Inorganica Chimica Acta, 46 (1980) 275–280
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Studies on the Structure of Oxalato Binuclear Mo(III) Complexes of Amino Acids

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Received May 10, 1980

Reaction of the molybdenum(III) compound $Mo(OH)_3$ *with ligands* $C_2O_4^{2-}$ *and L, gave complexes* $[Mo_2OC_2O_4L_2(H_2O)_4]\cdot xH_2O$ *(L = α-alanine, x = 2; L = β-phenyl-α-alanine, x = 0; L = 4-hydroxyproline, x = 2). The complexes are formulated and structures proposed on the basis of analyses and physical measurements. The binuclear complexes contain the μ-oxo-μ-oxalato-dimolybdenum(III) group.*

Introduction

As it follows from review [1] of the molybdenum bridge complexes, relatively scarce experimental data are available on the structure of Mo(III) complexes. The molybdenum compounds with amino acids and the organic sulphur compounds are interesting as models of enzymes, such as xanthine oxidase [2–4], aldehyde oxidase [5], nitric reductase [6, 7] and nitrogenase [8, 9]. It is suggested that Mo(III) plays the role of the active catalyst in the model Mo–cysteine system [10]. Recently, Mo(III) was believed to be present also in nitrogenase, which was confirmed by the following evidence:

a) reduction of N_2 and C_2H_2 is catalysed by the inorganic Mo(III) species over the wide temperature and pressure range [11, 12];

b) the satisfactory model of the nitrate reduction is based upon the $Mo(H_2O)_6^{+3}$ cation [13];

c) observation of the EPR signal of Mo(III) in the nitrate reductase [14–16].

Since molybdenum plays the role of the electron carrier between the substrate and coenzyme and between the substrate and iron in enzymes, the mechanism of that process required explanation. To this purpose the redox reactions were examined. Although a number of papers dealing with that problem has been recently published [17–21], neither has the mechanism of the redox reaction of the binuclear $Mo_2O_4^{+2}$ centre been explained, nor has the formation mode of the active catalyst deriving from that core been recognized. Owing to this it appeared reasonable to undertake the investigations on the Mo(III) bondings with amino acids to elucidate their structures. Such studies would complete and broaden our knowledge about these compounds.

Experimental

Preparations

All reactions and manipulations were carried out under argon atmosphere.

The starting substance for the syntheses was molybdenum(III) hydroxide, which was prepared by the following method. A solution of ammonium molybdate (5×10^{-3} kg) in water (4×10^{-1} dm^3) was reduced electrolytically using a gauze platinum (55×10^{-4} m^2) as cathode and a graphite rod immersed in 10% hydrochloric acid as anode. The cathode compartment was separated from the anode compartment by a Pucall compound cylinder. The electrolytic process was carried out a 2A and 8–10 V for 6 hours. For a complete deareation, argon was passed through the solution. Concentrated ammonia was then run into the reduced solution and the resulting precipitate was filtered off, washed with boiling water, and after washing away the SO_4^{2-} ions, dried in a vacuum desiccator over P_2O_5.

μ-oxo-μ-oxalato-bis[diaquo(α-alanine)molybdate-(III)] dihydrate, $[Mo_2OC_2O_4(C_3H_7NO_2)_2(H_2O)_4]\cdot 2H_2O$ *(1)*

Stoichiometric amounts of oxalic acid and α-alanine were added to a suspension of the $Mo(OH)_3$ in water (3×10^{-1} dm^3). The suspension was boiled until its volume decreased to 1/3 of the original. Then acetone (0.5 dm^3) was added to the filtered reaction solution and left to stand for 2–3 days. After that time the complex precipitated as an oil on the bottom. After decanting the parent solution and washing the oil several times with acetone the complex was obtained as a powder. The complex was then dried in a desiccator filled with argon over P_2O_5. *Anal.* , Found: C, 16.96; H, 3.90; N, 5.00; Mo, 33.17; H_2O, 18.60%. Calcd.: C, 16.56; H, 4.17; N, 4.85; Mo, 33.07; H_2O, 18.62%.

TABLE I. Magnetic Susceptibility Data for the Complexes.

