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Magnetic and Electrochemical Properties of Transition Metal Complexes with Multiple Metal-to-Metal Bonds. II. $[Ru_2(C_3H_7COO)_4]^{n+}$ with $n = 0$ and 1

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Average magnetic susceptibilities of $[Ru_2(C_3H_7COO)_4]Cl$ in the solid state in the temperature interval 60–300 K and in solution at 300 K are interpreted in terms of a quartet ground state which has $g_{av} = 2.13$ and large positive zero-field splitting ($2D \approx 12$ cm^{-1}) and shows weak antiferromagnetic exchange coupling in the solid state. Frozen-solution esr spectra at 77 and 4.2 K are in accordance with this and give $g_\parallel = 2.1 \pm 0.1$ and $g_\perp = 2.18$. The hyperfine pattern observed at 4.2 K is interpreted in terms of coupling to two equivalent ruthenium nuclei. $|A_\parallel| = (9 \pm 3) \times 10^{-3}$ cm^{-1} and $|A_\perp| = (31 \pm 1) \times 10^{-4}$ cm^{-1} for ^{99}Ru. Rotating-disk electrode polarography and cyclic voltammetry show that $[Ru_2(C_3H_7COO)_4]^+$ can be reduced through a quasireversible transfer of a single electron. The value of $E_{1/2}$ varies from 0.00 to −0.34 V vs. sce depending on the solvent. Complex formation with chloride ions is found to be a slow process which has an important effect upon the redox behavior in dichloromethane solution.

Introduction

Of the numerous compounds now known which contain multiple metal-to-metal bonds, those of the type $Ru_2(O_2CR)_4X$ (X = a univalent ion) are of special interest because they contain the metal atoms in formally different oxidation states (+2, +3) and because they have been reported to have three unpaired electrons.[1] The structure of one representative member of the series, $Ru_2(O_2CC_3H_7)_4Cl$, has been determined, and a tentative suggestion has been put forward to account for the presence of three unpaired electrons rather than only one.[2] However, the data concerning the magnetic and electrochemical properties of these systems have been very scant and much more detailed knowledge was considered necessary as a basis for more thoroughly understanding their electronic structures. This paper provides such data.

Experimental Section

Esr spectra were recorded on the instruments described in part I of this series.[3]

Magnetic Susceptibilities. Measurements on the solid state were made by the Faraday method by S. Kallesoe, Chemistry Department I, H. C. Orsted Institute, Copenhagen. An earlier version of the instrument has been described briefly.[4] Later modifications include application of a Hall probe field-controlled, magnet power supply giving a magnetic field that varies as a trapezoidal function of time. The temperature is continuously variable according to linear or nonlinear programs. The force on the sample is recorded by a Cahn RG electrobalance. At zero and maximum magnetic fields the force and corresponding temperature are punched on paper tape *via* analog to digital converters thus allowing direct computer processing. The measurements were performed relative to $Hg[Co(NCS)_4]$[5] and are believed to have absolute accuracy of 0.5%. Reproducibility and noise level of the instrument is at least 10 times better, however. Measurements on solutions were performed using the Gouy method and the nmr method[6] on a Varian HA 100 nmr spectrometer. Aqueous solutions of nickel(II) chloride were used as calibrants.

Electrochemical reactions were studied by cyclic voltammetry and rotating-disk electrode polarography employing a Beckman "Electroscan 30" with accessories.

The $[Ru_2(C_3H_7COO)_4]Cl$ was prepared according to the literature method.[1] The product was recrystallized twice from butyric acid.

Results

Static Susceptibility Measurements. Measurements of susceptibilities of methanol solutions of two different samples with the concentrations 1 and 3% w/w according to the nmr and Gouy methods all gave the result $\chi'_M = (6.91 \pm 0.05) \times 10^{-3}$ cgsu/mol at 300 K with a diamagnetic correction of -278×10^{-6}. This value differs approximately 35% from an earlier measurement.[1]

Faraday measurements on two powdered samples in the temperature range 60–300 K showed Curie–Weiss temperature dependence. The results were fitted by a least-squares procedure to the polynomial expression

