and Se_8 samples, for the purpose of comparison. These spectra were recorded at a resolution of ~ 2 cm^{-1}. The frequency values of the features marked in Figure 1 are accurate to ± 2 cm^{-1}. The strong band around 470 cm^{-1} in pure S_8 has been assigned to S–S stretching vibrations.[6-8] The bands at and below 244 cm^{-1} in S_8 are due to the deformation modes of S_8 rings. The Se–Se stretching vibration is assigned to the band at 251 cm^{-1} in pure Se_8.[9,10] All of the Se_8 deformation vibrations occur at and below 111 cm^{-1} (Figure 1). Many additional features are seen in the spectra of Se_nS_{8-n} mixed crystals.[11,12] The spectra can be classified into two groups: (i) the band(s) around 360 cm^{-1} and (ii) the bands below 220 cm^{-1} (Figure 1). The first group is easily assigned to S–Se stretching vibrations.[12,13] The second group arises from the skeleton deformations of Se_nS_{8-n} ring systems. Thus, it is clear from the above discussion that S–S, S–Se, and Se–Se stretching vibrations appear in the Raman spectra of sulfur–selenium eight-membered rings in the regions where their presence can be unambiguously established.[13] This brings us to the central point of this communication that the band corresponding to Se–Se stretching vibrations is seen in all of the Se_nS_{8-n} mixed-crystal spectra (Figure 1), indicating thereby the existence of Se–Se *homonuclear bonds* in these crystals. This is contrary to the published reports that the Se_nS_{8-n} mixed crystals should not contain Se–Se bonds.[4,14] The Se–Se stretching band is seen at a slightly higher frequency in the Se_nS_{8-n} compounds than in the pure Se_8 rings (Figure 1). Thus there is no possibility of this band being due to a skeleton-deformation mode. The fact that the Se–Se stretching band is seen at slightly higher frequency in the mixed crystals than in the pure Se_8 system also suggests that the band is primarily due to the stretching vibrations of neighboring Se atoms in rings containing both Se and S and does not arise only from Se_8 impurity, if any is present in the mixed-crystal samples. The conclusion that the Se–Se stretching band seen in the Raman spectra of "low Se content" sulfur–selenium mixed crystals (spectra B–D in Figure 1) cannot be due *only* to the Se_8 impurity is also supported by the fact that the Se–Se stretching band around 250 cm^{-1} and the Se_8 skeleton-deformation band around 110 cm^{-1} have nearly equal intensities in the Raman spectrum of Se_8 (spectrum F in Figure 1). But the intensity of the Se–Se stretching band in the Raman spectra of mixed crystals with low selenium content is many times greater than the intensity of any feature seen around 111 cm^{-1} in their spectra (Figure 1). This indicates that a major part of the intensity of the Se–Se stretching band in these mixed crystals *must* arise from Se_nS_{8-n} moieties *other than* Se_8 but having Se–Se bonds. Clearly the variation in the intensities of these two bands indicates that any argument based on the assignment of the two bands to only one chemical species, namely, Se_8 impurity, has to be completely discarded. We have studied Se_nS_{8-n} mixed crystals of more than 20 different compositions and recorded the spectra of each sample several times, on two different spectrometers. The samples with as low a selenium content as to give a nominal composition of $Se_{0.05}S_{7.95}$ also showed the "Se–Se stretching band" (Figure 1). These spectroscopic results indicate that selenium–sulfur moieties containing *homonuclear* Se–Se bonds are easily formed even in those mixed crystals in which there is nominally only one selenium atom per twenty rings. On the other hand, the S–S stretching band was not seen if the nominal content of sulfur dropped below that in Se_6S_2 (Figure 1). The near absence of the S–S stretching band in the spectrum of Se_6S_2 (spectrum E in Figure 1) cannot be accounted for only on the basis of the fact that the S–S stretching vibration is expected to be weaker than the Se–Se stretching vibration in the Raman spectrum. Our studies using an internal standard ($HgCl_2$) indicate that the Se–Se bonds are nearly 10 times stronger Raman scatterers than the S–S bonds in these mixed crystals if one uses the 6328-Å He–Ne line as the exciting radiation (the radiation used in the present work). This is consistent with the expected higher polarizability for the Se–Se bonds compared with that for the S–S bonds and can also be seen from the spectrum of $Se_{4.1}S_{3.9}$ (spectrum D in Figure 1) which should contain a nearly equal number of S–S and Se–Se homonuclear bonds. The above observations suggest that the formation of S–S homonuclear bonds is not favored in sulfur–selenium mixed crystals with low sulfur content.