$[Mo_2OC_2O_4(C_3H_7NO_2)_2(H_2O)_4]\cdot 2H_2O$		$[Mo_2OC_2O_4(C_9H_{11}NO_2)_2(H_2O)_4]$		$[Mo_2OC_2O_4(C_5H_8NO_3)_2(H_2O)_4]\cdot 2H_2O$	
T, (K)	χ_M^{cor} (c.g.s)	T, (K)	χ_M^{cor} (c.g.s)	T, (K)	χ_M^{cor} (c.g.s)
78	407.76	78	251.0	77	290.1
101	425.17	101	334.3	101	248.3
114	413.56	115	321.1	114	251.6
127	419.36	131	249.6	127	211.7
141	401.96	143	238.5	140	149.3
156	407.76	156	241.2	154	110.8
169	396.16	161	235.0	167	157.3
182	401.96	184	226.7	180	146.0
195	384.55	200	195.4	195	124.0
209	384.55	212	223.2	207	104.1
222	378.75	242	202.4	220	137.3
237	378.75	251	226.7	234	110.8
256	361.35	278	195.4	252	117.4
265	367.15	295	188.2	264	124.0
281	355.55			281	117.4
297	367.15			297	104.1

μ-oxo-μ-oxalato-bis[diaquo(DL-β-phenyl-α-alanine)-molybdate(III)], $[Mo_2OC_2O_4(C_9H_{11}NO_2)_2(H_2O)_4]$ *(II), and μ-oxo-μ-oxalato-bis[diaquo(L-4-hydroxyproline)molybdate(III)] dihydrate*, $[Mo_2OC_2O_4(C_5H_8NO_3)_2(H_2O)_4]\cdot 2H_2O$ *(III)*

The complex (II) was obtained by boiling the suspension of the molybdenum (III) hydroxide with stoichiometric amounts of DL-β-phenyl-α-alanine and oxalic acid under conditions described above. Similar conditions for molybdenum(III) hydrixode, L-4-hydroxyproline and oxalic acid yield complex (III). *Anal.* Calcd.: C, 34.50; H, 4.02; N, 4.02; Mo, 27.56; H_2O, 10.34%. for (II): Found: C, 34.09; H, 3.95; N, 4.10; Mo, 27.89; H_2O, 9.60%. *Anal.* Calcd: C, 21.70; H, 4.25; N, 4.21; Mo, 28.89; H_2O, 16.26%. for (III): Found: C, 21.66; H, 4.45; N, 4.28; Mo, 29.34; H_2O, 16.00%.

Analyses

Molybdenum was determined gravimetrically as Mo_2O_3 after oxidation of Mo(III) to Mo(VI) with 30% H_2O_2 solution and treating with 5% 8-hydroxyquinoline in 4 *M* acetic acid solution. The precipitate was calcined to constant weight at 600 °C. The oxidation state of molybdenum was determined by permanganate titration on cooling under argon atmosphere. The samples of the same weight (1.2×10^{-3} kg) of complexes *(I)*, *(II)* and *(III)* were prepared and they required 2.64×10^{-2}, 2.20×10^{-2} and 2.31×10^{-2} dm^3 of 0.093 *N* permanganate, respectively. The percentage of molybdenum present in the complexes is in good agreement with the results obtained by gravimetric method.

Carbon, hydrogen and nitrogen were determined by the semi-microanalytical methods. Water was determined by heating the complexes in an atmosphere of argon using a thermobalance model MOM Budapest 3427-T.

Physical Measurement

IR spectra of the compounds were recorded in the ranges 400–4000 cm^{-1} (potassium bromide discs) and 50–500 cm^{-1} (nujol mulls) with a Perkin-Elmer Model 621 and Perkin-Elmer Model 180 spectrophotometer, respectively. UV and visible solution and reflectance spectra were recorded with a Hitachi spectrophotometer in the range 12000–50000 cm^{-1}. Magnetic susceptibilities were measured on powdered samples using the Gouy method in the temperature range 77–300 K.

Results and Discussion

General Properties of the Complexes

The complexes were obtained as dark crimson powder solids. The dry solids could be handled in air although they oxidized slowly within several days. The complexes were soluble in cold water but not in organic solvents.

