^{-1}.[17] It is therefore concluded that the unpaired electron in the phosphine adduct occupies a significantly ligand-based MO. The epr signal (observed, *e.g.*, at $G = 2.01$ in $CoS_4C_4Ph_4 \cdot (OPh)_3$) shows the complete (though small) hyperfine splitting of Co^{59} as well as splitting due to phosphorus.[18] It appears that, for practical purposes, the complexes $CoS_4C_4Ph_4 \cdot PR_3$ are isoelectronic with $NiS_4C_4Ph_4^-$, which is supported by the similarity of the electronic spectra shown in Figure 7. Similarly, the ion $CoS_4C_4Ph_4^-$ appears to be isoelectronic with $NiS_4C_4Ph_4$. The infrared spectrum of the $AsPh_4^+$ salt, for example, exhibits the three characteristic bands of the metal bisdithion system at frequencies not very different from those of the neutral nickel compound ($\omega_1 = 1385$, $\omega_2 = 1140$, and $\omega_3 = 862$ cm^{-1}, respectively). Moreover, the complex is green as the nickel species and exhibits an intense band in the near-infrared region at 820 mμ ($NiS_4C_4Ph_4$: 866 mμ). These analogies must not be carried too far since the five-coordinated phosphine adducts obviously contain nonplanar $MS_4C_4R_4$ units. This causes differences in the mixing of the metal and ligand orbitals compared to the planar species. Similarly, the anion $Co(MNT)_2^-$ has different properties from $CoS_4C_4Ph_4^-$. For example, it lacks the characteristic intense near-infrared transition. Consequently, it is better described as a Co(III) complex with "conventional" MNT dianions as the ligands. We ascribe this difference in the electronic structure to the inductive effect of the CN groups. For the binuclear iron complex III a planar structure is proposed in which the metal atoms are both formally +3 and the dithion resonance takes place across the sulfur bridge (Figure 8). That this is possible follows from group-theoretical considerations. Assuming a molecular symmetry D_{2h}, the 3p π orbitals of the bridging sulfur atoms transform as B_{1u}

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(17) G. N. Schrauzer and V. P. Mayweg, *J. Am. Chem. Soc.*, **87**, 1483 (1965).

(18) Measurements performed by Dr. E. Genser, Emeryville. These results will be published separately.

Table I

Complex	Formula	Mp (dec), °C	*Anal.* Calcd/Found C	H	S	P	M	Mol wt
$FeS_4C_4H_4\cdot P(n\text{-}C_4H_9)_3$	$C_{16}H_{31}S_4PFe$	98	43.7/43.5	7.1/7.3	29.2/28.6	7.0/7.2	12.7/12.7	
$FeS_4C_4Ph_4\cdot P(C_6H_5)_3$	$C_{46}H_{35}S_4PFe$	228	68.8/68.6	4.4/4.4	16.0/14.7	3.9/3.0	7.0/6.95	803/870
$FeS_4C_4Ph_4\cdot P(n\text{-}C_4H_9)_3$	$C_{40}H_{47}S_4PFe$	192	64.8/64.0	6.5/6.5	17.2/16.5	4.2/4.2	7.5/7.4	
$FeS_4C_4Tol_4\cdot P(n\text{-}C_4H_9)_3$	$C_{44}H_{55}S_4PFe$	173	66.1/65.8	6.9/7.2	16.0/15.4	3.9/3.9	7.0/6.9	
$FeS_4C_4Ph_3\cdot P(OC_6H_5)_3$	$C_{46}H_{35}S_4O_3PFe$	208	64.9/62.1	4.1/42	15.2/15.9	3.6/3.7	6.6/6.8	
$CoS_4C_4Ph_4\cdot P(C_6H_5)_3$	$C_{46}H_{35}S_4PCo$	209	68.5/68.3	4.4/4.4	15.9/14.3	3.8/3.4	7.3/7.3	806/810
$CoS_4C_4Tol_4\cdot P(n\text{-}C_4H_9)_3$	$C_{44}H_{55}S_4PCo$	208	66.1/65.8	6.9/7.2	16.0/15.4	3.9/3.9	7.0/6.9	
$CoS_4C_4Ph_4\cdot P(OC_6H_5)_3$	$C_{46}H_{35}S_4O_3PCo$	175	64.7/63.8	4.1/4.0	15.0/14.7	3.6/3.8	6.9/7.1	
$CoS_4C_4Ph_4\cdot P(n\text{-}C_4H_9)_3$	$C_{40}H_{47}S_4PC_0$	165	64.4/64.0	6.3/6.4				