It is known that the dissociation energies of the various bonds in the systems are in the order S–S > Se–S > Se–Se.[14] Also, sulfur and selenium molecules are known to break into radical fractions even at room temperature.[15] The existence of Se–Se bonds in the Se_nS_{8-n} ring systems with low selenium content can be explained by assuming that after one Se atom has been introduced into a sulfur molecule, the next Se atom radical can attack this moiety easily at a Se–S bond rather than at a S–S bond, leading to the formation of a Se–Se bond. On the other hand, in a selenium-rich system, an incoming S-atom radical will preferably break a Se–Se bond rather than a S–S or S–Se bond, which results in a lower probability for the formation of S–S homonuclear bonds in a system with low sulfur content.

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Registry No. S_8, 10544-50-0; Se_8, 12597-33-0.

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EPR Evidence for the Formation of the Mixed-Chelate (Diethyldithiocarbamato)(diethyldithiophosphato)copper(II) Complex in Solutions

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Diethyldithiocarbamate (dtc^-) and diethyldithiophosphate (dtp^-) anions are typical bidentate ligands which form four-membered chelate ring structures with various metal ions.[1] Cu(II) complexes of these ligands with a bis-chelate coor-

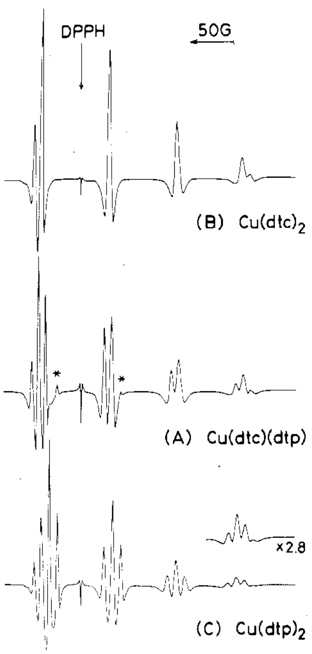

Figure 1. Second-derivative EPR spectrum of Cu(dtc)(dtp) compared with those of $Cu(dtc)_2$ and $Cu(dtp)_2$ in toluene at room temperature. (A) Cu(dtc)(dtp): The spectrum was obtained from the toluene solution of reaction b with a molar ratio of $(dtc\cdot)_2/[Cu(dtp)]_4 = 1$ and concentration of $[Cu(dtp)]_4$ 0.91×10^{-3} M. The absorption peaks with asterisks are assigned to $Cu(dtp)_2$, indicating that the disproportionation (reaction a) takes place to a slight extent: $g_0 = 2.045$, $A_0(^{63}Cu) = 72.5$, $A_0(^{65}Cu) = 77.8$, $A_0(^{31}P) = 7.8$ [$g_z = 2.086$, $A_z(^{63}Cu) = 163.3$, $A_z(^{65}Cu) = 174.4$, $A_z(^{31}P) = 7.9$]. (B) $Cu(dtc)_2$: $g_0 = 2.045$, $A_0(^{63}Cu) = 74.1$, $A_0(^{65}Cu) = 79.6$ [$g_z = 2.088$, $A_z(^{63}Cu) = 165.6$, $A_z(^{65}Cu) = 177.4$]. (C) $Cu(dtp)_2$: $g_0 = 2.046$, $A_0(^{63}Cu) = 69.1$, $A_0(^{65}Cu) = 74.9$, $A_0(^{31}P) = 9.2$ [$g_z = 2.086$, $A_z(^{63}Cu) = 161.3$, $A_z(^{65}Cu) = 172.6$, $A_z(^{31}P) = 9.2$]. Anisotropic values obtained from the frozen-solution spectra (not shown) are given in parentheses. $g_\perp$ and $A_\perp$ values can be estimated by assuming axial symmetry from the relations $g_\perp = (3g_0 - g_z)/2$ and $A_\perp = (3A_0 - A_z)/2$. Hf and shf coupling constants are in 10^{-4} cm^{-1}.

