

Cu(II) charge-transfer absorption. This latter absorption is exhibited by a variety of tetragonal Cu(II)-amine complexes in the 240-270-nm spectral region.³⁷

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Supplementary Material Available: Listings of structure factor amplitudes and experimental and calculated magnetic susceptibility data for 1 (28 pages). Ordering information is given on any current masthead page.

Notes

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Potentiometric Investigation of Molybdenum(VI) Equilibria at 25 °C in 1 M NaCl Medium

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The well-established method of equilibrium analysis by potentiometric titration in a medium of constant and high ionic strength has been used by several authors to obtain information about the various mono- and polynuclear species which may exist in acidified molybdate solutions.¹⁻⁵ In the pH range for which the degree of protonation is less than 1.5, results of these studies were interpreted mainly in terms of hexa-, hepta- and octamolybdates,¹⁻⁵ in addition to the monomeric species HMoO₄⁻ and Mo(OH)₆.⁶ Sasaki and Sillén⁴ found a series of heptamolybdates to predominate in 3.0 M NaClO₄ medium, viz., (8, 7), (9, 7), (10, 7), and (11, 7), the numbers referring to the values of *p* and *q* in the general formula H_{*p*}(MoO₄)_{*q*}^{*p-2q*}. From the results of an investigation in 1.0 M NaCl, Aveston et al.² also proposed a series of heptamers but considered the octameric ion (12, 8) more likely than the (11, 7) species. These authors based their findings on other experimental methods as well. Schwing³ concluded that the species (8, 6), (8, 7), and probably also (9, 6) exist in 3.0 M NaCl medium.

The potentiometric data from the above-mentioned studies were subsequently treated by Sillén⁷ with his "species selector" program LETAGROP. Although the reaction model giving the best fit in each case included the polynuclear ions (8, 7), (9, 7), (10, 7), and (11, 7), no single model could satisfy all three sets of data with respect to the selection criteria adopted in the program.

More recently Baldwin and Wiese⁵ conducted a potentiometric investigation in 1 M Mg(ClO₄)₂ medium, and again using the program LETAGROP for the treatment of their data, they found as major polynuclear components the ions (8, 6) and (9, 8).

Although medium effects may account for some of the inconsistencies, it appears as if potentiometric data as such do not lead to a complete description of all the simultaneous condensation and protonation equilibria of molybdenum(VI) in acid solution. However, the interpretation of results obtained by other important experimental methods, e.g., en-

thalpimetric and kinetic methods, depends heavily on values of equilibrium constants determined by potentiometry. For instance the results of an extensive kinetic study by temperature jump,⁸ which pointed to the (12, 8) species rather than the (11, 7), were interpreted by using the equilibrium constants reported by Aveston et al.;² the values of β_{9,7} and β_{10,7} had, however, to be adjusted by 1 log unit to give the best fit between observed and calculated relaxation times. This discrepancy and the need for reliable equilibrium constants for use in the treatment of results of an extensive calorimetric investigation of molybdenum(VI) equilibria in 1 M NaCl medium, currently being conducted in our laboratory, necessitated the present investigation.

Experimental Section

Reagents and Materials. All reagents were of analytical grade (Merck p.a.) and solutions were prepared with deionized distilled water. Sodium chloride solution was prepared from recrystallized NaCl and standardized by drying samples to constant weight at 130 °C. Prior to recrystallization, a saturated solution of salt was allowed to stand for about a week during which time some impurities precipitated. Sodium molybdate, Na₂MoO₄·2H₂O, was purified and recrystallized as described by Sasaki and Sillén.⁴ The stock solution, standardized gravimetrically by precipitation of molybdate as PbMoO₄,⁹ was kept in a polythene bottle. Hydrochloric acid was standardized indirectly against potassium hydrogen phthalate by titration with sodium hydroxide.

Potentiometric Measurements. The experiments were carried out as titrations at 25.0 ± 0.1 °C in a waterbath starting with 100 mL sodium molybdate and adding hydrochloric acid from a 10 mL buret. Sodium chloride was used to maintain the chloride concentration of the solutions at 1.0 M. A stream of nitrogen, free from carbon dioxide, was presaturated with 1.0 M NaCl and used for stirring the solution.

The hydrogen ion concentration, *h*, of the solution was determined by measuring the emf accurate to ±0.1 mV with a Beckman Research pH meter employing Beckman glass (39000) and Beckman calomel (39071) electrodes. The electrode system was standardized by a similar titration of 1 M NaCl with hydrochloric acid and the value of *E*⁰ determined from the measured emf values (in mV) by using eq 1.

$$E = E^{\circ} + 59.15 \log h \quad (1)$$

A value for *E*⁰ was determined before each titration of molybdate with acid and checked afterwards by a single emf measurement of the same solution used to determine *E*⁰. The titration data were considered acceptable only if the difference between the *E*⁰ values was ≤0.3 mV. Titrations were carried out at -log *h* values ranging from 6.5 to 2 at the following (initial) molybdenum(VI) concentrations: 0.0005, 0.001 (two), 0.002, 0.005, 0.01, 0.05, and 0.10 M. Of these, 324 experimental points corresponding to a degree of protonation of ≤1.5 were used in the computation of the stability constants.