Table II

Complex	Mp (dec), °C	CO stretching frequencies, cm^{-1}			*Anal.* Calcd/Found	
$Fe_2(CO)_6S_2C_2Ph_2$	126	2090	2045	1990	C, 46.2/46.0	H, 1.9/2.1[a]
$Fe_2(CO)_6S_2C_2(CH_3)_2$	76–77	2090	2040	2010	C, 30.2/30.5	H, 1.5/1.7; Mol wt 398/400
$Fe_2(CO)_6S_2C_2(p\text{-tolyl})_2$	128	2090	2040	2010	C, 48.1/48.8	H, 2.6/2.9; Mol wt 550/558
$Fe_2(CO)_6S_2C_2(p\text{-anisyl})_2$	129	2080	2040	1995	C, 45.4/45.7	H, 2.4/2.6; S, 11.0/0.51
$Fe_2(CO)_6S_2C_2H_2$[b]	54–55	2070	2030	1995	C, 26.2/26.1	H, 0.55/0.54

[a] This complex was described in ref 12, and a total analysis was given. [b] Vacuum-sublimed sample.

and B_{3g}. The B_{1u} combination therefore will overlap with the pair of the $4p_z$ iron orbitals thus connecting the B_{1u} π-MO's of the $S_2C_2Ph_2$ ligands with each other. All properties of III are in accord with this formulation. It should be pointed out that labile addition compounds of III with phosphines do exist, which, however, proved rather unstable and difficult to isolate. An X-ray crystallographic structure determination of III is in progress.

Experimental Section

Preparation of $FeS_4C_4Ph_4$ (Complex II). Ferrous sulfate ($FeSO_4\cdot 7H_2O$), 100 g, dissolved in 400 ml of water–methanol, 1:1, was slowly added to 1 l. of a refluxing "Thioester Solution" prepared from 100 g of benzoin and 100 g of P_4S_{10} in xylene. The reaction mixture was refluxed for 2 hr. The solution was filtered and the residue washed several times with methanol. The remaining black crystals were dried at 120°; they decomposed at 295° and were sufficiently pure for the subsequent experiments.

Anal. Calcd for $C_{28}H_{20}S_4Fe$: C, 62.2; H, 3.73; S, 23.7; Fe, 10.3. Found: C, 62.4; H, 3.76; S, 23.0; Fe, 9.6.

By essentially the same method the analogous complexes $FeS_4C_4R_4$ (R = *p*-tolyl and *p*-anisyl) were obtained. These complexes proved sufficiently soluble to be recrystallized from methylene chloride.

(a) $FeS_4C_4(p\text{-tolyl})_4$ (mp 244° dec). *Anal.* Calcd for $C_{32}H_{28}S_4Fe$: C, 64.4; H, 4.7; S, 21.5. Found: C, 64.8; H, 4.9; S, 21.3.

(b) $FeS_4C_4(p\text{-anisyl})_4$ (mp 272° dec). *Anal.* Calcd for $C_{32}H_{28}O_4S_4Fe$: C, 58.3; H, 4.3; S, 19.4; Fe, 8.4. Found: C, 59.1; H, 4.5; S, 20.2; Fe, 8.8.

Preparation of $Fe_2S_2(S_2C_2Ph_2)_2$ (Complex III). Complex II, 2 g, was suspended in 30 ml of toluene and was kept at a temperature from 190 to 200° in a sealed tube for 4 days. The black residue was collected and extracted at first with petroleum ether and subsequently with CS_2. A violet solution resulted from which the complex was isolated by adding petroleum ether (bp 60–80°). The black crystals of complex III are stable up to 360°; yield, 0.8 g (66%).