dination, i.e., $Cu(dtc)_2$ and $Cu(dtp)_2$, have been studied most extensively in particular by means of EPR methods.[2] The electronic nature of Cu–S bonding as well as the extent of spin delocalization over the four-membered chelate rings has been characterized on the basis of EPR parameters obtained.[2] However, such studies are limited to the bis-chelate complexes, and there seems to be no report on the mixed-chelate complex of the Cu(dtc)(dtp) type. Such a ternary complex may provide us with further insight into the coordination nature of dtc and dtp ligands. Furthermore, mixed-chelate complexes have currently come to be of particular interest because of their possible structural and electronic properties distinct from those of bis-chelate complexes and because of their potential biological significance.[3] In this note we report EPR evidence for the formation of Cu(dtc)(dtp) in solutions together with the EPR parameters obtained for the mixed-chelate complex.

Three different procedures were employed for the in situ formation of mixed chelate Cu(dtc)(dtp) complexes in solution: (a) chelate ring exchange between $Cu(dtc)_2$ and $Cu(dtp)_2$, $Cu(dtc)_2 + Cu(dtp)_2 = 2Cu(dtc)(dtp)$; (b) oxidation of tetrakis((diethyldithiophosphato)copper(I)), $[Cu^{I}(dtp)]_4$, with tetraethylthiuram disulfide, $(dtc\cdot)_2$, $[Cu^{I}(dtp)]_4 + 2(dtc\cdot)_2 = 4Cu^{II}(dtc)(dtp)$; (c) chelate ring displacement of $Cu(dtc)_2$ by dtpH followed by decomposition of dtcH, $Cu(dtc)_2 + dtpH = Cu(dtc)(dtp) + dtcH$, $Cu(dtc)(dtp) + dtpH = Cu(dtp)_2 + dtcH$, and $dtcH = (C_2H_5)_2NH + CS_2$. All the reactions were run in a nitrogen atmosphere by using a reaction vessel fitted with an EPR sample tube and were followed by in situ EPR measurements with a conventional X-band spectrometer. Benzene, toluene, and dichloromethane were used as solvents with no significant difference in the results.

A typical EPR spectrum which can be assigned to the mixed-chelate complex Cu(dtc)(dtp) is shown in Figure 1A. Quite similar spectra were obtained from the solutions of reaction a containing equimolar amounts of $Cu(dtc)_2$ and $Cu(dtp)_2$ and from the solutions of reaction b with $(dtc\cdot)_2/[Cu(dtp)]_4$ molar ratio less than 2. Reactions a and b proceeded immediately at room temperature, while reaction c proceeded rather slowly unless a large excess of dtpH was added to the $Cu(dtc)_2$ solutions. EPR spectra from the solution of reaction c changed gradually from the spectrum of $Cu(dtc)_2$ to that of $Cu(dtp)_2$, the spectrum assignable to Cu(dtc)(dtp) being observed at an intermediate stage in support of the reaction scheme given above.

It is evident from Figure 1A that each of the four hf (hyperfine) lines characteristic of the copper nucleus (^{63}Cu, ^{65}Cu, $I = {}^3/_2$) is further split into two components by shf (superhyperfine) interaction with the phosphorus nucleus (^{31}P, $I = {}^1/_2$), in marked contrast to the spectra of $Cu(dtc)_2$ and $Cu(dtp)_2$ (Figure 1B,C). Shf splittings due to one phosphorus nucleus unambiguously support the assignment of spectrum A to the mixed-chelate complex.

