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Cysteine and Cysteine Ester Complexes with Molybdenum(V) and Molybdenum(VI)

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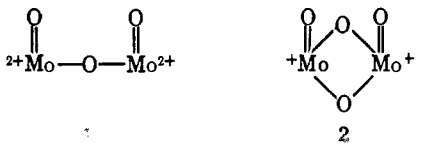
Sodium cysteinate reacts with Mo(V) in aqueous solution to form a crystalline, doubly oxygen-bridged binuclear Mo(V) complex containing 1 mol of ligand *per* molybdenum atom (**3**). Under similar conditions cysteine esters give singly bridged species (**4**) as purple, microcrystalline solids which, in solution in organic media, undergo ligand expulsion to form yellow, crystalline doubly bridged analogs of **3**. The Mo(V) derivatives are diamagnetic. Dichlorodioxomolybdenum(VI) with cysteine esters forms yellow crystalline mononuclear dioxomolybdenum(VI)-bis(thiolato) derivatives (**6**). Infrared and electronic absorption spectra were determined.

The implication of molybdenum in the function of several metaloenzymes[1,2] and particularly in the nitrogen-fixing enzyme nitrogenase[3] prompted us to study the coordination chemistry of molybdenum with α-amino acid ligands. The redox enzyme xanthine oxidase is a thiolo enzyme which is thought to involve molybdenum–sulfur bonding.[1] The molybdoprotein constituent of nitrogenase is also a sulfur-containing enzyme,[3] and it is tentatively presumed to contain molybdenum–sulfur linkages, although with much less compelling evidence than in the xanthine oxidase case. Accordingly, our initial studies have involved the amino acid cysteine and its derivatives.

Although a considerable body of literature deals with molybdenum–sulfur complexes,[4,5] prior to the completion of the present work only one reference was encountered specific to cysteine–molybdenum complexes, that being a spectroscopic study by Spence and Chang.[6] They concluded that in the pH range 4–6, cysteine and Mo(VI) form several complexes having cysteine:Mo mole ratios varying from 3:1 to 1:1 depending upon concentration. On the other hand, Mo(V) appeared to form only a 1:1 complex with cysteine over the pH range 3–6, this complex being so "weak" that rapid oxidation to Mo(VI) occurred when it was exposed to air. The results of our isolation work do not entirely support the conclusions of Spence and Chang, but our conditions were somewhat different.

Syntheses

When molybdenum pentachloride is dissolved in concentrated hydrochloric acid, it is hydrolyzed to molybdenum(V) oxytrichloride which is stabilized as the complex ion $MoOCl_5^{2-}$. In more dilute acid (2–6 *N*) the monomeric ion dimerizes to oxygen-bridged binuclear species, *e.g.*, **1** or **2**.[7] When a solution of $MoCl_5$ in 3 *N* hydrochloric acid at room temperature was treated with cysteine and the solution was alkalized with sodium hydroxide, the initially brown solution deposited a tan solid in the pH range 2–3. At pH 7 the solid dissolved to form an amber solution which, upon dilution with ethanol, deposited a water-soluble, amber, crystalline complex (**3**) as a sodium (or guanidinium) salt having a cysteine:Mo ratio of 1:1. Composition and spectral data indicated it to have a structure formally derived from species **2**. The elemental composition of this complex requires the inclusion of two molecules of water in the molecular formulation and it was at first assumed that the compound had a structure of type **3a**.[8] However, recent X-ray crystallographic analysis of the compound by Knox and Prout[9] shows that it has structure **3b** in which cysteine is tridentate and the water is hydrogen-bonded to carboxylate oxygen.



