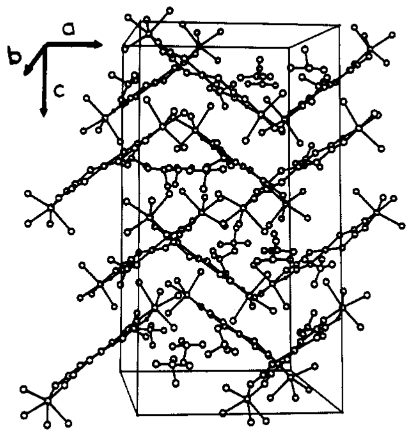


Figure 7. Crystal packing diagram for **1**.

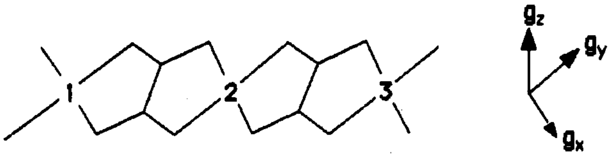
change-narrowed signal in a monoclinic lattice, one of the principal directions is along the 2-fold *b* axis.

Discussion

The ground state for compounds **1** and **2** is a spin doublet delocalized on three magnetic centers and well separated in energy from the first excited states. The description of such triad states is still the subject of theoretical and experimental studies.[6-12] The knowledge of the molecular **g** tensor could provide in principle interesting information on the nature of the triad state, especially if it is possible to correlate this molecular tensor with the three local **g** tensors.[12,13] Actually, that is why we have undertaken the single-crystal EPR study reported in this note. Owing to the absence of evident intermolecular exchange pathways, we thought to obtain molecular tensors. In fact, the EPR spectra are exchange-averaged and the **g** tensors for both **1** and **2** are related to the lattice as a whole and not to the trinuclear cation. From magnetic susceptibility measurements, we have been able to estimate the magnitude J of the interaction between a molecule and its neighbor in **1**. J is found to be of the order of the wavenumber. It has been shown[4,14,15] that when the interaction between two magnetic centers noted a and b is such as

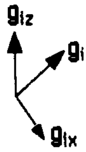
$$|J| > \tfrac{1}{2}\beta H|g_a - g_b| \qquad (6)$$

then the exchange-averaging conditions are filled. In the present case, the structure of the trinuclear cation may be schematized as and $\mathbf{g}_a$ (or $\mathbf{g}_b$) is related to the local tensors through



$$\mathbf{g}_a = (2\mathbf{g}_1 - \mathbf{g}_2 + 2\mathbf{g}_3)/3 \qquad (7)$$

Each copper(II) is roughly in an elongated tetragonal environment, so that its local $\mathbf{g}_i$ tensor is oriented as shown with $g_{iz} > g_{ix}$ and g_{iy}. It follows from (7) that $\mathbf{g}_a$ is expected to be oriented as shown at the right of the scheme of the structure. According to the crystal packing diagram[16] for **1** shown in Figure 7 and taking $g_{iz} = 2.18$ and $g_{ix} = g_{iy} = 2.07$, the largest and smallest $|g_a - g_b|$ values may be estimated as 0.026 and 0.006, respectively. It follows that $|J|$ is actually large enough to lead to exchange-narrowing effects, whatever the direction of the magnetic field may be.



In any direction of the *ac* plane for **1**, g retains a value close to the highest principal value (see Figure 3). Since the z axes perpendicular to the mean planes of the four magnetically nonequivalent trinuclear cations are almost located in this *ac* plane, this result confirms that the highest principal value of each molecular tensor is along the z direction. In other respects, although the trinuclear species in **1** and **2** are very similar, the crystal tensors are different, due to the differences of space groups and crystal packings.

A last question would deserve a comment, namely why the intermolecular interactions are so pronounced. This behavior might well be due to the presence of sulfur atoms in the periphery of the trinuclear cations and to relatively short intermolecular S···S contacts. As a matter of fact, there are several S···S contacts of the order of van der Waals radii. All involve a sulfur atom linked to the central copper and another one linked to a terminal copper. Owing to the specific diffuseness of their valence orbitals, the sulfur atoms could be involved in Cu–S···S–Cu-exchange pathways.

