of the same acceptor suggests that the latter are weaker. Also the 1:2 adducts in both the earlier report and the present study have more negative ΔIS values than the 1:1 adducts indicating the expected decrease in stability. The difference is small probably suggesting that the second ligand is bound much more weakly than the first. We are presently investigating other adducts of tin(II) halides to determine how widely the observed ΔG–ΔIS relationship holds.

The relatively low solubility of the tin(II) halide adducts hampered solution studies of the compounds. Small solubility was found in aniline and some more polar solvents but the latter caused loss of trimethylamine apparently via displacement reactions especially in the case of the 1:2 adducts. Aniline was satisfactorily employed as a solvent for ^{1}H NMR studies of the 1:1 adducts which gave singlets for methyl proton resonances with the chemical shifts noted in the Experimental Section. In the case of the boron(III) halide–trimethylamine complexes, methyl proton chemical shifts are reported[8f] to reflect adduct stabilities, so it was of interest to ascertain whether any similar relationship exists in the $SnX_2 \cdot N(CH_3)_3$ adducts. The chemical shifts of the 1:1 species give a reasonably good linear correlation ($R = 0.994$) when plotted vs. ΔG. The validity of the correlation assumes the absence of ligand exchange processes but this was not proven experimentally. Again, the limited data available mitigate against broad interpretation of the relationship at the present time but it is, nevertheless, interesting that even a limited correlation should exist between proton magnetic resonance and Mössbauer isomer shifts in adducts such as these. Evidently both these parameters are directly influenced by the same flow of charge which gives rise to the donor–acceptor bonding.

NMR parameters are not presented for the 1:2 adducts because there was evidence from time-dependent changes in the NH_2 protons of the solvent (aniline) that dynamic processes were occurring in those solutions. The nature of these reactions has not yet been elucidated.

It was hoped initially that the infrared spectra of the adducts would also provide information concerning the strengths of the donor–acceptor interaction in the adducts. However, no sensible interpretation of the IR band complexation shifts, etc., could be made, in part because positive assignment of tin–nitrogen stretching modes was not possible with the instrumentation available. Strong broad bands were observed between 500 and 600 cm^{-1} which appeared to be associated with adduct formation. We may note in this regard that Donaldson et al.[14] also reported problems in the interpretation of IR spectra of the pyridine adducts of $SnCl_2$ and $SnBr_2$.

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Registry No. $SnF_2 \cdot N(CH_3)_3$, 63528-07-4; $SnCl_2 \cdot N(CH_3)_3$, 63528-08-5; $SnBr_2 \cdot N(CH_3)_3$, 63528-09-6; $SnI_2 \cdot N(CH_3)_3$, 63528-10-9; $SnF_2 \cdot 2N(CH_3)_3$, 63528-11-0; $SnCl_2 \cdot 2N(CH_3)_3$, 63528-12-1; $SnBr_2 \cdot 2N(CH_3)_3$, 63528-13-2; $SnI_2 \cdot 2N(CH_3)_3$, 63528-14-3; SnF_2, 7783-47-3; $SnCl_2$, 7772-99-8; $SnBr_2$, 10031-24-0; SnI_2, 10294-70-9.

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Magnetic Properties of Oxygen-Bridged Binuclear Chromium(III) Complexes with 2,2′-Bipyridine and 1,10-Phenanthroline

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Magnetic susceptibilities of dimers of the type $[(N\text{-}N)_2Cr(OH)_n(O)_{2-n}Cr(N\text{-}N)_2]^{n+2}$ ($n = 2, 1, 0$; N-N = 2,2′-bipyridine or 1,10-phenanthroline) have been measured within the temperature range 5–300 K. The results are interpreted in terms of an antiferromagnetic coupling giving singlet–triplet separations ranging from ca. 40 cm^{-1} ($n = 2$) to ca. 110 cm^{-1} ($n = 0$). For $n = 2$ the data were fitted by least squares to the Heisenberg isotropic exchange model. Inclusion of a biquadratic exchange term did not improve the fitting significantly. Slightly different coupling constants were found for different salts of the phenanthrolinediol ($n = 0$). Via the angular overlap model the results are compared with the antiferromagnetism in the μ-oxo-bis{pentaamminechromium(III)} ion.