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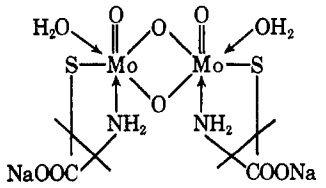
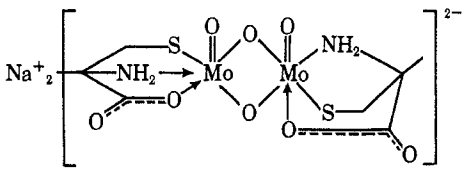


3a

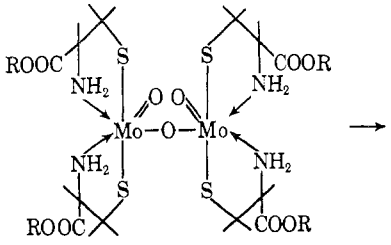


3b

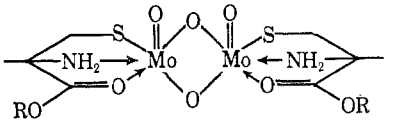
(1) A. E. Dennard and R. J. P. Williams, *Transition Metal Chem.*, **2**, 115 (1966).
(2) (a) L. S. Meriwether, W. F. Marzluff, and W. G. Hodgson, *Nature*, **212**, 465 (1966); (b) R. C. Bray and L. S. Meriwether, *ibid.*, **212**, 467 (1966).
(3) R. W. F. Hardy and E. Knight, Jr., in "Progress in Phytochemistry," L. Reinhold, Ed., John Wiley and Sons, Inc., New York, N. Y., 1968, p 387.
(4) P. C. H. Mitchell, *Coord. Chem. Rev.*, **1**, 315 (1966).
(5) F. W. Moore and M. L. Larson, *Inorg. Chem.*, **6**, 998 (1967).
(6) J. T. Spence and H. H. Y. Chang, *ibid.*, **2**, 319 (1963).
(7) P. C. H. Mitchell, *Quart. Rev.* (London), **20**, 103 (1966).
(8) A. Kay and P. C. H. Mitchell, *Nature*, **219**, 267 (1968), reported their independent preparation, by different methods, of a compound identical with **3**. They came to the same conclusion concerning its gross structure.
(9) J. R. Knox and C. K. Prout, *Chem. Commun.*, 1227 (1968).

When dissolved in hydrochloric acid, **3** gives a deep red color with thiocyanate characteristic of the Mo(V) ion. The 1:1 ligand to metal ratio required by formulation **3** is consistent with the ratio found by Spence and Chang in their spectral studies on the interaction of cysteine and Mo(V) in solution.[6] However, the different electronic absorption spectra indicate that we are dealing with different species (see below). Compound **3** was obtained whether the reaction was carried out in air or under nitrogen, although the crude product obtained in air contained a small amount of by-product cystine which was removed during recrystallization. The solid, crystalline chelate is quite stable in air or in solution in the absence of air, but solutions exposed to air undergo slow oxidation with formation of cystine. Aqueous solutions of the sodium salt **3**, when treated with 2 equiv of a strong acid, deposit an amorphous solid from which the crystalline sodium salt can be regenerated by dissolution in sodium hydroxide and alcohol precipitation, although in very low yield. Under conditions described for the preparation of **3** from Mo(V) the Mo(VI) compounds MoO_2Cl_2 or $MoOCl_4$ with cysteine gave cystine and complex **3** as the only isolable products. Thus, extensive and rapid reduction of Mo(VI) to Mo(V) had occurred even though the work of Spence and Chang[6] indicated that appreciable reduction of Mo(VI) by cysteine occurs preferably at pH ≤ 5.

Under similar conditions cysteine methyl or ethyl ester also formed a tan solid at around pH 2; when alkalized to pH 7 this solid turned magenta and appeared under microscopic examination to be microcrystalline. The magenta products had compositions corresponding to the singly bridged structures **4**. The ethyl ester (**4b**) dissolved readily in organic solvents to



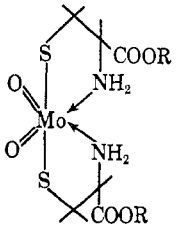
4a, R = CH_3
b, R = C_2H_5



5a, R = CH_3
b, R = C_2H_5

give magenta solutions (*e.g.*, λ_{max} 504 mμ in chloroform). Acetone or acetonitrile solutions of **4b** decolorized on standing (or more rapidly on being heated) and deposited a bright yellow crystalline solid, recrystallizable from acetonitrile and having the composition of the doubly bridged structure **5b**. Although direct proof is lacking, it is formulated with carbonyl group coordination by analogy with the tridentate nature of cysteine in **3**. The decolorization was accelerated by addition of a small amount of water to the organic solvent, but under these conditions conversion to the yellow product was erratic. In some such experiments it was accompanied by an amorphous intractable solid which seemed to be a polymeric modification. In 6 *N* hydrochloric acid solution compounds **4** and **5** gave strongly positive thiocyanate tests for Mo(V).

