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The Preparation and Optical and Electron Spin Resonance Spectra of Some *trans*-Tetrachlorodialkoxomolybdates(V)

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Molybdenum pentachloride was dissolved in methanol and treated with a base such as pyridine and *trans*-tetrachlorodimethoxomolybdates(V) were obtained. The complexes were characterized by analysis, electronic and infrared spectra, and electron spin resonance (esr) methods. The esr demonstrated that the compounds were predominantly *trans* isomers. For the solid pyridinium compound in methanol glass $g_{\parallel} = 1.9700$, $g_{\perp} = 1.934$, $A = -77.8 \times 10^{-4}$ cm^{-1}, $B = -32.9 \times 10^{-4}$ cm^{-1}, and the isotopic contact term, K, is -44.7×10^{4} cm^{-1}. Absorptions attributed to the $b_2 \rightarrow b_1$ transitions (based on the *trans*, D_{4h}, configuration) are observed at about 14 and 23 $\times 10^3$ cm^{-1}. Two charge-transfer bands are also observed. An ethoxo complex was also prepared by alkoxide exchange between a methoxo complex and solvent ethanol.

Introduction

In this laboratory we have been interested in the preparation and esr spectra of paramagnetic chloroalkoxo complexes,[1,2] and other groups have studied various Mo(V), W(V), V(IV), and Ti(III) complexes and especially the "yl," or MO^{n+}, complexes by esr methods.[3-6] Recently Funk, Schmeil, and Scholz reported the preparation of some chloroalkoxo complexes and some chloride alkoxides of Mo(V),[7] which appeared to be of interest for studies of electronic, infrared, and esr spectra. The authors[7] had reported only preparations and analyses. Therefore, we undertook the preparation and characterization of these compounds and report here results for a series of *trans*-tetrachlorodimethoxomolybdates(V) and a *trans*-tetrachlorodiethoxomolybdate(V).

Experimental Section

Materials.—Molybdenum pentachloride was obtained from K & K Laboratories and was used without further purification. Reagent grade methanol was refluxed with magnesium turnings and then was distilled at 65°. Absolute ethanol was further dried with sodium and then was distilled at 78–79°. Pyridine and quinoline were obtained from Matheson Coleman and Bell and were dried by refluxing over barium oxide and distilling. Tetramethylammonium chloride was Eastman White Label grade and was dried for 8 hr at 100°.

Solvents used in esr studies were reagent grade and were purified by a repeated melt–freeze–pump sequence, after which they were distilled and swept and stored with prepurified nitrogen. Each solvent was distilled into an esr sample tube containing a molybdenum compound and the tube was then sealed.

Prepurified nitrogen and anhydrous HCl were obtained from Matheson and were used without further purification.

Analyses.—Molybdenum was determined by titration of Mo(V) with Ce(IV) in 3 *M* HCl after the complex had been decomposed in the aqueous acid. Chloride was determined by the indirect Volhard method. Carbon, hydrogen, and nitrogen were determined by Spang Microanalytical Laboratory, Ann Arbor, Mich.

Spectra.—Visible–ultraviolet spectra of various solutions were measured with a Cary Model 14 spectrophotometer, and infrared spectra were determined in Nujol mulls with a Unicam SP-200 spectrophotometer.

X-Band esr spectra at 297 and 77°K were determined on a Varian V-4500-10A spectrometer and were recorded on an *X-Y* recorder with the *X* axis proportional to magnetic field strength. A Hall probe was used as a field sensor. First- and second-derivative curves were recorded. Hyperfine splittings were measured by means of a Hewlett-Packard 524C frequency counter, which was checked against aqueous $VOSO_4$, aqueous $K_3[Cr(CN)_5NO]$, and peroxylamine disulfonate.[8-10]

Peak separations were measured by means of markers, corresponding to measured proton frequencies, placed at 10–15-gauss intervals on the recorded spectra by means of simultaneous recording of esr and proton signals.