Introduction

A number of papers from this laboratory[2–7] have dealt with oxygen-bridged polynuclear complexes of chromium(III) and cobalt(III), including studies of their molecular and crystal structures[2–4,6] and their spectral and magnetic properties.[6,7] Among the complexes were salts of $[Cr(N\text{-}N)_2OH]_n^{2n+}$, having N-N = 2,2′-bipyridine and 1,10-phenanthroline,[5] which were shown to be binuclear and thus to belong to the class of structures called diols.[5] Since these two chromium diols are rather robust over a wide pH range, it was possible to isolate and characterize[5] the perchlorates of the novel complex cations of the types μ-hydroxo-μ-oxo-bis[bis(N-N)chromium(III)] and

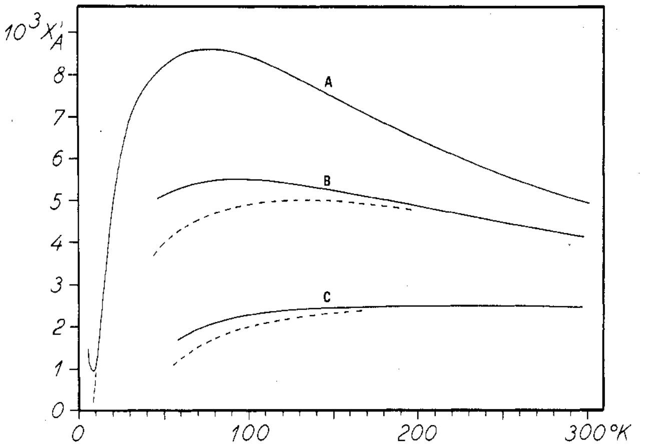

Figure 1. Magnetic susceptibilities of di-μ-oxygen-bridged 2,2′-bipyridinechromium(III) complexes. The solid lines each represent 800–1200 points of measurement. Dotted lines refer to calculated values according to the Heisenberg model with $g = 2$: (A) $[(bpy)_2Cr(OH)_2Cr(bpy)_2](ClO_4)_4 \cdot 2H_2O$ and calculated for $J = 37.41$ cm^{-1}; (B) $[(bpy)_2Cr(OH)OCr(bpy)_2](ClO_4)_3 \cdot 4H_2O$ and calculated for $J = 60$ cm^{-1}; (C) $[(bpy)_2CrO_2Cr(bpy)_2](ClO_4)_2 \cdot 2H_2O$ and calculated for $J = 120$ cm^{-1}.

di-μ-oxo-bis[bis(N-N)chromium(III)]. There are conflicting reports on the magnetic properties of salts of $[Cr(phen)_2OH]_2{}^{4+}$.[8-11] The magnetism of the other members of the two series has not been investigated earlier. They constitute excellent objects for studies of the influence of the bridging ligands on the magnitude of the magnetic coupling (exchange paths in the "superexchange models"). We expected a regular variation of the coupling parameters through each of the series, probably with similarities between corresponding bipyridine and phenanthroline complexes.

All the binuclear chromium(III) complexes studied earlier have indicated antiferromagnetic coupling which has been interpreted in terms of the Heisenberg–Dirac–Van Vleck model, in a few cases expanded by the inclusion of biquadratic and cubic exchange terms.[12] Ferromagnetism in chromium(III) systems has been found only in the coupling between the fourth nearest neighbors in ruby.[13] In binuclear complexes of other metals, ferromagnetism has been observed only in a few nickel(II) and copper(II) complexes.[12]

The two series of complexes discussed in this paper represent hitherto unknown intermediates between the weakly coupled acid rhodo, erythro, and other di-μ-hydroxo-chromium(III) complexes and the strongly coupled basic rhodo complex.

Experimental Section

Magnetic susceptibilities were determined by the Faraday method on powdered samples in the temperature range 5.0–300 K at magnetic fields in the range 5000–15 000 G (0.5–1.5 T). $Hg[Co(NCS)_4]$ was used as a calibrant.[14] The temperature was measured with a 0.07% Fe–Au vs. chromel thermocouple, calibrated against the vapor pressure of liquid helium, solid and liquid nitrogen, and solid carbon dioxide and against melting isopentane, diethyl ether, mercury, and water. The linearity was checked by the observation of Curie law behavior of $Gd_2(SO_4)_3 \cdot 8H_2O$. Preliminary reports on the automatically recording instrument have been presented earlier.[6,15] From two to five preparations of each complex followed by two or more susceptibility measurements in the temperature range 50–300 K were performed. The di-μ-hydroxo complexes were finally measured in the entire temperature range. The results are shown in Figures 1 and 2, representing typically 800–1200 points of measurements.

Preparations. The compounds were prepared as reported previously[5] for the basic complexes with minor modifications to improve the magnetic purity of the samples. The number of water of crystallization was determined by C, H, and N analyses. With the following modifications the reproducible results of Figures 1 and 2 were obtained.