Table I. Coefficients and Standard Deviations for the Magnetic Susceptibility of $[Ru_2(C_3H_7COO)_4]Cl$ According to Eq 1

n	a_n	σ_n
0	6.6	0.6
1	0.472	0.003
2	2.5×10^{-5}	4.1×10^{-5}

$$1/\chi'_M = \sum_n a_n T^n \qquad (1)$$

where T is the absolute temperature. From 1056 measurements two sets of 56 were randomly selected for the fitting procedure. The results are shown in Table I. All values of a_n for $n \geq 2$ were smaller than their standard deviations. At 300 K $\chi'_M = 6.74 \times 10^{-3}$ cgsu. The value of a_0 corresponds to a Weiss constant $\Theta = 14°$ and shows that $\partial\mu_{eff}/\partial T > 0$ as also found for the corresponding acetate complex.[1] The value of a_1 corresponds to $g_{av} = 2.13$ and 4.76 for spin quartet and doublet ground states, respectively. The assumption of a doublet ground state with $g_{av} = 4.76$ is inconsistent with the esr spectra discussed later.

In terms of the crystal structure,[2] showing that the chloride ions bridge adjacent dinuclear cations to form infinite zigzag chains, it is reasonable to suggest that the positive value of a_0 can be attributed to antiferromagnetic interactions between spin quartet states. Our data agree within the experimental uncertainty with a Heisenberg exchange model with the Hamiltonian $\mathcal{H} = JS_1S_2$ and with interaction between two spins of $S = {}^3/_2$, $g_{av} = 2.13$ and $J = 7.8$ cm^{-1}. In this fitting procedure we used the complete exponential expression for the susceptibility without any high-temperature approximations. In the high-temperature limit ($T >> J/k$) the susceptibility of such a system is of the form

$$\chi kt/Ng^2\mu^2 = \frac{5}{4}(1 - \frac{\alpha}{T}) \qquad (2)$$

where χ is the susceptibility per $S = {}^3/_2$ system, and α has the value $\alpha = 5J/4K$. The esr spectra discussed later show that the quartet state is not localized on a single ruthenium atom and a rigorous treatment of the exchange interaction would therefore include at least nearest neighbor interactions throughout infinite chains. For values of J/kT relevant here it has, however, been shown[7] that the susceptibility is almost independent of the length of the chain.

The high-temperature approximation of the susceptibility

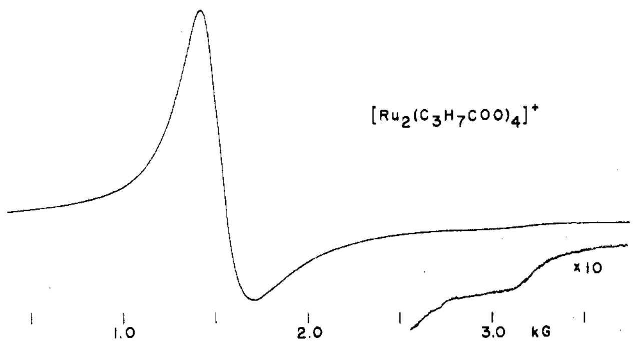

Figure 1. Frozen-solution esr spectrum of $[Ru_2(C_3H_7COO)_4]Cl$ in methanol at 77 K and 9.14 GHz.

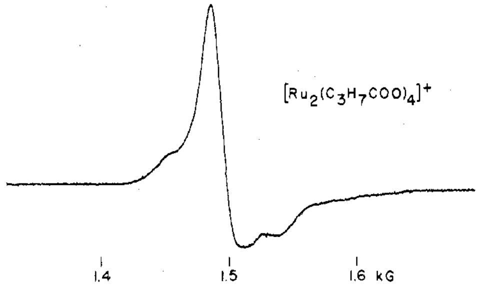

Figure 2. Frozen-solution esr spectrum of $[Ru_2(C_3H_7COO)_4]Cl$ in methanol at 4.2 K and 9.186 GHz. No other lines were observable below 9000 G.

of an infinite linear chain of spins with $S = {}^3/_2$ according to the Ising model with the Hamiltonian

$$\mathcal{H} = -2J\sum_i S_z^i S_z^{i+1} - g\mu H \sum_i S_z^i \tag{3}$$

is given by an expression similar to eq 2, but with $\alpha = 5J/k$.[8] Our data do, of course, fit equally well to this expression.

The deviation from the Curie law could be interpreted in terms of zero-field splitting of the quartet states. In this case

$$\chi = \frac{Ng^2\mu^2}{4kT}\,\frac{1 + 9\exp(-2D/kT)}{1 + \exp(-2D/kT)} \tag{4}$$

where $2D$ is the zero-field splitting. In the high-temperature limit eq 4 is equivalent to eq 2 with $\alpha = -4D/5k$. This model requires $2D = 24.3$ cm^{-1}, a value not in disagreement with the esr spectra. In this model χ is of course unaffected by magnetic dilution.