Values of *g* were determined (1) from the measured klyston frequency and the field strength and (2) by simultaneous recording of the spectrum of the complex and some reference substance such as phosphorus "doped" silicon in polyethylene, pitch in KCl, diphenylpicrylhydrazyl in benzene, peroxylamine disulfonate, and aqueous $K_3[Cr(CN)_5NO]$.

Magnetic Susceptibilities.—Bulk magnetic susceptibilities were determined at room temperature by the Gouy method. $Hg[Co(SCN)_4]$ was used as a standard.

Preparations.—The methoxo complexes were all prepared in the same manner as pyridinium tetrachlorodimethoxomolybdate(V).

Pyridinium Tetrachlorodimethoxomolybdate(V).—A 2.75-g sample of $MoCl_5$ (0.01 mole) was placed in a 1-l., three-necked, round-bottom flask, and the flask was continuously swept with dry, prepurified nitrogen. Then 8.1 ml (0.2 mole) of dry methanol was added dropwise, and the mixture was stirred and the flask cooled in an acetone–Dry Ice bath. HCl was liberated during the addition of methanol. After the $MoCl_5$ had dissolved, the dark green solution was treated dropwise with a 9:1 methanol:pyridine mixture and a lime-colored, crystalline solid separated immediately. The flask was stoppered and transferred to a drybox where the crystals were filtered in the dry nitrogen atmosphere and were washed with three 20-ml portions of anhydrous ethyl ether. *Anal.* Calcd for $C_7H_{12}NO_2Cl_4Mo$: C, 22.13; H, 3.18; N, 3.69; Cl, 37.33; Mo, 25.25. Found: C, 21.12; H, 2.88; N, 3.66; Cl, 37.33; Mo, 24.87.

Quinolinium Tetrachlorodimethoxomolybdate(V).—Quinoline in methanol was used instead of pyridine in the preparation.

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(1) R. A. D. Wentworth and C. H. Brubaker, Jr., *Inorg. Chem.*, **2**, 551 (1963); **3**, 47 (1964).

(2) P. G. Rasmussen, H. A. Kuska, and C. H. Brubaker, Jr., *ibid.*, **4**, 343 (1965).

(3) C. R. Hare, I. Bernal, and H. B. Gray, *ibid.*, **1**, 831 (1962).

(4) K. DeArmond, B. B. Garrett, and H. S. Gutowsky, *J. Chem. Phys.*, **42**, 1019 (1965).

(5) H. Kon and N. E. Sharpless, *J. Phys. Chem.*, **70**, 105 (1966).

(6) B. R. McGarvey, Symposium on Electron Spin Resonance, Michigan State University, Aug 1–3, 1966; sponsored by the Division of Physical Chemistry, American Chemical Society.

(7) H. Funk, F. Schmeil, and H. Scholz, *Z. Anorg. Allgem. Chem.*, **310**, 86 (1961).

(8) L. R. Dalton, J. D. Rynbrandt, E. M. Hansen, and J. L. Dye, *J. Chem. Phys.*, **44**, 3969 (1966).

(9) H. A. Kuska and M. T. Rogers, *ibid.*, **40**, 910 (1964).

(10) T. Cole, J. Kushida, and H. C. Heller, *ibid.*, **38**, 3915 (1963).

Anal. Calcd for $C_6H_{18}O_2NCl_4Mo$: C, 19.27; H, 4.79; N, 3.75; Cl, 32.98; Mo, 22.31. Found: C, 18.26; H, 4.74; N, 3.63; Cl, 32.90; Mo, 22.01.

Tetramethylammonium Tetrachlorodimethoxomolybdate(V).—Tetramethylammonium chloride in methanol was added in place of pyridine. *Anal.* Calcd for $C_6H_{18}O_2NCl_4Mo$: Cl, 37.93; Mo, 25.66. Found: Cl, 37.68; Mo, 25.64.