The g values and hf coupling constants obtained for Cu(dtc)(dtp) fall in the range between the values obtained for $Cu(dtc)_2$ and $Cu(dtp)_2$. Optical absorption measurements of Cu(dtc)(dtp) in toluene solutions showed an absorption maximum at 2.34×10^4 cm^{-1}, which was also intermediate between 2.30×10^4 and 2.38×10^4 cm^{-1} observed for $Cu(dtc)_2$[2a] and $Cu(dtp)_2$,[2f] respectively. Thus, the mixed-chelate complex has basically the mean bonding and electronic properties of the parent bis-chelate complexes. In fact, the EPR parameters for the mixed-chelate complex can be interpreted satisfactorily on the basis of square-planar coordination of dtc and dtp chelate ligands in which an unpaired electron is placed in the in-plane σ^* orbital. The bonding parameter, α^2, evaluated for comparative purposes according to eq 4 in ref 2c is found to be 0.54, indicating that the in-plane σ^* bonding is highly covalent. This value for α^2 is almost identical with those obtained for $Cu(dtc)_2$ and $Cu(dtp)_2$. It is, however, noted that the isotropic shf coupling constant (8.1 G) observed for Cu(dtc)(dtp) is smaller than that (9.7 G) for $Cu(dtp)_2$, implying that there is a significant difference in the extent of electron spin delocalization over the phosphorus 3s orbital (i.e., the spin densities calculated after Atkins and Symons[4] are 0.0022 and 0.0027 for Cu(dtc)(dtp) and $Cu(dtp)_2$, respectively).

Attempts to isolate and characterize the Cu(dtc)(dtp) complex as a crystalline solid have so far been unsuccessful. We obtained only the mixed crystals of $Cu(dtc)_2$ and $Cu(dtp)_2$ irrespective of many solvent systems and crystallization methods employed. The equilibrium constant of reaction a, $[Cu(dtc)(dtp)]^2/[Cu(dtc)_2][Cu(dtp)_2]$, is evidently much greater than the value 4 expected by statistical reasoning.[3] The driving force leading to greater stability of Cu(dtc)(dtp) in solutions is at present unknown.

Registry No. Cu(dtc)(dtp), 32506-53-9; $Cu(dtc)_2$, 13681-87-3; $Cu(dtp)_2$, 15611-25-3.

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Electrochemistry of Half-Sandwich and Trinuclear Sandwich Complexes Containing Phosphonate Ligands

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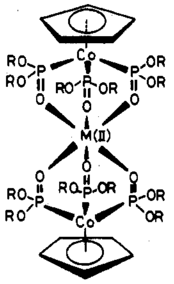
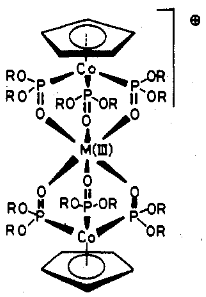
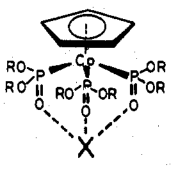
In a broad survey Dessy has reported[1,2] on the redox properties of 130 transition-metal π complexes and complexes with π-acceptor ligands. It is interesting to note that apart from the classical sandwiches ferrocene,[3] cobaltocene,[3] and bis(benzene)chromium[4] only very few *sandwich* or *half-sandwich* compounds are electrochemically oxidized or reduced to yield stable isolable metallocene ions. This has limited the use of electrochemical techniques for synthetic purposes in sandwich chemistry.[5,6] On the other hand much work has been devoted to the study of the electrochemical properties of such organometallic complexes from an analytical point of view.[7-9] To our knowledge only one example of an electrochemical formation of a *triple-decker compound* has been reported, namely, the oxidation of μ-cyclooctatetraene-bis(cyclopentadienylcobalt) by Geiger.[10] We have recently prepared a series of *trinuclear sandwich* complexes,[11,12] and we were interested to learn whether this new and interesting class of compounds shows redox properties comparable to those of the simple sandwiches cobaltocene, ferrocene, etc. or whether they undergo decomposition or ligand rearrangement reactions upon electrochemical oxidation or reduction. In this communication we present the preliminary findings on the trinuclear sandwich compounds **1**–**3**, **5** and **6** and the half-sandwich complex **9**.



