Crystallization of the solid residue from acetone/water and finally from methylene chloride/carbon tetrachloride yields 1.0 g (0.78 mmol) of **5**, PF_6 salt, as dark green crystals (yield 89%, mp 160 °C dec).

Anal. Calcd for $C_{34}H_{70}Co_3F_6O_{18}P_7$: C, 32.04; H, 5.54; Co, 13.87; F, 8.94; P, 17.01. Found: C, 32.15; H, 5.54; Co, 13.28, F, 8.84; P, 16.87.

Acknowledgment. This work was partially supported by the Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung. We thank Dipl.-Chem. W. Müller for measuring the magnetic susceptibility of **2** and **6**.

Registry No. **1**, 53322-15-9; **2**, 58438-21-4; **3**, 66403-09-6; **5**, PF_6 salt, 70850-85-0; **6**, BF_4 salt, 66245-41-8; **9**, 70850-86-1.

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Correspondence

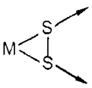
Disulfur Ligands in Transition-Metal Coordination and Cluster Compounds

Sir:

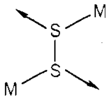
The investigation of complexes with diatomic ligands is of particular interest because of the information regarding basic aspects of homogeneous catalysis[1] (e.g., the type of transition metal–ligand interaction) which may be obtained and because of the bioinorganic relevance of O_2 and N_2 complexes. Despite the fact that several review papers about O_2 and N_2 complexes have been published (in accordance with the large number of original papers concerning this topic), there are only a few papers about S_2 complexes (for notation see ref 2). The nature of the metal–ligand bonding, the different types of metal–disulfur geometries that exist, and preparative methods have not been discussed. In this latter context, it should be pointed out that most of the S_2 complexes have been obtained accidentally.[5,6]

The preparative methods for S_2 complexes can be classified according to the nature of the reagent involved in the reaction. S_2 ligands may be introduced into a complex by (1) a positive S_2 group (agent: $S_2^{\delta+}Cl_2$),[7] (2) a neutral S_2 group (agent: S_8),[8] and (3) a negative S_2^{2-} group (agent: S_2^{2-} in polysulfide solution).[9,10] In the case of (1) and (2), the sulfur species are reduced[7,8] and the central atom is oxidized (assuming that the S_2 ligand in the complex has a negative charge; see below). Dioxygen complexes can only be prepared according to method 2 (with O_2 as reagent in an oxidative addition (oxad) reaction) or 3 (by using H_2O_2).

A further question to be considered is the mode of attachment of the disulfur group to metal ions. A large variety of structural types exists denoted as Ia–d, IIa–c, and III in Table I. The complexes can be categorized according to the number of sulfur atoms in the basic structures Ia (side-on S_2 coordination) and IIa (bridging S_2 ligand) coordinated to other



Ia



IIa

metal centers (the arrows indicate the possibility of further coordination). It is to be noted that Ia and IIa are also important structural types in the case of O_2 complexes. Complexes are known where the S_2 group links two (Ib, IIa), three (Ic, IIb), or four metal atoms (Id, IIc), in the course of which the sulfur atoms are bound to one, two, or even three metal atoms (in Id). There is no other simple ligand which is as versatile as S_2 in its mode of coordination.

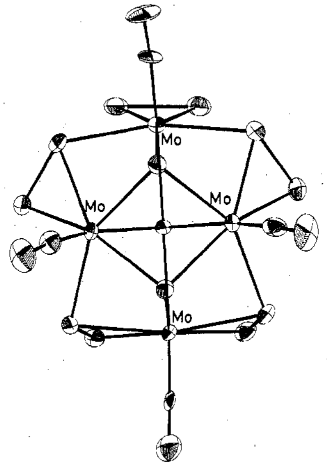


Figure 1. Structure of $[Mo_4(NO)_4S_3(S_2)_5]^{4-}$ (ORTEP plot) in $(NH_4)_4[Mo_4(NO)_4S_{13}]\cdot 2H_2O$ (see Table I).

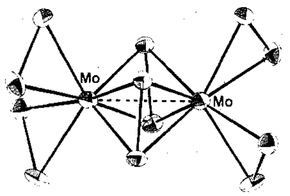
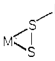
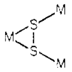
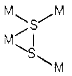
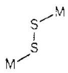
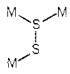
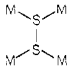
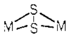


Figure 2. Structure of $[Mo_2(S_2)_6]^{2-}$ (ORTEP plot) in $(NH_4)_2[Mo_2(S_2)_6]\cdot 2H_2O$ (for details see ref 9 and 17).