This work shows how one must be careful when interpreting powder EPR spectra of polymetallic species. Even if the molecular units seem to be well isolated within the crystal lattice, the spectrum may be exchange-averaged and therefore less informative than expected.

Acknowledgment. We are most grateful to Dr. F. Robert who helped us to determine the indices of the crystal faces.

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Contribution from the Sektion Chemie,
Karl-Marx-Universität Leipzig, DDR-7010 Leipzig,
Talstrasse 35, GDR, and Anorganisch Chemisch Laboratorium,
J. H. van't Hoff Instituut, Universiteit van Amsterdam,
Nieuwe Achtergracht 166,
1018 WV Amsterdam, The Netherlands

Ion-Pair Charge Transfer (IPCT) between Bipyridinium Cations and the Tetracarbonylcobaltate Anion. Spectroscopy and Thermal and Photochemical Reactions

H. Knoll,*[1a,b] R. Billing,[1a] H. Hennig,[1a] and D. J. Stufkens[1b]

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Introduction

In recent years, increasing attention has been paid to the photochemical reactivity of coordination compounds altered in their second sphere.[2] Such changes can, e.g., be accomplished

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(1) (a) Karl-Marx-Universität Leipzig. (b) Universiteit van Amsterdam.

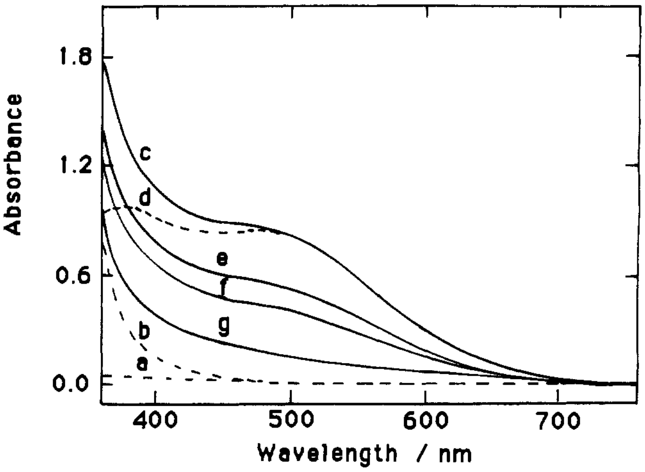

Figure 1. Electronic absorption spectra: (a) $PPN^+Co(CO)_4^-$ (5×10^{-3} M in CH_2Cl_2); (b) $DMBPY^{2+}(PF_6^-)_2$ (5×10^{-3} M in CH_2Cl_2); (c) $PPN^+Co(CO)_4^-/DMBPY^{2+}(PF_6^-)_2$ (both 5×10^{-3} M in CH_2Cl_2); (d) $DMBPY^{2+}Co(CO)_4^-PF_6^-$ (in CH_2Cl_2, spectrum obtained by subtracting spectra a and b from spectrum c); (e) mixture c with 5×10^{-3} M TBAP added; (f) mixture c with 10^{-2} M TBAP added; (g) mixture c in acetone.

by the formation of contact ion pairs, which may give rise to charge-transfer transitions not exhibited by the separate ions or by ion pairs with other counterions.[2-5] In order to observe these transitions separately at the low-energy side of the absorption bands and to use visible light for the initiation of photochemical reactions, their free energy should be moderately positive. On the other hand, it must not be too low in order to exclude thermal reactions.

$Co(CO)_4^-$ (E_{red} of $^{\bullet}Co(CO)_4$ estimated as ca. 0.2 V vs NHE[6]) is known to form contact ion pairs with different complex cobalt cations,[6-8] Tl^+,[9] and pyridinium cations.[10,11] Recently, the IPCT photochemistry of some of these ion pairs has been studied.[6,8,11] Until now no IPCT transitions have been reported for contact ion pairs between $Co(CO)_4^-$ and bipyridinium cations, which are molecular electron relays widely used in photochemical electron-transfer-reaction systems. In this paper, we report the results of a study on the contact ion pair formation between $Co(CO)_4^-$ and the cations 1,1′-dimethylbipyridinium-2,2′ ($DMBPY^{2+}$, $E_{red} = -0.72$ V vs NHE[12]) and 1,1′-dimethylbipyridinium-4,4′ (MV^{2+}, $E_{red} = -0.44$ V vs NHE[12]), which were considered to be good candidates for low-energy IPCT transitions in view of their reduction potentials. The ion pairs have been prepared by mixing the bipyridinium salts as hexafluorophosphates either with $Na^+Co(CO)_4^-$ or with bis(triphenylphosphoranylidene)ammonium tetracarbonylcobaltate ($PPN^+Co(CO)_4^-$).

