structurally related vanadium complex $(\pi\text{-}C_5H_5)_2V_2(CO)_5$.[6c] Since chromium is smaller than vanadium, a secondary bonding interaction between C(1) and the remote chromium atom is expected to be weaker than the corresponding interaction in the vanadium complex.

The ir spectrum of $[(\pi\text{-}(CH_3)_5C_5)Cr(CO)_2]_2$ is consistent with the structural findings above. Carbonyl stretching frequencies (1876, 1857 cm^{-1}, KBr)[8] were found in the region usually assigned to terminal carbonyl groups. Two bands are expected from group theory considerations (point group C_i), one for each unique carbonyl group; presumably, the lower frequency corresponds to carbonyl 1. The ir spectrum of $(\pi\text{-}C_5H_5)_2V_2(CO)_5$ shows five carbonyl stretching bands; the low-frequency band (1815 cm^{-1}, KBr)[21] is considerably below those found in $[(\pi\text{-}(CH_3)_5C_5)Cr(CO)_2]_2$ and this is also consistent with a greater degree of bridging in the former compound. The pmr spectrum[8] of $[(\pi\text{-}(CH_3)_5C_5)Cr(CO)_2]_2$ showed only a sharp singlet at τ 8.37 due to the methyl pro-

tons. Either the difference in shielding of nonequivalent methyl groups is too small to be detected on the nmr time scale or the molecule exhibits fluxional properties in solution. The second explanation is favored, particularly since $(\pi\text{-}C_5H_5)_2V_2(CO)_5$, with nonequivalent vanadium atoms, also showed a singlet pmr spectrum.[21]

(21) E. O. Fischer and R. J. J. Schneider, *Chem. Ber.*, 103, 3684 (1970).

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Model Compounds of Biological Molybdenum. I. Flavin and Mixed-Ligand Complexes of Molybdenum(IV) and -(V)

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The first solid flavin complexes of molybdenum(IV) have been isolated and characterized by dta, tga, ir, vis–uv, nmr, and epr data. Their general formulation is MoOCl$_3$(H-flavine), with the organic ligand being a monocation complexed as a bidentate ligand through its primary binding site, C=O(4) and N(5). Ir data are cited in support of this mode of bonding. The first solid molybdenum(V)–flavine complex has been isolated and partially characterized; its epr spectrum suggests that it is monomeric. Mixed-ligand complexes of oxomolybdenum(IV) containing both a flavine molecule and a sulfur-donor ligand have been synthesized for the first time. It is believed that these compounds may approximate the first coordination sphere environment of molybdenum in certain biological-molybdenum species.

It is now well established that molybdenum is an essential component of at least five different redox enzymes.[1-3] Despite a very large number of papers, which deal mainly with studies of the mammalian enzyme xanthine oxidase, several important questions remain unanswered. (1) What is (are) the oxidation state(s) of the metal in the resting enzymes, and what oxidation state changes take place during normal substrate turnovers? (2) Do atom as well as electron transfers involving the molybdenum take place during turnovers? (3) What groups (*e.g.*, from coenzyme flavines and/or from the apoenzyme itself) are permanently attached to the molybdenum, and what groups (if any) attach and detach during turnovers? In other words, what does the immediate (first coordination sphere) environment of the molybdenum look like before, during, and after a redox turnover? We have been preparing and characterizing a number of compounds of molybdenum with the aim of simulating the active sites of biological molybdenum, with the emphasis on the oxidation state of the metal and its first

coordination sphere environment. These compounds are then to be assayed for their redox behavior with various redox substrates including the actual biological substrates. In this paper we describe the preparation and characterization of 12 new compounds of molybdenum in oxidation states IV and V. (See Table I.) A later paper will deal with the pertinent redox reactions of these and other new products.

