

CHELATES OF MOLYBDENUM(VI) WITH CITRATE AND MALATE

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The interaction of MoO_4^{2-} ions with citrate and malate, respectively, has been studied by potentiometric neutralization titrations in aqueous solutions at pH 4–7. The equilibrium constants of chelate formation have been determined for $\text{MoO}_2(\text{OH})(\text{citH}_{-1})^{3-}$, $\text{MoO}_2(\text{citH}_{-1})^{2-}$, $\text{MoO}_2(\text{OH})(\text{malH}_{-1})^{2-}$, and $\text{MoO}_2(\text{malH}_{-1})^{4-}$. The way of bonding of the citrate and malate ligands to the central Mo(VI) atom is discussed.

Citric acid, like other α -hydroxy acids, is conventionally used for masking Mo(VI) in acid solutions. The complexes emerging from the reactions of Mo(VI) with citric (H_3cit) and malic (H_2mal) acids and their salts in aqueous solutions have been studied by using diverse methods^{1–7} and different hypotheses as to their structure have been proposed; component ratios of 1 : 1, 2 : 1, and 1 : 2 have been suggested, the importance of the presence of the alcoholic group in the chelating agent has been stressed, and molybdate is supposed to enter the reaction in its protonated form⁸. A potentiometric neutralization study⁹ of the formation of the malic chelate revealed that two protons and two binegative malate anions are used up for the complexation of an MoO_4^{2-} anion. No stepwise complex formation was observed, and a single mononuclear complex with two malate ligands was found in weakly acid to neutral solutions in the presence of excess reagent. The malate ligand, similarly as the hydroxyacetate ligand⁹, is bonded to the central atom *via* two oxygen donor atoms, one from the alcoholic group and one from the carboxy group.

Compendia on stability constants of metal ion complexes^{10–13} contain no data of Mo(VI) chelates with malate or citrate.

EXPERIMENTAL

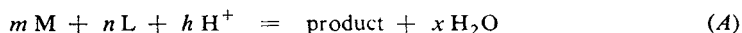
Chemicals and Apparatus

Chemicals used were of reagent grade purity (Lachema, Brno). Sodium molybdate was recrystallized from hot water; its concentration in the stock solution was determined by acidimetric titration in the presence of sorbitol¹⁴. The concentrations of the stock solutions of malic and citric acids were determined by alkalimetric titration. Potentiometric titrations with nitric acid (0.1 mol l^{-1}) were performed with an apparatus for automatic recording, comprising ABU-12,

PHM-26, TTT-11, and SBR-2 instruments fitted with a G 202 B glass electrode and a K 401 calomel electrode (all Radiometer, Copenhagen). The Nernstian response of the electrode was checked by titrating a strong base (NaOH) with a strong acid (HNO₃). The pH-meter was adjusted prior to each titration by means of a phosphate buffer at pH 6.50 ± 0.02 (Radiometer, Copenhagen).

Calculations

The experimental data from the potentiometric titrations were evaluated on an EC 1033 computer at the Computer Institute, Purkyně University in Brno, using various programs which seek for the optimum chemical model, *i.e.*, a set of reactions



characterized by the parameters m , n , and h and the equilibrium constant K_{mnh} , which leads to the minimum difference between the observed and calculated values of a suitable physico-chemical quantity. Minimized is the U value, *i.e.*, the sum of squares of the individual differences.

The programs POLET (refs¹⁵⁻¹⁷) and LETAGROP Z+ETA (ref.¹⁸) compare the observed and calculated values of function Z , which is the average amount-of-substance (mol) of one-component bonded in the complex, per mol of the other component (both bonded and free). The MINQUAD program (ref.¹⁹) compares the observed values of all analytical concentrations with calculated data; the variable treated by the LETAGROP E-TITR program²⁰ is the potential of an ion selective electrode. The input data for these programs include the characteristics of the chemical model (*i.e.*, the parameters m , n , h , and the K_{mnh} estimate), concentrations of the solutions used, and directions for minimization. The programs POLET and LETAGROP Z+ETA require, in addition, the pH and the Z -function values to be entered. For the programs MINQUAD and LETAGROP E-TITR, the input data also include the potential measured, parameters of the potentiometric measurement (these can also be minimized by the program), and volume of titrant added. All of these programs optimize the K_{mnh} values; only POLET (1985) (ref.²¹) allows also the parameters m , n , and h to be optimized. The optimum constants are presented in the form²² $\log K \pm s(\log K)$. The constants are mixed type, the hydrogen ion activity and the concentrations of the other components being used for their calculation.