Equation 2 predicts $\chi'_M = 7.08 \times 10^{-3}$ cgsu at 300 K for a dilute solution ($\alpha = 0$). The experimental value was $(6.91 \pm 0.05) \times 10^{-3}$. This suggest that zero-field splitting is important and that there is a small antiferromagnetic interaction in the solid state where the susceptibility is 6.74×10^{-3} cgsu at 300 K. In the high-temperature limit the contributions to α from zero-field splitting and exchange interaction are additive, and we therefore obtain the crudely estimated parameters $2D \approx 12$ cm^{-1} and $J \approx 4$ cm^{-1} from eq 2 and 4. Measurements at temperatures lower than 60 K would greatly improve the accuracy of these numbers. The results of the foregoing comparison between susceptibilities of the solid and the solution might be questioned in view of the observation that complex formation in solution has some importance for the redox behavior. However, as discussed later there is no evidence from the esr spectra that complex formation with different solvents has any significant influence on the magentic properties.

Esr Spectra. The frozen-solution X-band spectra at 77 and 4.2 K are shown in Figures 1 and 2, respectively. Spectra were identical in each of the following solvents: methanol, dichloromethane, and dimethylformamide–water–methanol in the volume ratios 1:1:2. At 77 K the line widths are very large and temperature dependent, probably because of relaxation phenomena. The hyperfine pattern is not visible and only approximate g factors can be obtained. The relevant spin Hamiltonian is

$$\begin{aligned}\mathcal{H} = {}& \mu[g_\parallel H_z S_z + g_\perp(H_x S_x + H_y S_y)] + \\ & D[S_z^2 - S(S+1)/3] + E(S_x^2 - S_y^2) + \\ & A_\parallel S_z(I^1{}_z + I^2{}_z) + A_\perp[S_x(I^1{}_x + I^2{}_x) + \\ & S_y(I^1{}_y + I^2{}_y)]\end{aligned} \tag{5}$$

for $S = {}^1/_2$ or ${}^3/_2$ with the D and E terms absent for $S = {}^1/_2$. The spectrum in Figure 1 gives $g_\parallel = 2.10 \pm 0.10$ and $g_\perp = 4.20 \pm 0.10$ ($g_{av} = 3.4 \pm 0.2$) in terms of an $S = {}^1/_2$ system or $g_\parallel = g_\perp = 2.10 \pm 0.10$ in terms of an $S = {}^3/_2$ system with $|2D| \gg g\mu H$. A comparison with the static susceptibility data rules out the first possibility. The X- and Q-band spectra showed no additional lines below 18,000 G. We therefore conclude[9] that $|2D| > 2.2$ cm^{-1}. For such a system the position of the low-field line will correspond to $2g_\perp$ and the Hamiltonian eq 5 is simplified to the doublet Hamiltonian, and the earlier described[3] diagonalization and computer simulation procedure can be applied.

At 4.2 K the hyperfine pattern is partly revealed. Because of the rather low signal-to-noise level of the liquid helium temperature spectrometer the parallel orientation lines, expected around 3100 G, as observed at 77 K with a Varian E-6 spectrometer, were not detected. These lines are expected to have approximately 1% of the intensities of the perpendicular lines[9] at 1500 G. A low-intensity spectrum at 4.2 K could be explained in terms of a negative D value. But there was no evidence of increasing intensity with increasing temperature in agreement with the sign of D obtained from static susceptibility measurements.

Naturally occurring ruthenium consists of seven different isotopes, two of which have nonzero nuclear magnetic moments, thus giving rise to the six magnetically different dimers as shown in Table II.

Table II. Magnetically Different Ruthenium Dimers[a]

Compn	% abundance	I^1	I^2	μ^1	μ^2
^{99}Ru–^{99}Ru	1.64	$^5/_2$	$^5/_2$	−0.63	−0.63
^{99}Ru–^{101}Ru	4.36	$^5/_2$	$^5/_2$	−0.63	−0.69
^{101}Ru–^{101}Ru	2.88	$^5/_2$	$^5/_2$	−0.69	−0.69
^{99}Ru–Ru	17.98	$^5/_2$	0	−0.63	0
^{101}Ru–Ru	23.84	$^5/_2$	0	−0.69	0
Ru–Ru	49.29	0	0	0	0

[a] Ru without superscript refers to the nonmagnetic nuclei ^{96}Ru, ^{98}Ru, ^{100}Ru, ^{102}Ru, and ^{104}Ru.

