dium sulfide) and the dramatic rate increase observed in melts that initially contained sodium sulfide but also a source of sodium thiosulfate, which was found in the melt subsequent to a similar experiment. A sequence of reactions that is consistent with the results of this study for the oxidation of graphite in pure sodium sulfate using argon is represented by eq 2, 4, 13, 14, 17, and 18. The overall process is represented by eq 7. Sodium sulfate is consumed under these conditions.

$$Na_2SO_4 \rightleftarrows SO_2 + Na_2O_2 \quad (17)$$

$$Na_2O_2 + C \rightarrow Na_2O + CO \quad (2)$$

$$Na_2O_2 + CO \rightarrow Na_2O + CO_2 \quad (4)$$

$$SO_2 + Na_2O \rightarrow Na_2SO_3 \quad (18)$$

$$Na_2SO_3 + 3C \rightarrow Na_2S + 3CO \quad (13)$$

$$Na_2SO_3 + 3CO \rightarrow Na_2S + 3CO_2 \quad (14)$$

Sodium Carbonate/Sodium Sulfate–Inert Sparge Gas. In sodium carbonate/sodium sulfate mixed melts with argon, a sequence of reactions proposed for the oxidation of graphite may be represented by eq 2, 4, 5, 10, 13, and 14, in which the overall process is represented by eq 7.

$$Na_2SO_4 + Na_2CO_3 \rightarrow CO_2 + Na_2SO_3 + Na_2O_2 \quad (10)$$

$$Na_2O_2 + C \rightarrow Na_2O + CO \quad (2)$$

$$Na_2O_2 + CO \rightarrow Na_2O + CO_2 \quad (4)$$

$$Na_2SO_3 + 3C \rightarrow Na_2S + 3CO \quad (13)$$

$$Na_2SO_3 + 3CO \rightarrow Na_2S + 3CO_2 \quad (14)$$

$$Na_2O + CO_2 \rightleftarrows Na_2CO_3 \quad (5)$$

There are other reactions possible between the species discussed, and indeed, there may be other species involved in these complex systems. Even though the reaction sequences presented are consistent with the data presently available, they may not be the only sequences capable of explaining the results.

To understand more about the chemistry of graphite oxidation in sodium carbonate/sodium sulfate mixed melts, it will be necessary to determine how the concentrations of the ionic species in the melt change with variations in the reaction conditions and how they relate to the reaction rate. Such studies are presently under way.

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Registry No. Graphite, 7782-42-5; Na_2SO_4, 7757-82-6; Na_2CO_3, 497-19-8; Na_2S, 1313-82-2.

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Some Observations on the Solution Chemistry of Molybdenum(II) Trifluoroacetate

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Solutions of molybdenum(II) trifluoroacetate in pyridine have been shown to contain not the axial bis(pyridine) adduct known in the solid state but a species with both bidentate and monodentate carboxylate ligands. Ring opening and closing proceed with an apparent free energy barrier ($\Delta G^{\ddagger}$) of ca. 13 kcal/mol. Evidence is presented for dissociative control of this process.

Introduction

Some years ago, Cotton[1] established that binuclear molybdenum(II) carboxylates such as molybdenum trifluoroacetate form axially symmetrical adducts with pyridine and other Lewis bases. Recently, Andersen[2,3] has described two additional reactions: the formation of binuclear complexes containing equatorial bases (with certain phosphines) and the formation of monuclear complexes (with isocyanides). Cotton[4] has reported the structures of two equatorial adducts.

We have begun[5] to investigate the solution chemistry of binuclear molybenum(II) complexes in order to establish the species present in solution and the mechanisms by which these complexes react. We report here the behavior of molybdenum(II) trifluoroacetate in pyridine-containing solutions. Our results indicate that this complex rearranges from the axial adduct to an equatorial adduct in the presence of excess pyridine. A ring opening–closing process occurs in solution; we report a ^{19}F NMR study of the process.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer Model 580 recording spectrophotometer. Electronic spectra were measured on a Cary 17 spectrophotometer. NMR spectra (^{19}F, 84.67 MHz) were recorded on a Varian EM-390 spectrophotometer; temperatures were calibrated in terms of the chemical shifts of methanol and ethylene glycol samples.[6] Conductivities were measured at room temperature with a Beckman RC-18A bridge. Pyridine, toluene, and benzene were redistilled (pyridine from KOH pellets) and stored over 4A molecular sieves in dark bottles. Molybdenum trifluoroacetate was prepared by literature methods[7] and characterized spectroscopically.

