S_2 ligand, external and perpendicular to the metal–metal bond, is of importance. It is to be pointed out that the complexes can be obtained by direct methods.[19] We believe that the chemistry of disulfur complexes will be a source of interest to chemists in the future.

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the Minister für Wissenschaft und Forschung (NRW) for financial support.

Registry No. Na_2S_2, 22868-13-9.

References and Notes

(1) M. M. Taqui Khan and A. E. Martell, "Homogeneous Catalysis by Metal Complexes", Vol. 1, Academic Press, New York and London, 1974.

(2) In the text the term disulfur complexes is used in agreement with the notation of dioxygen complexes,[3,4] though, as will be shown, it is chemically more reasonable to define the known ones as S_2^{2-} complexes (see also ref 3). S_2^{2-} complexes of Nb^{V}, Nb^{IV}, Mo^{VI}, Mo^{V}, Mo^{IV}, Mo^{III}, Mn^{I}, Fe^{III}, Fe^{II}, Co^{III}, Co^{II}, Rh^{III}, and Ir^{III} are known and are all diamagnetic. For most of the complexes the 18-electron requirement is fulfilled for the metals.

(3) L. Vaska, *Acc. Chem. Res.*, **9**, 175 (1976).

(4) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", Wiley-Interscience, New York, 1972.

(5) K. Mennemann and R. Mattes, *Angew. Chem.*, **89**, 269 (1977).

(6) V. Küllmer, E. Röttinger, and H. Vahrenkamp, *J. Chem. Soc., Chem. Commun.*, 782 (1977).

(7) J. Marcoll, A. Rabenau, D. Mootz, and H. Wunderlich, *Rev. Chim. Miner.*, **11**, 607 (1974).

(8) $[Ir(S_2)(dppe)_2]Cl$ has been prepared following this method. But because of the nature of the reaction (oxad with $Ir^{I} \rightarrow Ir^{III}$) and the S–S distance in the complex, it is not appropriate to use the term the "molecular unit S_2 as a ligand" (A. P. Ginsberg and W. E. Lindsell, *Chem. Commun.*, 232 (1971)).

(9) A. Müller, W. O. Nolte, and B. Krebs, *Angew. Chem., Int. Ed. Engl.*, **17**, 279 (1978).

(10) A Müller, S. Sarkar, R. G. Bhattacharyya, S. Pohl, and M. Dartmann, *Angew. Chem., Int. Ed. Engl.*, **17**, 535 (1978).

(11) H. G. von Schnering and W. Beckmann, *Z. Anorg. Allg. Chem.*, **347**, 231 (1966).

(12) The reactivity of sulfur, which is tricoordinated, is reduced (H. Vahrenkamp, *Angew. Chem., Int. Ed. Engl.*, **14**, 322 (1975)).

(13) $[Mo_3^{IV}S(S_2)_6]^{2-}$ and $[Mo^{V}(S_2)_6]^{2-}$ are examples of the rule that, for the transition elements Mo, W, and Re with d^n configuration, cluster types are expected to be dumbbell shaped (in the case where $n = 1$), triangular ($n = 2$), tetrahedral ($n = 3$), and octahedral ($n = 4$) (here n also indicates the number of metal–metal bonds originating from each metal atom) if the ligands only have a weak ligand field such as halogen or sulfur.

(14) See A. B. P. Lever and H. B. Gray, *Acc. Chem. Res.*, **11**, 348 (1978).

(15) Our measurements.

(16) P. M. Treichel and G. P. Werber, *J. Am. Chem. Soc.*, **90**, 1753 (1968).

(17) A. Müller, W. O. Nolte, and B. Krebs, to be submitted for publication in *J. Am. Chem. Soc.*

(18) A. Müller, S. Pohl, M. Dartmann, J. P. Cohen, J. M. Bennet, and R. M. Kirchner, *Z. Naturforsch., B*, **34**, 434 (1979). For a very simple preparation method of $(NH_4)_2[Mo_3S(S_2)_6]\cdot nH_2O$ (the compound contains variable amounts of water: $n = 0–2$) and $(NH_4)_2[Mo_2(S_2)_6]\cdot 2H_2O$ see A. Müller, R. G. Bhattacharyya, and B. Pfefferkorn, *Chem. Ber.*, **112**, 778 (1979).

(19) For a novel type of a generation of a triangular metal–S_2 moiety by an intramolecular redox reaction during the condensation of $MO^{VI}O_2S_2^{2-}$ to $[Mo_2^{V}O_2S_2(S_2)_2]^{2-}$ see W. Rittner, A. Müller, A. Neumann, W. Bäther, and A. C. Sharma, *Angew. Chem.*, in press.