Computer simulation showed that nuclear species with $J = I^1 + I^2 = 5$ (8.88%) would have lines with intensities too low to be observed with the applied spectrometer, even if these lines were well separated from other lines. The two outer lines in Figure 2 are thus ascribed to $J = {}^5/_2$ (41.82%) and directly give the total multiplet splitting ($5A_\perp$). The result of a computer simulation including $J = 0$ and $J = {}^5/_2$ species with the parameters $g_\parallel = 2.03$, $g_\perp = 2.18$, $A_\parallel = 93 \times 10^{-4}$ cm^{-1}, and $A_\perp = 31 \times 10^{-4}$ cm^{-1} (A values for $\mu = -0.63$) is shown in Figure 3. The value of $g_\parallel$ was chosen to give the g_{av} value determined earlier but was unimportant for this part of the spectrum. $A_\parallel$ has an influence on the second-order shifts of the perpendicular orientation lines. A series of simulations revealed that $2|A_\perp| < |A_\parallel| < 4|A_\perp|$. The information directly obtained from the liquid helium temperature spectrum is $g_\perp = 2.18$, $|A_\perp| = 31 \times 10^{-4}$ cm^{-1}, and $|A_\parallel| = (9 \pm 3) \times 10^{-3}$ cm^{-1}.

The esr spectra do not conclusively settle the question of magnetic equivalence of the two ruthenium nuclei but show that it is unreasonable to assume that the quartet state is

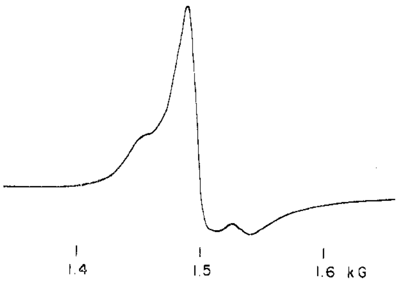

Figure 3. Computer-simulated random orientation esr spectrum including the following species: 49.27% with $S = {}^3/_2, I = 0, g_{\parallel} = 2.03, g_{\perp} = 2.18$; 17.86% with $S = {}^3/_2, I = {}^5/_2$, unchanged g factors, $A_{\parallel} = 93 \times 10^{-4}$ cm^{-1}, $A_{\perp} = 31 \times 10^{-4}$ cm^{-1} ($\mu = -0.63$ BM); 23.96% with $S = {}^3/_2, I = {}^5/_2$, unchanged g factors, and A values corresponding to $\mu = -0.69$. Single-molecule spectra with lorentzian line widths of 25 G were added for every step of 0.1° in the polar angle θ. Only the perpendicular orientation part of the spectrum is shown.

localized at one of the ruthenium nuclei in the dimers. This would correspond to 29.79% having $I = {}^5/2$ and 70% having $I = 0$ which is not in agreement with the intensities observed in Figure 2.

Electrochemical Properties. Rotating-disk electrode polarography and cyclic voltammetry were investigated at 25° at platinum, gold, and carbon electrodes in the following solvents: (A) 0.1 *M* TBAP in dichloromethane, (B) 0.1 *M* TEAC in dichloromethane, (C) 0.1 *M* TBAP in acetonitrile, (D) 0.1 *M* TEAC in acetonitrile, (E) 0.1 *M* TBAP in ethanol, and (F) 0.1 *M* TEAC in ethanol (TBAP = tetrabutylammonium perchlorate and TEAC = tetraethylammonium chloride). The results were almost independent of the electrode material but medium dependent. The maximum potential range covered was −2 to +2 V *vs.* sce in solvent C. The other solvents imposed narrower potential intervals. Apart from completely irreversible and complicated reactions below −1.1 and above +1.6 *vs.* sce the only redox reaction for $[Ru_2(C_3H_7COO)_4]Cl$ is a reduction in the potential range 0 to −0.4 V *vs.* sce, with the exact voltage being dependent on the medium. In solvent A a two-step reduction is observed; in all other solvents, only a single-step reduction. Examples of cyclic voltammograms are shown in Figures 4 and 5.