Table I. Data for Solutions of Molybdenum Trifluoroacetate in Pyridine

infrared,[a] cm^{-1}	1713 (br), 1617, 1611
NMR,[b] ppm	−70.5, −73.3
equiv conduct,[c,d] Ω^{-1} mol^{-1} cm^2 [e,d]	<1.5
Raman,[e] cm^{-1}	343
electronic,[f] nm	502

[a] Thin-film spectrum; 1750–1300-cm^{-1} region. [b] ^{19}F, negative shifts upfield from $CFCl_3$; $T = -30$ °C. [c] Measured on 0.0050 M solutions of $Mo_2(O_2CCF_3)_4$ at room temperature (ca. 23 °C); a value of 30.6 Ω^{-1} mol^{-1} cm^2 was measured for Et_4NClO_4 under identical conditions. [d] Measurements were complicated by slow air oxidation of the dilute solutions employed. Solutions and cells were purged with argon before measurements were made; a 50% increase in conductivity was noted over a 1-h period. In the presence of air, conductivity increased by more than a factor of 3. [e] Mo–Mo stretching vibration from ref 1. [f] Calculated from data in ref 6.

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Samples for NMR spectroscopy were prepared by dissolving weighed amounts of molybdenum trifluoroacetate in argon-purged solvents to constant volume under argon. A constant amount of $CFCl_3$ was added as internal standard. Samples were then capped. Without argon purging, line widths measured above 45 °C were nonreproducible and broader than those observed with argon-treated samples. Line widths at half-height ($\Delta\nu_{1/2}$) were measured and converted to rate data by using standard methods.[8,9]

Results and Discussion

Solution Species. Cotton[1] originally reported that the axial adduct $Mo_2(O_2CCF_3)_4(py)_2$ crystallizes from red solutions of the trifluoroacetate in pyridine. Andersen[2] later reported that $CDCl_3$ solutions of this adduct give a singlet in the ^{19}F NMR spectrum. We observe two lines (Table I) in the ^{19}F NMR spectrum of molybdenum trifluoroacetate in pyridine solution at −30 °C, with relative areas (5% error) of 1:1.0 over the temperature range −30 to −5 °C. This result indicates that the axial adduct is not the principal species present in pyridine solution. A comparison of chemical shifts with Andersen's data on phosphine adducts[2] suggests that the downfield resonance comes from bidentate trifluoroacetate ligands. Three separate lines of evidence suggest that the upfield signal comes from monodentate trifluoroacetate rather than free ligand. First, the conductivity data (Table I) indicate that the complex is a nonelectrolyte in solution; free trifluoroacetate ion is not present in appreciable amounts. Second, trifluoroacetate salts give a third line (−73.2 ppm) in the NMR spectrum. Third, the infrared band at 1713 cm^{-1} indicates monodentate trifluoroacetate. Andersen's equatorial phosphine adducts[2] give infrared absorption in the 1660–1670-cm^{-1} region. Cotton's solid-state results[4] suggest that this absorption be assigned to a carboxylate strongly bound to an equatorial site and more weakly bound to an axial site on the same metal center. The higher frequency observed in pyridine solution is more consistent with a purely monodentate carboxylate ligand than an equatorial–axial nonbridging bidentate carboxylate. Our observations suggest a solution species having two bidentate and two monodentate trifluoroacetate ligands, with two pyridine ligands in equatorial positions. Pyridine ligands also probably occupy the axial sites (see below).