Results and Discussion

Treatment of Data. The equilibria for the various possible condensation and protonation reactions can be represented by the general equation

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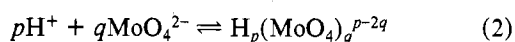
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Table I. Values for the Equilibrium Constants, $\log(\beta_{pq} + 3\sigma)$, of Molybdenum(VI) Species, $H_p(MoO_4)_q^{p-2q}$, Included in Various Reaction Models

model	$HMoO_4^-$ $\log \beta_{1,1}$	$Mo(OH)_6$ $\log \beta_{2,1}$	$HMo_2O_7^{2-}$ $\log \beta_{3,2}$	$Mo_7O_{24}^{6-}$ $\log \beta_{8,7}$	$HMo_7O_{24}^{5-}$ $\log \beta_{9,7}$	$H_2Mo_7O_{24}^{4-}$ $\log \beta_{10,7}$	$H_3Mo_7O_{24}^{3-}$ $\log \beta_{11,7}$	$Mo_8O_{26}^{4-}$ $\log \beta_{12,8}$	$HMo_8O_{28}^{7-}$ $\log \beta_{9,8}$	σ_Z
A ^a	3.57 ± 0.03	7.28 ± 0.02		52.79 ± 0.01	57.48 ± 0.01	61.04 ± 0.03	63.52 ± 0.01			0.0069
A ^b	3.55 ± 0.12	7.20 ± 0.12		52.81 ± 0.03	57.39 ± 0.06	61.02 ± 0.09	63.40 ± 0.15			0.0069
B ^a	3.55 ± 0.03	7.30 ± 0.02		52.77 ± 0.01	57.52 ± 0.01	60.84 ± 0.05		71.70 ± 0.06		0.0072
B ^b	3.53 ± 0.15	7.26 ± 0.10		52.80 ± 0.06	57.42 ± 0.06	60.84 ± 0.15		71.56 ± 0.18		0.0078
A ^c	3.56 ± 0.02	7.31 ± 0.02		52.79 ± 0.01	57.47 ± 0.05	60.99 ± 0.05	63.36 ± 0.25			0.0058
B ^c	3.56 ± 0.02	7.33 ± 0.02		52.60 ± 0.01	57.52 ± 0.01	60.82 ± 0.08		71.57 ± 0.12		0.0052
C ^c	3.59 ± 0.02	7.32 ± 0.02		52.54 ± 0.05	57.52 ± 0.02	60.93 ± 0.06	63.59 ± 0.15			0.0058
D ^c	3.58 ± 0.02	7.34 ± 0.02		52.58 ± 0.05	57.51 ± 0.02	60.83 ± 0.06		71.53 ± 0.13		0.0054
E ^c	3.40 ± 0.05	7.11 ± 0.06	14.84 ± 0.10	52.80 ± 0.01	57.44 ± 0.01	60.87 ± 0.05	63.59 ± 0.12			0.0046
F ^c	3.39 ± 0.05	7.16 ± 0.05	14.81 ± 0.10	52.80 ± 0.01	57.45 ± 0.01	60.77 ± 0.06		71.53 ± 0.10		0.0043

^a Results of present investigation: $Z \leq 1.5$; 324 data points. ^b Results of Aveston et al.:² $Z \leq 1.5$; 61 data points. ^c Results of present investigation: $Z \leq 1.4$; 268 data points.



The analytical concentrations of acid and molybdate, denoted by H and B , are given by

$$H = h + \sum ph^p b^q \beta_{pq} \quad (3)$$

$$B = b + \sum qh^p b^q \beta_{pq} \quad (4)$$

where h and b are the free concentrations of hydrogen and molybdate ions and β_{pq} is the overall equilibrium constant for the formation of species $H_p(MoO_4)_q^{p-2q}$. The degree of protonation, Z , is defined by

$$Z = (H - h) / B \quad (5)$$

Combination of eq 3, 4, and 5 then yields the following expression for Z

$$Z = \sum ph^p b^q \beta_{pq} / (b + \sum qh^p b^q \beta_{pq}) \quad (6)$$

Values for Z for titration points were calculated by means of eq 5. With use of these Z values and the corresponding h values, eq 6 was solved by a nonlinear least-squares method, in which the error mean square $(n - k)^{-1} \sum (Z_{\text{exptl}} - Z_{\text{calcd}})^2$ is minimized by means of stepwise Gauss-Newton iterations on the constants β_{pq} , n being the number of data points and k the number of constants. A package program BMDX85¹⁰ has been adapted for this purpose. Provision was made in a subroutine for an iterative computation of b from the total molybdenum concentration, B , for each data point using eq 4.