The reaction of MoO_2Cl_2 in water with the sodium salt of methyl or ethyl cysteinate or, alternatively, the reaction of cysteine ester hydrochlorides with sodium molybdate gave the molybdenum(VI)–bis(thiolato) compounds (**6**) as yellow, crystalline solids in high



6a, R = CH_3
b, R = C_2H_5

yield (~80%). No 3:1 complexes comparable to that suggested by the solution studies of Spence and Chang[6] could be isolated. These Mo(VI) chelates were recrystallized from ethanol, although the ethyl ester (**6**, R = C_2H_5) was converted to an amorphous, presumably polymeric solid when heated too long in solution. In other experiments the sodium salts of cysteine and S-benzylcysteine failed to react with Mo(V), while N-acetylcysteine and glycine gave brown intractable sludges whose infrared spectra lacked ligand absorption.

Infrared Spectra

The main features of the infrared spectra of complexes **3**–**6** are summarized in Table I. The bands of most interest are those in the 900–1000-cm^{-1} region assignable to Mo=O stretching[5,7,10,11] and those in the 450- and 750-cm^{-1} regions characteristic of Mo–O–Mo bridge-stretching modes.[5] Complexes of the type $(L_2Mo{=}O)_2O$ are reported to show a single Mo=O stretching mode in the 930–970-cm^{-1} region,[5] and indeed the cysteine methyl ester derivative **4a** shows a single though somewhat broad band at 925 cm^{-1}. On the other hand, the ethyl ester **4b** shows a doublet centered at 925 cm^{-1}, both peaks being of about equal intensity. The doubly bridged derivatives **3** and **5** show three or four bands in the Mo=O stretch region. With respect to dioxomolybdenum(VI) derivatives, it has generally been considered that existence of two bands in the 900-cm^{-1} region implies *cis* orientation

(10) C. G. Barraclough, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 3552 (1959).
(11) M. D. Joesten, *Inorg. Chem.*, **6**, 1598 (1967).

TABLE I

INFRARED SPECTRA OF MOLYBDENUM–CYSTEINE DERIVATIVES[a]

	Assignment and freq, cm^{-1}					
	NH_2	C=O	NH_2		MoOMo	
Compd	str	(or COO)	bend	Mo=O	Antisym	Sym
3	3210 vs[b]	1580–1630 vs		970, 945, 925 vs, triplet	730 vs	425 vs
4a	3230 s	1720 vs	1560 m	925 s, singlet		425 w
4b	3240 s	1720 vs	1550 m	925 s, doublet		425 w
5a	3275 w	1750 vs	1574 m	995 w	739 vs	478 m
	3220 s	1730 vs	1550 m	978 vs		415 w
	3185 vs			950 m		
	3100 s			925 w		
5b	3230 vs	1738 vs	1560 s	980 vs	735 vs	470 s
	3180 vs		1541 s	945 s		410 m
	3100 vs			935 m		
				900 w		
6a (fibrous)	3285 vs	1730 vs	1558 s	992 s		
	3245 vs			948 s		
	3160 s			895 vs		
6a (prisms)	3310 vs	1720 vs	1570 vs	998 w		
	3250 vs			932 s		
				910 vs doublet		
				880 vs		
6b	3280 s	1748 vs	1555 s	900 vs		
	3235 s			868 vs		

[a] Nujol mulls. [b] Also 3450 cm^{-1} vs assigned to H_2O.