$[(bpy)_2Cr(OH)OCr(bpy)_2](ClO_4)_3 \cdot 4H_2O$. This product was obtained as larger golden crystals when using twice the amounts of solvents (water at 70 °C and 2 M lithium hydroxide). The crystals were washed with 50 mL of concentrated aqueous ammonia, only, at 0 °C. For recrystallization 1 g was dissolved on the filter in about 100 mL of water at room temperature, and to the yellow solution was added 25 mL of concentrated ammonia, followed by 25 mL of saturated aqueous sodium perchlorate. The solution was cooled to 0 °C. The precipitate was washed with 10 mL of cold concentrated ammonia and dried over silica gel. Anal. Calcd for $[Cr_2(C_{10}H_8N_2)_4O(OH)](ClO_4)_3 \cdot 4H_2O$: C, 42.44; H, 3.65; N, 9.90; Cl, 9.39. Found: C, 42.9; H, 3.7; N, 10.0; Cl, 9.5.

$[(bpy)_2CrO_2Cr(bpy)_2](ClO_4)_2 \cdot 2H_2O$. The brown precipitate was allowed to crystallize from the cooled basic solution (0 °C) without adding sodium perchlorate. Anal. Calcd for $[Cr_2(C_{10}H_8N_2)_4O_2](ClO_4)_2 \cdot 2H_2O$: C, 48.25; H, 3.64; N, 11.25; Cl, 7.12. Found: C, 48.2; H, 3.7; N, 11.2; Cl, 6.2. The low chlorine content may be explained by substitution of perchlorate by hydroxyl ions from the strongly basic solution.

$[(phen)_2Cr(OH)OCr(phen)_2](ClO_4)_3 \cdot 2H_2O$. The brown crystals were washed with 100 mL of concentrated ammonia (0 °C). Anal. Calcd for $[Cr_2(C_{12}H_8N_2)_4O(OH)](ClO_4)_3 \cdot 2H_2O$: C, 48.36; H, 3.13; N, 9.40; Cl, 8.92. Found: C, 48.4; H, 3.2; N, 9.4; Cl, 9.2.

$[(phen)_2CrO_2Cr(phen)_2](ClO_4)_2 \cdot 5H_2O$. Lithium perchlorate in only 10% excess of the stoichiometric amount was used to precipitate the dark brown perchlorate from the cooled basic solution (0 °C). The product was dried over silica gel. Anal. Calcd for $[Cr_2(C_{12}H_8N_2)_4O_2](ClO_4)_2 \cdot 5H_2O$: C, 50.32; H, 3.70; N, 9.78; Cl, 6.19. Found: C, 50.5; H, 3.6; N, 9.8; Cl, 6.1.

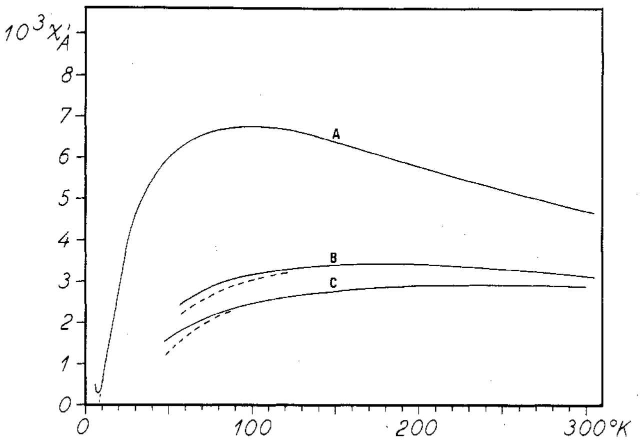

Figure 2. Magnetic susceptibilities of di-μ-oxygen-bridged 1,10-phenanthrolinechromium(III) complexes. The solid lines each represent 800–1200 points of measurement. Dotted lines refer to calculated values according to the Heisenberg model with $g = 1.986$: (A) $(-)_D[(phen)_2Cr(OH)_2Cr(phen)_2](ClO_4)_4 \cdot 3H_2O$ and calculated for $J = 44.87$ cm^{-1}; (B) $[(phen)_2Cr(OH)OCr(phen)_2](ClO_4)_3 \cdot 2H_2O$ and calculated for $J = 90$ cm^{-1}; (C) $[(phen)_2CrO_2Cr(phen)_2](ClO_4)_2 \cdot 5H_2O$ and calculated for $J = 105$ cm^{-1}.

Results

The magnetic susceptibilities of the oxygen-bridged complexes are shown in Figures 1 and 2. The temperature variations of the susceptibilities of the di-μ-hydroxo complexes were found to be close to the predictions of the simple Heisenberg model. By a least-squares procedure[16] the data were fitted to the Hamiltonian

$$H_{ab} = \sum_{a,b} g\beta HS + J \cdot S_a \cdot S_b - j(S_a \cdot S_b)^2 \qquad (1)$$

The data were corrected for diamagnetism. Constant susceptibility contributions (temperature-independent paramagnetism) and the molar fractions of chromium compounds with a Curie law temperature dependence (impurities) were used as parameters in the fitting procedure. The results are shown in Table I. It is seen that introducing the restriction $j = 0$ had no significant influence on the variance to degrees of freedom ratio. Hence, there is no statistical justification of the biquadratic term in the Hamiltonian in the present cases.