Working Procedure

Four series of aqueous solutions were titrated with acid titrant solution. In Series One, the solutions contained sodium molybdate (M) together with sodium citrate (Na₃cit) or sodium malate (Na₂mal) (L). The corresponding concentrations c_M and c_L are given in Table I. In the solutions of Series Two, citrate or malate were present in the same concentrations as in Series One, molybdate, however, was absent. In Series Three, on the contrary, sodium molybdate was titrated in the absence of the salts of the organic hydroxy acids. And solutions of Series Four had the same ionic strength as those of the other series, so that their titration curve allowed us to establish the amount of acid requisite for attaining a certain pH in solution free from any of the component of the systems studied. The difference between the acid consumption for attaining the same pH in the solutions of Series One and Series Four determines the take-up of protons for the complex formation, for the protonation of the free reagent, and for the protonation of the nonbonded molybdate. The analogous differences for Series Two and Four and for Series Three and Four allow the protonation of the nonbonded reagent and of the MoO₄²⁻ anion, respectively, to be evaluated.

TABLE I
 Calculated $\log K_{mnh}$ values at $20 \pm 1^\circ\text{C}$, $I = 0.2$ (KNO_3), for $M = \text{MoO}_4^{2-}$ and $L = \text{cit}^{3-}$ (No 1-13) or mal^{2-} (No 14-26)

No	c_M mmol l $^{-1}$	c_L mmol l $^{-1}$	pH ^a	POLET calculations			MINIQUAD calculations				
				$\log K_{011}$	$\log K_{012}$	$\log K_{013}$	$\log K_{111}$	$\log K_{112}$	$\log K_{113}$		
1	0	28	7.4-3.8								
2	0	14	7.4-2.8								
3	0	5.6	7.0-4.2	5.58 ± 0.01	9.81 ± 0.01	12.64 ± 0.02					
4	0	2.8	6.8-3.0								
5	10	14	7.8-3.6	$\log K_{111}$	$\log K_{112}$	$\log K_{113}$	$\log K_{111}$	$\log K_{112}$	$\log K_{113}$		
6	10	28	7.8-4.6	8.48 ± 0.03	15.68 ± 0.01	20.62 ± 0.01	8.48 ± 0.03	15.68 ± 0.01	20.62 ± 0.01		
7	2	2.8	7.2-4.8	8.19 ± 0.02	15.46 ± 0.04	20.25 ± 0.02	8.19 ± 0.02	15.46 ± 0.04	20.25 ± 0.02		
8	2	5.6	7.4-4.6	8.17 ± 0.17	15.61 ± 0.04	20.48 ± 0.02	8.17 ± 0.17	15.61 ± 0.04	20.48 ± 0.02		
9	0.91	1.27	7.0-4.4	8.39 ± 0.09	15.62 ± 0.01	20.55 ± 0.02	8.39 ± 0.09	15.62 ± 0.01	20.55 ± 0.02		
10	0.91	2.55	7.0-4.6	—	15.27 ± 0.03	19.90 ± 0.04	—	15.27 ± 0.03	19.90 ± 0.04		
11	20	14	7.8-4.6	—	15.38 ± 0.03	20.21 ± 0.05	—	15.38 ± 0.03	20.21 ± 0.05		
12	4	2.8	7.4-4.4	—	15.51 ± 0.05	20.86 ± 0.07	—	15.51 ± 0.05	20.86 ± 0.07		
13	1.82	1.27	7.0-4.4	—	15.57 ± 0.04	20.69 ± 0.05	—	15.57 ± 0.04	20.69 ± 0.05		

$\log K_{111} = 8.28 \pm 0.05^b$
 $\log K_{112} = 15.57 \pm 0.01^c$
 $\log K_{113} = 20.42 \pm 0.03^d$

		$\log K_{011}$	$\log K_{012}$	$\log K_{011}$	$\log K_{012}$
14	0	40	6.8-3.8		
15	0	20	6.6-3.4		
16	0	8	6.1-3.7	4.65 ± 0.01	7.94 ± 0.01
17	0	4	5.9-3.7		
}					
				$\log K_{112}$	$\log K_{122}$
18	10	20	7.6-4.2		
19	10	40	7.8-4.6	13.68 ± 0.04	15.60 ± 0.04
20	20	40	7.8-5.0		
21	2	4	6.5-4.1		
22	2	8	6.5-4.7	13.78 ± 0.02	15.50 ± 0.07
23	4	8	6.7-4.9		
24	0.91	1.82	6.1-4.5		
25	0.91	3.64	6.3-4.5	13.77 ± 0.02	15.50 ± 0.09
26	1.82	3.64	6.3-4.9		
}					
				13.71 ± 0.04	15.56 ± 0.04