Thermogravimetric Analyses

In order to determine the water content of the complexes thermogravimetric analyses were carried out. For the complex *(I)* the first decrease in weight of 7.3% was observed at about 100 °C due to the loss

TABLE II. Assignments of the Main Infrared Bands.[a]

Complex (*I*) ($\mathrm{cm^{-1}}$)	Complex (*II*) ($\mathrm{cm^{-1}}$)	Complex (*III*) ($\mathrm{cm^{-1}}$)	Assignment	Literature
3430 s	3420 s	3440 s	$\nu_s(\mathrm{O{-}H})$	
3120 s, br	3120 s, br	3150 s, br	$\nu(\mathrm{N{-}H})$	
1670 vs, br	1675 vs, br	1655 vs, br	$\delta(\mathrm{H{-}O{-}H})$	
1340 m	1320 m	1310 m	$\nu_s(\mathrm{C{-}O}) + \delta(\mathrm{O{=}C{-}O})$	
1120 m	1130 m	1180 m	$\delta(\mathrm{C{-}H})$	
954 m	960 m	960 m	$\nu_s(\mathrm{C{-}O}) + \delta(\mathrm{O{=}C{-}O})$	
905 m	905 m	905 m	$\delta(\mathrm{O{=}C{-}O}) + \nu(\mathrm{Mo{-}O})$	[34]
740 s	747 s	745 s	$\nu_{as}(\mathrm{Mo}\diagup^{\mathrm{O}}\diagdown\mathrm{Mo})$	
	700 m	690 m	$\delta(\mathrm{O{=}C{-}O})$	
525 m	535 m	535 m	$\nu_s(\mathrm{Mo}\diagup^{\mathrm{O}}\diagdown\mathrm{Mo})$	
478 m	479 m	475 m	$\nu_{as}(\mathrm{Mo{-}N})$	[46, 48]
310 w	352 w	350 w	$\nu(\mathrm{Mo{-}O})_{am}$	[46, 48]
300 vw	300 vw	300 vw	$\nu(\mathrm{Mo{-}O})_{ox}$	[47]

[a] Band intensities indicated by v (very), s (strong), m (medium), w (weak), and br (broad).

of two molecules of water from the outer coordination sphere. The large decrease in weight equal to 41.5% observed at 300 °C is thought to result from the simultaneous loss of two alanine molecules together with four inner sphere water molecules. The decrease in weight of 5% observed for complex (*II*) at 200 °C and of 40.5% at about 355 °C corresponds to the loss of four inner sphere molecules of water and two amino acid molecules, respectively. For the complex (*III*) 5% loss of weight occurs at about 155 °C due to the loss of two molecules of water from the outer coordination sphere. The subsequent loss in weight equal to 42% observed at 300 °C results from the loss of two amino acid molecules together with four inner sphere molecules of water, analogously with the case of complex (*I*).

Magnetic Properties

The results of magnetic susceptibility measurements are given in Table I. The molar susceptibilities were calculated for the whole molecules of dimers taking into account the appropriate diamagnetic corrections. Because of the nearly temperature-independent and small values of the magnetic susceptibilities, no magnetic moments were calculated for individual complexes. The observed paramagnetism was assumed to result from the monomeric impurities. The percentage of these impurities estimated according to the method of Trzebiatowska *et al.* [22], was equal to 0.3% for complex (*III*). These magnetic moments are much below the spin only value for molybdenum (III) (3.88 B.M.) indicating spin pairing between adjacent molybdenum atoms as found for many complexes of molybdenum(III) [23] and molybdenum(V) [24].

On the basis of the results of the analysis of vibrational spectra, the diagram for compounds containing angular oxygen bridge of C_{2v} symmetry of a system given by Trzebiatowska [25] was assumed to be relevant for the complexes studied. The lack of temperature dependence of magnetic susceptibility over the temperature range studied implies that the energy difference between $e_g{}^*$ (b_2) and $b_{1u}{}^*$ (a_2) considerably exceeds the kT value. Therefore it seems reasonable to assume the following electronic structure of the core: $(b_{2g}{}^*)^2(e_g{}^*)^4$.