Table I. Results of the Digital Fitting Procedure for the Susceptibilities of the Di-μ-hydroxo Complexes

	$(-)_D[(phen)_2Cr(OH)_2Cr(phen)_2](ClO_4)_4\cdot 3H_2O$[21]		$[(bpy)_2Cr(OH)_2Cr(bpy)_2](ClO_4)_4\cdot 2H_2O$	
J, cm^{-1}	44.34 (9)[a]	44.87 (2)	36.97 (5)	37.41 (8)
j, cm^{-1}	0.06 (1)	Fixed to zero	0.06 (6)	Fixed to zero
g[b]	1.987 (3)	2.005 (2)	2.000 (2)	1.998 (3)
TIP, cgs units	4 (2) × 10^{-5}	5 (2) × 10^{-5}	2 (2) × 10^{-5}	3 (2) × 10^{-5}
Contamination with Curie behavior, mol %	0.15 (6)	0.17 (4)	0.7 (2)	0.7 (3)
Degrees of freedom (*f*)	895	895	785	785
Variance/*f*	1.08	1.20	0.30	0.35

[a] Numbers in parentheses indicate standard deviations. [b] Refer to the discussion of accuracy in the Results.

Table II. Singlet-Triplet Separations in Di-μ-oxygen Bridged Complexes

	J, cm^{-1}
$(-)_D[(phen)_2Cr(OH)_2Cr(phen)_2](ClO_4)_4\cdot 3H_2O$[a]	44.87 (2)
$[(phen)_2Cr(OH)_2Cr(phen)_2](NO_3)_4\cdot 4H_2O$	45
$[(phen)_2Cr(OH)_2Cr(phen)_2](NO_3)_4\cdot 8H_2O$	42
$[(phen)_2Cr(OH)OCr(phen)_2](ClO_4)_3\cdot 2H_2O$[b]	90
$[(phen)_2CrO_2Cr(phen)_2](ClO_4)_2\cdot 5H_2O$[c]	105
$[(bpy)_2Cr(OH)_2Cr(bpy)_2](ClO_4)_4\cdot 2H_2O$[a]	37.41 (8)
$[(bpy)_2Cr(OH)OCr(bpy)_2](ClO_4)_3\cdot 4H_2O$[d]	60
$[(bpy)_2CrO_2Cr(bpy)_2](ClO_4)_2\cdot 2H_2O$[e]	120

[a] For further details of parameter fitting see Table I. [b-e] Estimates of impurities of protonated forms: (*b*) 3%; (*c*) 4%; (*d*) 11%; (*e*) 5%.

Application of three independent energy parameters for the ground state made the fitting procedure diverge. The *g* factors obtained by susceptibility methods are correlated with the molecular weight assumed, the molar susceptibilities being proportional to g^2. The accuracy of the *g* factors should therefore not be evaluated from the standard deviations but merely from the accuracies of the elemental analyses of the samples. 1% is expected corresponding to 0.5% for the *g* factors. This explains why our fitting procedure could give *g* factors slightly exceeding 2, a result which obviously appears unreasonable.

The μ-oxo complexes all showed varying deviations from eq 1. Initially the susceptibilities varied from one sample to the next. This was not unexpected in view of the extreme preparative conditions. In accordance with analytical results and obvious intuitional feelings we considered minimum susceptibility as a criterion for maximum purity. This was our guide in optimizing the preparative procedure by which we obtained a maximum decrease in susceptibility of 7% at 60 K. The persistent deviations from the isotropic exchange model found for complexes with μ-oxo ligands were interpreted in terms of contamination with their protonated forms. No digital fitting of the data was attempted. The best and reproducible measurements are shown in Figures 1 and 2, and the resultant coupling parameters and estimated amounts of contamination obtained in this way are shown in Table II.

While the kinetic and thermodynamic stability of the diols in solution has been discussed previously,[5] it seems necessary to emphasize a few chemical properties of the μ-oxo-bridged complexes in relation to the magnetic properties. Firstly, the solubilities of the basic complexes as perchlorates are, not unexpectedly, much higher than those of the diols as seen from the isolation conditions given above. This problem combined with those introduced by the values of the acidity constants[5] could explain the presence of small fractions of the corresponding acid in the basic complexes. This would hardly be detectable in the elemental analyses but much more so in the susceptibilities at low temperatures. Secondly, in basic solution the simple acid–base equilibration competes with two different decomposition reactions, viz., cleavage of one or two oxygen bridges and replacement of one or more ligating nitrogens by hydroxyl ions. From previous experiments[5] we cannot exclude that these two reactions are both in operation. The first type of decomposition is expected to lead to the greater increase in susceptibility since the second type leaves the bridging system intact.