Whereas S_2 complexes with only end-on bonded S_2 ligands are not known, S_2 groups are side-on and end-on bonded to different metal atoms in the novel complex $[Mo_4(NO)_4(\mu_4\text{-}S)(\mu_3\text{-}S)_2(S\text{-}\mu\text{-}S)_4(S_2)]^{4-}$ which we recently isolated and which contains sulfur in five different valence states (see Figure 1). A novel compound containing *only S_2 ligands* could also be obtained (see Figure 2).

Concerning the disulfur complexes, a bridging S_2 group external and roughly perpendicular to a metal–metal bond (type III) is of special importance due to its power of stabilizing metal clusters. This type of coordination occurs in $[Mo_2$-

Table I. Types of Metal–Disulfur Geometries

type	compd	ν(S–S),[h] cm^{-1}	d(S–S), Å	ref
Ia 	$[MoO(S_2)_2(COS\text{-}CO_2)]^{2-}$	530	2.03 (2)	*a*
Ib 	$[Mo_4(NO)_4S_{13}]^{4-}$	548, 533, 506	2.048 (7)	*b*
Ic 	$[Mn_4S_4(CO)_{15}]$		2.07	*c*
Id 	$[Mn_4S_4(CO)_{15}]$		2.09	*c*
IIa 	$[Co_2(S_2)(CN)_{10}]^{6-}$	490		*d*
IIb 	$[Cp_4Co_4S_6]$		2.01	*e*
IIc 	$[SCo_3(CO)_7]_2S_2$		2.042 (14)	*f*
III 	$[Mo_2(S_2)_6]^{2-}$	530	2.043 (5)	*g*

[a] Reference 5. [b] A. Müller, W. Eltzner, and N. Mohan, *Angew. Chem., Int. Ed. Engl.*, **18**, 168 (1979). [c] See ref 6. [d] H. Siebert and S. Thym, *Z. Anorg. Allg. Chem.*, **399**, 107 (1973). [e] V. A. Uchtmann and L. F. Dahl, *J. Am. Chem. Soc.*, **91**, 3756 (1969). [f] D. L. Stevenson, V. R. Magnuson, and L. F. Dahl, *J. Am. Chem. Soc.*, **89**, 3727 (1967). [g] See ref 9. Another example of this type is $Fe_2S_2(CO)_6$, the structure of which has been described by C. H. Wei and L. F. Dahl, *Inorg. Chem.*, 4, 1(1965). [h] It should be noted that the vibration is often strongly coupled. This has been shown by us for $[Mo_3S(S_2)_6]^{2-}$ by using ^{92}Mo and ^{100}Mo isotopes.

Table II. S–S Distances and ν(S–S) Vibrational Frequencies

	medium	d(S–S), Å	ν(S–S), cm^{-1}
S_2 ($^3\Sigma_g^-$)	matrix, gas phase	1.887[a]	719[b]
S_2^- ($^2\Pi_g$)	alkali halide host (KI)		594[c]
S_2^{2-} ($^1\Sigma_g^+$)	solid Na_2S_2	2.13[d]	446[e]

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$(S_2)_6]^{2-}$ (being the first complex with only S_2 ligands) and $[Mo_3S(S_2)_6]^{2-}$, which is the only known isolated transition-metal–sulfur cluster (Figures 2 and 3). The central units $\{M_2(S_2)_2\}$[9] and $\{M_3(S)(S_2)_3\}$[10] with tricoordinated sulfur occur in isolated "clusters" as well as in solid-state structures (e.g., in MoS_2Cl_3,[7] $Mo_3S_7Cl_4$,[7] and NbS_2Cl_2).[11,12]

A comparison of the d(S–S) values and ν(S–S) frequencies of the complexes with those of S_2 ($^3\Sigma_g^-$, ..., $(\pi_g^*)^2$), S_2^- ($^2\Pi_g$, ..., $(\pi_g^*)^3$), and S_2^{2-} ($^1\Sigma_g^+$, ..., $(\pi_g^*)^4$) (Table II) demonstrates that the values lie between those of S_2^- and those of S_2^{2-}. Taking into account that the S–S distances are expected to be smaller in the complexes than in free S_2^{2-} (the repulsion between the lone electron pairs of the S atoms should be smaller in the complex), it seems reasonable to consider the known compounds as disulfido complexes. This also appears chemically sound, as on this basis the properties of known complexes (e.g., magnetism and structure[9,10,11,13]), their formation (e.g., oxad reaction with S_n; see above and ref 8), and the resulting oxidation numbers of the central atoms[5,9,10,11,13] can be explained.