R = C_2H_5
1, M(II) = Co
2, M(II) = Fe
3, M(II) = Hg
4, M(II) = Cu



R = C_2H_5
5, M(III) = Co
6, M(III) = Fe
7, M(III) = Ln



R = C_2H_5
8, X = H
9, X = Na

Results and Discussion

$[(C_5H_5)Co(P(O)(OC_2H_5)_2)_3]_2Co$ (1). From our investigation of the reactivity of **1** we know that this complex is extremely stable toward oxidation.[13] It can be dissolved, e.g., in concentrated nitric acid, and recovered quantitatively upon dilution with water. It is readily protonated but not oxidized by nitric acid. In fact we have not been able so far to prepare the cation **5** from the corresponding neutral compound **1** by chemical means.

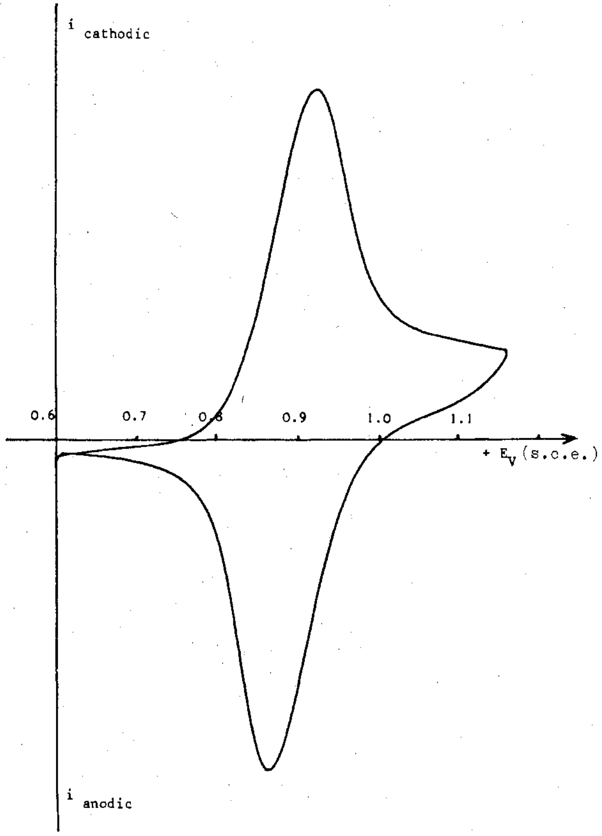


Figure 1. Thin-layer linear potential sweep voltammogram of 0.001 M $[(C_5H_5)Co(P(O)(OC_2H_5)_2)_3]_2Co$ (**1**) in CH_2Cl_2; 0.2 M $[Bu_4N]PF_6$, at carbon electrode; scan rate 0.001 V s^{-1}.

A polarographic study of a 0.001 M solution of **1** in methylene chloride with 0.2 M $[Bu_4N]PF_6$ as supporting electrolyte shows that this compound is not reducible and not oxidizable at the dropping mercury electrode (DME) in the accessible potential range of the system (+0.8 to −1.9 V vs. SCE). The cyclic voltammogram of this solution using glassy carbon as the working electrode shows, however, an oxidation peak at +1.02 V. This oxidation is electrochemically reversible even for a sweeping rate of 0.01 V s^{-1}. In thin-layer linear potential sweep voltammetry at a carbon electrode this oxidation process remains reversible even for the very slow scanning rate of 0.001 [V s^{-1}] (see Figure 1). The comparison of the area of the oxidation peak of **1** with that of the monoelectronic reduction of cobalticinium ion to cobaltocene shows that the oxidation of **1** is monoelectronic. By controlled-potential coulometry at +1.3 V we have confirmed that the oxidation is a one-electron process and that the cation is stable in methylene chloride solution. Such solutions remain actually unchanged for several days and the reduction at +1.0 V leads quantitatively back to the starting material.

By electrolysis of **1** on a preparative scale (see Experimental Section) we have been able to isolate **5** as the PF_6 salt. The compound is a dark green solid which dissolves readily in polar organic solvents such as chloroform, methylene chloride, acetone, and nitromethane. The stability of such solutions is remarkable in view of the high oxidation potential. The kinetic stability of **5** is probably due to the difficulty of getting a reducing agent close enough to the central cobalt(III). The X-ray structure determination[14] of the analogous copper compound **4** shows indeed that the 12 OC_2H_5 groups are shielding the central atom very effectively. This is also in line with our observation that the corresponding lanthanide

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