IR Spectra

Positions of the main bands and assignments are listed in Table II. In order to confirm the assumption derived from the results of magnetic measurements, the structure of the compounds was further studied by IR spectroscopy. Hewkin *et al.* [26] have reported occurrence of asymmetric stretching vibrational bands around 860 $\mathrm{cm^{-1}}$ (ν_{as} $\mathrm{M_2O}$) in the IR spectra of bridged linear systems, where M designates a transition metal atom, as well as deforming vibration giving rise to the spectral band below 200 $\mathrm{cm^{-1}}$. The existence of the complexes of the above type has been reported by several recent studies [25, 27]. In the case of angular complexes vibrations ν_s, ν_{as} and ν_δ ($\mathrm{M_2O}$) give bands at 558 $\mathrm{cm^{-1}}$, 772 $\mathrm{cm^{-1}}$ and 220 $\mathrm{cm^{-1}}$ for $\mathrm{Cr_2O_7^{2-}}$ [28, 29] and at 550 $\mathrm{cm^{-1}}$, 750 $\mathrm{cm^{-1}}$ and 220 $\mathrm{cm^{-1}}$ for $\mathrm{V_2O_7^{2-}}$ [30, 31], respectively; for $[\mathrm{W_2O_{11}(H_2O)_2}]^{2-}$, ν_s

occurs at 556 cm^{-1} and ν_{as} at 790 cm^{-1}. The complexes with double oxygen bridge (M_2O_2) exhibit three IR active frequencies. For the molybdenum complexes stretching vibrations appear in the ranges 720 cm^{-1}–760 cm^{-1}, 490 cm^{-1}–670 cm^{-1} and 240 cm^{-1}–335 cm^{-1} [32].

Several complexes were synthesized by Mitchell and Scarle [23] by the reaction of dioxochloromolybdenum(III) $[Mo_2O_2Cl_2(H_2O)_6]$ with organic ligands. All of them exhibit intensive broad bands in the IR spectra in the region 670–690 cm^{-1} which they assigned to vibrations of a molybdenum–oxygen–molybdenum bridging system. The spectrum of the oxo-chloride in this region was similar to that of the molybdenum(V) complex $(Me_4N)_2[Mo_2O_4Cl_4(H_2O)_6]$ for which assignments have been made [33] for a doubly bridged structure (M_2O_2), *viz.* ν_s, 720 cm^{-1}; ν_{as}, 675 cm^{-1} and ν_δ, 705 cm^{-1}. The intensity is greatest for the ν_{as} band; the ν_s and ν_δ bands appear as shoulders. As expected, it was at lower wavenumbers in the molybdenum(III) complexes than in the molybdenum(V) complexes.

Since the IR spectra of our complexes show no bands either for the complex (*I*) within the range 810–890 cm^{-1}, or for complexes (*II*) and (*III*) within the range 820–890 cm^{-1}, an occurrence of linear oxygen bridge has been excluded. The lack of any band for complexes (*I*), (*II*) and (*III*) over the ranges 600–720 cm^{-1}, 610–690 cm^{-1} and 560–700 cm^{-1}, respectively, suggests that the (M_2O_2) core does not exist there. On this basis we have suggested that vibrations at 740 cm^{-1}, 747 cm^{-1} and 745 cm^{-1} for complexes (*I*), (*II*) and (*III*), respectively, should be assigned to the asymmetric vibration, while the vibrations at 525 cm^{-1} for complex (*I*) and at 535 cm^{-1} for complex (*II*) and complex (*III*) should be assigned to symmetric vibration of angular oxygen bridge.

IR spectra were further analyzed in order to ascertain whether the oxalate residue is bound as a simple chelate group or as a bridging one. For the $(PyrH)_4[Mo_2O_3(C_2O_4)(NCS)_6]$ complex the bands at 908 cm^{-1} and 810 cm^{-1} have been attributed to the vibrations originating from the oxalate bridge [34]. Thus the band occurring at 905 cm^{-1} in the IR spectra of the present study is likely to have the same origin. We have failed to identify the vibration around 810 cm^{-1} because of the occurrence of closely strong broad band at 790 cm^{-1}.