In the two-step reduction in Figure 4 with approximate $E_{1/2}$ values of 0.00 and −0.34 V *vs.* sce the peak currents of the reaction at 0.00 V gradually decreased and peak currents at −0.34 V simultaneously increased by addition of chloride ions. At a concentration of 0.1 *M* as in solvent B the reaction at 0.00 V has disappeared as seen from Figure 5. The potential separations between the cathodic and anodic peaks of the two reactions are independent of the chloride concentration but strongly dependent on the potential sweep rate. For very slow potential sweeps (2 mV sec^{-1}) the peak separation for both steps approached 60 mV. The ratios between the peak currents $i_p{}^c/i_p{}^a$ of each step remain 1.0 ± 0.1 independent of the sweep rate and the chloride concentration. The ratio betweeen the cathodic peak currents of the two steps was independent of the potential sweep rate in the range 200–2 mV sec^{-1}. We interpret these observations in terms of the reaction scheme shown in eq 6. One or two chloride ions may be involved. Since two separate reduction reactions are observed the rate constants for the chloride complex formation reaction are small.

In the other solvents, B to F, where either the solvent or the added chloride ions can act as ligands, single-electron quasireversible reductions were observed. In all cases $i_p{}^a/i_p{}^c = 1$, and $i_p{}^c\nu^{-1/2}$ and $\Psi\nu^{1/2}$ were independent of ν. ν is the potential sweep rate, and Ψ is the dimensionless reaction parameter for a quasireversible electron transfer defined according to Nicholson.[10] The values of $E_{1/2}$ were 0.00 V *vs.* sce in solvents C and E, −0.15 V in F, and −0.34 V in B.

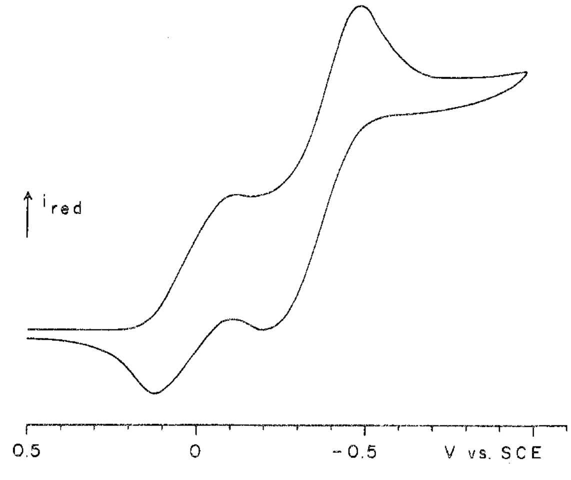

Figure 4. Cyclic voltammogram for $[Ru_2(C_3H_7COO)_4]Cl$ in 0.1 *M* tetrabutylammonium perchlorate in dichloromethane; potential sweep rate 10 mV sec^{-1}

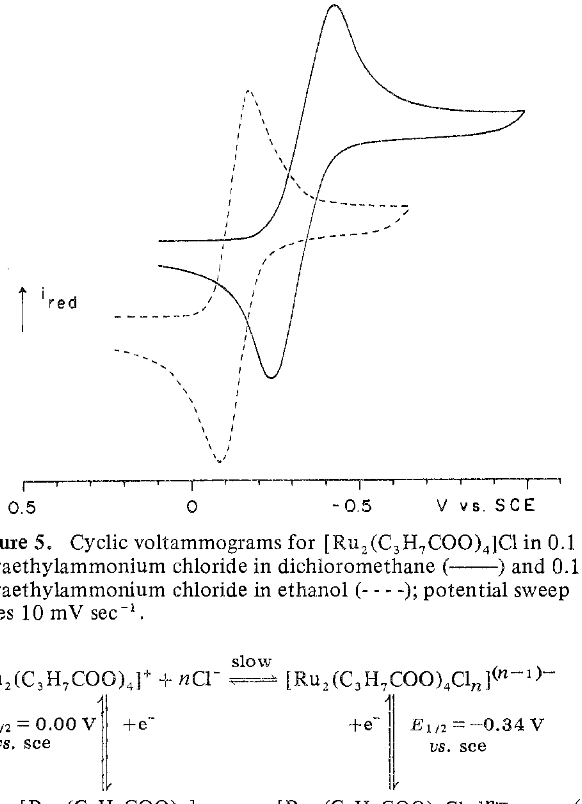

Figure 5. Cyclic voltammograms for $[Ru_2(C_3H_7COO)_4]Cl$ in 0.1 *M* tetraethylammonium chloride in dichloromethane (——) and 0.1 *M* tetraethylammonium chloride in ethanol (- - - -); potential sweep rates 10 mV sec^{-1}.