In Chart I are shown structural formulas, compound names, and name abbreviations for the ligands employed in this work. For the four flavine ligands 3-6 the abbreviation takes on an initial H when the complex forms, since N(1) becomes protonated. Thus HEAMIA, HTMIA, HRTA, and HRTB stand for the respective flavine molecules after they are complexed resulting in the generalized structure
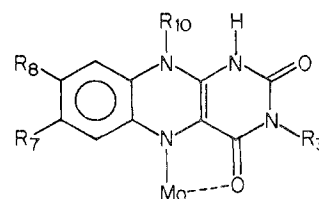
(1) R. C. Bray and T. C. Swann, *Struct. Bonding (Berlin)*, 11, 107 (1972).
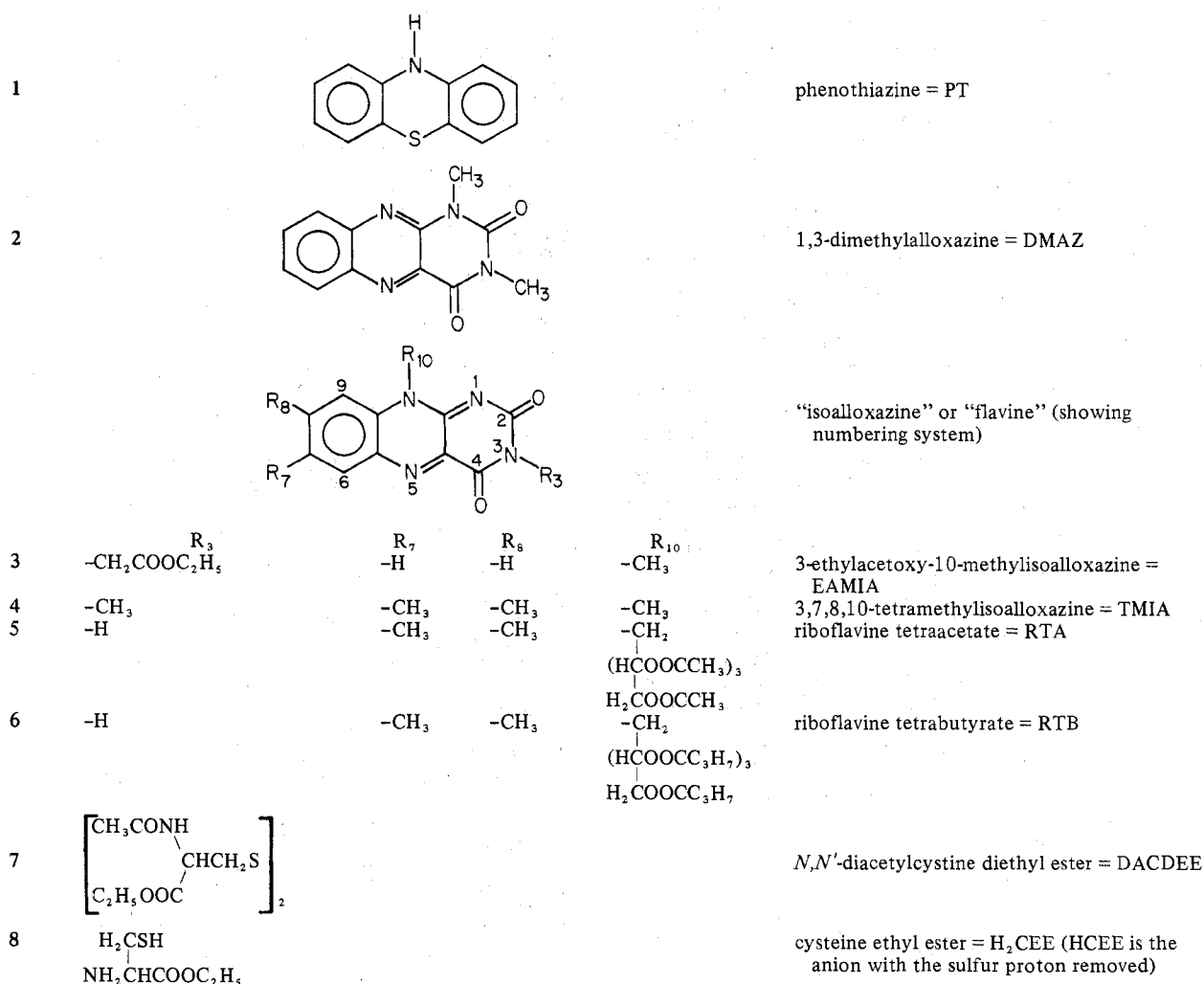(2) J. T. Spence, *Coord. Chem. Rev.*, 4, 475 (1969).
(3) E. L. Stiefel, *Proc. Nat. Acad. Sci. U. S.*, 70, 988 (1973).

Table I. New Compounds of Molybdenum(V) and -(IV)[a]—Elemental Analyses[b]

	Calcd				Found			
Compd	C	H	N	Other	C	H	N	Other
PTMoO$_2$Cl$_2$; C$_{12}$H$_9$NSMoO$_2$Cl$_2$	36.20	2.28	3.52		35.65	2.41	3.49	
PTMoOCl$_4$; C$_{12}$H$_9$NSMoOCl$_4$	31.82	2.00	3.09	7.08 (S)	31.21	2.39	3.07	6.50 (S)
MoOCl$_3$(TMIA)·HCl; C$_{14}$H$_{14}$N$_4$O$_2$MoOCl$_3$·HCl	32.01	2.89	10.67		31.84	2.98	10.48	
MoOCl$_3$(HEAMIA); C$_{15}$H$_{15}$N$_4$O$_4$MoOCl$_3$	33.76	2.83	10.49	17.98 (Mo) 19.93 (Cl)	33.35	2.75	10.52	16.5 (Mo) 19.8 (Cl)
MoOCl$_3$(HTMIA)·0.5HCl	33.08	3.07	11.01	18.88 (Mo) 24.43 (Cl)	32.71	2.97	11.14	18.6 (Mo) 22.6 (Cl)
MoOCl$_3$(HRTB); C$_{33}$H$_{45}$N$_4$O$_{10}$MoOCl$_3$	45.24	5.18	6.39	10.95 (Mo) 12.14 (Cl)	43.75	5.04	6.29	10.8 (Mo) 11.7 (Cl)
Atom ratios	33	45	4	1 (Mo) 3 (Cl)	33	45.25	4.065	1.017 (Mo) 2.99 (Cl)
MoOCl$_3$(HRTA)·HCl; C$_{25}$H$_{29}$N$_4$O$_{10}$MoOCl$_3$·HCl	37.50	3.78	7.04		37.40	3.79	6.74	
MoOCl$_3$(HTMAZ)·1.5HCl; C$_{14}$H$_{15}$N$_4$O$_2$MoOCl$_3$· 1.5HCl	30.89	3.05	10.28		31.15	2.97	10.62	
Mo$_2$OCl$_4$(HCEE)$_2$; C$_{10}$H$_{22}$N$_2$O$_4$S$_2$Mo$_2$OCl$_4$	18.52	3.42	4.32		18.82	3.86	4.21	
MoOCl$_2$(DACDEE)·3HCl; C$_{14}$H$_{24}$N$_2$O$_6$S$_2$- MoOCl$_2$·3HCl	24.99	4.04	4.16		24.82	4.03	3.67	
MoOCl$_2$(HCEE)(HTMIA)·2HCl; C$_{19}$H$_{24}$N$_5$O$_4$- SMoCl$_2$·2HCl	33.83	3.89	10.39		33.53	4.07	9.91	
MoOCl$_2$(DACDEE)(HTMIA)·2HCl; C$_{28}$H$_{38}$N$_6$O$_8$S$_2$MoOCl$_2$·2HCl	37.08	4.45	9.27		36.60	4.49	9.72	

[a] The first three compounds contain Mo(V); the remainder are Mo(IV) compounds. [b] Elemental analyses for the ligands prepared in this work are reported at the end of each preparation description in the Experimental Section.