The Raman and electronic spectra reported by Cotton[1,7] (Table I) also support our structural assignment. The lowest energy electronic transition (ca. 500 nm) occurs at somewhat longer wavelength than usual for complexes with bidentate carboxylates (ca. 440 nm).[10] The Mo–Mo stretching vibration (343 cm^{-1}) occurs at lower frequency than usual for complexes with four bidentate carboxylates.[11] These results are very consistent with more recent literature reports[12] of complexes containing fewer than four bidentate carboxylates. The reported Raman spectrum also rules out an alternative interpretation of the NMR spectrum: that more than one type of complex is present (for example, equal amounts of two complexes, one with only bidentate carboxylate groups, the other with only monodentate).

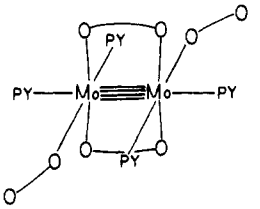
While the spectroscopic data of Table I establish the basic structure of the solution species, they do not establish which, or how many, of the possible geometric isomers are present.

Table II. Coalescence Temperature for Ring Opening–Closing in Mixed Solvents

solvent[a]	T_c, °C	solvent[a]	T_c, °C
pyridine	13	pyridine–toluene[b]	
pyridine–benzene[b]		1:1	4
1:3	0	1:3	2
1:7	−7	1:7	−13
		1:15	−18
		1:100	<−25

[a] Samples were prepared by dissolving molybdenum trifluoroacetate in solvent of desired composition to give 0.50 mL solution. $CFCl_3$ (0.05 mL) was then added as an internal standard. [b] Expressed as volume ratio, measured at 25 °C.

Two reports[4,13] of related complexes in the solid state suggest the isomer shown as a probable solution species.



The rather unequal line widths observed in the NMR spectrum at −30 °C (3.1 and 4.1 Hz) suggest to us that more than one isomer is present. We have not successfully resolved either peak because an exchange process contributes to the line widths. We have not detected a Mo–Mo stretching vibration (ca. 350 cm^{-1}) in the infrared because other bands interfere; detection of this mode would indicate that at least one noncentrosymmetric isomer was also present. The two infrared absorptions at 1617 and 1611 cm^{-1} are consistent with the presence of more than just the centrosymmetric isomer depicted above.[14]

We have also examined solutions of molybdenum trifluoroacetate in pyridine–benzene and pyridine–toluene mixtures. Interpretation of NMR data is complicated by an exchange process. Both NMR and electronic spectra suggest that benzene or toluene solutions of $Mo_2(O_2CCF_3)_4(py)_2$ contain mainly the axial adduct. With additional pyridine, the axial adduct is converted to the two monodentate–two bidentate species. We suggest that the solution species is the axially solvated $Mo_2(O_2CCF_3)_4(py)_4$. We estimate the room-temperature (23 °C) equilibrium constant for this process (eq 1) as ca. 10 M^{-2} from the electronic spectra.

$$Mo_2(O_2CCF_3)_4(py)_2 + 2py \rightleftharpoons Mo_2(\mu\text{-}O_2CCF_3)_2(OCOCF_3)_2(py)_4 \quad (1)$$

Although exchange broadening complicates the NMR spectra, data at −30 °C suggest a larger constant (perhaps as large as 10^3 M^{-2}) at that temperature.

Our observations raise several points for further considerations. We note first that Andersen[2] found equatorial adducts containing monodentate carboxylate ligands only with small, basic phosphines. Our results suggest that such complexes should form, at least in solutions containing excess base, with other classes of small, basic donors. The solid-state structure adopted by these complexes will reflect the relative packing energies of and the ease of interconversion between possible structures. A second question involves the solution structures of other families of binuclear molybdenum(II) complexes. In an earlier study of molybdenum(II) complexes with alkyl xanthate ligands,[5] we found no evidence for unusual behavior