^a Experimental points were read in pH steps of 0.2 over the region indicated; ^{b-d} LETAGROP Z+ETA and LETAGROP E-TTTR calculations: ^b 8.52 ± 0.29 and 8.38 ± 0.17; ^c 15.84 ± 0.09 and 15.99 ± 0.03; ^d 20.99 ± 0.25 and 21.39 ± 0.02, respectively.

RESULTS

At the beginning of the titration, all solutions were virtually neutral. The formation of the molybdate complex with citrate or malate is associated with acid consumption at $\text{pH} \lesssim 8$, protonation of the nonbonded reagents appears at pH about unity lower, and protonation of the MoO_4^{2-} ion, in solutions still more acidic (Fig. 1). The differences between the titration curves for solutions of Series Two and Four were used to calculate function Z_L , providing the average amount-of-substance (mol) of hydrogen ions bonded *per* mol of reagent in the cit^{3-} or mal^{2-} form. This function enabled us to determine the acidity constants of citric and malic acids; the logarithms of their reciprocal values are given in Table I. Function Z is the average amount-of-substance of bonded hydrogen ions per mol of molybdate in the MoO_4^{2-} form; this function served for the calculation of the complex formation. Data of molybdate protonation in the absence of chelating agents were taken from ref.²³

When seeking for the optimum model to account for the shape of the titration curves for the molybdate-citrate system No 12 (Table I), the nonbonded reagent was assumed to exist as the cit^{3-} , Hcit^{2-} , H_2cit^- , and H_3cit species. The protonation constants of cit^{3-} in the absence of Mo(VI) were determined beforehand and the values were no more varied during the optimization. The assumption of the formation of the mononuclear complex with the ratio $M : L = 1 : 2$ (reaction (A) with parameters 1, 2, 2) led to a marked disagreement between the observed and calculated values. A reasonable agreement ($U = 0.21$) was attained if citrate was assumed to coordinate to molybdate in the 1 : 1 ratio (reaction (A) with parameters 1, 1, 1; 1, 1, 2; and 1, 1, 3). This agreement improved further ($U = 0.038$) when the molybdate protonation constants²³ $K_{102} = 10^{7.5}$ and $K_{708} = 10^{58.1}$ were introduced (these quantities were not optimized by the program). For the optimum, $U = 0.034$,

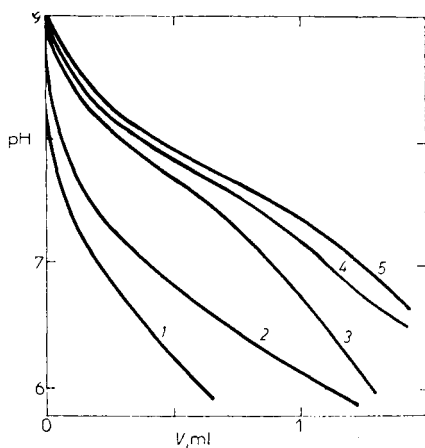


FIG. 1

Titration curves for the titration of solutions of sodium molybdate and sodium citrate with nitric acid, $c_{\text{HNO}_3} = 0.1 \text{ mol l}^{-1}$. Initial volume 5 ml; $c_{\text{Na}_2\text{MoO}_4}$, $c_{\text{Na}_3\text{Cit}}$ (mmol l^{-1}): 1 0, 14; 2 0, 28; 3 10, 14; 4 10, 28; 5 20, 14

reaction (A) with parameters 1, 1, 1 had to be excluded. The formation of the citrate complex with these parameters was not proved in all of the solutions studied. Calculations showed that this complex shares less than 2% of the Mo(VI) present in solutions No 9–12 (Table I) and no more than 16% in solutions No 5–8. Considerably higher fractions of Mo(VI) in solutions No 5–12 are bonded in complexes with parameters 1, 1, 2 (up to 80%) and 1, 1, 3 (up to 90%). For the complexation study, the program largely treated the experimental points from several titration curves simultaneously (Table I). Only for the molybdate-citrate system, the titrations were evaluated one at a time by means of the POLET program; Table I shows that the formation of the complex with parameters 1, 1, 1 was not proved in solutions with excess molybdate or with low concentrations of citrate at $c_L - c_M < 2 \text{ mmol l}^{-1}$.