Our present experimental results do not favor one of the two explanations. The observation, for example, that the bipyridine complexes show the largest deviations from the Heisenberg model can be explained by their higher solubilities as well as by their faster rate of decomposition in basic solution. However, we interpret our results in terms of the explanation involving acid–base equilibria for two reasons. Firstly, only this assumption could give us a quantitative estimate of the amounts of impurities. Secondly, this will give us worse case estimates for the reasons mentioned above.

In view of these problems we do not consider our magnetic data for the μ-oxo-bridged complexes, in contrast to those for the diols, as sufficiently reliable to allow a detailed analysis of the magnetic coupling model, viz., inclusion of biquadratic exchange terms, etc. We have, however, obtained a good estimate of the singlet–triplet separations.

Discussion

The coupling constants found for the bipyridine- and phenanthrolinediols as seen from Table I are significantly larger than those published for other diols.[12] Our values for the phenanthrolinediol perchlorate and nitrate hydrates are comparable to those found for the chloride and iodide,[10,11] and it thus supports the doubt cast[11] on an earlier report on the iodide.[8] As seen from Table II the coupling constants are almost equal for different salts of the phenanthrolinediol. Surprisingly, we found no need to introduce biquadratic exchange terms but found perfect agreement with the simple isotropic coupling model. The effects of intermolecular coupling or a calibration error on the temperature scale in the earlier work[11] might be responsible for this difference.

As seen from Table II corresponding bipyridine and phenanthroline complexes give rise to comparable coupling constants, and apart from the di-μ-oxo-phenanthroline complex (see below) the bipyridine complexes show slightly smaller couplings than the corresponding phenanthroline complexes. The magnetic coupling between the chromium atoms in both series of complexes increases with each step of deprotonation. In the bipyridine series this variation is regular in contrast to the phenanthroline series. The relatively small increase in *J* in going from the μ-hydroxo-μ-oxo-phenanthroline complex may be caused by steric hindrance. From the recently elucidated molecular structures[10,11] of salts of the phenanthrolinediol it is known that the coordination geometry around the chromium atoms is distorted from the ideal octahedron. The two sets of almost parallel phenanthroline molecules in the dimer seem to repel each other. This may be caused by the π-electron clouds and is expected to increase inversely with the Cr–Cr distance which is likely to be shorter in the μ-oxo complexes. The separation between the planes of the two phenanthroline molecules is approximately 1.9 Å. The crystal structure of the pure ligand itself is not known. In the similar phenanthrene[17] the molecules are situated in a parallel ar-

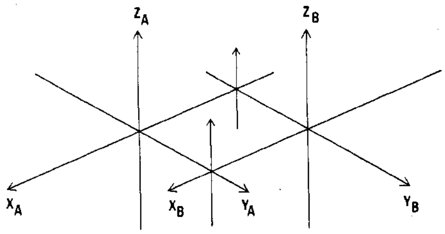

Figure 3. Skeleton of a di-μ-bridged chromium(III) dimer illustrated in a simplified rectangular coordinate system for definition of orbital overlaps of significance for the magnetic interactions.

rangement with a plane separation of 3.6 Å. The bipyridine molecules have a degree of freedom not present in phenanthroline, viz., a twist around the single bond making the two 2-pyridyl planes nonparallel. This twist, which is observed in several bipyridine complexes, will release the strain. This effect may also be responsible for the greater kinetic stability in solution of the μ-hydroxo bridges in the bipyridinediol.[5]

The magnetic properties of the μ-oxo-bis{pentaammine-chromium(III)} ion,[6] here referred to as the basic rhodo ion, have been interpreted in terms of the angular overlap model including configuration interaction with excited charge-transfer states.[7] A similar treatment is possible for the di-μ-oxo complexes. In analogy with the ligand field matrix elements for a single center[18] the two-center interactions may be defined[19]

$$\langle \mathrm{d_{ia}} | V_{\mathrm{ab}} | \mathrm{d_{jb}} \rangle = \sum_{\mathrm{q}} \sum_{\lambda\omega} \sum_{\mathrm{n}} (e_{\lambda\omega\mathrm{nqa}})^{1/2} (e_{\lambda\omega\mathrm{nqb}})^{1/2} F_{\lambda\omega}(\mathrm{d_{ia}}, \mathrm{L_{nq}}) F_{\lambda\omega}(\mathrm{d_{jb}}, \mathrm{L_{nq}}) \tag{2}$$