Pyridinium Tetrachlorodiethoxomolybdate(V).—Preparation was effected by alkoxide exchange in ethanol. A small sample of $C_5H_6N[Mo(OCH_3)_2Cl_4]$ was dissolved in a minimum quantity of hot ethanol, a dark green solution was produced, and, upon cooling, light green needles separated. The needles proved to be $C_5H_6N[Mo(OC_2H_5)_2Cl_4]$. *Anal.* Calcd for $C_9H_{16}O_2NCl_4Mo$: C, 26.49; H, 3.95; N, 3.43; Cl, 34.76; Mo, 23.52. Found: C. 26.45; H, 3.86; N, 3.56; Cl, 34.35; Mo, 23.52.

Results and Discussion

The tetrachlorodialkoxomolybdates(V) which have been prepared were made by a variation of the methods of Funk, Schmeil, and Scholz,[7] but we have been unsuccessful with the exact procedures they described for pyridinium tetrachlorodimethoxomolybdate(V). We have also succeeded in preparing a quinolinium and a tetramethylammonium salt of the $Mo(OCH_3)_2Cl_4^-$ anion. By exchange of methoxide in ethanol, we have prepared pyridinium tetrachlorodiethoxomolybdate(V). All of the salts are decomposed slowly by the atmosphere: HCl is given off and a brown residue is formed. The pyridinium salts are soluble in methanol and ethanol, but the quinolinium and tetramethylammonium salts are only slightly soluble in the alcohols. These latter two salts were rather more soluble in acetone–alcohol mixtures, in which their electronic spectra were measured.

Infrared spectra of all of these compounds correspond to the ions pyridinium, quinolinium, and tetramethylammonium and *not* to ligand or unbound pyridine or quinoline. All of the compounds have an absorption between 1040 and 1050 cm^{-1} which can be attributed to C–O stretching of a coordinated alkoxo group,[1,11] and no O–H band could be detected. Thus, the infrared spectra indicate alkoxo groups are coordinated and pyridine and quinoline are not.

The important features of the electronic spectra are given in Table I. Each compound has two absorptions which may be attributed to d–d transitions[3-5] at about 14,000 and 23,000 cm^{-1}. In addition, two charge-transfer bands at about 33,000 and 40,000 cm^{-1} are found. The two d–d transitions should probably be the $b_2 \rightarrow e$ and $b_2 \rightarrow b_1$ in D_{4h} symmetry (which is required by the esr data below). The $b_2 \rightarrow a_1$ transition and a low-energy charge-transfer band[5] are probably hidden by the large 23,000-cm^{-1} band.

Bulk magnetic susceptibilities are given in Table II.

Electron spin resonance spectra were obtained on powdered samples and on diluted powders (with KCl or other alkali chlorides as diluents) at 297°K and on various solutions at 297 and 77°K (as glasses). The ^{95}Mo–^{97}Mo hyperfine spectrum was observed. Both nuclei have $I = {}^5/_2$ and slightly different moments (-0.9099 and -0.9290 for ^{95}Mo and ^{97}Mo, respectively).

Table I

Electronic Spectra of Tetrachlorodialkoxomolybdates(V) in Solutions at 25°

Compound	Solvent	Absorption, cm^{-1}	ϵ
$C_5H_6N[Mo(OCH_3)_2Cl_4]$	Methanol	13,900	27
		23,100	1.64×10^2
		32,800	1.63×10^3
		39,060	6.54×10^3
$C_9H_8N[Mo(OCH_3)_2Cl_4]$	Methanol–acetone	14,200	~ 10
		23,150	$\sim 2 \times 10^2$
		32,260	$\sim 2 \times 10^3$
		43,010	$\sim 10^4$
$(CH_3)_4N[Mo(OCH_3)_2Cl_4]$	Methanol–acetone	13,900	~ 10
		22,075	$\sim 10^2$
		31,250	$\sim 2 \times 10^3$
		45,600	$\sim 10^4$
$C_5H_6N[Mo(OC_2H_5)_2Cl_4]$	Ethanol	14,150	15.4
		23,525	202
		33,900	2.6×10^3
		39,140	14.6×10^3