It has been univocally demonstrated in the present study that four water molecules exist in the inner coordination sphere of the complexes. Assuming the octahedral configuration of each central ion [35], we suggest that oxalate anion is linked to both molybdenum atoms. Although the possibility of the presence of simple chelate oxalato groups in the complexes should be taken into account, the resulting nonequivalency of two molybdenum atoms in these dimers would be unjustified. By comparison of the spectra of the complexes under study with those of free or metal-coordinated amino-acids [36], we find that amino acids coordinate through oxygen of carboxylic group and nitrogen of amino group.

Electronic Spectra

Interpretation of the electronic spectra of the examined compounds have created difficulties. The UV and visible spectroscopy, very useful in studies of energetic levels distribution in monomeric complex ions and in studies of the inner and outside coordination sphere, is of little value in studies of structure of polynuclear ions [34, 37–40]. The quantum mechanics calculations made usually by the SCCC MO [41] method do not always give satisfactory results, because of the complexity of a system. The complete discrepancy between the calculated and experimental data [42] of the electron transition of the $[Re_2Cl_8]^{2-}$ ion seems to be a good example. The spectral contours of complexes under investigation was subjected to the Gaussian analysis. With the parameters for that peak available, it is now possible to subtract it from the overall absorption envelope and then to repeat the process for the next peak. In this way, the peaks are subtracted sequentially until they are all removed [43–45]. Neither the construction of the energy diagram nor the more detailed interpretation of the obtained results was successful because of the lack of some data (bonding length, angle value, group symmetry). All those difficulties are responsible for the analytical character of interpretation of the electronic spectra of the synthesized complexes. In each case the general contour of electronic spectrum was composed by one weak band and a few shoulders. The precise positions of the absorption bands maxima were determined by the Gaussian analysis of the spectral contour.

In the spectra of complexes (*I*) and (*III*) four component bands were distinguished, while in the spectrum of the complex (*II*) six bands were. The first two bands, considering their position and intensity, were attributed to the d–d transitions. The other bands were assigned to the charge-transfer and to the inner ligand transitions (Table III). Comparison of the reflectance spectra of the dimeric Mo(III) complexes in the solid with the absorption spectra of their aqueous solutions revealed marked similarities. That fact allowed us to conclude that although the structure and/or composition of those compounds could be somewhat different in the solid state from that in solution, their basic structural units are obviously identical.

TABLE III. Electronic Spectrum of Compounds Experimental.

Designations of consecutive bands	Transitions energies (cm^{-1})	Extinction coefficient (mol dm^{-1} cm^{-1})	Half width (cm^{-1})	Assigned transition energies
		$[Mo_2OC_2O_4(C_3H_7NO_2)_2(H_2O)_4]\cdot 2H_2O$		
ν_1	20200	230	7200	d–d
ν_2	26200	450	5000	d–d
ν_3	33600	1630	7600	M(d)–L(π^*)
ν_4	41400	10700	8000	charge transfer
ν_5	>50000	–	–	inner-ligand
		$[Mo_2OC_2O_4(C_9H_{11}NO_2)_2(H_2O)_4]$		
ν_1	19200	170	5200	d–d
ν_2	26700	365	6000	d–d
ν_3	32000	150	2000	inner-ligand
ν_4	33900	1610	6500	M(d)–L(π^*)
ν_5	41000	10750	7400	charge transfer
ν_6	48500	7450	4000	inner-ligand
ν_7	>50000	–	–	inner-ligand
		$[Mo_2OC_2O_4(C_5H_8NO_3)_2(H_2O)_4]\cdot 2H_2O$		
ν_1	19600	195	5800	d–d
ν_2	26400	460	5600	d–d
ν_3	32900	1950	5300	M(d)–L(π^*)
ν_4	41000	11900	8400	charge transfer
ν_5	>50000	–	–	inner-ligand

Conclusion

Since the direct resolution of a structure of the obtained complexes was impossible, the indirect methods have been applied; vibrational spectra have been examined and the magnetic susceptibility has been measured. On the basis of the data obtained from the above reported methods we have proposed the empirical formulae of the compounds under examination, in which the oxalate anion is treated as the bridging ligand.

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