$\mathrm{d_i}$ refers to the d orbitals, $\lambda\omega$ to $\sigma,\pi x,\pi y$ bonding, n counts the common ligands L, q is the orbitals on these ligands, $F_{\lambda\omega}$ is a fractional overlap factor, and $e_{\lambda\omega\mathrm{nq}}$ is a semiempirical radial dependent parameter. In the basic rhodo ion the most important contribution to the magnetic coupling comes from π interactions of the types $\langle zx_{\mathrm{a}} | V_{\mathrm{ab}} | zx_{\mathrm{b}} \rangle$ and $\langle yz_{\mathrm{a}} | V_{\mathrm{ab}} | yz_{\mathrm{b}} \rangle$, where the z axis is defined as the fourfold axis through Cr–O–Cr. These "exchange paths" proceed via the oxygen p_x and p_y orbitals, giving rise to two maximum π overlaps.

The coordinate system of Figure 3 represents the di-μ-oxo complexes, assuming 90° bonding angles. The only nonzero metal interactions via the oxygens of importance for the ground states of the coupled $\mathrm{t_2}^3(\mathrm{a}) \times \mathrm{t_2}^3(\mathrm{b})$ configuration are $\langle zx_{\mathrm{a}} | V_{\mathrm{ab}} | yz_{\mathrm{b}} \rangle$ and $\langle yz_{\mathrm{a}} | V_{\mathrm{ab}} | zx_{\mathrm{b}} \rangle$. Both involve oxygen p_z orbitals. They correspond to two maximum π overlaps as for the basic rhodo ion, and not surprisingly they therefore give rise to identical exchange parameters. The $\mathrm{t_2}^3 \times \mathrm{t_2}^3$ configuration includes states with $S = 0$, 1, 2, and 3, and the low-spin charge-transfer configuration $\mathrm{t_2}^2\mathrm{t_2}^4$ includes $S = 0$, 1, and 2. As an example of the calculation of the interaction we calculate the quintet matrix element. The skeleton of the molecule consists of the metal and ligating atoms and has the symmetry D_{2h}. The z axis is assumed to be parallel to the z axes in Figure 3. The quintet functions are

$$\begin{aligned} |{}^5\mathrm{A_g}\rangle = (1/6^{1/2}) | & yz_{\mathrm{a}} zx_{\mathrm{a}} xy_{\mathrm{a}} (\overline{yz}_{\mathrm{b}} zx_{\mathrm{b}} xy_{\mathrm{b}} + yz_{\mathrm{b}} \overline{zx}_{\mathrm{b}} xy_{\mathrm{b}} \\ & + yz_{\mathrm{b}} zx_{\mathrm{b}} \overline{xy}_{\mathrm{b}}) - (\overline{yz}_{\mathrm{a}} zx_{\mathrm{a}} xy_{\mathrm{a}} + yz_{\mathrm{a}} \overline{zx}_{\mathrm{a}} xy_{\mathrm{a}} \\ & + yz_{\mathrm{a}} zx_{\mathrm{a}} \overline{xy}_{\mathrm{a}}) yz_{\mathrm{b}} zx_{\mathrm{b}} xy_{\mathrm{b}} \rangle \end{aligned} \tag{3}$$

$$\begin{aligned} |{}^5\mathrm{A_g}\mathrm{CT}\rangle = (1/2) | & zx_{\mathrm{a}} xy_{\mathrm{a}} yz_{\mathrm{b}} zx_{\mathrm{b}} \overline{zx}_{\mathrm{b}} xy_{\mathrm{b}} \\ & + yz_{\mathrm{a}} xy_{\mathrm{a}} yz_{\mathrm{b}} \overline{yz}_{\mathrm{b}} zx_{\mathrm{b}} xy_{\mathrm{b}} + yz_{\mathrm{a}} \overline{yz}_{\mathrm{a}} zx_{\mathrm{a}} xy_{\mathrm{a}} yz_{\mathrm{b}} xy_{\mathrm{b}} \\ & + yz_{\mathrm{a}} zx_{\mathrm{a}} \overline{zx}_{\mathrm{a}} xy_{\mathrm{a}} zx_{\mathrm{b}} xy_{\mathrm{b}} \rangle \end{aligned} \tag{4}$$

Here CT refers to the charge-transfer configuration and bars indicate β spins. The matrix element of configuration interaction is

$$\begin{aligned} \langle {}^5\mathrm{A_g} | V_{\mathrm{ab}} | {}^5\mathrm{A_g}\mathrm{CT} \rangle & = -(1/24^{1/2})(4\langle zx_{\mathrm{a}} | V_{\mathrm{ab}} | yz_{\mathrm{b}} \rangle + 4\langle yz_{\mathrm{a}} | V_{\mathrm{ab}} | zx_{\mathrm{b}} \rangle) \\ & = -(4/6^{1/2}) e_{\pi\mathrm{O}} \end{aligned} \tag{5}$$