The titration curves for the molybdate-malate system were evaluated similarly as for the molybdate-citrate system. Formation of mononuclear complexes with one and also with two ligands was observed. The complex with two ligands, with parameters 1, 2, 2, predominates in solutions at higher concentrations of malate, the complex with one ligand, with parameters 1, 1, 2, in dilute malate solutions. In solutions No 18–20 (Table I), the amount of Mo(VI) bonded in the complexes with one and two ligands does not exceed 65% and 56%, respectively. When diluted with a tenfold volume of 0.2M-KNO₃, the solutions (No 24–26) contain as much as 95% Mo(VI) in the form of the 1 : 1 complex and no more than 9% Mo(VI) in the form of the complex with two ligands.

The experimental Z(pH) data were evaluated by the POLET program, occasionally also by LETAGROP Z+ETA (Table I). The experiment was repeated and the data of potential *versus* volume of acid added were evaluated by the MINQUAD and LETAGROP E-TITR programs. Table I demonstrates that the various evaluation procedures ultimately lead to identical qualitative characteristics (parameters m , n , h) and to a reasonable agreement of quantitative characteristics (K_{mnh}). Data for solution No 15 were also evaluated by the POLET (1985) program; the m , n , h , and K_{mnh} values minimized in this manner (Table II) bear out the correctness of the

TABLE II

Optimization by POLET (1985) program, data for solution No 5 (Table I). Only for this case the parameters m , n , h are not integers

$\log K_{mnh} \pm s(\log K)$	$m \pm s(m)$	$n \pm s(n)$	$h \pm s(h)$
8.48 ± 0.03	1.043 ± 0.041	1.021 ± 0.033	1.018 ± 0.043
15.38 ± 0.03	0.999 ± 0.008	1.002 ± 0.008	2.001 ± 0.005
20.23 ± 0.04	1.005 ± 0.009	1.006 ± 0.009	3.006 ± 0.010

chemical model used. The citrate complex with parameters 1, 1, 1 either does not form at all in the solutions studied or it forms to a negligible extent only. This is also documented by the s ($\log K$) values in Table I and the $s(m)$, $s(n)$, and $s(h)$ values in Table II, which are considerably higher for this complex than for the remaining ones. A survey of the observed complexation equilibria is presented in Table III.

DISCUSSION

Hydroxyacetic acid forms with Mo(VI) only a complex with the ratio M : L = 1 : 2 in weakly acid solutions. Its formation is shown in Formula I; the coordination of ligands to the hydrated molybdate anion is accompanied by condensation of water, as indicated by rectangles in the formula. The interaction of $\text{MoO}_2(\text{OH})_4^{2-}$ with hydroxyacetic acid occurs without participation of hydrogen ions, whereas during the reaction with the hydroxyacetate anion, a hydrogen ion must be supplied to each coordinated hydroxyacetate. The reaction patterns of hydroxyacetic acid with Mo(VI) are also followed by other aliphatic α -hydroxy acids⁹.

Malic and citric acid can be derived from hydroxyacetic acid by successive substitution of the hydrogen atoms at the carbon atom by CH_2COOH groups: $\text{HOOC}-\text{CH}_2\text{OH} \rightarrow \text{HOOC}-\text{CH}(\text{OH})-\text{CH}_2\text{COOH} \rightarrow \text{HOOC}-\text{C}(\text{OH})(\text{CH}_2\text{COOH})_2$. Both of them can bond to the central atom similarly as hydroxyacetic acid, with the formation of a five-membered chelate ring; moreover, however, malic acid has one and citric acid, two additional carboxy groups which are also capable of bonding to the central atom. So the malate ligand can form two chelate rings (Formula II), a five-membered one and a six-membered one, and the citrate ligand may form three rings (Formula III), a five-membered one and two six-membered ones. Steric

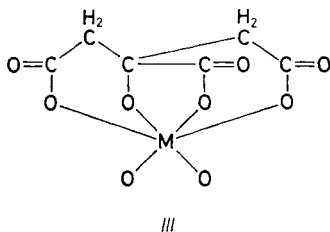
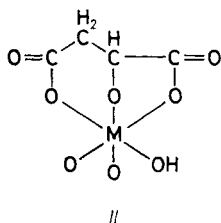
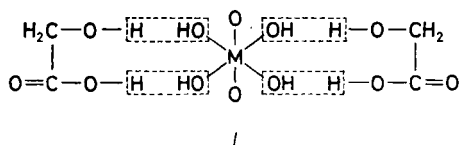
TABLE III

