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Medium Effects in Weakly Coupled Electron-Transfer Processes. Calculation of Inner-Sphere Reorganizational Energies at Zero Ionic Strength

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The solvent dependence of the intervalence transition (IT) band of the very weakly coupled binuclear (2,8-dithiadispiro-[3.1.3.1]decane)decaamminediruthenium(II,III) hexafluorophosphate was studied. No correlation could be discerned with any solvent parameter. A dependence of the optical band of the ruthenium binuclear complex, E_{op}, on the ionic strength of the medium was observed, with some solvents showing stronger effects than others. When ionic strength studies were performed and the extrapolated values at zero ionic strength were employed, a correlation of $E_{op}{}^0$ with $1/D_{op} - 1/D_s$ was observed. The calculated inner-sphere reorganizational energy, λ_i, was 25 kcal/mol. The calculated slope of the plot of $E_{op}{}^0$ against $1/D_{op} - 1/D_s$ was 20.7 whereas the measured value was only 2.02. These results indicate that the dielectric continuum model is not appropriate for theories used in analyzing IT bands of very weakly coupled mixed-valence complexes.

Introduction

Electron-transfer reactions between ions and molecules in solution, both intermolecular and intramolecular, have been the subject of intense experimental and theoretical investigation during the past three decades.[1-11] Of considerable current interest is the mechanism of electron transport in biological systems; these commonly involve a complex system of metalloenzymes, which pass the electron successively over comparatively long distances from one member to another having a slightly lower potential. One of the problems encountered in studying such processes or in modeling them arises from the fact that the metalloproteins are often bound to lipid material. In addition to making such proteins difficult or impossible to isolate, the lipid may play some undetermined role in the electron-transfer process itself.[12] A general feature of biological electron-transfer processes is that the metals involved in transferring the electron are very weakly coupled electronically.

The in vitro reactions of metalloproteins are generally studied in aqueous buffers that may not model effectively the conditions found in living organisms. It is often tacitly assumed that the electron-transfer process is not very sensitive to such environmental parameters as the dielectric constant of the medium or the precise mixture and kind of salts present. Recently, experimental and theoretical evidence has been advanced which suggests that the rate of electron transfer between small molecules or between a metalloprotein and an attached ruthenium complex is affected by the relative motion of nearby solvent molecules.[13,14]

In the usual theoretical treatments of electron transfer, no specific ion-pairing interactions are assumed.[1-5] The theories also usually presume that the solvent forms a dielectric continuum around the reacting species although this is known to be a poor approximation. There is a growing body of evidence, both theoretical and experimental, on thermal electron transfers, which indicates that significant noncontinuum effects operate on the kinetics and thermodynamics of both heterogeneous (electrode) and homogeneous electron-transfer reactions. These effects are especially strong for transition-metal complexes bearing ammine or aqua ligands.[13-25] In the absence of high concentrations of ions, specific solute–solvent interactions are the main sources of these noncontinuum effects, especially via hydrogen bonding. Therefore, in simple redox systems, the role of solvent dielectric and dynamical properties has commanded careful scrutiny. Recently, noncontinuum effects have been observed in intervalence electron-transfer processes as well. Curtis et al.[26] have noted that in solvents with low donor numbers, i.e. DN < 14, substantial spectral shifts were induced in measured intervalence bands as a result of ion pairing between the $(bpy)_2ClRu^{II}$–pyz–$Ru^{III}(NH_3)_5{}^{4+}$ cation and various anions. They reported, for example, that the λ_{max} with Br^- present was 1008 nm, whereas with PF_6^- as counterion it was 1332 nm. The concentrations of anion in solution were not given.[26] In any event, the extent of ion pairing that results will depend inversely on the dielectric constant of the solvent, directly on the changes of the ions involved, and directly on the concentrations of the ions. In a more recent paper, Drickamer and Hendrickson et al.[27] described the concentration dependence of mixed-valent biferrocenium triiodide dissolved in nitrobenzene or dichloromethane. They concluded that in the 0.24–24 mM range, the IT band contour of biferrocenium triiodide in nitrobenzene is likely a superposition of variable amounts of two IT bands, one for an ion-paired cation and the other for a non-ion-paired cation. The increase in E_{op} with increasing concentration was thought to reflect an increasing percentage of ion-paired mixed-valent cations that have a higher energy IT band than does the non-ion-paired cations because the ion pairing probably introduces a zero-point energy separation between the two vibronic states of the cation.