of the oxo substituents.[5,7,12] The cysteine methyl ester derivative **6a** was isolated in two crystalline forms, one fibrous and the other prismatic; both showed at least two Mo=O stretch bands and the *cis* orientation of the molybdenyl oxygen atoms is consistent with the results of preliminary X-ray analysis.[13] However, the ethyl ester **6b**, which presumably should be geometrically equivalent to **6a**, showed only one strong, sharp band at 900 cm^{-1}. It does, however, show a very strong band at 868 cm^{-1}. Similar lower energy bands are also found in the spectra of **3**, **4a**, **4b**, and **5b**. Cotton and Wing have assigned an 860-cm^{-1} band to an antisymmetrical Mo–O–Mo stretching mode.[12] On the other hand, Moore and Larson have assigned the 430–435 and 766–810 cm^{-1} regions to symmetrical and antisymmetrical O-bridge stretching.[5] We find that the singly bridged Mo(V) derivatives **4** and the Mo(VI) compounds **6** show weak or no absorption in these regions, but the doubly bridged compounds **3** and **5** show very prominent bands at around 410–425 and 735–750 cm^{-1}. One is tempted to assign the bands around 470 cm^{-1} to Mo–S stretching[5] except that such bands are present in the spectra of several nonsulfur-containing molybdenum complexes (*e.g.*, Mo(V) and Mo(VI) complexes with ethylenediaminetetraacetate) and are absent in the S-bonded derivative **3**. The ligand bands of the ester derivatives are all sharp and well resolved, whereas in the sodium cysteinato compound **3** the ligand bands are considerably broadened in analogy with the zinc analogs.[14] If, indeed, the ester derivatives **5** involve carbonyl group coordination, the bonding must be very weak since the carbonyl absorption bands are not appreciably different in position or shape from those in the Mo(VI) esters **6** in which carbonyl coordination is precluded.

(12) F. A. Cotton and R. M. Wing, *Inorg. Chem.*, **4**, 867 (1965).
(13) Personal communication from L. J. Guggenberger of this laboratory.
(14) H. Shindo and T. L. Brown, *J. Am. Chem. Soc.*, **87**, 1904 (1965).

Electronic Absorption Spectra

The major electronic absorption bands for chelates **3**–**6** are listed in Table II. In aqueous solutions exposed to air the sodium cysteinato chelate **3** is unstable; the band at 307 mμ undergoes significant attenuation within hours at room temperature and the peak maximum shifts to longer wavelength. This degradation is probably oxidative. When stored under nitrogen and manipulated with exclusion of air, such solutions are much more stable but nevertheless show similar spectral changes on standing. A 10^{-4} *M* solution of compound **3** in 10^{-1} *N* hydrochloric acid (air free) showed a weak absorption maximum at 298 mμ, the

TABLE II

ELECTRONIC ABSORPTION SPECTRA

Compd	Solvent	λ_{max}, mμ	ϵ_{max}
3	H_2O	307	11,800[a]
4b	$CHCl_3$	330	7,550[b]
		504	13,500[b]
5b	CH_3CN	276	9,050
		288	8,900
6a[c]	$CHCl_3$	262	7,330
		354	5,400

[a] Freshly prepared in distilled water at pH 5.6; after 3 days λ_{max} was 317 mμ and the extinction was reduced to one-fourth the initial value. [b] Freshly prepared; after 90 min the long-wavelength-band extinction had decayed to about half the initial value. [c] **6b** was identical within experimental error.

same wavelength reported by Spence and Chang[6] for a molybdenum(V)–cysteine complex formed in solution. The 307-mμ band characteristic of the sodium salt was not restored by neutralization of the acid solution; thus the compound had undergone extensive structural change.

The magenta ethyl ester complex **4b**, in chloroform, has a visible absorption band at 504 mμ very much like the analogous xanthate complexes, $Mo_2O_3(ROCS_2)_4$, which absorb at 506 mμ.[5] This cysteine ester derivative is very unstable in solution; in reagent grade chloroform stabilized with ethanol, the absorbance of the 504-mμ band decreases to about 50% of that of a freshly prepared solution within 90 min at room temperature. This decay is probably partly a result of the ligand expulsion referred to above although oxidation may also have taken place. The intensities of the bands listed in the table suggest that they are S–Mo charge-transfer bands.

Summary

The existence of this group of cysteine–molybdenum derivatives lends support to the possible association of either Mo(V)[2] or Mo(VI)[6] with cysteine residues in molybdenum-containing enzymes although caution must be used in attempting to correlate the compositions or structures of these complexes with the metal environment in a native enzyme.

Experimental Section

Methods and Materials.—Infrared and electronic spectra were determined, respectively, with Perkin-Elmer Model 621 and Cary Model 15 spectrophotometers.

L-Cysteine and its derivatives were obtained from Mann Research Laboratories and the molybdenum halides were obtained from Alfa Inorganics, Inc.