Equilibrium Constants and Reaction Models. Values calculated for equilibrium constants of various mono- and polynuclear species, corresponding to several different reaction models, are given in Table I. In the light of previous work, models A and B may be regarded as important alternatives in terms of which a satisfactory description of molybdenum(VI) equilibria in the range $Z \leq 1.5$ can be given. With use of these models to compare the results of the present investigation with those of Aveston et al.,² it is seen (Table I) that the agreement between the $\log \beta_{pq}$ values of all the species concerned is excellent. This finding is important in view of the observation by Honig and Kustin⁸ that values of $\log \beta_{9,7}$ and $\log \beta_{10,7}$ reported by Aveston et al.² had to be reduced by 1 log unit to obtain the best fit between observed and calculated relaxation times in a temperature jump study at 25 °C in 1.0 M NaNO₃ medium. Following Aveston et al.² these authors interpreted their results in terms of model B. However, model B should not be considered unacceptable for this reason because other factors might be responsible for the deviations.⁸

It has been suggested by Aveston et al.² that more precise and extensive data than their own could perhaps facilitate a better choice between various possible reaction models. The data of the present investigation is not claimed to be more accurate but it is more extensive, the rather small standard deviations of the equilibrium constants being a direct consequence of the large number of data points used in the computations. Taking the standard deviation in Z , σ_Z , as a criterion to determine which model best fits the experimental data, it is seen that model A fits better than model B, again in agreement with the results of Aveston et al.² However, when the data of the latter authors were recalculated by Sillén,⁷ he used only 51 of the 62 data points, apparently neglecting those points for which $1.4 \leq Z \leq 1.5$, and obtained smaller values for σ_Z , finding model C to give the best fit.

For any system of consecutive overlapping equilibria it is safer not to calculate equilibrium constants from Z values which might be affected by species other than those accommodated in a particular model. This precaution has also been taken in the subsequent treatment of the data of this inves-

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tigation, and only those points for which $Z \leq 1.4$ were used. This resulted in a much better fit for models A and B; σ_Z improved so much for model B that it now gave the better fit. In further calculations, addition of the (9, 8) species to model A, giving model C, caused no change to the fit, while adding it to model B (giving model D) actually resulted in a small increase in the value of σ_Z . Thus, having taken into account models previously selected to give either very good or best fits between experimental and calculated Z values for measurements in 1 M NaCl medium, results of this investigation show that the smallest σ_Z value is obtained for model B.

Subsequently various other combinations of possible species were considered in an attempt to find a model that would give an even better fit than model B. A marked improvement in σ_Z could, however, only be obtained by adding the dimeric species (3, 2) to either model A or B; of these two models, E and F, the latter fits best.

Since dimeric species in the cationic state have been shown to exist in strong acid medium,¹¹ the possibility that lower protonated dimers such as a neutral (4, 2) species and a singly charged anion (3, 2) will occur at higher pH seems reasonable. From a statistical point of view the (3, 2) species is acceptable since the value of the stability constant, $\beta_{3,2}$, is greater than 3 times its standard deviation which corresponds, technically at least, to a confidence level of better than 99%.⁷

Obviously this result can not be regarded as sufficient evidence for the existence of a (3, 2) species, but it does show that the possible presence of this dimer should be taken into account in future investigations of molybdenum(VI) equilibria, especially at relatively low concentrations. Although model F has given the best fit, it should be pointed out that the rather small difference between the σ_Z values for models E and F does not justify a final choice between the (11, 7) and (12, 8) species, i.e., between the ions $H_3Mo_7O_{24}^{3-}$ and $Mo_8O_{26}^{4-}$. However, results of X-ray scattering and Raman measurements carried out on a series of 2.0 M lithium molybdate solutions in the range $Z \leq 1.5$, which have just been reported (at the time of writing), are found to be best interpreted in terms of the formation of the $Mo_8O_{24}^{6-}$ ion;¹² the existence of the $Mo_7O_{24}^{6-}$ ion in solution has been reconfirmed as well.