Faculty of Chemistry
The University
D-4800 Bielefeld, West Germany

A. Müller*
W. Jaegermann

Received August 23, 1978

A Reinvestigation of the Hexacyanocobaltate(III) Photosolvation in Water/Ethanol Solvent Systems

Sir:

We have recently studied the photoaquation of $Co(CN)_6^{3-}$ in a variety of water/alcohol solvent mixtures, in order to obtain information about the medium effects on this photoreaction.[1] We found that in the mixed solvents used the same photoaquation reaction (eq 1) occurred as in water solution

$$Co(CN)_6^{3-} + H_2O \xrightarrow{h\nu} Co(CN)_5H_2O^{2-} + CN^- \tag{1}$$

and that the photoaquation quantum yields correlated well with the solvent viscosity, exhibiting a continuous decrease as the solvent viscosity was increased. This observation led us to conclude that the $Co(CN)_6^{3-}$ photoaquation proceeded by a dissociative primary process coupled with a cage-recombination mechanism.

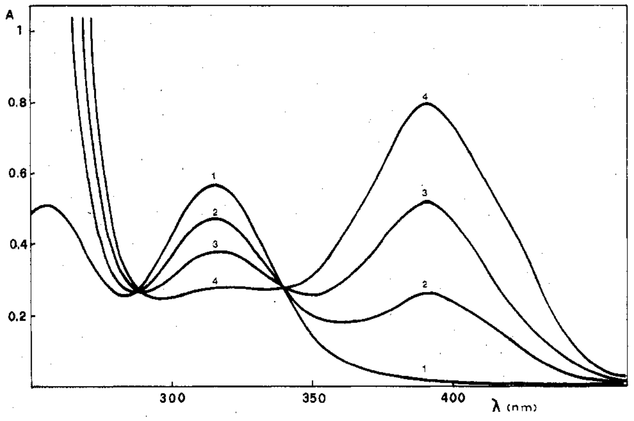

Figure 1. Spectral changes of $Co(CN)_6^{3-}$ in ethanol solution upon irradiation at 313 nm ($[Co(CN)_6^{3-}] = 3 \times 10^{-3}$ M): (1) nonirradiated solution, (2) solution irradiated for 2 h, (3) solution irradiated for 5 h and 15 min, (4) solution irradiated up to constant absorbance.

Later on, Wong and Kirk[3] reinvestigated the solvent dependence of the $Co(CN)_6^{3-}$ photoreaction in aqueous mixed-solvent systems and concluded that the correlation with viscosity found was "more apparent than real", since they thought that the observed quantum yield reduction was caused by errors in the spectrophotometric calculation. This conclusion was essentially[4] drawn on the basis of a study of the photosolvation reactions of $Co(CN)_6^{3-}$ in nonaqueous solvents published by Nakamaru, Jin, Tazawa, and Kanno (NJTK).[6] In NJTK's paper it was reported that (i) the irradiation of solutions of $Co(CN)_6^{3-}$ in dried ethanol, methanol, acetonitrile, DMF, or pyridine in the first ligand field band caused the photosolvation reaction (eq 2), (ii) the photosolvation quantum

$$Co(CN)_6^{3-} + S \xrightarrow{h\nu} Co(CN)_5S^{2-} + CN^- \tag{2}$$

yields in these nonaqueous solvents (calculated spectrophotometrically by assuming for $Co(CN)_5S^{2-}$ the spectrum obtained from exhaustive photochemistry of $Co(CN)_6^{3-}$ in the S solvent) were almost the same as that in aqueous solution, and (iii) in water/ethanol solvent mixtures no isosbestic points were observed, and the spectral variations upon irradiation were similar to those observed in pure water or ethanol as the content of water or ethanol increased.

In order to settle this argument, we have reexamined the problem, and, as a sample, we have studied the photosolvation reaction of $Co(CN)_6^{3-}$ both in pure ethanol and in ethanol/water mixtures. The spectral changes obtained upon irradiation at 313 nm[7] of $Co(CN)_6^{3-}$ in ethanol solution are shown in Figure 1. These spectral changes qualitatively agree with those of NJTK,[6] indicating that the same photosolvation reaction occurs also in our conditions. However, the molar absorptivities for the ethanol-monosubstituted compound obtained by complete photolysis[8] of $Co(CN)_6^{3-}$ are quite higher than those reported in the NJTK paper, e.g., ϵ_{392} 282 L mol^{-1} cm^{-1} instead of ϵ_{392} 184 L mol^{-1} cm^{-1}.[6] This fact suggests that in NJTK's experiments an incomplete conversion of $Co(CN)_6^{3-}$ to the ethanol-monosubstituted product was achieved. The experimental reason for this incomplete conversion is presently

0020-1669/79/1318-2633$01.00/0 © 1979 American Chemical Society

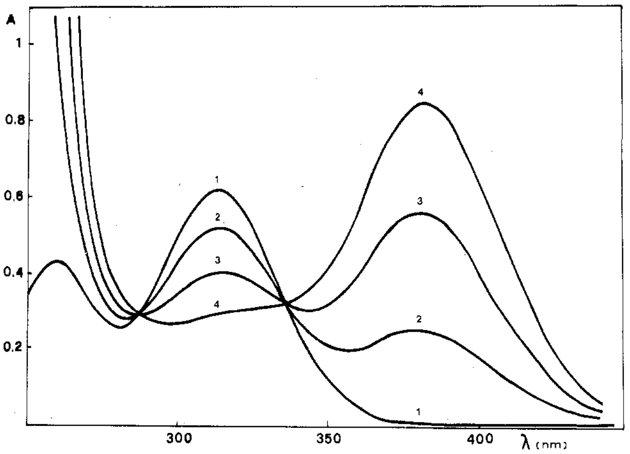

Figure 2. Spectral changes of $Co(CN)_6^{3-}$ in 60% ethanol/40% water solution containing 0.1 N H_2SO_4 upon irradiation at 313 nm ($[Co(CN)_6^{3-}] = 3 \times 10^{-3}$ M): (1) nonirradiated solution, (2) solution irradiated for 1 h, (3) solution irradiated for 3 h and 20 min, (4) solution irradiated up to constant absorbance.