Chart I

1   phenothiazine = PT

2   1,3-dimethylalloxazine = DMAZ

"isoalloxazine" or "flavine" (showing numbering system)

	R$_3$	R$_7$	R$_8$	R$_{10}$	
3	–CH$_2$COOC$_2$H$_5$	–H	–H	–CH$_3$	3-ethylacetoxy-10-methylisoalloxazine = EAMIA
4	–CH$_3$	–CH$_3$	–CH$_3$	–CH$_3$	3,7,8,10-tetramethylisoalloxazine = TMIA
5	–H	–CH$_3$	–CH$_3$	–CH$_2$ (HCOOCCH$_3$)$_3$ H$_2$COOCCH$_3$	riboflavine tetraacetate = RTA
6	–H	–CH$_3$	–CH$_3$	–CH$_2$ (HCOOCC$_3$H$_7$)$_3$ H$_2$COOCC$_3$H$_7$	riboflavine tetrabutyrate = RTB

7
$$\left[\begin{array}{c} CH_3CONH \\ \diagdown \\ CHCH_2S \\ \diagup \\ C_2H_5OOC \end{array} \right]_2$$
N,N'-diacetylcystine diethyl ester = DACDEE

8
$$\begin{array}{c} H_2CSH \\ | \\ NH_2CHCOOC_2H_5 \end{array}$$
cysteine ethyl ester = H$_2$CEE (HCEE is the anion with the sulfur proton removed)

Experimental Section

A. Preparation of Compounds. 1. 1,3,7,8-Tetramethylalloxazine, C$_{14}$H$_{14}$N$_4$O$_2$ = TMAZ. This compound was prepared by the methylation of lumichrome (7,8-dimethylalloxazine, available commercially). A 5.0-g (0.02-mol) sample of lumichrome was mixed with 100 ml of acetone, 18 g of anhydrous K$_2$CO$_3$, and 17 g (0.12 mol) of CH$_3$I. The solution was heated under reflux for 24 hr, cooled, filtered, and evaporated to dryness under vacuum. The residue was recrystallized twice from acetone and its purity was

checked by thin-layer chromatography (tlc); 90% yield. *Anal.* Calcd for $C_{14}H_{14}N_4O_2$: C, 62.21; H, 5.22; N, 20.73. Found: C, 62.26; H, 5.29; N, 20.90.

2. Riboflavine Tetraacetate, $C_{25}H_{28}N_4O_{10}$ = RTA. The procedure used was that of Kyogoku and Yu,[4] and yellow flaky crystals were obtained in 85% yield. The purity of the compound was checked by tlc. *Anal.* Calcd for $C_{25}H_{28}N_4O_{10}$: C, 55.14; H, 10.29; N, 5.18. Found: C, 54.00; H, 10.05; N, 5.03.

3. Cysteine Ethyl Ester Hydrochloride Hemihydrate, $C_5H_{11}NO_2$·HCl·0.5H_2O ($C_5H_{11}NO_2$ = H_2CEE). This compound was prepared by the procedure of Cherbuliez and Plattner,[5] and it had a melting point of 117–121°. *Anal.* Calcd for $C_5H_{13}ClNO_{2.5}S$: C, 30.84; H, 6.74; N, 7.19. Found: C, 30.13; H, 6.27; N, 7.15.

4. *N,N'*-Diacetylcystine Diethyl Ester, $C_{14}H_{24}N_2O_6S_2$ = DACDEE. The procedure used for this preparation was that of Cherbuliez and Plattner,[5] and the product melted at 121–123°. *Anal.* Calcd for $C_{14}H_{24}N_2O_6S_2$: C, 44.19; H, 6.36; N, 7.37. Found: C, 44.10; H, 6.56; N, 7.46.

5. 3,7,8,10-Tetramethylisoalloxazine, $C_{14}H_{14}N_4O_2$ = TMIA. This compound was prepared by two different procedures.

(a) 4-Bromo-5-nitro-*o*-xylene was prepared first by the method of Guzzo and Tollin.[6] The reaction of this compound with CH_3NH_2 and atmospheric pressure hydrogenation of the subsequent product using the procedure of Selbin, *et al.*,[7] for both reactions yielded the desired reactant 2-amino-*N*,4,5-trimethylaniline (I). The other reactant required to make TMIA, methylalloxan (II), was prepared by the method of Fischer.[8] Then equimolar amounts of II and the hydrochloride of I were dissolved separately in minimum amounts of water, mixed, and heated at 60° for 15 min. A precipitate began to form immediately in the brown-black solution. Filtration and washing with water to produce the crude TMIA was followed by recrystallization from 95% ethanol; mp 319–321°. *Anal.* Calcd for $C_{14}H_{14}N_4O_2$: C, 62.22; H, 5.22; N, 20.72. Found: C, 61.98; H, 5.16; N, 20.96.