We have extensively investigated electron-transfer mechanisms[28] in the ruthenium spiro binuclear complex I and have determined that the electron movement between the metal centers is facilitated by a hyperconjugating mechanism due to the strained nature of the four-membered rings.[29] Electron tunneling is a predominant

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(1) Marcus, R. A. *J. Phys. Chem.* **1956**, *24*, 906.
(2) Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155.
(3) Hush, N. S. *J. Chem. Phys.* **1958**, *28*, 962.
(4) Hush, N. S. *Trans. Faraday Soc.* **1961**, *57*, 557.
(5) Hush, N. S. *Prog. Inorg. Chem.* **1967**, *8*, 391.
(6) Creutz, C.; Taube, H. *J. Am. Chem. Soc.* **1969**, *91*, 3988.
(7) Creutz, C.; Taube, H. *J. Am. Chem. Soc.* **1973**, *95*, 1086.
(8) Sutin, N. *Acc. Chem. Res.* **1982**, *15*, 275.
(9) Creutz, C. *Prog. Inorg. Chem.* **1983**, *30*, 1.
(10) Newton, M. D.; Sutin, N. *Annu. Rev. Phys. Chem.* **1983**, *30*, 441.
(11) Meyer, T. J. *Acc. Chem. Res.* **1978**, *4*, 94.
(12) Wainio, W. W. *Biol. Rev.* **1983**, *58*, 131.
(13) Gray, H. B. Presented at the 193rd National Meeting of the American Chemical Society, Denver, CO, April 5–10, 1987; paper INOR59.
(14) Warshel, A. Presented at the 193rd National meeting of the American Chemical Society, Denver, CO, April 5–10, 1987; paper INOR20.
(15) Meyer, U.; Kotocova, A.; Gutmann, V.; Gergev, W. *J. Electroanal. Chem. Interfacial Electrochem.* **1977**, *100*, 875.
(16) Gutmann, V. *Electrochim. Acta* **1978**, *21*, 661.
(17) Gritzner, G.; Danksagmuller, K.; Gutmann, V. *Electrochim. Acta* **1979**, *72*, 177.
(18) Meyer, U.; Gergev, W.; Gutmann, V.; Rechberger, P. Z.; *Z. Anorg. Allg. Chem.* **1980**, *464*, 200.
(19) Kotocova, A.; Meyer, U. *Collect. Czech. Chem. Commun.* **1980**, *45*, 335.
(20) Hupp, J. T.; Weaver, M. J. *J. Phys. Chem.* **1985**, *89*, 1601.
(21) Hupp, J. T.; Weaver, M. J. *J. Phys. Chem.* **1984**, *88*, 1860.
(22) Hupp, J. T.; Weaver, M. J. *Inorg. Chem.* **1984**, *23*, 3639.
(23) Tweedle, M. F.; Wilson, L. J. *J. Am. Chem. Soc.* **1976**, *98*, 4824.
(24) Zhu, T.; Su, C. H.; Schaeper, D.; Lemke, B. K.; Wilson, L. J.; Kadish, K. M. *Inorg. Chem.* **1984**, *23*, 4345.
(25) Kadish, K. N.; Das, K.; Schaeper, D.; Merrill, C. L.; Welch, B. R.; Wilson, L. J. *Inorg. Chem.* **1980**, *19*, 2816.
(26) Chang, J. P.; Fung, E. Y.; Curtis, J. C. *Inorg. Chem.* **1986**, *25*, 4233.
(27) Lowery, M. D.; Hammack, W. S.; Drickamer, H. G.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1987**, *109*, 8019.
(28) Stein, C. A.; Lewis, N. A.; Seitz, G. *J. Am. Chem. Soc.* **1982**, *104*, 2596.