$$\begin{tikzcd}
{[Ru_2(C_3H_7COO)_4]^+ + nCl^-} \arrow[r, shift left, "\text{slow}"] \arrow[d, shift left, "+e^-"] \arrow[d, leftarrow, shift right, "{E_{1/2} = 0.00\ \text{V}\ \textit{vs.}\ \text{sce}}"'] & {[Ru_2(C_3H_7COO)_4Cl_n]^{(n-1)-}} \arrow[l, shift left] \arrow[d, shift right, "+e^-"'] \arrow[d, leftarrow, shift left, "{E_{1/2} = -0.34\ \text{V}\ \textit{vs.}\ \text{sce}}"] \\
{[Ru_2(C_3H_7COO)_4]} \arrow[d, "\text{slow}"'] & {[Ru_2(C_3H_7COO)_4Cl_n]^{n-}} \arrow[d, "\text{slow}"'] \\
\text{decompn products} & \text{decompn products}
\end{tikzcd} \qquad (6)$$

Rotating-disk electrode polarograms gave rise to plots of E *vs.* log $(i_L - i)/i$ with slopes decreasing with ν and the rate of rotation. In solvent B, for example, at $\nu = 2$ mV sec^{-1} and 0.5 rotations sec^{-1} the slope was 70 mV, close to the value of 60 mV expected for a single-electron transfer but still slightly dependent upon the rotation rate.

Properties of $[Ru_2(C_3H_7COO)_4]$. In spite of many attempts[11] crystalline samples of $[Ru_2(RCOO)_4]$ have never been obtained, although the species probably exist in solution. We were unable to change this state of affairs. A thorough investigation of the magnetic properties was therefore impossible. For such a system with an even number of electrons a singlet or triplet ground state could be expected.

Electrolytic reduction of $[Ru_2(C_3H_7COO)_4]Cl$ in solution did not give rise to extra peaks in the frozen-solution esr spectrum at 77 K. The black powdered material prepared in a similar way as the corresponding diruthenium tetraacetate[11] was close to being diamagnetic. This provides an indication that the ground state may be a singlet.

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Registry No. $[Ru_2(C_3H_7COO)_4]Cl$, 53370-31-3.

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Magnetic and Electrochemical Properties of Transition Metal Complexes with Multiple Metal-to-Metal Bonds. III. Characterization of Tetrapotassium and Tripotassium Tetrasulfatodimolybdates

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The compounds $K_4Mo_2(SO_4)_4{\cdot}2H_2O$ (**1**) and $K_3Mo_2(SO_4)_4{\cdot}3.5H_2O$ (**2**) have been prepared by reaction of $K_4Mo_2Cl_8$ with 0.1 *M* sulfuric acid at 25°. Both compounds have been identified and structurally characterized by X-ray crystallography. The former is the hydrate of a compound previously reported by Bowen and Taube; the latter is a new, paramagnetic compound. Compound **1** crystallizes in space group $C2/c$ with unit cell dimensions $a = 17.206$ (3) Å, $b = 10.193$ (2) Å, $c = 10.061$ (2) Å, and $\beta = 94.92$ (2)°, $Z = 4$; 1217 reflections for which $F_o^2 > 3\sigma(F_o^2)$ were used to solve and refine the structure to $R_1 = 0.028$ and $R_2 = 0.036$. Compound **2** also crystallizes in space group $C2/c$. The unit cell dimensions are $a = 30.654$ (4) Å, $b = 9.528$ (1) Å, $c = 12.727$ (1) Å, and $\beta = 97.43$ (1)°, $Z = 8$; 2341 reflections with $F_o^2 > 3\sigma(F_o^2)$ were used to solve and refine the structure to $R_1 = 0.026$ and $R_2 = 0.033$. The important structural unit in each compound is the $Mo_2(SO_4)_4{}^{n-}$ ion in which four bidentate sulfate ions, related by a fourfold axis, serve as bridges across the strongly bonded pair of molybdenum atoms. The $Mo_2(SO_4)_4{}^{4-}$ ion is diamagnetic with Mo–Mo = 2.111 (1) Å. The $Mo_2(SO_4)_4{}^{3-}$ ion is paramagnetic with one unpaired electron (1.65 ± 0.01 BM; $g_{av} = 1.90 \pm 0.01$) and an Mo–Mo distance of 2.164 (2) Å. From cyclic voltammetry and rotating-disk electrode polarography in 9 *M* H_2SO_4 it was shown that the two ions are related by a half-wave potential of +0.22 V *vs.* sce. The decomposition rate of $Mo_2(SO_4)_4{}^{3-}$ in solution is enormously variable, depending, *inter alia*, upon the condition of the electrode surfaces. By controlled-potential electrolysis a concentration sufficient for esr study was generated, and the following results were obtained: $g_\parallel = 1.891$, $g_\perp = 1.909$, $g_{av} = 1.903$, $|A_\parallel| \times 10^4 = 45.2$ cm^{-1}, $|A_\perp| \times 10^4 = 22.9$ cm^{-1}, where the hyperfine coupling is to ^{95}Mo.