(b) TMIA was also prepared (in better overall yield) by the reaction of I with alloxan, followed by methylation of the product with CH_3I and K_2CO_3 in dry acetone. Equimolar amounts of alloxan and I were allowed to react in dilute HCl for 15 min at 60°. The crude 7,8,10-trimethylisoalloxazine (lumiflavine) (III) was separated by filtration, washed with water, and vacuum dried. A 5.0-g (0.02-mol) sample of crude III was mixed with 100 ml of acetone, 10 g of anhydrous K_2CO_3, and 8.5 g (0.06 mol) of CH_3I. The solution was heated under reflux for 24 hr and then filtered and evaporated to dryness under vacuum. The crude product was recrystallized from CH_2Cl_2–petroleum ether. *Anal.* Calcd for $C_{14}H_{14}N_4O_2$: C, 62.22; H, 5.22; N, 20.72. Found: C, 62.38; H, 5.28; N, 20.82.

6. 3-Ethylacetoxy-10-methylisoalloxazine, $C_{15}H_{14}N_4O_4$ = EAMIA. This compound was prepared by the reaction of ethyl bromoacetate with 10-methylisoalloxazine using a modification of the original procedure.[9] 10-Methylisoalloxazine (IV) was prepared by the reaction of methylalloxan with *N*-methyl-*o*-phenylenediamine as described by Guzzo and Tollin.[6] *N*-Methyl-*o*-phenylenediamine (V) was prepared from *o*-chloronitrobenzene using methods described by us earlier.[7] A slurry of 5.12 g (0.023 mol) of IV and 10 g (0.072 mol) of anhydrous K_2CO_3 was prepared in 80 ml of dry dimethylformamide (DMF). While the slurry was continuously stirred at room temperature, 17.2 g (0.103 mol) of ethyl bromoacetate in a 1:1 mixture with DMF was slowly added. After the addition was complete, the solution was heated at 60° for 2 hr. The resulting dark green-black solution was filtered and then evaporated to dryness under vacuum. The residue was recrystallized from dry $CHCl_3$ and dried under vacuum; yield 80%. The purity of the product was checked by tlc. *Anal.* Calcd for $C_{15}H_{14}N_4O_4$·0.25H_2O: C, 56.52; H, 4.58; N, 17.57. Found: C, 56.75; H, 4.37; N, 17.56.

7. Riboflavine Tetrabutyrate, $C_{33}H_{44}N_4O_{10}$ = RTB. This was purchased from Tokyo Tanabe Pharmaceutical Co. in "purified" condition, recrystallized from 1:1 (by volume) CH_2Cl_2–petroleum ether, and then checked for purity by tlc.

8. Phenothiazine, $C_{12}H_9NS$ = PT. This was purchased from

Eastman in technical grade, recrystallized by us twice from dry, reagent grade benzene, and checked for purity by tlc.

All of the following complex compounds of molybdenum were prepared in a dry nitrogen atmosphere glove bag. For the results of elemental analyses of these following compounds, see Table 1.

9. Phenothiazine Cation Radical Dichlorodioxomolybdate(V), $C_{12}H_9NSMoO_2Cl_2$ = PTMoO_2Cl_2. To 0.17 g (0.85 mmol) of phenothiazine in 10 ml of dry CH_3CN was added 10 ml of a CH_3CN solution containing 0.17 g (0.85 mmol) of MoO_2Cl_2. The resulting orange-black solution was poured into 500 ml of anhydrous diethyl ether, whereupon a green-black precipitate formed immediately. The compound was removed by filtration, washed with ether, and vacuum dried; yield ~20%.

10. Phenothiazine Cation Radical Tetrachlorooxomolybdate-(V), $C_{12}H_9NSMoOCl_4$ = PTMoOCl_4. This unique molybdenum compound has already been reported in a brief communication by us[10] and so we detail here only its preparation and elemental analyses. A solution of 0.55 g (2.15 mmol) of $MoOCl_4$ in 20 ml of dry chloroform was added to 25 ml of a solution of 0.43 g (2.17 mmol) of phenothiazine in dry chloroform. A very dark precipitate formed immediately. The compound was separated by filtration, washed with dry solvent, and vacuum dried. The epr spectrum of the compound established the presence of both the organic free radical and monomeric Mo(V); yield 90%, mp 190–191° dec.

11. (3,7,8,10-Tetramethylisoalloxazine)trichlorooxomolybdenum(V) Monohydrochloride, $C_{14}H_{14}N_4O_2MoOCl_3$·HCl = MoOCl_3-(TMIA)·HCl. To 25 ml of a dry chloroform solution of 0.195 g (0.71 mmol) of $MoCl_5$ was added 0.114 g (0.42 mmol) of the ligand in 25 ml of the same solvent. (Due to the extreme reactivity of $MoCl_5$ with oxygen and water, it was weighed out in a drybox.) The olive green precipitate, which formed immediately upon mixing, was filtered, washed with fresh solvent, and vacuum dried; yield 85%.

12. 3-Ethylacetoxy-10-methylisoalloxazine Trichlorooxomolybdate(IV), $C_{15}H_{15}O_4MoOCl_3$ = MoOCl_3(HEAMIA). To 0.35 g (1.5 mmol) of $MoCl_4$ dissolved in $CHCl_3$ was added 0.407 g (1.3 mmol) of the ligand dissolved in 20 ml of $CHCl_3$. The very dark purple precipitate which formed immediately was filtered, washed with fresh solvent, and vacuum dried; yield 68%. The epr spectrum of the solid exhibited a signal which corresponded to less than 0.01 spin/molecule.

13. 3,7,8,10-Tetramethylisoalloxazine Trichlorooxomolybdate-(IV) Hemihydrochloride, $C_{14}H_{14}N_4O_2MoOCl_3$·0.5HCl = MoOCl_3-(HTMIA)·0.5HCl. To 25 ml of a solution of 0.295 g (1.2 mmol) of $MoCl_4$ in $CHCl_3$ was added 0.243 g (0.98 mmol) of the ligand in 25 ml of $CHCl_3$. The very dark purple product which formed immediately was isolated, washed, and dried as with previous products; yield 70%.