$e_{\pi\mathrm{O}}$ is the π-bonding parameter for oxygen, connected to the spectroscopic parameter Δ for oxygen through the equation $\Delta = \Delta_\sigma - \Delta_\pi = 3e_\sigma - 4e_\pi$. In a similar way the other matrix elements are obtained as

$$\begin{aligned} \langle {}^3\mathrm{B_{2u}} | V_{\mathrm{ab}} | {}^3\mathrm{B_{2u}}\mathrm{CT} \rangle & = -(40^{1/2}/3) e_{\pi\mathrm{O}} \\ \langle {}^1\mathrm{A_g} | V_{\mathrm{ab}} | {}^1\mathrm{A_g}\mathrm{CT} \rangle & = -(4/3^{1/2}) e_{\pi\mathrm{O}} \end{aligned} \tag{6}$$

In first order the ground states are suppressed proportional to the squares of these matrix elements and inversely proportional to the energy of the charge-transfer states. If the energies of these states are assumed to be high and equal, the result is an antiferromagnetic coupling according to the Landé rule, equally well described by the Heisenberg spin Hamiltonian $H_{\mathrm{ab}} = J{\cdot}S_{\mathrm{a}}{\cdot}S_{\mathrm{b}}$ with $J = (8/9)e_{\pi\mathrm{O}}{}^2/E_{\mathrm{CT}}$. The same result was found for the basic rhodo ion. In this model deviations from the Landé rule can be explained in terms of different energies of the $^5\mathrm{A_g}$, $^3\mathrm{B_{2u}}$, and $^1\mathrm{A_g}$ states of the $\mathrm{t_2}^2\mathrm{t_2}^4$ charge-transfer configuration. The splitting of these is caused by two-center exchange interactions and therefore expected to be small. Only in accidental cases such a splitting would cause deviations from Landé rule for the four ground states in a way described by the two-parameter model including J and j. We refer to Table I where it is shown that our susceptibility data for the di-μ-hydroxo complexes showed no evidence of deviations from Landé rule corresponding to a biquadratic exchange term.

As seen from Table II, the J values for the di-μ-oxo complexes are significantly smaller than 450 cm^{-1} as found for the basic rhodo complex.[6] Several factors may be of importance for this difference. Firstly, the Cr–O distances are likely to be larger than the 1.80 Å as found in the basic rhodo ion, and the radial parameter e_π decreases strongly with increasing distance. Secondly, the zx and yz orbitals responsible for the magnetic coupling are involved in the ligand π orbitals in the phenanthroline and bipyridine complexes but not in the basic rhodo ion. The extent of this effect is not known. Thirdly, the Cr–Cr distance in the di-μ-oxo complexes is expected to be slightly smaller than 2.9 Å as found for the phenanthrolinediol and thereby much smaller than 3.60 Å as in the basic rhodo complex. Direct metal interactions of the types $\langle xy_{\mathrm{a}} | V_{\mathrm{ab}} | xy_{\mathrm{b}} \rangle$ and $\langle xy_{\mathrm{a}} | V_{\mathrm{ab}} | z^2{}_{\mathrm{b}} \rangle$ give antiferromagnetic and ferromagnetic contributions, respectively. These contributions are probably small and negligible, respectively. Fourthly, the Cr–O–Cr angles are likely to exceed 90° as found in the phenanthrolinediol.[10,11] Thereby the π interactions via oxygen p_z orbitals remain unchanged for fixed distances, and p_x and p_y orbitals become involved in further π bonding. The relative importance of this can be calculated via the angular overlap model once structural data are available.

The magnetic coupling in μ-hydroxo complexes are persistently smaller than in the corresponding μ-oxo complexes. In terms of the angular overlap model this is difficult to understand unless it is assumed that the hydrogen atom is placed out of the xy plane in Figure 3. Otherwise the oxygen p_z orbital and thereby $\langle zx_{\mathrm{a}} | V_{\mathrm{ab}} | yz_{\mathrm{b}} \rangle$ and J would remain unchanged on protonation. Out-of-plane bonding would, however, highly decrease the π bonding. The slight difference in bond lengths expected can hardly account for the difference in coupling. We therefore suggest a hydrogen position in μ-hydroxo complexes somewhat related to that expected for an sp^3 hybridization on oxygen as it was recently found for the carbon atom in di-μ-methoxy complexes.[20]

If x-ray and neutron diffraction data were available, most of our qualitative arguments could become semiquantitative within the framework of the angular overlap model. The overwhelming problem will be the process of growing large crystals of the μ-oxo complexes.