Anal. Calcd for $C_{28}H_{20}S_6Fe_2$: C, 50.4; H, 3.0; S, 28.9; Fe, 16.8. Found: C, 50.5; H, 3.1; S, 29.4; Fe, 16.4.

Similarly, the complexes $Fe_2S_2(S_2C_2R_2)_2$ with R = *p*-tolyl and *p*-anisyl were obtained.

(a) $Fe_2S_2(S_2C_2(p\text{-tolyl})_2)_2$ *Anal.* Calcd for $C_{32}H_{28}S_6Fe_2$: C, 53.7; H, 3.9; S, 26.8; Fe, 15.6. Found: C, 53.5; H, 3.8; S, 27.0; Fe, 15.8.

(b) $Fe_2S_2(S_2C_2(p\text{-anisyl})_2)_2$. *Anal.* Calcd for $C_{32}H_{28}S_6O_4Fe_2$: C, 49.3; H, 3.6; S, 24.6; Fe, 14.3. Found: C, 48.6; H, 3.5; S, 24.4; Fe, 14.7.

Preparation of $Fe_2S_2(S_2C_2Ph_2)_2$ from Diphenylacetylene, Sulfur, and Iron or Iron Carbonyls. Diphenylacetylene (4 g) and sulfur (5 g) were refluxed under nitrogen with 5 g of finely divided metallic iron, 5 g of $Fe(CO)_5$, or 5 g of $Fe_3(CO)_{12}$, in 30 ml of toluene, for 24 hr. After filtration the residue was extracted with CS_2. After evaporation of the solvent, the residue was treated with petroleum ether whereby it converted into a gray product consisting mainly of sulfur, tetraphenylthiophene, and the complex. Prolonged extraction with petroleum ether gave a product essentially free of sulfur and tetraphenylthiophene. It was redissolved in CS_2, and the crystallization was induced by slowly adding petroleum ether. The yield was 970 mg (13% of theoretical amount based on diphenylacetylene), using $Fe_3(CO)_{12}$ (with iron powder or $Fe(CO)_5$ the yields were considerably lower).

Preparation of $CoS_4C_4Ph_4$ (Complex V). To 1.5 l. of a "Thioester Solution" in xylene prepared from 100 g of P_4S_{10} and 150 g of benzoin, 150 g of $ClCl_2\cdot 6H_2O$ in 400 ml of water was slowly added. The reaction mixture was heated for 1 hr on a steam bath. The crystalline precipitate was filtered, washed with methanol, and dried. For further purification it was extracted with benzene. The black, diamagnetic, crystalline compound decomposed above 360°.

Anal. Calcd for $C_{28}H_{20}S_4Co$: C, 61.9; H, 3.7; Co, 10.9; S, 23.9. Found: C, 62.3; H, 4.0; Co, 10.6; S, 22.8.

By the same method the compounds $CoS_4C_4R_4$ (R = *p*-tolyl and *p*-anisyl) were prepared.

(a) $CoS_4C_4(p\text{-tolyl})_4$ (mp 294° dec). *Anal.* Calcd for $C_{32}H_{28}S_4Co$: C, 64.0; H, 4.7; S, 21.4; Co, 9.8. Found: C, 63.7; H, 4.9; S, 20.6; Co, 10.0.

(b) $CoS_4C_4(p\text{-anisyl})_4$ (mp 275° dec). *Anal.* Calcd for $C_{32}H_{28}O_4S_4Co$: C, 58.0; H, 4.2; S, 19.3; Co, 8.9. Found: C, 57.4; H, 4.1; S, 26.2; Co, 8.6.