14. Riboflavine Tetrabutyrate Trichlorooxomolybdate(IV), $C_{33}H_{44}N_4O_{10}MoOCl_3$ = MoOCl_3(HRTB). A 15-ml $CHCl_3$ solution of 0.60 g (0.92 mmol) of the ligand was added to 25 ml of a $CHCl_3$ solution of 0.251 g (1.05 mmol) of $MoCl_4$. The solution immediately turned very dark purple, almost black, but no precipitate formed. The solution was evaporated under vacuum to half the original volume and then an equal volume of dry cyclohexane was added. The resulting solution in a tightly stoppered flask was cooled for 3 hr in an ice bath whereupon the product was precipitated. The product was isolated by filtration, washed with cyclohexane, and vacuum dried; yield 80%.

15. Riboflavine Tetraacetate Trichlorooxomolybdate(IV) Monohydrochloride, $C_{25}H_{29}N_4O_{10}MoOCl_3$·HCl = MoOCl_3(HRTA)·HCl. A 25-ml $CHCl_3$ solution of 0.60 g (1.1 mmol) of the ligand was added to a 25-ml $CHCl_3$ solution containing 0.364 g (1.5 mmol) of $MoCl_4$. The solution turned very dark purple-black but no precipitate formed. The solvent was removed under vacuum and the residue was taken up in 10 ml of dry CH_2Cl_2. Gradual precipitation of the product was effected by adding petroleum ether until precipitation just started and then cooling the tightly stoppered flask in an ice bath. The product was isolated by filtration, washed with 1:1 petroleum ether–dichloromethane, and vacuum dried; yield 74%.

16. (1,3,7,8-Tetramethylalloxazine Trichlorooxomolybdate(IV) Sesquihydrochloride, $C_{14}H_{16}N_4O_2MoOCl_3$·1.5HCl = MoOCl_3-(HTMAZ)·1.5HCl. To a solution of 0.15 g (0.63 mmol) of $MoCl_4$ in 25 ml of $CHCl_3$ was added 0.10 g (0.37 mmol) of the ligand in 25 ml of $CHCl_3$. The solution immediately turned purple-black, but no precipitate formed. The solution was reduced to half-volume under vacuum and cooled in an ice bath whereupon the purple-black product precipitated. It was isolated by filtration, washed with cold CH_2Cl_2, and vacuum dried; yield 75%.

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(8) E. Fischer, *Justus Liebigs Ann. Chem.*, **215**, 304 (1882).

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17. Bis(ethyl cysteinato)tetrachloro-μ-oxo-dimolybdenum(IV), $C_{10}H_{22}N_2O_4Mo_2Cl_4O = (HCEE)Cl_2MoOMoCl_2(HCEE)$. To 0.133 g (0.56 mmol) of $MoCl_4$ in 25 ml of $CHCl_3$ was added 0.072 g (0.43 mmol) of cysteine ethyl ester hydrochloride dissolved in a mixture of 25 ml of $CHCl_3$ and 1 ml of absolute C_2H_5OH. A dark brown precipitate formed immediately and was filtered, washed with $CHCl_3$, and vacuum dried; yield 51%.

18. (*N,N*'-Diacetylcystine diethyl ester)dichlorooxomolybdenum(IV) Trihydrochloride, $C_{14}H_{24}N_2O_6S_2MoOCl_2 \cdot 3HCl = MoOCl_2 \cdot (DACDEE) \cdot 3HCl$. To 0.27 g (1.1 mmol) of $MoCl_4$ dissolved in 25 ml of $CHCl_3$ was added 0.30 g (0.75 mmol) of the ligand dissolved in 10 ml of $CHCl_3$. A brown oil settled out of the solution. The $CHCl_3$ was decanted and dry petroleum ether was added to the oil, causing it to solidify and permitting its isolation by filtration and vacuum drying.

19. Adduct of Cysteine Ethyl Ester and 3,7,8,10-Tetramethyl-isoalloxazine with Dichlorooxomolybdenum(IV) Dihydrochloride, $C_{19}H_{24}N_5O_4SMoOCl_2 \cdot 2HCl = MoOCl_2(HCEE)(HTMIA) \cdot 2HCl$. To 0.13 g (0.67 mmol) of the cysteine ethyl ester compound (preparation no. 3 above) dissolved in 50 ml of CH_3CN was added 0.36 g (0.71 mmol) of the Mo–TMIA complex (preparation no. 13 above) dissolved in 70 ml of CH_3CN. The color of the resulting solution was less intense than that of the molybdenum–flavine complex solution alone. No precipitate formed. All of the solvent was drawn off under vacuum and the black residue was taken up in 25 ml of dry CH_2Cl_2. Petroleum ether was then added to the solution until precipitation just commenced and then the tightly stoppered solution was cooled to 0°. The product was filtered, washed with CH_2Cl_2–petroleum ether, and vacuum dried; yield 50%.

20. Adduct of *N,N*'-Diacetylcystine Diethyl Ester and 3,7,8,10-Tetramethylisoalloxazine with Dichlorooxomolybdenum(IV) Dihydrochloride, $C_{28}H_{38}N_6O_8S_2MoOCl_2 \cdot 2HCl = MoOCl_2(DACDEE)(HTMIA) \cdot 2HCl$. To 60 ml of a CH_3CN solution containing 0.22 g (0.43 mmol) of the Mo–TMIA complex was added 0.15 g (0.39 mmol) of the DACDEE compound (preparation no. 4 above) dissolved in 10 ml of CH_3CN. No precipitate formed, so the solvent was removed under vacuum and the solid residue was taken up in 25 ml of CH_2Cl_2. Petroleum ether was added to initiate precipitation and then the mixture was cooled in an ice bath to complete the process. The black precipitate was filtered, washed with CH_2Cl_2–petroleum ether, and vacuum dried.