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Registry No. $(-)_D[(phen)_2Cr(OH)_2Cr(phen)_2](ClO_4)_4$, 59204-27-2; $[(phen)_2Cr(OH)_2Cr(phen)_2](NO_3)_4$, 31351-95-8; $[(phen)_2CrO(OH)Cr(phen)_2](ClO_4)_3$, 31351-96-9; $[(phen)_2CrO_2Cr(phen)_2](ClO_4)_2$, 31282-17-4; $[(bpy)_2Cr(OH)_2Cr(bpy)_2](ClO_4)_4$, 31418-78-7; $[(bpy)_2CrO(OH)Cr(bpy)_2](ClO_4)_3$, 31542-02-6; $[(bpy)_2CrO_2Cr(bpy)_2](ClO_4)_2$, 31282-16-3.

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Di-μ-oxo, μ-Oxo-μ-sulfido, and Di-μ-sulfido Complexes of Molybdenum(V) with EDTA, Cysteine, and Cysteine Ester Ligands. Preparation and Electrochemical and Spectral Properties

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Preparative methods and electrochemical and spectral properties are reported for binuclear Mo(V) complexes containing di-μ-oxo ($Mo_2O_4^{2+}$), μ-oxo-μ-sulfido ($Mo_2O_3S^{2+}$), and di-μ-sulfido ($Mo_2O_2S_2^{2+}$) centers coordinated to EDTA, cysteine, and ethyl cysteinate ligands. The μ-oxo-μ-sulfido complexes are prepared here for the first time, and improved synthetic procedures are reported for the di-μ-sulfido complexes. Infrared and electronic absorption spectra of these compounds are sensitive to substitution of sulfur atoms into the bridge system. The systematic changes upon bridge modification are useful in characterizing the compounds and in clarifying assignments of Mo–O and Mo–S bridge stretching frequencies. The EDTA and cysteine complexes undergo electrochemical reduction in a single four-electron step to Mo(III) dimers in aqueous buffers. Although the ease of reduction and electrochemical reversibility of the $Mo^V{}_2/Mo^{III}{}_2$ couple increase with insertion of S into the bridge system, the Mo(III) dimers become increasingly unstable upon bridge sulfur substitution. The corresponding ethyl cysteinate complexes are reduced by successive one-electron transfers in dimethyl sulfoxide to Mo^V–Mo^{IV} and $Mo^{IV}{}_2$ species. The chemical stability of these reduced products increases in the sequence $Mo_2O_4 < Mo_2O_3S < Mo_2O_2S_2$. The different behavior of sulfido bridging is attributed to greater lability of Mo^{III}–S bonds in the former case and to greater electron delocalization by sulfur atoms over the binuclear framework in the latter.

Binuclear molybdenum(V) complexes are currently of interest as models for the redox centers of molybdenum-containing enzymes. A number of complexes containing di-μ-oxo and di-μ-sulfido bridging units have been prepared,[1-8] and the structural features and physical and chemical properties of these compounds have been discussed in recent reviews.[9-12] Relatively little has been reported on species containing the intermediate μ-oxo-μ-sulfido bridging moiety. Preparation and study of such compounds would be of interest in understanding the effect of sulfur-bridging atoms on the properties of the binuclear molybdenum unit.

We have previously reported on the electrochemical[13,14] and catalytic[15,16] properties of the di-μ-oxo species $Mo_2O_4(EDTA)^{2-}$ and $Mo_2O_4(Cys)_2{}^{2-}$. The latter compound is one of the most widely studied chemical models for the molybdenum-containing site of nitrogenase,[17] and its behavior mimics that of the enzyme in many respects. As a continuation of our studies on the redox properties of binuclear molybdenum centers, we have synthesized a series of complexes containing $Mo_2O_3S^{2+}$ cores coordinated to EDTA, cysteine, and ethyl cysteinate ligands. The spectral and electrochemical properties of these compounds are reported in this paper and compared with those of the $Mo_2O_4^{2+}$ and $Mo_2O_2S_2^{2+}$ analogs. The results of this study demonstrate that replacement of oxygen by sulfur bridging atoms exerts a significant and systematic influence on the infrared and electronic spectral properties and electrochemical behavior of the binuclear molybdenum(V) unit.

During the course of this work it was found that some procedures previously published for preparation of di-μ-sulfido complexes could not be applied successfully to the compounds we wished to prepare. In addition, no synthetic methods were available for preparation of μ-oxo-μ-sulfido complexes. In this work simple synthetic procedures are described which are generally applicable to the direct preparation of complexes containing $Mo_2O_3S^{2+}$ and $Mo_2O_2S_2^{2+}$ cores and which are particularly effective for preparation of the water-soluble sulfido-bridged Mo(V) derivatives. Since the completion of this work several μ-O-μ-S bridged Mo(V) complexes with