unclear. Using our molar absorptivities for $Co(CN)_5C_2H_5OH^{2-}$, we have obtained a quantum yield of 0.18 for the photosolvation reaction (eq 2). The same value would be obtained from NJTK's data by replacing their molar absorptivities of the photoproduct with ours.

The spectral changes obtained upon irradiation at 313 nm of $Co(CN)_6^{3-}$ in 60% ethanol/40% water solution containing 0.1 N H_2SO_4 are shown in Figure 2. In this mixed solvent two isosbestic points can be seen, as in acidic aqueous solution or in pure ethanol.[9] The features of the spectral changes, e.g., the wavelengths of the isosbestic points and the λ_{max} of the photoproduct, are appreciably the same as those obtained in aqueous solution and slightly but definitely different from those obtained in pure ethanol. This fact indicates that under these conditions the predominant photosolvation reaction is water substitution (reaction 1), as we assumed in our previous study.[1] It must be pointed out, however, that even if some ethanol-monosubstituted compound was formed, it would not cause any appreciable error in the spectrophotometric calculation of the quantum yield, since at 382 nm, where the quantum yield was calculated, both $Co(CN)_5H_2O^{2-}$ and $Co(CN)_5C_2H_5OH^{2-}$ have the same molar absorptivity (ϵ_{386} 280 L mol^{-1} cm^{-1}). In solutions containing a higher concentration of the alcoholic solvent, e.g., 80% ethanol/20% water, the spectral changes were intermediate between those obtained in pure water or ethanol, as found by NJTK.[6]

The results reported in this paper show that the quantum yield of 0.25, previously obtained for the $Co(CN)_6^{3-}$ photosolvation in 60% ethanol/40% water mixtures,[1] is correct.

The conclusion drawn by Wong and Kirk that in the ethanol/water solvent systems used in ref 1 and 3 the quantum yield remains practically unchanged with respect to pure water is shown to be wrong. In fact, this conclusion was based on (i) the incorrect hypothesis that water and ethanol efficiently compete as entering ligands in the photosolvation and (ii) the use of a previously reported erroneous spectrum for the ethanol-monosubstituted product.

Registry No. $Co(CN)_6^{3-}$, 14897-04-2; $Co(CN)_5H_2O^{2-}$, 14842-83-2; $Co(CN)_5C_2H_5OH^{2-}$, 70749-49-4.

References and Notes

(1) F. Scandola, M. A. Scandola, and C. Bartocci, *J. Am. Chem. Soc.*, **97**, 4757 (1975).
(2) L. Moggi, F. Bolletta, V. Balzani, and F. Scandola, *J. Inorg. Nucl. Chem.*, **28**, 2589 (1966).
(3) C. F. C. Wong and A. D. Kirk, *Can. J. Chem.*, **54**, 3794 (1976).
(4) The data reported by Wong and Kirk[3] in nonalcoholic solvents must be interpreted with caution for the following reasons: (i) contrary to what happens with alcoholic solvents, the spectrum of $Co(CN)_6^{3-}$ undergoes a marked shift in going from water to water/acetonitrile mixtures, indicating that the photophysics of the complex may be changed, (ii) in water/poly(vinylpyrrolidone), as in similar polymeric systems studied by Natarajan,[5] the viscosity may not be related to the structure of the solvent cage, as the solution is likely to be strongly inhomogeneous.
(5) P. Natarajan, *J. Chem. Soc., Chem. Commun.*, 26 (1975).
(6) K. Nakamaru, K. Jin, A. Tazawa, and M. Kanno, *Bull. Chem. Soc. Jpn.*, **48**, 3486 (1975).
(7) This wavelength seemed more appropriate for minimizing the inner-filter effect of the photoproduct than the 365-nm wavelength used by NJTK.[6]
(8) We verified that the thermal and photochemical anation of $Co(CN)_5C_2H_5OH^{2-}$ by CN^- was practically negligible under our conditions.
(9) The lack of isosbestic points observed by NJTK[6] in ethanol/water mixtures is probably due to the use of solutions not buffered at acid pH values.[2]

Centro di Studio sulla Fotochimica e
Reattività degli Stati
Eccitati dei Composti di Coordinazione
del CNR
Istituto Chimico dell'Università
Ferrara, Italy

Nanda Sabbatini*
Roberto Rossi
Maria Anita Scandola
Franco Scandola

Received August 4, 1978