Preparative Procedures. Sodium Cysteinatomolybdenum(V) (3).—In 25 ml of 3 *N* hydrochloric acid was dissolved 2.7 g (10 mmol) of molybdenum pentachloride and to the chilled solution was added 5.25 g (30 mmol) of L-cysteine hydrochloride monohydrate dissolved in 20 ml of water. While being stirred magnetically the solution was brought to pH 7 by the addition of 6 *N* sodium hydroxide solution using a pH meter. At about pH 3 a light brown solid formed, but it dissolved on further addition of alkali. The deep amber solution was treated with an equal volume of ethanol and refrigerated overnight. The amber platelets were collected and redissolved in water (25 ml/g) to which was then added an equal volume of ethanol. The mixture was allowed to stand at room temperature for 0.5 hr and was filtered through a fine-frit glass filter to remove a trace of white, insoluble material. The filtrate was again treated with an equal volume of ethanol. On standing at room temperature for 1 hr additional the solution deposited deep orange platelets which were collected and dried *in vacuo* over phosphorus pentoxide; yield 2.1 g (74% based on molybdenum); mp >200°. *Anal.* Calcd for $Na_2Mo_2C_6H_{14}N_2O_{10}S_2$ (formula wt 576.2): Na, 8.0; Mo, 33.3; C, 12.5; H, 2.5; N, 4.9; S, 11.1. Found: Na, 7.3; Mo, 33.7; C, 13.2; H, 2.4; N, 4.5; S, 11.7.

When a solution of 1.25 g of molybdenum oxytetrachloride and 3.5 g of L-cysteine in 3 *N* hydrochloric acid was treated as above, there was obtained 0.8 g of crude product. This was dissolved in 20 ml of water and the insoluble solid was collected on a filter; the infrared spectrum of this solid was identical with that of L-cystine. The filtrate was diluted with 40 ml of ethanol and chilled to obtain 0.3 g of the crystalline salt **3**.

The **guanidinium salt** was prepared by adding a solution of 0.3 g of guanidinium chloride in 5 ml of water to a filtered solution of the sodium salt (0.4 g) in water (10 ml). The solution was chilled in ice water, and the amber needles were collected, washed quickly with ice-cold water, and vacuum dried. *Anal.* Calcd for $Mo_2C_8H_{26}N_8O_{10}S_2$ (formula wt 650.5): Mo, 29.5; C, 14.8; H, 4.0; N, 17.2. Found: Mo, 30.2; C, 15.1; H, 3.5; N, 17.4.

Tetrakis(ethyl cysteinato)molybdenum(V) (4b).—To an ice-cold solution of 2.7 g (10 mmol) of molybdenum pentachloride in 25 ml of 3 *N* hydrochloric acid was added 3.7 g (20 mmol) of L-cysteine ethyl ester hydrochloride, and the solution was diluted with 100 ml of ice-cold water. The solution was magnetically stirred and brought to pH 7.5 with ice-cold 6 *N* sodium hydroxide solution, small pieces of ice being added to keep the solution cold during neutralization. The initially brown solid which separated at around pH 3 turned magenta as alkalization was continued. The cold mixture was stirred for an additional 5 min, and the microcrystalline solid was collected on a medium-frit glass filter and washed quickly with 100 ml of ice-cold water. The water-wet filter cake was quickly transferred to a desiccator and dried under vacuum over phosphorus pentoxide; yield 2.6 g (62%); mp ~110–120° dec. *Anal.* Calcd for $Mo_2C_{20}H_{40}N_4O_{11}S_4$ (formula wt 832.5): Mo, 23.1; C, 28.8; H, 4.8; N, 6.7; S, 15.4. Found: Mo, 23.1; C, 28.4; H, 4.9; N, 6.4; S, 15.3. The **methyl ester** was prepared in similar fashion and comparable yield; mp ~110–125° dec. *Anal.* Calcd for $Mo_2C_{16}H_{32}N_4O_{11}S_4$ (formula wt 776.5): Mo, 24.8; C, 24.8; H, 4.1; N, 7.2; S, 16.5. Found: Mo, 25.8; C, 24.1; H, 4.2; N, 6.8; S, 16.0.