Experimental Section

$Na^+Co(CO)_4^-$ was prepared as described[13] and further used in order to prepare $PPN^+Co(CO)_4^-$[14] from PPN^+Cl^- (Aldrich). The bipyridinium salts have been prepared from the bipyridines (Lachema) by methylation with CH_3I and exchange of the iodide by PF_6^- by means of precipitation with $NH_4^+PF_6^-$ in water. The solvents were dried by standard procedures, distilled, and stored under nitrogen. All samples were handled by means of the Schlenk-technique. Electronic absorption spectra were measured on a Perkin-Elmer Lambda 5 UV/vis spectrophotometer, equipped with a Model 3600 data station. IR spectra were recorded on a Nicolet 7199 B FTIR interferometer with a liquid-nitrogen-cooled MCT detector.

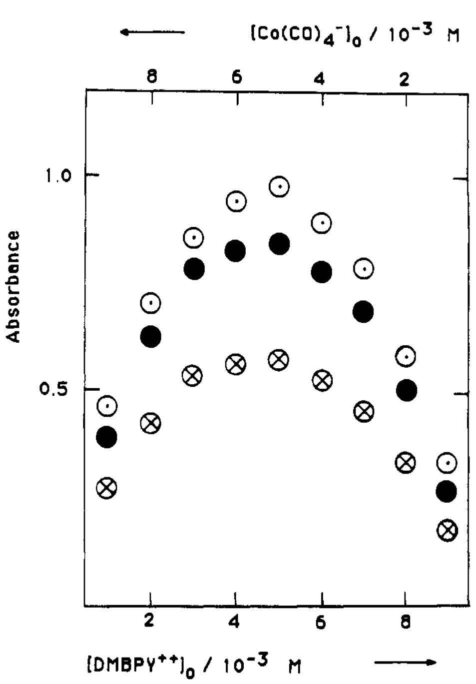

Figure 2. JOB plot of the absorbance of the IPCT transition (corrected for the absorbance of the initial ion pairs) for mixtures of $DMBPY^{2+}(PF_6^-)_2$ and $PPN^+Co(CO)_4^-$ in CH_2Cl_2: (⊗) 550 nm; (●) 470 nm; (⊙) 375 nm.

Results and Discussion

Spectroscopy. The colorless solutions of $DMBPY^{2+}(PF_6^-)_2$ and $PPN^+Co(CO)_4^-$ in CH_2Cl_2 immediately turned red upon mixing. Figure 1 shows the UV/vis spectra of the separate components, the mixtures in CH_2Cl_2 and acetone, and a mixture with added tetra-*n*-butylammonium perchlorate (TBAP). The decrease of the low-energy absorption band upon going from CH_2Cl_2 to the more polar acetone and by adding the inert TBAP proves that this transition is due to ion-pair formation. Because of solubility problems the variation of solvents was restricted.

The JOB plot in Figure 2 clearly shows that essentially an 1:1 ion-pair was formed. The slightly asymmetric behavior might be caused by a small amount of 1:2 aggregates or might be due to mixing of an 1:1 ion pair with an 1:2 ion-pair. In an equation for the absorbance of the IPCT transition