Since the equilibrium constants of a number of species likely to occur in acidified molybdenum(VI) solution have been verified, their values can now be applied with greater confidence to interpret or evaluate data obtained by other experimental techniques. For instance, values for equilibrium constants are essential for the determination of enthalpy and entropy quantities of individual species from calorimetric data for this system of overlapping equilibria. Such thermodynamic data together with structural information of characterized species should provide a much better understanding of the true nature of the system. As yet, no satisfactory explanation can be given as to why only certain species predominate under a given set of conditions. In fact, the question as to what accounts for the critical stability of a particular polynuclear configuration has yet to be answered for the whole field of isopoly and heteropoly complexes and not merely for molybdenum(VI) isopolyions.

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Registry No. $HM_oO_4^-$, 14259-84-8; $Mo(OH)_6$, 13597-71-2; $HM_o_2O_7^-$, 72004-03-6; $Mo_7O_{24}^{6-}$, 12274-10-1; $HM_o_7O_{24}^{3-}$, 12371-76-5; $H_2Mo_7O_{24}^{4-}$, 12371-78-7; $H_3Mo_7O_{24}^{3-}$, 52015-50-6; $Mo_8O_{26}^{4-}$, 12346-58-6; $HM_o_8O_{28}^{7-}$, 53237-16-4.

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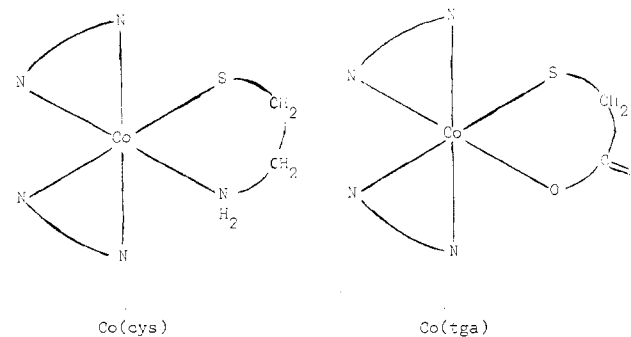
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Ligating Ability of the Coordinated Thiolato Sulfur Atom. 2.¹ The Crystal Structure of $\{[(en)_2Co(SCH_2COO)]_2Ag\}(ClO_4)_3$, a Model for an Inner-Sphere Electron-Transfer Precursor Complex

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Recently we have examined the interactions of (thiolato)cobalt(III) complexes with the soft metals Ag(I) and CH_3Hg^{II} and reported equilibrium association constants¹ for these metals with $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ and $[(en)_2Co(SCH_2COO)]^+$ (hereafter referred to as Co(cys) and Co(tga), respectively). Supportive of that study, we now present the



single-crystal X-ray structure determination of the 2:1 adduct $\{[Co(tga)]_2Ag\}(ClO_4)_3$ which clearly indicates sulfur to be the bridging atom between cobalt(III) and silver(I). Changes in the cobalt coordination sphere accompanying the binding of the coordinated thiolato sulfur atom to silver are important with respect to the changes one might expect when a potentially reducing metal (e.g., Cu(I), Cr(II), Co(I)) approaches a (thiolato)cobalt(III) compound to form the precursor complex in prelude to inner-sphere electron transfer.²

Experimental Section

$\{[Co(tga)]_2Ag\}(ClO_4)_3$ was prepared by the addition of $AgClO_4$ to an acidic solution of $[Co(tga)]ClO_4^3$ in approximate stoichiometric ratios. Typically, 10 mL (0.018 M) of $[Co(tga)]ClO_4$ was mixed with 3 mL (1.0 M) of $HClO_4$ and 1 mL (0.09 M) of $AgClO_4$. The solution was allowed to stand at room temperature for a few days until large red crystals formed. The rate of crystal formation is very dependent on $HClO_4$ concentration.

Precession photographs of the title complex indicated a monoclinic unit cell with systematic absences consistent with the space groups⁴ $C2/c$ and Cc ($h+k = \text{odd}$ for hkl and $l = \text{odd}$ for $h0l$). A crystal of approximate dimensions $0.23 \times 0.21 \times 0.11$ mm was mounted on a Syntex P1 diffractometer (Mo $K\alpha$, graphite monochromator), and unit cell parameters were confirmed by precisely centering on 19 pairs of reflections at $\pm(18^\circ \leq 2\theta \leq 25^\circ)$: $a = 16.267$ (5) Å, $b = 8.9885$ (7) Å, $c = 22.145$ (4) Å, $\beta = 99.82$ (2)°, $V = 3190.4$ Å³, $Z = 4$, $\rho_{\text{calc}} = 1.967$ g cm⁻³. Equipment and methods of data collection have previously been described.⁵ Within the sphere $2.5 \leq 2\theta \leq 60^\circ$, 5639 reflections were scanned, resulting in 3350 unique, observed ($I > 2\sigma(I)$) reflections. Four standard reflections were measured between every 36 test reflections to provide a drift correction that exhibited long-term, random variation and ranged from 0.94 to 1.02. Gaussian absorption

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