Introduction

There is now an enormous number of species containing the dimolybdenum(II) entity, with a quadruple Mo–Mo bond coordinated by ligands of very diverse types, for example H_2O, Cl^-, CH_3^-, $C_3H_5^-$, PR_3, RCO_2^-, etc.[1] A particularly important type of ligand is the bidentate bridging type which is sterically adapted to form two approximately parallel donor bonds, one to each of the two metal atoms in the Mo≣Mo group or other, similar, dinuclear coordination center. The carboxylato anions, RCO_2^-, are the commonest, but others include amidino ions, $R'NC(R)NR''^-$, triazino ions, $RNNNR'^-$, thiocarboxylato ions, $RCOS^-$, xanthato ions, $ROCS_2^-$, carbonate ion, OCO_2^{2-}, and sulfate ion, $O_2SO_2^{2-}$. The first $M_2(SO_4)_4{}^{n-}$ species reported was that postulated to occur in $K_4MO_2(SO_4)_4$ by Bowen and Taube.[2] In this laboratory the $Re_2(SO_4)_4{}^{2-}$ ion has been prepared and characterized as its sodium salt.[3]

We have previously reported[4] that X-ray crystallographic and Raman data for $K_4Mo_2(SO_4)_4{\cdot}2H_2O$, the hydrated form of Bowen and Taube's compound, verify the presence of the $Mo_2(SO_4)_4{}^{4-}$ ion and that the singly oxidized derivative, $Mo_2(SO_4)_4{}^{3-}$, can also be isolated and characterized crystallographically.[5] In this paper, we shall describe the structures of the two compounds $K_4Mo_2(SO_4)_4{\cdot}2H_2O$ and $K_3Mo_2(SO_4)_4{\cdot}3.5H_2O$ in full detail and also report on their redox properties and the bulk magnetic and electron spin resonance characteristics of the paramagnetic $Mo_2(SO_4)_4{}^{3-}$ ion.

Experimental Section

Preparation of Compounds. The anhydrous compound $K_4Mo_2(SO_4)_4$ was prepared by the method of Bowen and Taube[2] with slight modifications. Crude $K_4Mo_2Cl_8$[6] (1.0 g) was stirred under nitrogen with 0.1 *M* H_2SO_4 (100 ml) at room temperature for 3 hr. The product was precipitated by adding excess solid K_2SO_4. The pink solid was filtered under nitrogen, washed with ethanol and ether, and dried for a few minutes under vacuum at room temperature.

Crystals of $K_3Mo_2(SO_4)_4{\cdot}3.5H_2O$ were obtained by slow diffusion of a saturated solution of K_2SO_4 in 0.1 *M* H_2SO_4 into a solution of $K_4Mo_2(SO_4)_4$ in 0.1 *M* H_2SO_4 through a medium-porosity sintered-glass disk under nitrogen in the apparatus described previously.[7] Crystals of the oxidized complex formed as bladelike, lavender needles, easily distinguishable from $K_4Mo_2(SO_4)_4$, which usually reprecipitated as a pink powder. The crystals appeared to be stable to air and moisture.

Satisfactory crystals of $K_4Mo_2(SO_4)_4{\cdot}2H_2O$ were also obtained by the diffusion method. However, it proved quite difficult to obtain a suitably crystalline product; very dilute solutions of $K_4Mo_2(SO_4)_4$ appeared to produce the best crystals. The crystals formed as rose red platelets which appeared to be air and moisture stable.