Survey of complex equilibria studied ($I = 0.2(\text{KNO}_3)$, $t = 20 \pm 1^\circ\text{C}$)

Reaction	$\log K$
$\text{MoO}_2(\text{OH})_4^{2-} + \text{cit}^{3-} + \text{H}^+ = \text{MoO}_2(\text{OH})_2(\text{citH}_{-1})_4^{4-} + 2 \text{H}_2\text{O}$	8.3 ^a
$\text{MoO}_2(\text{OH})_4^{2-} + \text{cit}^{3-} + 2 \text{H}^+ = \text{MoO}_2(\text{OH})(\text{citH}_{-1})_3^{3-} + 3 \text{H}_2\text{O}$	15.6
$\text{MoO}_2(\text{OH})_4^{2-} + \text{cit}^{3-} + 3 \text{H}^+ = \text{MoO}_2(\text{citH}_{-1})_2^{2-} + 4 \text{H}_2\text{O}$	20.4
$\text{MoO}_2(\text{OH})(\text{citH}_{-1})_3^{3-} + \text{H}^+ = \text{MoO}_2(\text{citH}_{-1})_2^{2-} + \text{H}_2\text{O}$	4.8
$\text{MoO}_2(\text{OH})_4^{2-} + 2 \text{mal}^{2-} + 2 \text{H}^+ = \text{MoO}_2(\text{malH}_{-1})_2^{4-} + 4 \text{H}_2\text{O}$	15.6 (16.2) ^b
$\text{MoO}_2(\text{OH})_4^{2-} + \text{mal}^{2-} + 2 \text{H}^+ = \text{MoO}_2(\text{OH})(\text{malH}_{-1})_2^{2-} + 3 \text{H}_2\text{O}$	13.7

^a In the solutions studied the reaction did not occur or it occurred to a low extent only; ^b ref.⁹

problems are to be expected for the Formula III. Substitution of the hydroxy group in malic acid by an amino group gives aspartic acid, for the derivative of which the existence of a five-membered ring and a six-membered ring (chelation analogous to Formula II) has been proved²⁴. This justifies the assumption that Formulas II and perhaps also III are sterically feasible. In the reaction of molybdate with the mal^{2-} or cit^{3-} anions, a hydrogen ion must be supplied per coordinated carboxy group; this is necessary for water to be formed by condensation similarly as in Formula I.



If concentrated solutions of salts of polyfunctional α -hydroxy acids, tartrate²⁵ or malate, are reacted, mononuclear Mo(VI) complexes with the $M:L = 1:2$ ratio are formed similarly as in the case of hydroxyacetate. The ligand is bonded in them *via* an alcoholic and a carboxy group to form a single five-membered chelate ring. If, however, the concentration of anions of the polyfunctional α -hydroxy acids in question is sufficiently low, the remaining functional groups can bond as well. A 2:2 complex thus forms with tartrate²⁵ and a 1:1 complex, with malate (Formula II). The Mo(VI) citrate chelate characterized by Formula III forms in acid solutions at $\text{pH} \approx 4$; as the acidity is lowered, one of the six-membered chelate rings splits up, and in alkaline medium at $\text{pH} > 7$ the complex decomposes. The

second chelate ring in the mononuclear Mo(VI) complexes with oligodentate malate or citrate ligands increases the chelate stability. Thus citrate, forming several chelate rings in coordination to Mo(VI), is a suitable reagent for the titrimetric determination of Mo(VI), whereas tartrate, which bonds *via* a single chelate ring, is not^{7,26}.

The oligodentate citrate ligand has analogous possibility of bonding to the central metal as the tetradentate anion of nitrilotriacetic acid. The crucial difference between the properties of these chelones is in the ability of the donor atom, that is common to all the chelate rings of the complex, to form bonds to the central atom. Whereas the donor atom of the amino group in nitrilotriacetic acid bonds to metal cations readily even in rather acid solutions, the strong bonding between the metal cation and the alcoholic oxygen of hydroxy acids only establishes after the dissociation of hydrogen from the complexed hydroxy group in alkaline medium^{27,28}. However, if citrate is reacted with hydroxy compounds of metal ions stable also in acid solutions, such as boric, molybdic, or germanic acids, the alcoholic hydrogen is eliminated by condensation to water, and stable citrate complexes form in acid medium as well.

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