B. **Analytical and Physical–Chemical Measurements.** C, H, and N analyses were carried out by our own staff employing standard commercial analyzers. Occasional double checks were made by sending samples to the Galbraith Laboratories, Inc., Knoxville, Tenn. These latter laboratories are where Mo, Cl, and S analyses were performed.

Visible–uv spectra were recorded on a Cary Model 14. Ir spectra were recorded using Beckman IR-7 and IR-10 instruments or a Perkin-Elmer Model 180. A Du Pont Model 900 thermal analyzer was used for dta studies and a Du Pont Model 950 thermogravimetric analyzer was used for tga studies.

The dta and tga curves were consistent with our formulation of these compounds as pure substances but revealed that all of the compounds melted with decomposition. Both sets of curves further supported the existence and separate loss on heating of HCl molecules formulated in the original molecules.

Electron paramagnetic resonance spectra were recorded with a JEOLCO esr spectrometer, Model JES-3BS-X, using 100-kc modulation and measuring the field with a precision nmr gaussmeter. Solid $K_3Mo(CN)_8$ was used as a standard in the spin concentration measurements. A Varian HA-100 nmr spectrometer was used to obtain nmr spectra.

Results and Discussion

A. **Molybdenum(V) Compounds.** The properties of $PTMoOCl_4$, and in particular its unique epr spectrum, have already been reported by us.[10] In the solid state there is one fairly broad (55 G) asymmetric signal at $\langle g \rangle = 1.98$. In solution there are two clearly separate signals at 1.95 (the Mo(V) electron) and 2.006 (the cation radical electron), and each corresponds to one full electronic charge. The analogous compound $PTMoO_2Cl_2$ exhibits a very similar epr spectrum in the solid state, with $\langle g \rangle = 1.99$ and peak-to-peak signal width of 36 G. A spin concentration study of this signal showed a concentration of roughly two unpaired electrons per molecule. Unfortunately a solution epr spectrum could

not be obtained for this compound due to its insolubility in all solvents which do not decompose it. Nevertheless we do feel that this compound also represents a unique pentavalent molybdenum species since we know of no other compound which contains the dichlorodioxomolybdate(V) anion. Furthermore there is indication from the esr $\langle g \rangle$ value that this unique anion is complexed by the phenothiazine cation radical just as in the case of the $PTMoOCl_4$ compound. In the latter case there is evidence[10] for the complexing of this same free radical to the metal in the $MoOCl_4^-$ species.

The only other Mo(V) compound reported here, $MoOCl_3$-(TMIA)·HCl, could not be thoroughly characterized due to its instability. In the polycrystalline solid, it did exhibit a Mo(V) epr signal at $\langle g \rangle = 1.954$ and a spin concentration of *ca.* 0.8 spin/molecule, which suggests that it is monomeric. Its ir spectrum exhibited strong bands at 986 cm^{-1} (Mo=O), 1755 cm^{-1} (C=O(2)), and 1702 cm^{-1} (C=O(4)). (The (2) and (4) refer to oxygens at the no. 2 and 4 positions on the isoalloxazine ring (*vide supra*).) Since TMIA itself exhibits these C=O bands at 1705 and 1670 cm^{-1}, respectively, the increase in each of these frequencies in the complex suggests that neither of the carbonyl oxygens is attached to the metal. This is in sharp contrast to the Mo(IV) compounds (*vide infra*) where the frequency of the C=O(2) increases and that of the C=O(4) decreases from the ligand to the complex. The olive green Mo(V) compound produces a red-orange solution in CH_3CN, whereas all of the molybdenum(IV)–flavine complexes are purple-black solids which produce deep purple solutions in CH_3CN. $MoOCl_3(TMIA)$·HCl exhibits a complicated visible-uv solution spectrum with absorption maxima at 513, 476, 440, 404, 340, and 318 nm. By contrast the analogous Mo(IV) compounds exhibit only three maxima in this same region (*vide infra*).

B. **Molybdenum(IV) Compounds.** These flavine-containing complexes represent, to our knowledge, the first such Mo(IV) complexes to be isolated. Numerous studies from several other laboratories[11] have dealt with *solution* interactions between flavine molecules and molybdenum in different oxidation states. Thus our initial efforts were directed toward establishing the mode of binding of the isoalloxazine moiety to the molybdenum. Ligation may possibly occur through the "primary binding site," *viz.*, chelation through N(5) and C=O(4), through N(1) and C=O(2) (much less likely because of four-membered ring formation and steric hindrance), through the N(5) and N(10), or through either of the latter acting alone. In Table II we have summarized the pertinent ir data which we feel very strongly support the binding of the flavine to the Mo(IV) through the primary binding site, *viz.*, C=O(4) and N(5). It can be seen that in each case (the four isoalloxazine and the one alloxazine compounds) the stretching frequency for C=O(2) increases and that of C=O(4) decreases on going from ligand to complex. The basis for our assignments of the carbonyl bands, C=O(2) and C=O(4), follows. The most recent ir study of isoalloxazines which includes assignments of carbonyl frequencies seems to be a 1960 paper,[12] in which the higher frequency band was assigned to C=O(4) and the lower one to C=O(2). However, since 1970, several crystal structure investigations of isoalloxazines have been reported.[13] They

(11) G. Colovos and J. T. Spence, *Biochemistry*, **11**, 2542 (1972); P. Kroneck and J. T. Spence, *J. Inorg. Nucl. Chem.*, **35**, 3391 (1973); T. Huang and G. P. Haight, *J. Amer. Chem. Soc.*, **93**, 611 (1971); L. W. Amos and D. T. Sawyer, *Inorg. Chem.*, **13**, 78 (1974).