0020-1669/89/1328-3796$01.50/0

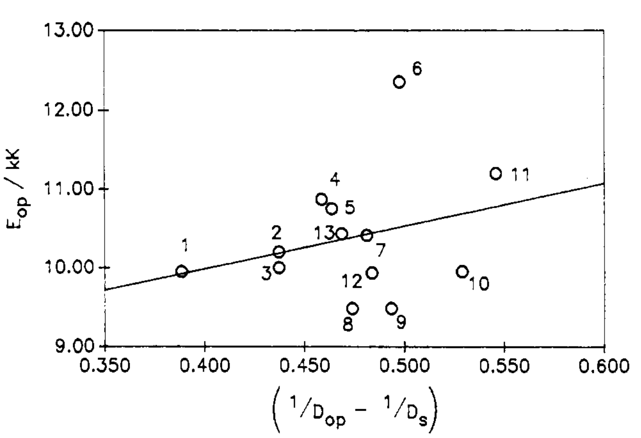

Figure 1. Dielectric continuum plot of the energy of the intervalence transfer band uncorrected for ionic strength against $1/D_{op} - 1/D_s$. Key: 1, benzonitrile; 2, dimethyl sulfoxide; 3, methyl butyl ketone; 4, dimethylformamide; 5, dimethylacetamide; 6, nitromethane; 7, propylene carbonate; 8, methyl ethyl ketone; 9, acetone; 10, acetonitrile; 11, D_2O; 12, *N*-methylformamide; 13, formamide.

feature in this weakly coupled binuclear complex, and Hopfield's theory[39,40] was shown to apply. In an earlier paper,[30] we showed that a significant ionic strength dependence of the IT band occured in *N*-methylformamide and dimethyl sulfoxide. This was attributed to ion pairing between the highly charged mixed-valent binuclear (5+) complex and anions introduced into the solution.

In the present work, we attempted to calculate the inner-sphere reorganizational energy λ_i by performing solvent studies and employing relationships that are based on the dielectric continuum approximation. Several studies on more strongly coupled systems have indicated that good correlations exist except for certain solvents, especially water, which often is irregular.[31,38] Our results were unexpectedly erratic, and we detail in this paper the origin of this peculiar behavior.

Experimental Section

Chemicals and Reagents. All solvents were purchased from Aldrich Chemical Co. Inc. and were either Gold Label or spectrophotometric grade. They were stored over molecular sieves under argon. Cerium ammonium nitrate (G. F. Smith Chemical Co.) was dissolved in dry acetonitrile (spectrophotometric grade), the solution filtered, and the solvent partially removed with a rotary evaporator. The bright yellow precipitate was washed with a copious quantity of diethyl ether and was then vacuum-dried at ambient temperature for 3 h. The dry Ce(IV) salt was stored in amber bottles under argon. Sodium trifluoroacetate (Lancaster Synthesis Ltd.) was recrystallized from hot acetone (spectrophotometric grade) and was stored in plastic bottles under argon. The complex (2,8-dithiadispiro[3.1.3.1]decane)decaamminediruthenium(II) hexafluorophosphate, $[(NH_3)_5RuS_2C_8H_{12}Ru(NH_3)_5](PF_6)_4$, was prepared as described previously.[28]

Spectral Measurements. The near-infrared spectra were recorded on a Perkin-Elmer Lambda 9 spectrophotometer interfaced to an IBM PC/XT microcomputer and an Epson HI-80 plotter. The spectrophotometer was controlled by a commercial software package (Softways). Background correction and data analysis were provided by the same software. Graphs were constructed with Sigma-Plot (Jandel Scientific). The concentrations of the binuclear diruthenium(II) complex and Ce(IV) were equal and were maintained as constant as possible ((5.0 ± 0.8) × 10^{-3} M). No concentration dependence was observed over this range.

Results

It is usual to describe the energy (λ or E_{op}) of the IT band as arising from two contributions—an inner-sphere reorganizational energy, λ_{in}, resulting from stretching and compressing of intermuclear bonds within the mixed-valence species, prior to electron transfer, and λ_{out}, which results from reorientation of solvent molecules. Therefore, the following equation results:[1,2,32]