Table II

Magnetic Susceptibilities and Moments of the Alkoxo Molybdenum(V) Compounds

Compound	Temp, °K	Susceptibility, $10^4\chi_M$, cgs units/mole	Moment, BM
$C_5H_6N[Mo(OCH_3)_2Cl_4]$	297	1225	1.71
$C_9H_8N[Mo(OCH_3)_2Cl_4]$	297	1370	1.81
$(CH_3)_4N[Mo(OCH_3)_2Cl_4]$	298	1235	1.72
$C_5H_6N[Mo(OC_2H_5)_2Cl_4]$	296	1469	1.88

Spectra of the solids and glasses could be resolved into parallel and perpendicular components, which requires that at least most of the compound be an isomer with axial symmetry: the *trans* isomer with D_{4h} symmetry. Sample spectra are shown in Figure 1.

Since the hyperfine splittings are on the order of 50 gauss, the high-field approximation cannot be applied rigorously and the paramagnetic electron spin operators lie along the resultant of the applied magnetic field and nuclear magnetic moment vectors. The perturbation of the Zeeman transition resulting from the hyperfine interaction was corrected by means of the following equations

$$h\nu = g\beta H_0$$

for isotropic g

$$H_0 = H_m + \langle a\rangle m_I + \frac{\langle a\rangle^2}{2H_m}[I(I + 1) - m_I^2] + \frac{\langle a\rangle^3}{4H_m^2}$$

for $g_{\parallel}$

$$H_0 = H_m + Am_I + \frac{B^2}{2H_m}[I[I + 1) - m_I^2]$$

for $g_{\perp}$

$$H_0 = H_m + Bm_I + \frac{(A^2 + B^2)}{4H_m}[I(I + 1) - m_I^2]$$

where H_m is the magnetic field position of the esr line due to the component m_I of the nuclear spin I, ν is the klystron frequency and a, A, and B are the nuclear

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(11) C. G. Barraclough, D. C. Bradley, J. Lewis, and I. M. Thomas, *J. Chem. Soc.*, 2601 (1961).

TABLE III

ESR SPECTRA AND DERIVED QUANTITIES FOR TETRACHLORODIALKOXOMOLYBDATES(V) [a]

Sample	Temp, °K	$\langle g \rangle$	$\langle a \rangle$	$g_{\parallel}$	$g_{\perp}$	A, $cm^{-1} \times 10^{-4}$	B, $cm^{-1} \times 10^{-4}$
$C_5H_6N[Mo(OCH_3)_2Cl_4]$							
Powder	297	1.9396		1.9690	1.9249		
Diluted powder	297	1.9396		1.9690	1.9249		
Methanol	297	1.9463	47.69				
	77			1.9700	1.934	77.8	32.9
Acetone	297	1.9478	46.68				
Dimethylformamide	297	1.9453	46.93				
	77			1.9673	1.934	75.1	33.0
Pyridine	297	1.9374	42.83				
				1.9711	1.926	67.5	30.5
Ethylene dichloride	297	1.9463	45.96				
Dimethyl sulfoxide	297	1.9437	48.00				
	77			1.9705	1.934	74.7	33.0
Ethanol	297	1.9461	47.70				
	77			1.9704	1.934	76.3	33.4
$C_9H_8N[Mo(OCH_3)_2Cl_4]$							
Powder	297	1.9355		1.9601	1.9232		
Diluted Powder	297	1.9355		1.9601	1.9232		
Methanol	297	1.9456	47.84				
	77			1.9667	1.935	77.7	32.9
$(CH_3)_4N[Mo(OCH_3)_2Cl_4]$							
Powder	297	1.9397		1.9706	1.9243		
Diluted Powder	297	1.9397		1.9706	1.9243		
Methanol	297	1.9459	47.99				
	77			1.9676	1.935	78.0	33.0
$C_5H_6N[Mo(OC_2H_5)_2Cl_4]$							
Powder	297	1.9422		1.9609	1.9328		
Diluted powder	297	1.9422		1.9609	1.9328		
Ethanol	297	1.9460	47.94				
	77			1.9680	1.935	77.8	33.0
Methanol	297	1.9460	47.92				
	77			1.9680	1.935	77.8	33.0