$$A_{IP} = [IP]d\epsilon_{IP} \qquad (1)$$

where $d = 1$ cm and $[IP] = [\{DMBPY^{2+}PF_6^-Co(CO)_4^-\}]$ given by

$$K_{IP} = [IP]/\{[DMBPY^{2+}]_0 - [IP]\}\{[Co(CO)_4^-]_0 - [IP]\} \qquad (2)$$

the asymmetry can be accounted for by a not further specified additional term linearly dependent on $[Co(CO)_4^-]$. For the special conditions of our experiments, an average value for $K_{IP} = (120 \pm 50)$ M^{-1} with $\epsilon = (560 \pm 270)$ M^{-1} cm^{-1} for 470 nm was calculated by means of nonlinear regression analysis. The ϵ-value is in the same order of magnitude as in the case of ion pairing of $Co(CO)_4^-$ with other cations, including pyridinium.[9,10,11] K_{IP} is much less, probably also due to the presence of competing counter ions in the in situ preparation of the ion pairs in this work. Compared with the very recent work of Kochi et al.,[11] the IPCT transition in our case of $DMPBY^{2+}$ (470 nm) is at higher energy with respect to the reduction potential. This might be due to the higher Franck–Condon energy of the IPCT transition going from an essentially undistorted tetrahedral $Co(CO)_4^-$ (see below) donor

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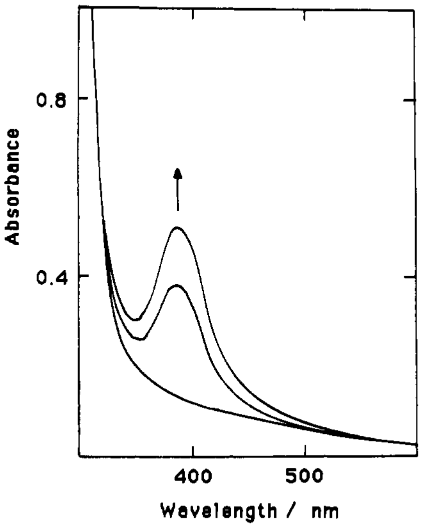

Figure 3. UV/vis spectral changes upon irradiation of mixture c of Figure 1 (10^{-1} M PPh_3 added, IR cell 0.02 cm) at 514.5 nm.

anion in the contact ion pair. Ion pairing in metal carbonyl chemistry can also be monitored by means of IR spectroscopy.[9,11,13,15,16] The IR spectra of the cobaltate solutions of Figure 1 showed hardly any difference in intensity for the strong C–O stretching vibration at about 1890 cm^{-1}. Moreover, no other band showed up in this wavenumber region, but only significantly small changes in bandwidths were observed. This is obviously due to different interactions in the ion pairs and/or their concentrations. Although the addition of TBAP decreases the IPCT absorption, see Figure 1, the bandwidth of the CO stretching vibration is not significantly altered. Thus, a similar contact ion pair seems to be formed upon replacement of $DMBP^{2+}$ by the tetra-*n*-butylammonium cation, which has, however, no low-energy IPCT transition, since a low-lying π^*-orbital is lacking in the latter cation. The solubility of $Na^+Co(CO)_4^-$ is much less than 5×10^{-3} M in CH_2Cl_2. Stirring a suspension of $Na^+Co(CO)_4^-$ and $DMBPY^{2+}(PF_6^-)_2$ gives an increasing C–O stretching mode in the solution. This indicates that the $Co(CO)_4^-$ anion dissolves by ion-pair formation with $DMBPY^{2+}$. The final relative bandwidth is increased compared with the corresponding mixture by using $PPN^+Co(CO)_4^-$ as cobaltate source. This result clearly shows that ion-pair equilibria in organic solvents are dependent on the initial ion pairs.

Thermal Reactions. The solutions of the ion-pair with $DMBPY^{2+}$ are stable for some hours so that photochemistry could be studied separately from thermal reactions, see below. On the other hand, mixing $MV^{2+}(PF_6^-)_2$ with $PPN^+Co(CO)_4^-$ or $Na^+Co(CO)_4^-$ in CH_2Cl_2 or acetone caused the color to change to blue with bands at 390 and 606 nm, indicating the formation of MV^+. In acetone, the intensity of these bands increased within 3 h at room temperature until a maximum was reached and then slowly decreased. With an absorption coefficient of 13 800 M^{-1} cm^{-1},[17] the extent of maximum conversion toward equilibrium can be estimated to be about 5%. As a plot of the increasing absorbance at 606 nm revealed approximately first order kinetics with $k_3 = 5 \times 10^{-5}$ s^{-1}, the rate-determining step is the redox reaction within the ion pair, reaction 3. The fate of the cobalt radical is not yet

$$\mathrm{MV^{2+}Co(CO)_4^-PF_6^- \rightarrow MV^+PF_6^- + {}^{\bullet}Co(CO)_4} \qquad (3)$$

clear. Because of the strong blue color of the mixtures we did not further study the IPCT behavior and photochemistry of $MV^{2+}Co(CO)_4^-$.