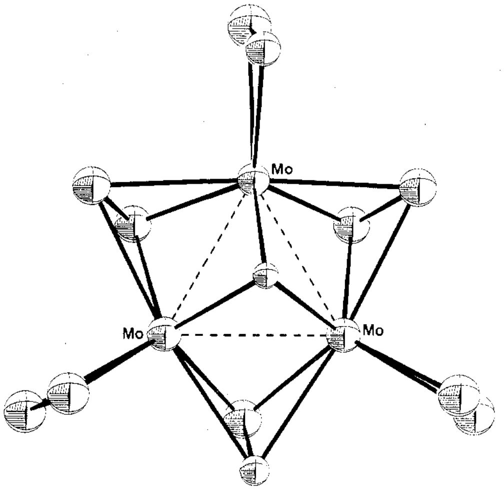
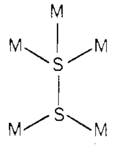
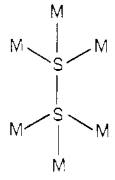


Figure 3. Structure of $[Mo_3S(S_2)_6]^{2-}$ (ORTEP plot) in $(NH_4)_2[Mo_3S(S_2)_6]$ (for details see ref 10 and 18).

Due to the side-on coordination of the S_2 unit, the π_g^* level splits, according to the loss of cylindrical symmetry, into an in-plane orbital π_h^*, forming a strong σ bond to the metal and an out-of-plane π_v^* orbital with no bonding character and higher energy. The longest wavelength band of the MS_2 chromophore with the ground state $(\pi_h)^2(\pi_v)^2(\pi_h^*)^2(\pi_v^*)^2d^n(M)$ should be assigned to a $\pi_v^* \rightarrow$ d LMCT transition (for S_2^{2-} complexes as well as for side-on bonded O_2 complexes[14] having a central atom with a high oxidation state). The corresponding band is observed at nearly 21 cm^{-1} × 10^3 in compounds like $[MoO(S_2)_2(CO_2COS)]^{2-}$,[15] $(\pi\text{-}C_5H_5)_2NbS_2Cl$,[16] $(\pi\text{-}C_5H_5)_2NbS_2Br$,[16] and NbS_2Cl_2[11] and is responsible for the red color of these compounds. The energy of the $\pi_v^* \rightarrow$ d transitions is lower in S_2 complexes than in comparable O_2 complexes.[14] It increases with decreasing optical electronegativity of M.

Most likely complexes with S_2^- ligands (supersulfido) can be isolated. Complexes with an S_2^{2-} group linking more than four metal atoms (with S atoms forming four bonds) corresponding to IId and IIe should exist also.


IId


IIe

Further information about the nature of the metal–ligand interaction may be obtained from condensation reactions of metal atoms with molecular S_2 in low-temperature matrices, by which it is possible to prepare binary nonionic transition-metal–sulfur complexes and clusters. Disulfur can now be generated for the first time at rather low temperatures by heating $Cs_2[Mo_2(S_2)_6]$ up to 150 °C according to a reduction (Mo)–oxidation (S_2^{2-}) process (reductive elimination) whereby it is possible to codeposit S_2 in low-temperature matrices. This has been proven by mass and Raman matrix-isolation spectroscopy.

The S_2 complex chemistry is interesting because of the large variety of the modes of coordination of S_2. S_2 ligands favor high coordination numbers (e.g., 9 for $[Mo_2(S_2)_6]^{2-}$ and $[Mo_3S(S_2)_6]^{2-}$) and are suitable for stabilizing metal clusters since an optimum shielding of the metal atom is achieved through the high coordination numbers arising due to the smallness of the MS_2 angles (ca. 60°). Regarding the stability of a metal–metal bond, the presence of a symmetrical bridging

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.

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(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.
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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

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

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.

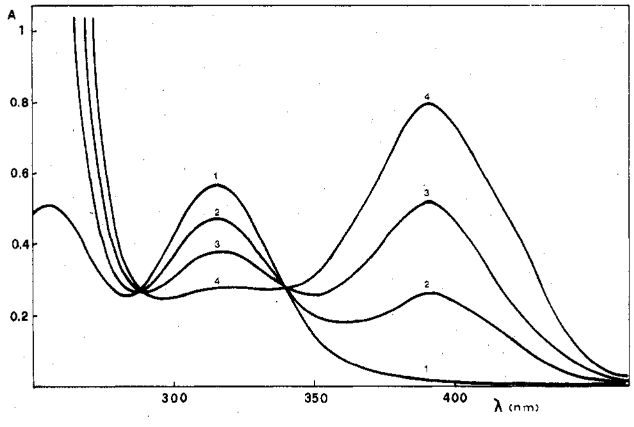

Figure 1. Spectral changes of $Co(CN)_6^{3-}$ in ethanol solution upon irradiation at 313 nm ($[Co(CN)_6^{3-}] = 3 \times 10^{-3}$ M): (1) nonirradiated solution, (2) solution irradiated for 2 h, (3) solution irradiated for 5 h and 15 min, (4) solution irradiated up to constant absorbance.

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

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

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