$$\lambda = \lambda_{in} + \lambda_{out} \qquad (1)$$

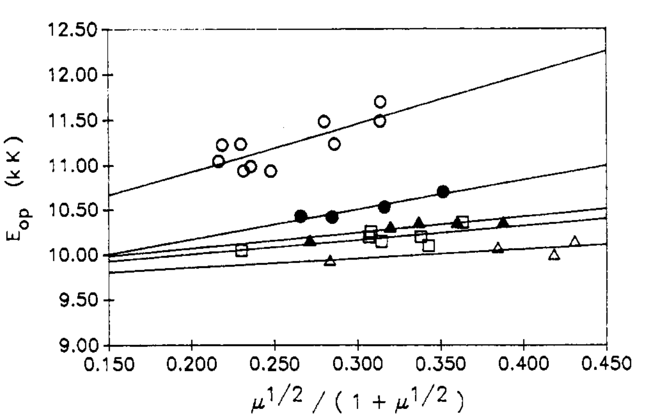

Figure 2. Guntelberg plot of the energy of the intervalence transfer band at various ionic strengths. Key: open circles, D_2O; solid circles, formamide; open triangles, dimethyl sulfoxide; solid triangles, dimethylformamide; open squares, *N*-methylformamide.

Table I. Parameters for the Analysis of Data from the Intervalence Transition Bands in Various Solvents Extrapolated to Zero Ionic Strength

solvent[a]	E_{op}^0	$1/D_{op} - 1/D_s$	slope[b]	AN[c]
D_2O	9.85	0.550	5.31	54.8
formamide	9.51	0.469	3.32	39.8
DMSO	9.65	0.437	1.04	19.3
DMF	9.72	0.464	1.76	16.0
NMF	9.69	0.484	1.58	32.0

[a] DMSO is dimethyl sulfoxide, DMF is dimethylformamide, and NMF is *N*-methylformamide. [b] These are the slopes of the lines in Figure 2. [c] AN is acceptor number. These are taken from ref 37.

The dielectric continuum model is then usually employed to describe the solvent reorganization contribution, resulting in eq 2,

$$\lambda_{out} = (\Delta e)^2(\tfrac{1}{2}a_1 + \tfrac{1}{2}a_2 - 1/R)(1/D_{op} - 1/D_s) \qquad (2)$$

originally derived by Marcus[32] to describe intermolecular electron transfer, where Δe is the charge transferred, a_1 and a_2 are the radii of the two reactants, R is the distance between their centers, D_{op} is the optical dielectric constant, and D_s is the static dielectric constant of the medium. A plot of $1/D_{op} - 1/D_s$ vs E_{op} then should produce a straight line with an intercept of λ_{in}.

The results we obtained, shown in Figure 1, were unexpected. No correlation could be discerned. We had earlier shown that the wavelength maximum of the intervalence transition band (IT band) for this binuclear complex was sensitive to the ionic strength of the medium.[30] The ionic strength in the previous study was adjusted with tetra-*n*-butylammonium hexafluorophosphate (TBAH), which caused precipitation of the binuclear complex in all solvents except dimethyl sulfoxide and *N*-methylformamide. In the present work, sodium trifluoroacetate was used to adjust the ionic strength, since its more soluble nature allowed a wider variety of solvents to be studied. The oxidant was changed from $[Fe(bpy)_3](PF_6)_3$ to Ce(IV) for the same reason. The ionic strength studies are shown in Figure 2. Application of eq 1 using the values of E_{op} extrapolated to zero ionic strength (Table I) gives the line shown in Figure 3. There was no systematic variation in extinction coefficients with ionic strength. The ranges of the extinction coefficients were 33 ± 3 in dimethyl formamide, 32 ± 4 in formamide, 32.9 ± 0.3 in *N*-methylformamide, 34 ± 7 in dimethyl sulfoxide and 34 ± 7 in D_2O.

Discussion

Although the theories commonly employed to describe intervalence electron-transfer processes do not explicity consider environmental perturbations on the reacting system, experimentally, as is shown in the present work, such perturbations are known to occur. Thus, the energy of the potential energy surface, for any particular state, is determined by these perturbations as well

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(29) Stein, C. A.; Lewis, N. A.; Seitz, G.; Baker, A. D. *Inorg. Chem.* **1983**, *22*, 1124.
(30) Lewis, N. A.; Obeng, Y. S. *J. Am. Chem. Soc.* **1988**, *110*, 2306.
(31) Callahan, R. W.; Keene, F. R.; Meyer, T. J.; Salmon, D. J. *J. Am. Chem. Soc.* **1977**, *99*, 1064.
(32) Marcus, R. A. *J. Phys. Chem.* **1963**, *67*, 853.