[a] Uncertainties in $\langle g \rangle$ range between 0.002 and 0.0008; $g_{\parallel}$, between 0.0002 and 0.0009; $g_{\perp}$, between 0.0002 (in powders) and 0.002 (in glasses); A, from 0.08 to 0.1 cm^{-1}; B, from 0.3 to 0.5 cm^{-1}.

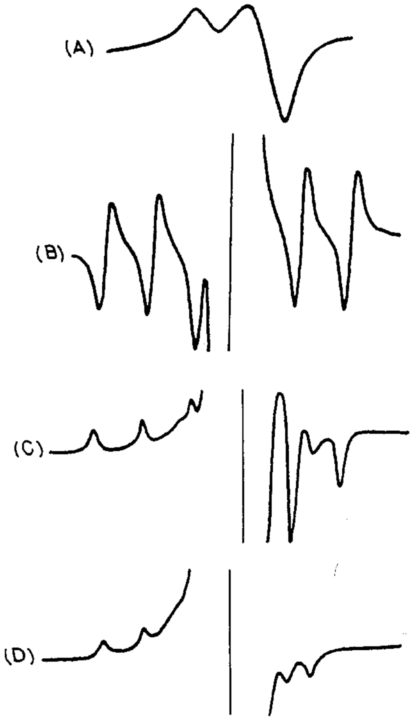

Figure 1.—Electron paramagnetic resonance spectra of $C_5H_6N[Mo(OCH_3)_2Cl_4]$ at 9.5 kMc: (A) powder spectrum at 297°K; (B) solution spectrum in DMF at 297°K; (C) spectrum in DMF glass at 77°K; (D) spectrum in DMSO glass at 77°K.

hyperfine splitting constants. These corrections are necessarily reiterative; they were performed by use of a program designed for this specific application[12] and were carried out on the MSU control data 3600 computer. Ten iterations were carried through, but it resulted that only the first two would have been necessary.

In Table III are listed the esr parameters for the various tetrachlorodialkoxomolybdates(V) in the solid phase and in various solutions. The values of g and A and B are in line with those obtained for other molybdenum(V) complexes.[3–6]

When $C_5H_6N[Mo(OCH_3)_2Cl_4]$ is dissolved in ethanol, the initial spectrum resembles that of the same compound in methanol, but over some minutes it changes to that which corresponds to the corresponding ethoxo complex in ethanol. However, when the ethoxo complex is dissolved in methanol, very little change of the spectrum is observed and g and A and B are essentially those for the ethoxo complex in ethanol. It seems that the equilibrium constant for the replacement of methoxide by ethoxide is very large.

When $C_5H_6N[Mo(CH_3)_2Cl_4]$ is dissolved in dimethyl sulfoxide (DMSO), the spectrum is gradually changed

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[12] L. R. Dalton, J. D. Rynbrandt, V. A. Nicely, and J. L. Dye, private communication.

from that typical of the tetrachlorodimethoxo complex to the spectrum whose parameters are given in Table II. The product also shows axial symmetry at 77°K. The addition of excess HCl to the solution causes the spectrum to revert to the original form. It seems that chloride is displaced by DMSO and that the process is reversible.

It appears likely that some ligand exchange may also have occurred in pyridine.

At present we are making an extensive study of the kinetics and equilibria in the ethoxide–methoxide exchange and the chloride–DMSO exchange.