Preparation of the Phosphine Adducts. The complexes (*e.g.*, II or V), in amounts of about 3.0 g, were refluxed in 40 ml of benzene under nitrogen with a small excess of the phosphine for about 4 hr. The filtered reaction solution was evaporated under reduced pressure. The residue was redissolved in CH_2Cl_2 and crystallization of product induced by the addition of methanol. The crystallization from this solvent mixture was repeated for further purification. The complex $FeS_4C_4H_4$ with tributylphosphine was obtained by treating the black, insoluble reaction product of $Na_2S_2C_2H_2$ with $FeSO_4$ with an excess of tributylphosphine in benzene. The reaction solution was filtered and worked up as indicated above. The analogous cobalt complex, $CoS_4C_4H_4\cdot P(n\text{-}Bu)_3$, is apparently less stable and decomposed during work-up. (See Table I.)

Reaction of Complexes $MS_4C_4R_4$ with $Fe(CO)_5$ (Preparation of Complexes $Fe_2(CO)_6S_2C_2R_2$). The complex $MS_4C_4R_4$ (about 2 g) was dissolved in a small amount of benzene and refluxed with an excess of $Fe(CO)_5$ (10 ml) until there was no further color change of the solution. The excess of $Fe(CO)_5$ and the solvent were evaporated *in vacuo*. The residue was dissolved in acetone and treated with 2 *N* HCl after filtration. Red crystals of the complexes precipitated, which were collected and recrystallized from methanol-water. (See Table II.)

Thermal Decomposition of $Fe_2(CO)_6S_2C_2Ph_2$. Complex IV (2.0 g) was heated until it completely decomposed. The volatile organic decomposition product was distilled off and identified as diphenylacetylene (melting point, mixture melting point, comparison of infrared spectra with authentic sample). The nonvolatile residue consisted of FeS as evidenced by its behavior with acids.

Reaction of $Fe_2(CO)_6S_2C_2Ph_2$ with Sulfur. Complex IV (1.5 g) was heated in an autoclave with 2 g of sulfur in 15 ml of toluene, for 15 hr at 130°. Work-up as described in the preparation of III from $Fe_3(CO)_{12}$, S, and diphenylacetylene afforded 755 mg, or 78% of the theoretical amount, of complex III.

Preparation of Salts of $FeS_4C_4Ph_4^-$ and $CoS_4C_4Ph_4^-$. To complex II (5.5 g suspended in 50 ml of methanol) 2.5 ml of anhydrous hydrazine was added. A brown-red solution resulted to which 2.1 g of tetraethylammonium bromide or 4.2 g of tetraphenylarsonium chloride dissolved in 25 ml of methanol was slowly added. A green precipitate formed which was collected and washed with methanol. Further purification was achieved by extraction with acetonitrile in an atmosphere of nitrogen. From the concentrated acetonitrile solution the products crystallized on cooling, forming dark green crystals. The cobalt compounds were obtained analogously. The salts proved to be diamagnetic (Gouy method).

Anal. (a) Calcd for $N(C_2H_5)_4^+FeS_4C_4Ph_4^-$ ($C_{36}H_{40}S_4NFe$) (mp ~214° dec): C, 64.5; H, 6.0; S, 19.0; Fe, 8.3; N, 2.1. Found: C, 64.5; H, 6.6; S, 18.0; Fe, 7.9; N, 2.1.

(b) Calcd for $As(C_6H_5)_4^+FeS_4C_4Ph_4^-$ ($C_{52}H_{40}S_4AsFe$) (mp ~112° dec): C, 67.6; H, 4.4. Found: C, 67.8; H, 4.4.

(c) Calcd for $N(C_2H_5)_4^+CoS_4C_4Ph_4^-$ ($C_{36}H_{30}S_4NCo$) (mp ~198° dec): C, 64.4; H, 6.0; S, 18.8; Co, 8.7; N, 2.1. Found: C, 64.4; H, 6.0; S, 17.0; Co, 8.4; N, 2.2.

(d) Calcd for $As(C_6H_5)_4^+CoS_4C_4Ph_4^-$ ($C_{52}H_{40}S_4AsCo$) (mp ~98° dec): C, 67.3; H, 4.3. Found: C, 67.5; H, 4.6.