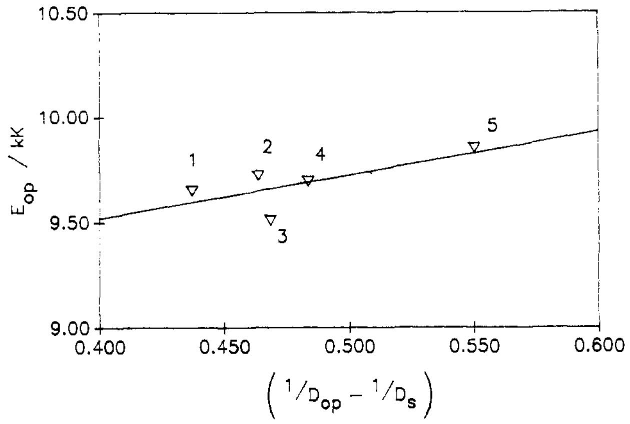

Figure 3. Dielectric continuum plot of the energy of the interalence transition band at zero ionic strength against $1/D_{op} - 1/D_s$. Key: 1, dimethyl sulfoxide; 2, dimethylformamide; 3, formamide; 4, *N*-methylformamide; 5, D_2O.

as by the local polarization around the complex induced by the solvent. The energy of the intervalence transition, $E_{op}(\mu)$, may therefore be described by eq 3, where $E_{op}{}^0$ is the energy change

$$E_{op}(\mu) = E_{op}{}^0 + \Delta G(\mu) \tag{3}$$

in the absence of environmental perturbations due mainly to the orientation of solvent molecules around the complex and $\Delta G(\mu)$ is the sum of the environmental perturbations representing all noncontinuum terms, arising mainly from specific solvent-solute interactions (such as H bonding) and ion pairing or aggregation effects.

Normally, a solid has a D_s much smaller than that of the corresponding liquid, typically by a factor of 10 or more. Thus, eq 2 predicts that a large shift to lower energy should occur in a frozen medium. To test this idea, Drickamer and Hendrickson et al.[33] employed pressure-induced freezing of biferrocenium and $(bpy)_2ClRu\text{-}pyz\text{-}RuCl(bpy)_2{}^{2+}$ cations in deuterated nitromethane, acetonitrile, and nitrobenzene. The shifts in energy of the IT bands observed upon freezing the solution were negligible. In a later paper,[34] the same group examined the effect of pressure-induced freezing on the energy of the mixed-valent diferrocenylacetylene cation and found that the peaks in this case shifted by about 1800 cm^{-1} to lower energy but that this was still less than 40% of the shift predicted to occur by eq 2. From these observations, Drickamer and Hendrickson et al. concluded, and their conclusion is reinforced by the present paper and our earlier communication,[30] that the dielectric continuum model is inadequate in accounting for the behavior of IT bands.

Since the noncontinuum contribution to eq 3 is expected to be ionic strength dependent, it should be possible to isolate the solvent polarization contribution to the measured optical transition, i.e. $E_{op}{}^0$. This contribution would be the intercept, on the energy axis, of the Guntelberg modification of the Debye-Huckel[35] plot arising from eq 4.

$$E_{op} = E_{op}{}^0 + \frac{2z_1z_2A\mu^{1/2}}{1 + \mu^{1/2}} \tag{4}$$

These intercepts, for the solvents employed in the present study, are listed in Table I. These calculated values of E_{op} have been extrapolated to zero ionic strength to remove the effects of ion pairing and therefore should correlate with the theories that are based on the continuum model. Figure 3 shows that this expectation is realized. It is interesting to note that the value of E_{op} measured in D_2O and extrapolated to zero ionic strength is in agreement with the dielectric continuum model, although, in other work in which ion pairing has been a neglected parameter, this solvent had been described as anomalous.[31] Probably, because of its extensive D-bonding network, ion pairing and H bonding to ammines on the ruthenium is more serious in this solvent and can be detected even in more strongly coupled systems such as the ruthenium binuclears containing pyrazine as the bridging ligand, in which electron transfer occurs on a time scale similar to that of solvent rearrangement. Thus, most solvents correlated well with the dielectric continuum model for these binuclears, leaving water as an anomalous solvent.