Bis(ethyl cysteinato)molybdenum(V) (5b).—The transformation of the violet tetrakis compound (**4b**) to the yellow bis analog (**5b**) proved to be difficultly reproducible but was best carried out with freshly prepared **4b**. In one instance 0.2 g of the tetrakis compound was dissolved in 30 ml of acetone at room temperature. The magenta solution was filtered to remove a trace of insoluble material, and the filtrate was allowed to stand at room temperature for 1 hr and then stored at about −20° overnight. The brownish red solution was then boiled down to a volume of 10 ml, and the glistening yellow crystals were collected (~50 mg) and recrystallized from acetonitrile (75 ml/0.1 g); mp >200°. *Anal.* Calcd for $Mo_2C_{10}H_{20}N_2O_8S_2$ (formula wt 552.3): Mo, 34.7; C, 21.7; H, 3.7; N, 5.1; S, 11.6. Found: Mo, 35.2; C, 21.4; H, 3.5; N, 4.7; S, 10.9.

Bis(methyl cysteinato)molybdenum(V) (5a).—About half of the wet filter cake from a preparation of the tetrakis compound as described above was suspended in 50 ml of methanol, and the suspension was boiled gently on a steam bath for 15 min during which time the initially violet solid was converted to a yellowish, crystalline solid. It was collected on a filter and washed with methanol and ether; crude yield 0.6 g. For purification a 0.3-g portion was dissolved in 5 ml of warm dimethylformamide, the solution was filtered, and the filtrate was treated with 15 ml of methanol and chilled to obtain 0.1 g of beige, crystalline solid. *Anal.* Calcd for $Mo_2C_8H_{16}N_2O_8S_2$ (formula wt 524.3): Mo, 36.6; C, 18.4; H, 3.1; N, 5.3; S, 12.2. Found: Mo, 33.2; C, 18.4; H, 3.0; N, 5.2; S, 12.6.

Bis(methyl cysteinato)dioxomolybdenum(VI) (6a).—A solution of 2.0 g (10 mmol) of molybdenum(VI) dioxydichloride in 20 ml of ice-cold water was filtered (medium-frit glass filter) to remove a trace of extraneous solid, and the filtrate was chilled in an ice bath. This solution was magnetically stirred, and a freshly prepared solution of 3.42 g (20 mmoles) of L-cysteine methyl ester hydrochloride in 40 ml of 1 *N* sodium hydroxide was added all at once. A flocculent yellow solid separated almost immediately. An additional 40 ml of cold water was added, and stirring was continued for 15 min during which time the solid became granular. It was collected, washed with cold water, and vacuum dried; yield 3.2 g (80%); mp 149–150° dec. This material was obtained in two crystalline forms depending upon the recrystallization procedure.

a. **Fibrous Form.**—To 100 ml of vigorously boiling methanol was added 1.0 g of crude product, and boiling was continued for 1 min to obtain a clear yellow solution. It was filtered and immediately chilled in a wet ice–acetone bath whereupon the

product separated as fibrous yellow crystals. It was collected and vacuum dried to obtain 0.8 g of purified product; its melting point and infrared spectrum were identical with those of the crude form. *Anal.* Calcd for $MoC_8H_{16}N_2O_6S_2$ (formula wt 396.3): Mo, 24.2; C, 24.2; H, 4.1; N, 7.1; S, 16.2. Found: Mo, 23.9; C, 24.6; H, 4.2; N, 6.9; S, 16.3.

b. Prism Form.—A solution of 0.25 g of crude product in 50 ml of methanol was boiled gently for 5 min, filtered, and allowed to stand at room temperature for 2 hr. It was then refrigerated overnight to obtain 0.15 g of yellow-amber prisms contaminated with several clumps of feathery crystals; these were separated mechanically. The prism form melted at 150–151° dec. *Anal.* Found: C, 24.6; H, 4.2; N, 6.9.

Addition of a solution of 1.7 g of L-cysteine methyl ester hydrochloride in 10 ml of water to a vigorously stirred solution of 1.2 g of sodium molybdate dihydrate gave a good yield of product identical with the crude product obtained from molybdenum dioxydichloride.