Photochemical Reactions. Irradiation of a mixture of both 5×10^{-3} M $DMBPY^{2+}(PF_6^-)_2$ and $PPN^+Co(CO)_4^-$ in CH_2Cl_2 with the 514.5-nm laser line of an Ar ion laser did not cause any change in the UV/vis and IR spectra, obviously because of a fast back-reaction of the radicals formed by the charge-transfer transition. Addition of triphenylphosphine (10^{-1} M) and irradiation with 514.5-nm laser light caused the appearance of an absorption band at 390 nm (Figure 3). At the same time the $Co(CO)_4^-$ IR band at 1890 cm^{-1} decreased in intensity while two new bands showed up at 1957 and 1976 cm^{-1}, respectively. The new features at 390 nm and 1957 cm^{-1} belong to $Co_2(CO)_6(PPh_3)_2$;[7,18] the origin of the 1976-cm^{-1} band is not yet clear. $Co(CO)_3(PPh_3)_2^+$, which has a strong IR band at 2008 cm^{-1},[18] was not formed during this reaction.

Apparently, PPh_3 acts as a scavenger here for the ${}^{\bullet}Co(CO)_4$ radicals as in the case of the photochemical reaction of the $Co(Cp)_2^+Co(CO)_4^-$ ion pair;[6,11] see reactions 4 and 5. An initial

$$\mathrm{{}^{\bullet}Co(CO)_4 + PPh_3 \rightarrow {}^{\bullet}Co(CO)_3PPh_3 + CO} \qquad (4)$$

$$\mathrm{2\,{}^{\bullet}Co(CO)_3PPh_3 \rightarrow Co_2(CO)_6(PPh_3)_2} \qquad (5)$$

quantum yield of about 0.02 for the formation of $Co_2(CO)_6(PPh_3)_2$ was determined under our conditions with $[PPh_3] = 10^{-1}$ M. The irradiation of a mixture of $PPN^+Co(CO)_4^-$ with PPh_3 in the absence of $DMBPY^{2+}(PF_6^-)_2$ did not give any products.

The primary product of the charge-transfer transition is the $DMBPY^+$ radical cation, for which different lowest energy bands at 600[19] and 470 nm,[20] respectively, are given. As such an absorption band could not be detected, we conclude that $DMBPY^+$ is not formed in noticeable concentrations due to a secondary reaction of the cation radical, possibly with the solvent, re-forming the $DMBPY^{2+}$ dication. The photochemical reaction of the same mixture with added PPh_3 in acetone was much slower, also taking into account the smaller IPCT absorption. This is expected for the more polar solvent. Neither the 1957-cm^{-1} nor the 390-nm band is dominating in the spectra as found in CH_2Cl_2. Obviously acetone competes with PPh_3 for the ${}^{\bullet}Co(CO)_4$ radicals, reducing them at least in part.

These results show that IPCT occurs also in contact ion pairs without significant distortion of the tetrahedral structure of the tetracarbonylcobaltate anion. Therefore the interaction should be effected here mainly via the CO ligands and not directly by the metal, as for the ion pairs with complex cobalt cations and Tl^+. $DMBPY^{2+}/Co(CO)_4^-$ ion pairs give irreversible photochemical product formation only if the intermediate radicals are scavenged, in accordance with results on other pyridinium cations.[11]

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Contribution from the Department of Chemistry
and Center for Organometallic Research and Education,
University of North Texas, Denton, Texas 76203

Competitive CO Attack in $Fe(CO)_5$ Using Methanolic $[Et_4N][OH]$. IR Spectral Observation and Reactivity Studies of $[Fe(CO)_4(CO_2X)^-]$ (X = OH, OMe)

Sang Woo Lee, W. David Tucker, and Michael G. Richmond*

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The water gas shift reaction continues to receive attention in connection with carbon dioxide reduction processes and as a method to generate hydrogen from water gas.[1] Of the many