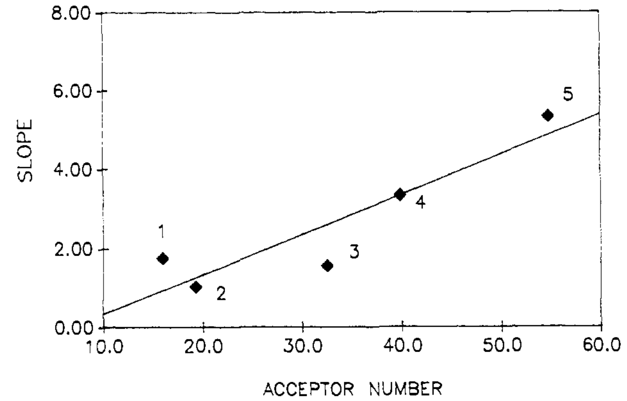

Figure 4. Slopes of the lines in Figure 2 plotted as a function of the acceptor number of the solvent. Key: 1, dimethylformamide; 2, dimethyl sulfoxide; 3, *N*-methylformamide; 4, formamide; 5, D_2O.

The slopes of the lines in Figure 2 are an estimate of the extent of ion pairing in a particular solvent. One might expect that a competition exists between the anions and the solvent for a place in the solvent sheath. The stronger the coordinating ability of the solvent, then, the more often it should be successful. Since the mixed-valence compound is a cation, one might anticipate a correlation with the "electron-donating" ability of the solvent or the donor number (DN).[36] This, however, was not the case, and a correlation was found instead with the acceptor number[36] of the solvent (Figure 4). Such correlations have been found before, and in the present case, it is an indication that it is the solvation of the anion, i.e. the counterion, rather than the solvation of the mixed-valence species itself which is important in controlling the energy of the intervalence process. Presumably, it is the solvated anions, not "bare" anions, that are involved in ion pairing with the mixed-valence species. For this reason, a significant dependence of the energy of the IT band on the counterion employed should be expected.

The value of λ_i estimated from the intercept of Figure 3 is 25 kcal/mol. This is considerably higher than those values calculated for more strongly coupled systems (10-16 kcal/mol),[41] indicating that the nuclear barrier to electron transfer is higher in the present system. Since the electron-transfer process is significantly nonadiabatic, there is sufficient time between subsequent electron transfers for each end of the binuclear complex to relax to a configuration appropriate for Ru(II) or Ru(III) bond lengths and for the medium to reorient itself to these new configurations as well. Under these circumstances, we see that theories based on the dielectric continuum approximation will be qualitatively correct, producing the straight line in Figure 3, but quantitatively incorrect in the value of the calculated slope. However, it should also be recognized that since the solvent dependence of the corrected E_{op} values (Table I) is relatively weak, it may be considered to be a constant, 9.7 ± 0.1, in all solvents. This arises because the slope of the line in Figure 3 is only 2.02 instead of the value of 20.7 calculated on the basis of the continuum model. A similar

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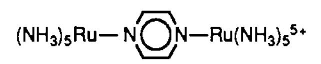
(33) Hammack, W. S.; Drickamer, H. G.; Lowery, M. D.; Hendrickson, D. N. *Chem. Phys. Lett.* **1986**, *132*, 231.
(34) Hammack, W. S.; Drickamer, H. G.; Lowery, M. D.; Hendrickson, D. N. *Inorg. Chem.* **1988**, *27*, 1307.
(35) Guntelberg, E. *Z. Phys. Chem.* **1926**, *123*, 199.
(36) Gutmann, V. *The Donor-Acceptor Approach to Molecular Interactions*; Plenum Press: New York, 1978.
(37) Mayer, U. *Coord. Chem. Rev.* **1976**, *21*, 159.
(38) Hupp, J. T.; Meyer, T. J. *J. Phys. Chem.* **1987**, *91*, 1001.
(39) Hopfield, J. J. Biophys. J. **1977**, *18*, 311.
(40) Hopfield, J. J. *Proc. Natl. Acad. Sci.* U.S.A. **1974**, *71*, 3640.
(41) Meyer, T. J. *Acc. Chem. Res.* **1978**, *11*, 94.

plot for the complex $[(bpy)_2ClRu(pyr)RuCl(bpy)_2]^{3+}$ has been constructed by Meyer et al.[31] In this case, we calculated that the theoretical slope was 3.2 and the measured slope was 4.3. The excellent agreement between theory and experiment for Meyer's experiments and the poor agreement obtained in the present work may be a reflection of the degree of adiabaticity in the systems. In other words, the influence of noncontinuum contributions becomes relatively more important as the degree of electronic coupling between the metal centers decreases. This was also observed in spectral measurements of IT bands performed under high pressures. We have reported[42] the effect of pressure on the IT band of the spiro binuclear complex I. A large red shift occurred as the pressure was increased from 1 to 1500 bar, indicating that significant interactions with the medium were occurring. For a strongly coupled system, the Creutz–Taube ion, II, no shift of the IT band could be observed over this pressure range.[43] Experiments are under way to test the generality of these observations.