Preparation of a Salt of the Dianion of III. Under conditions identical with those described above, the salt $(AsPh_4^+)_2Fe_2S_2(S_2C_2Ph_2)_2^{2-}$ was obtained.

Anal. Calcd for $C_{76}H_{60}Fe_2S_6As$: C, 63.9; H, 4.2; S, 13.5; Fe, 7.8. Found: C, 63.3; H, 4.4; S, 12.8; Fe, 7.6; mp 174–179° dec.

Polarographic Measurements (Performed by Dr. D. C. Olson). The polarographic measurements were made on an ORNL controlled-potential instrument, Model Q-1988 A, in DMF as the solvent, using an Ag|AgCl reference electrode in an aqueous 0.1 *M* LiCl solution. (See Table III.)

Table III

Compound	$E_{1/2}$ observed,[a] v Reversible	 Irreversible
$FeS_4C_4Ph_4 \cdot P(C_4H_9)_3$	−0.498	−1.089
$FeS_4C_4Ph_4 \cdot P(OC_6H_5)_3$	−0.366	−1.09
$FeS_4C_4H_4 \cdot P(n\text{-}C_4H_9)_3$	−0.556	−1.050
$CoS_4C_4Ph_4 \cdot P(n\text{-}C_4H_9)_3$	−0.430	−1.729
$CoS_4C_4Ph_4 \cdot P(OC_6H_5)_3$	−0.29	−1.04
$CoS_4C_4(p\text{-tolyl})_4 \cdot P(C_6H_5)_3$	−0.27	−1.06
$CoS_4C_4(p\text{-tolyl})_4 \cdot P(n\text{-}C_4H_9)_3$	−0.430	−1.279
$Fe_2S_2(S_2C_2Ph_2)_2$	−0.022, −0.530, −1.24, −1.87	

[a] Estimated number of electrons in each case = 1.

X-Ray Measurements (Performed by Dr. A. E. Smith, Emeryville). The complexes $FeS_4C_4(CF_3)_4$ and $CoS_4C_4(CF_3)_4$ were shown to be isomorphous by comparing the well-resolved X-ray powder patterns. The complex $Fe_2S_2(S_2C_2Ph_2)_2$ crystallizes in space group $P_{2/c}$, $a = 10.26$, $b = 11.57$, $c = 27.96$ A, $\beta = 114° 45'$, d(obsd) 1.60 ± 0.01 g/cm³, d (calcd, for 4 molecules per unit cell) 1.608, mol wt found 730. The crystals examined contained one molecule of CS_2 of crystallization per molecule of complex, mol wt calcd 730.6.

Infrared Spectra. The spectra were obtained from KBr pellets; only the bands ω_1, ω_2, and ω_3 characteristic of the metal–dithion system were reported (in cm^{-1}). (See Table IV.)

Table IV

Complex	ω_1	ω_2	ω_3
$FeS_4C_4Ph_4$	1378	1176, 1151	910, 982
$CoS_4C_4Ph_4$	1370	1170, 1152	902, 871
$FeS_4C_4Ph_4 \cdot PPh_3$	1380	1148	884
$FeS_4C_4Ph_4 \cdot P(n\text{-}C_4H_9)_3$	1392	1154	880
$FeS_4C_4H_4 \cdot P(n\text{-}C_4H_9)_3$	1371	1100	868
$CoS_4C_4Ph_4 \cdot PPh_3$	1403	1152	875
$CoS_4C_4Ph_4 \cdot P(n\text{-}C_4H_9)_3$	1415	1160	874
$Fe_2S_2(S_2C_2Ph_2)_2$	1400	1163	887
$FeS_4C_4Ph_4^-$, $N(C_2H_5)_4^+$	*a*	1175	910
$CoS_4C_4Ph_4^-$, $AsPh_4^+$	*a*	1145	860

[a] Obscured bands.

Electronic Spectra. The electronic spectra of the compounds shown in Figures 1 and 2 were obtained on a Cary 14 instrument.