(12) P. Hemmerich, B. Prijs, and H. Erlenmeyer, *Helv. Chim. Acta*, **43**, 372 (1960).

Table II. Ir and Visible-Uv Bands for Molybdenum(IV)-Flavine Complexes (in cm^{-1} and nm, Respectively)

Compd	Mo=O	C=O(2)	C=O(4)	N–H	Visible-uv				
MoOCl$_3$(HTMIA)·0.5HCl	980	1752	1595	3190	525		412		303	
TMIA		1705	1670			441		341		271
MoOCl$_3$(HEAMIA)	984	1730	1605	3120	509		393		304	
EAMIA		1718	1655			437		333		267
MoOCl$_3$(HRTB)	982	1728	1630	3130[a]	519		417		307	
RTB		1700	1663	3180		444		349		268
MoOCl$_3$(HRTA)·HCl	984	1740	1635	3130[a]	525		450		350	
RTA		1730	1670	3160		440		340		265
MoOCl$_3$(HTMAZ)·1.5HCl	982	1728	1625	3130	650 755		375		310 255	
TMAZ		1720	1675			386		334		250

[a] Since the ligands RTA and RTB have bands due to the N(3)–H stretch, the bands in the spectra of the complexes must include these along with those due to the newly formed N(1)–H stretch.

all show that the bond length of the C=O(2) is *shorter* than that of the C=O(4). Therefore we believe the correct assignment to be just the reverse of that in the 1960 paper.

Also listed in Table II are Mo=O stretching frequencies which represent the primary evidence that the starting MoCl$_4$ molecule hydrolyzes to the monooxo species in the course of the preparative reactions. The source of the water molecule which effects this hydrolysis is probably the ligands (which are never strictly anhydrous) and/or the solvents (which are likewise not totally anhydrous). The water molecule is also the source of the protons which form HCl molecules and, more importantly, which attach to N(1) in the flavine complexes (and presumably N(10) in the alloxazine complex). Evidence for these nitrogen-attached protons comes likewise from the ir spectra of the complexes, and Table II records the observed N–H stretching frequencies. The assignments of Mo=O and N–H stretching frequencies are quite straightforward inasmuch as the bands are the only strong absorptions in the respective ir regions which are present in the complexes but absent in the ligands.

We tentatively formulate the flavine complexes as six-coordinate species with oxomolybdenum(IV) complexed by one bidentate flavine molecule and three chloride ions. We believe that the oxygen in monooxo species comes from hydrolysis of the MoCl$_4$ by water molecules present in the ligand samples plus minute amounts present in the reaction solvents. The reactions were all carried out in very dilute solutions where the quantity of water required by the molybdenum is expected to be present without the need intentionally to add additional water. The values of Mo=O stretching frequency and the *absence* of lower frequency ir bands assignable to bridging Mo-O-Mo species and to other Mo(V)- and Mo(VI)-oxo formulations, as well as the mode of formation of the compounds, strongly support our formulation of these compounds as monooxo–molybdenum(IV) species but do not conclusively prove this formulation. The extra HCl molecules which are present in three of the four compounds may be present as weakly bound molecules attached by hydrogen to the flavine molecule, or the coordination number of the Mo(IV) may be increased to 7 by complexation of a fourth chloride and attachment of the proton to some basic site on the flavine.

The nmr spectra for TMIA and its Mo(IV) complex produced the resonances reported in Table III. Assignments were made in consultation with Professor Norman Bhacca of our department. The spin density data are for the free

(13) R. Norrestam and B. Stensland, *Acta Crystallogr., Sect. B,* **28**, 440 (1972); M. Vonglehn, *ibid.,* **28**, 434 (1972); T. D. Wade and C. J. Fritchie, *J. Biol. Chem.,* **248**, 2337 (1973). This last paper deals with the structure of metal complexes of flavines.

Table III. Chemical Shifts (in ppm from TMS) of the Proton Resonances for MoOCl$_3$(HTMIA)·0.5HCl and the Experimental Spin Densities for an Isoalloxazine Semiquinone

	N(3)–CH$_3$	C(6)–H	C(7)–CH$_3$	C(8)–CH$_3$	C(9)–H	C(10)–CH$_3$
MoOCl$_3$(HTMIA)·0.5HCl (in CD$_3$CN)	3.35	8.30	2.45	2.90	7.40	4.35
TMIA (in CDCl$_3$)	3.50	8.05	2.45	2.55	7.40	4.10
Spin density[14]	0.00[a]	0.14	0.00[a]	0.14	0.00[a]	0.14

[a] Value too small to measure.[14]
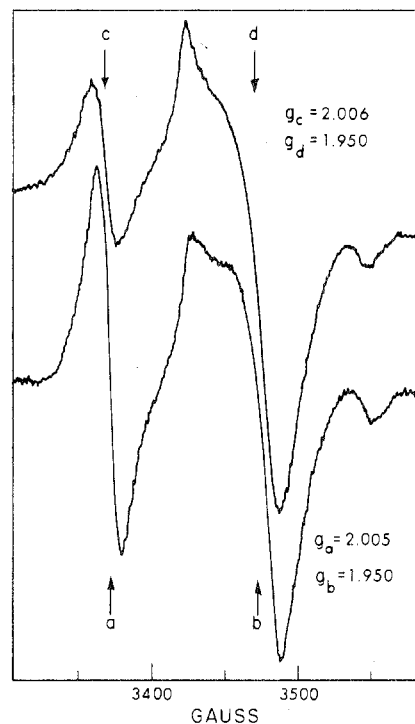
Figure 1. Epr spectrum of MoOCl$_3$(HEAMIA) in the solid state (upper curve) and in CH$_3$CN solution (lower curve) at ambient temperature.

radical semiquinone.[14] The observed chemical shifts in the complexed flavine suggest that they are Fermi contact in nature rather than pseudocontact.