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(42) Lewis, N. A.; Obeng, Y. S.; Taveras, D. V.; van Eldik, R. *J. Am. Chem. Soc.* **1989**, *111*, 924.

(43) Hammack, W. S.; Lowery, M. D.; Hendrickson, D. N.; Drickamer, H. G. *J. Phys. Chem.* **1988**, *92*, 1771.

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Solution Properties and Reactivity of the Aqua Ion of the Mo^{IV}_3 Incomplete Cuboidal Mo/S Cluster $[Mo_3S_4(H_2O)_9]^{4+}$

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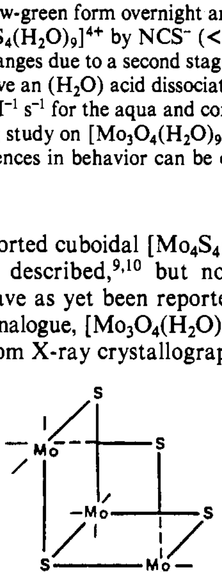
The green sulfido-bridged Mo^{IV}_3 ion $[Mo_3S_4(H_2O)_9]^{4+}$, prepared by decomposition of cuboidal $[Mo_4S_4(H_2O)_{12}]^{5+}$, exhibits solution behavior strikingly different from that of the previously studied red $[Mo_3O_4(H_2O)_9]^{4+}$. It is stable indefinitely in acidic solutions of pH < 1 and, unlike the μ-oxo analogue, does not react overnight with O_2 and ClO_4^-. It does however react (<1 min) with air-free solutions of aqua M^{2+} under reducing conditions ($NaBH_4$ or electrochemical) to yield mixed-metal cuboidal (or related) complexes $[Mo_3MS_4(H_2O)_{10}]^{4+}$ (e.g. M = Fe, Ni, Cu), whereas no corresponding reactions of $[Mo_3O_4(H_2O)_9]^{4+}$ are observed. In this reaction the three exposed μ-sulfido groups of Mo_3S_4 are activated by reduction of Mo^{IV}_3, and M^{2+} is incorporated (order not specified). No permanent electrochemical or chemical reduction of $[Mo_3S_4(H_2O)_9]^{4+}$ is observed, again in contrast to $[Mo_3O_4(H_2O)_9]^{4+}$, which is readily reduced to the Mo^{III}_3, and $Mo^{III}_2Mo^{IV}$ states. Similarly, by reaction of $[Mo_3S_4(H_2O)_9]^{4+}$ with $[Mo(H_2O)_6]^{3+}$ in the presence of $NaBH_4$, $[Mo_4S_4(H_2O)_{12}]^{5+}$ can be regenerated. The cube is also regenerated by first converting $[Mo_3S_4(H_2O)_9]^{4+}$ to the double cube $Mo_7S_8^{8+}$ and then leaving it to stand in 2 M HCl for a few days, when the cube and trimer are obtained in equal amounts. With 1 M NCS^- substitution to $[Mo_3S_4(NCS)_9]^{5-}$ occurs and yellow-green and red products can be separated chromatographically. From previous crystallographic studies the yellow-green product is assigned the N-bonded thiocyanato structure. The minority red product (~1% yields after chromatography) converts to the yellow-green form overnight and is possibly an S-bonded isomer. Stopped-flow kinetic studies on the 1:1 substitution of H_2O in $[Mo_3S_4(H_2O)_9]^{4+}$ by NCS^- ($<2 \times 10^{-3}$ M) were monitored at an isosbestic point at 362 nm, thereby avoiding contributions from small changes due to a second stage of reaction, isomerization of S- to N-bonded thiocyanate. The kinetics at 25 °C, $I = 2.00$ M ($LiClO_4$), give an (H_2O) acid dissociation constant $K_a = 0.22$ M for $[Mo_3S_4(H_2O)_9]^{4+}$ and formation rate constants k_1 and k_2 of 108 and 1120 $M^{-1}\,s^{-1}$ for the aqua and conjugate-base forms, respectively, $I = 2.00$ M ($LiClO_4$). These compare with values for the corresponding study on $[Mo_3O_4(H_2O)_9]^{4+}$, $I = 2.00$ M (LiPTS), for which k_2 is 230-fold less and no contribution from k_1 is observed. Differences in behavior can be explained by the electron-rich properties of the μ-S core ligands.