The isotopic contact terms, K, may be calculated from the equations

$$A = -K - \frac{4}{7}\beta^2 P + (g_{\parallel} - 2.0023)P + \frac{3}{7}(g_{\perp} - 2.0023)P$$

$$B = -K - \frac{2}{7}\beta^2 P + \frac{11}{14}(g_{\perp} - 2.0023)P$$

for a d^1 ion and assuming the electron is in the $b_2(d_{xy})$ orbital.[6] If P is taken for the "free ion" (55.0×10^{-4} cm^{-1} for Mo^{3+}, *i.e.*, the average for the two isotopes and a net charge of 3+ for the $Mo(OCH_3)_2{}^{3+}$ unit[6]), then we may also solve for $\beta^2 P$ and thus determine β^2.

From the relationship

$$\chi = -\frac{3}{2}\left[\frac{hca_0{}^3}{2.0023 g_n \beta_n \beta_e}\right]K$$

χ in atomic units may also be determined. To determine g_n we employed an average value for the two isotopes

$$g_n = \frac{{}^1/_2(-0.9099 - 0.9290)}{5/2}$$

In Table IV are listed the values of K, χ, β^2, and P_{complex} ($=\beta^2 P_{\text{ion}}$). These values are comparable to those obtained for other Mo(V) complexes[3-6] but the $-K$, and hence $-\chi$, are on the low side, which may indicate high ionic character. The β^2 are about 0.94 and suggest that the electron is essentially a b_2 electron.

Table IV

Values of the Isotopic Contact Term, K, and χ and β^2 for Tetrachlorodialkoxomolybdates(V) in Methanol Glasses at 77°K

Compound	$-K$, cm^{-1} × 10^4	$-\chi$, au	P, cm^{-1} × 10^4	β^2
$C_5H_6N[Mo(OCH_3)_2Cl_4]$	44.7	5.72	51.9	0.945
$(CH_3)_4N[Mo(OCH_3)_2Cl_4]$	44.9	5.74	51.8	0.944
$C_9H_8N[Mo(OCH_3)_2Cl_4]$	44.7	5.72	51.6	0.940
$C_5H_6N[Mo(OC_2H_5)_2Cl_4]$	44.8	5.73	51.6	0.940

In the work with Nb(IV) we were able to employ an approximate molecular orbital treatment and make some estimates of the bonding parameters. However, in the present case there seems to be a large uncertainty in the spin–orbit coupling constant[4,5] and since we are unable to locate the low-energy charge-transfer band and the $b_2 \rightarrow a_1$ transition, it seems wiser to postpone such a treatment.

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Cobalt(III)-Catalyzed Deuterium Exchanges on Ligands with Glycinate Rings[1]

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The isotopic exchange in acidic heavy water of cobalt(III) polyaminocarboxylic acid chelates containing glycinate ring structures was followed by nuclear magnetic resonance spectroscopy by observing decreases in spectral intensities. The exchange process, occurring by pseudo-first-order decay, was studied in the acidity range 0.05 to 0.5 M acid at 85, 95, and 103°. Intermediate isotopic enantiomeric species were observed to be formed at the out-of-plane methylene carbon while the in-plane methylene protons did not undergo direct isotopic exchange. A major consideration in elucidating various features of the exchange process was the stereochemistry of the individual ligand. An enol intermediate has been proposed for the exchange mechanism.

Introduction

Acidic D_2O solutions of ethylenediaminetetraacetatocobalt(III), $[(Co(EDTA)]^-$, when heated, were observed by nuclear magnetic resonance (nmr) spectroscopy to undergo a decrease in intensity of the acetate proton resonances, indicating that isotopic exchange was occurring. *trans*-1,2-Cyclohexanediamine-N,N′-tetraacetatocobaltate(III), $[Co(CyDTA)]^-$, and *dl*-1,2-propylenediamine-N,N′-tetraacetatocobaltate(III), $[Co(PDTA)]^-$, were also studied, providing additional insight into the isotopic exchange processes. Previous isotopic exchange studies of Co(III) chelates

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