The epr spectrum for MoOCl$_3$(HEAMIA), both in the solid state and in CH$_3$CN solution, reveals signals (Figure 1) both from a free radical, at $\langle g \rangle = 2.006$, and from Mo(V), at $\langle g \rangle = 1.950$. However, a spin density measurement shows that these signals represent less than 0.01 spin/molecule in

(14) A. V. Guzzo and G. Tollin, *Arch. Biochem. Biophys.,* **105**, 380 (1964).

Table IV. Pertinent Ir Bands for the Two S-Donor Ligands and Their Corresponding Mo(IV) Complexes (in cm^{-1})

Compd	Mo-O-Mo or Mo=O	Amide C=O	Ester C=O	S-H	N-H
Mo$_2$OCl$_4$(HCEE)$_2$	740		1738		3020
H$_2$CEE			1750	2480	3100
MoOCl$_2$(DACDEE)·3HCl	987	1590	1745		3310
DACDEE		1655	1743		3325

the complex. One interpretation that can be based on this fact is that the molybdenum(IV)-flavine complex is in equilibrium with a very small amount of molybdenum(V)-flavinesemiquinone complex and that at least for the latter species there is no difference in the solid complex and its solution species.

The Mo(IV)-HCEE and Mo(IV)-DACDEE complexes were prepared in the anticipation that they would further react with flavine ligands to produce mixed-ligand species. This hope faded when these two S-ligand compounds proved to be very insoluble in the required reaction solvents. Since these compounds were not useful for our purposes, we did not study them extensively. However, their pertinent ir spectral bands are listed in Table IV. We formulate the DACDEE compound as a monomeric oxomolybdenum(IV) complexed by at least two chlorides and by the DACDEE, probably *via* a sulfur atom and the amide oxygens. Evidence for the latter is the observed decrease in the C=O stretching frequency from 1655 to 1590 cm^{-1} on going from ligand to complex. The HCEE compound is formulated as a monooxobridged dimer on the basis of the absence of a Mo=O frequency and the clear presence at 740 cm^{-1} of a band assignable to the Mo-O-Mo stretching frequency.[15] The cysteine ethyl ester is probably bound to the molybdenum *via* all *three* of its potential ligand atoms, as was suggested[15] in the case of a Mo(V) complex with this same ligand.

Finally, the mixed-ligand (flavine and S-donor) complexes of Mo(IV) were prepared by allowing the S-donor ligand to react with the flavine complex. The pertinent ir bands for the two complexes are recorded in Table V. Since the ir

(15) L. R. Melby, *Inorg. Chem.*, **8**, 349 (1969).

Table V. Pertinent Ir Bands for the Mixed-Ligand Complexes and the Appropriate Ligands (in cm^{-1})

Compd	Mo=O	TMIA C=O- (2)	C=O- (4)	Ester C=O	Amide C=O	S-H	N-H[a]
MoOCl$_2$(HCEE)-(HTMIA)·2HCl	984	1715	1600	1740			2960
H$_2$CEE				1750		2480	3100
TMIA		1705	1670				
MoOCl$_2$(DACDEE)-(HTMIA)·2HCl	980	1715	1600	1738	1660		3280
DACDEE				1743	1655		3325

^{a} For the complexes these bands are broad and probably include the band due to the cysteine derivative N-H stretch as well as that due to the HTMIA N(1)-H formed in the complex.

spectra are so complicated, most of the assignments, with the exceptions of those for Mo=O, S-H, and N-H stretching frequencies, are quite tentative. However, they are consistent with the models put forth earlier in this paper for the Mo(IV) complexes containing one or the other of the two ligands. We believe that the first coordination sphere of the Mo(IV) contains a multiply bonded oxygen, two chloride ions, and each of the polydentate ligands bound through at least two ligand atoms.

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Complexes of Di(tertiary stibines). Group VIb Metal Carbonyl Halide Derivatives of Bis(diphenylstibino)methane

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The potentially bidentate antimony ligand (C$_6$H$_5$)$_2$SbCH$_2$Sb(C$_6$H$_5$)$_2$ (Dpsm) reacts immediately with the molybdenum and tungsten tetracarbonyl dihalides to yield M(CO)$_3$(Dpsm)$_2$X$_2$ (M = Mo, X = Cl, Br; M = W, X = Cl, Br, I) and Mo(CO)$_3$-(Dpsm)I$_2$. Under more vigorous conditions most of the tricarbonyls lose 1 mol of ligand and carbon monoxide to produce species of the type M(CO)$_2$(Dpsm)X$_2$. Structural and bonding assignments are based upon the interpretation of nmr and infrared spectral data. The types of Dpsm derivatives, their relative stabilities, and spectral data are compared with those for the known phosphorus and arsenic ligand complexes.

Introduction

Compared to the extensive investigations of transition metal carbonyl derivatives of amine, phosphine, and arsine mono- and polydentate ligands relatively few studies of analogous

stibine Lewis bases have been conducted.[1-9] In fact, there are only four reports describing reactions of metal carbonyls

(1) G. Booth, *Advan. Inorg. Chem. Radiochem.*, **6**, 1 (1964).
(2) M. Kilner, *Advan. Organometal. Chem.*, **10**, 115 (1972).