Introduction

The cyano complex $[Mo_3S_4(CN)_9]^{5-}$, obtained by treating $(NH_4)_2[Mo_3S(S_2)_6]$ with excess KCN,[1] was the first Mo_3S_4 core complex to be prepared.[1] Since then, others have been reported,[2-5] including the aqua ion $[Mo_3S_4(H_2O)_9]^{4+}$.[6-8] The procedure for the latter involves heating 1–2 M HCl solutions of cuboidal $[Mo_4S_4(H_2O)_{12}]^{5+}$.[8] The structure has been confirmed as $[Mo_3S_4(H_2O)_9]^{4+}$ by X-ray crystallographic structures on derivative complexes $Ca[Mo_3S_4(ida)_3]\cdot 11.5H_2O$ (ida = iminodiacetate) and $Cs_2[Mo_3S_4(C_2O_4)_3(H_2O)_3]\cdot 3H_2O$.[6,7] Solution properties of the distorted cuboidal $[Mo_4S_4(H_2O)_{12}]^{n+}$ ions (n = 4, 5, 6) have been described,[9,10] but no similar studies on $[Mo_3S_4(H_2O)_9]^{4+}$ have as yet been reported.

The Mo^{IV}_3 μ-oxo analogue, $[Mo_3O_4(H_2O)_9]^{4+}$, has been studied extensively.[11-14] From X-ray crystallography the $Mo_3S_4^{4+}$ and



$Mo_3S_4^{4+}$

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(1) Müller, A.; Reinsch, U. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 72.

(2) Howlander, N. C.; Haight, G. P., Jr.; Hambley, T. W.; Lawrence, G. A.; Rahmoeller, K. M.; Snow, M. R. *Aust. J. Chem.* **1983**, *36*, 377.

(3) Wieghardt, K.; Hermann, W.; Müller, A.; Ettzner, W.; Zimmermann, M. *Z. Naturforsch.* **1984**, *39B*, 876.

(4) Halbert, T. R.; McGauley, K.; Pan, W. H.; Czernuszewicz, R. S.; Stiefel, E. I. *J. Am. Chem. Soc.* **1984**, *104*, 1849.

(5) Cotton, F. A.; Llusar, R.; Marler, D. D.; Schwotzer, W. *Inorg. Chim. Acta* **1985**, *102*, L25.

(6) Shibahara, T.; Kuroya, H. *Polyhedron* **1986**, *5*, 357.

(7) Cotton, F. A.; Dori, Z.; Llusar, R.; Schwotzer, W. *J. Am. Chem. Soc.* **1985**, *107*, 6734.

(8) Martinez, M.; Ooi, B.-L.; Sykes, A. G. *J. Am. Chem. Soc.* **1987**, *109*, 4615.

(9) Sharp, C.; Sykes, A. G. *J. Chem. Soc., Dalton Trans.* **1988**, 2579.

(10) Ooi, B.-L.; Sharp, C.; Sykes, A. G. *J. Am. Chem. Soc.* **1989**, *111*, 125.

(11) (a) Ooi, B.-L.; Sykes, A. G. *Inorg. Chem.* **1988**, *27*, 310. (b) Hills, E. F.; Sykes, A. G. *J. Chem. Soc., Dalton Trans.* **1987**, 1397. (c) Harmer, M. A.; Richens, D. T.; Soares, A. B.; Thornton, A. T.; Sykes, A. G. *Inorg. Chem.* **1981**, *20*, 4155. (d) Richens, D. T.; Sykes, A. G. *Comments Inorg. Chem.* **1981**, *1*, 141. (e) Diebler, H.; Millan, C. *Polyhedron* **1986**, *5*, 539.