Bis(ethyl cysteinato)dioxomolybdenum(VI) (6b).—This compound was prepared similarly to the methyl ester analog; crude yield 3.3 g (77%); mp 127–128° dec. This material is very unstable in hot organic solvents; thus, heating in ethanol for as short a time as 2 min converted it to an amorphous, intractable solid. The following procedure gave purified crystalline product. To 6 ml of boiling ethanol was added 0.2 g of finely divided crude product, and the mixture was boiled for less than 1 min to effect dissolution; the solution was immediately filtered into a flask immersed in an ice bath and the filtrate was agitated while scratching the inner walls of the flask with a stirring rod. A bright yellow, crystalline solid separated and was quickly collected and vacuum dried; recovery, less than 50%. The melting point was unchanged. *Anal.* Calcd for $MoC_{10}H_{20}N_2O_6S_2$ (formula wt 424.4): Mo, 22.6; C, 28.4; H, 4.8; N, 6.6; S, 15.1. Found: Mo, 22.6; C, 28.1; H, 4.7; N, 6.3; S, 15.9.

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Spectral Study of Some New Low-Symmetry Oxomolybdenum(V) Complexes[1]

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The following new low-symmetry oxomolybdenum(V) complexes were synthesized and characterized by conductance, by magnetic susceptibility, and by infrared, visible–ultraviolet, and epr spectroscopy: $MoOX_3(\beta\text{-diketonate})^-$, where X = Cl or Br, and the β-diketones are benzoyltrifluoroacetone, dibenzoylmethane, hexafluoroacetylacetone, and thenoyltrifluoroacetone. Analysis of the electronic spectral data is carried out in detail and band assignments are made, somewhat securely for the ligand field spectral region and somewhat less certain for the charge-transfer and intraligand-transition spectral region.

Introduction

Until recently the interpretation of the spectra of compounds containing the oxomolybdenum(V) moiety MoO^{3+} has been predicated largely upon the treatment proposed by Gray and Hare[2] for the $MoOCl_5^{2-}$ ion. These workers presumed that the resemblance between this species and the oxovanadium(IV) entity (both of which are d^1 systems) was sufficient to permit utilization of very similar energy diagrams in both cases. This was a convenient assumption since Ballhausen and Gray[3] had previously examined oxovanadium(IV) by means of a Wolfsberg–Helmholtz type of calculation and obtained a model which seemed to explain many spectral features of that system. Although the Gray–Hare proposal has appeared to be satisfactory in many cases, some questions have arisen. This has led us to prepare and obtain spectra of several very low-symmetry oxomolybdenum(V) complexes in order to test the validity of the Gray–Hare assignments.

Experimental Section

A. Preparation of Compounds.[4]—All reagents and solvents used were reagent grade chemicals from common commercial sources except tetraethylammonium oxopentachloromolybdate(V) and tetraethylammonium oxotetrabromomolybdate(V) monohydrate. The former material was prepared using the procedure described by Palmer[5] as appropriate for $(NH_4)_2MoOCl_5$, with the substitution of tetraethylammonium chloride for ammonium carbonate in those instructions. The bromo complex was prepared as described by Bishop;[6] an aqueous solution of tetraethylammonium bromide was added to a solution of molybdenyl hydroxide dissolved in concentrated hydrobromic acid. A yellow-brown solid formed immediately, was recovered by filtration, and then was purified by recrystallization from ethanol.

(1) $[(C_2H_5)_4N][MoOCl_3(hfa)]$.—The liquid, hexafluoroacetylacetone, was added slowly to a hot, concentrated solution of

(1) Taken in part from the Ph.D. Dissertation of H. E. Pence, Louisiana State University, 1967.

(2) H. B. Gray and C. R. Hare, *Inorg. Chem.*, **1**, 363 (1962).

(3) C. J. Ballhausen and H. B. Gray, *ibid.*, **1**, 111 (1962).

(4) The ligand ions are designated by the following abbreviations: btfa, benzoyltrifluoroacetonate ion; dbm, dibenzoylmethanate ion; hfa, hexafluoroacetylacetonate ion; ttfa, thenoyltrifluoroacetonate ion.

(5) W. G. Palmer, "Experimental Inorganic Chemistry," Cambridge University Press, Cambridge, England, 1954.

(6) A. D. Bishop, M.S. Thesis, Louisiana State University, Baton Rouge, La., 1962.