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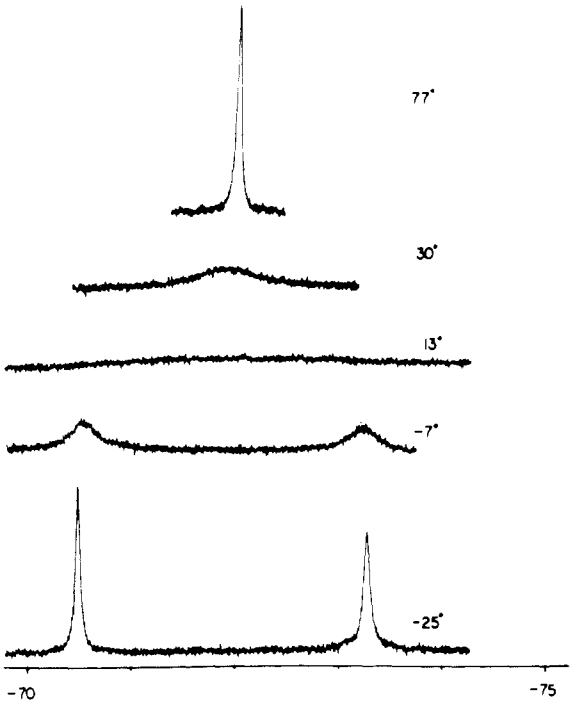
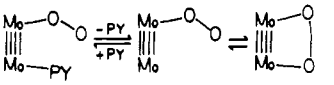


Figure 1. Selected ^{19}F NMR spectra of molybdenum trifluoroacetate in pyridine solution.

in pyridine solutions. This difference suggests to us that alkyl xanthate ligands are stronger donors to the Mo_2^{4+} core than are carboxylates. Finally, these results remind us of an obvious but easily forgotten point: there is no requirement that solution and solid-state structures be identical.

Variable-Temperature Behavior. When pyridine solutions of molybdenum trifluoroacetate are warmed from −30 to +75 °C, the ^{19}F NMR spectrum changes reversibly, as shown in Figure 1. The changes are independent of molybdenum trifluoroacetate concentration over the range 0.03–0.09 M; they are unaffected by small quantities of free trifluoroacetate ion. In pyridine–benzene or pyridine–toluene mixtures, similar changes occur, but at lower temperatures. Coalescence temperatures observed in various solvent mixtures are listed in Table II.

The spectra in Figure 1 indicate that monodentate and bidentate ligand environments become averaged as the temperature increases. A logical description of the mechanism is the ring closing-opening process shown in eq 2. The rate



(2)

increase observed with decreasing pyridine concentration suggests that the process in dissociatively controlled. The observed 1:1 ratio of monodentate to bidentate ligand populations, an equilibrium ratio, suggests that the exchange process involves closing one ring and opening another. These two events may be consecutive or concurrent.

Our mechanism is consistent with Mureinik's earlier suggestion[12a] that the reaction between $Mo_2Cl_8^{4-}$ and acetic acid is dissociatively controlled. The probable solution species, noted above, the solvated $Mo_2(\mu\text{-}O_2CCF_3)_2(O_2CCF_3)_2(py)_4$, is coordinatively saturated. Furthermore, all available low-energy molecular orbitals would be filled.[15] This situation is much like that of octahedral cobalt(III) complexes that also undergo dissociatively controlled substitutions.

In evaluating activation parameters, we note that exchange contributes to the observed line widths over the entire temperature range studied. In particular, we observe directly neither the no-exchange line widths ($\Delta\nu_{1/2}°$) nor the no-exchange chemical shift difference ($\nu_A° - \nu_B°$). We observe a constant chemical shift difference (220 Hz) at temperatures below −15 °C. If we use this value as the no-exchange shift difference (it should be close to the no-exchange value in any case), we calculate[8,9,16] an apparent free-energy barrier ($\Delta G^‡$) of 13 kcal/mol at coalescence (13 °C). Efforts to determine $\Delta H^‡$ and $\Delta S^‡$ (with use of the line width of free trifluoroacetate ion as an estimate of the no-exchange line width) led to markedly curved plots (concave upward) of ln (k/T) vs. $(1/T)$. This study was dropped at this point.

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Registry No. $Mo_2(O_2CCF_3)_4$, 36608-07-8; py, 110-86-1.

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