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(6) In this estimate we have used values of $10Dq = 21.8$ kK for $Co(NH_3)_5N_3^{2+}$ and $10Dq = 31.1$ kK for $Co(CN)_5N_3^{3-}$. Similar differences of $10Dq$ values are found for other acidopentaamminecobalt(III) and acidopentacyanocobaltate(III) complexes.
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(17) The quantities represented in Scheme I are as follows: the excitation energy, $h\nu$; an attractive or bonding contribution in the CTTM excited state $\{Co^{II}L_5(\cdot X)\}^*$, ΔH_{BE}; a repulsive or Franck–Condon contribution in the CTTM excited state, ΔH_{FC}; the enthalpy change associated with electron transfer within the $\{Co^{III}L_5,X^-\}$ ion pair, $\Delta H°_{IP}$; the enthalpy of hydrolysis of $Co^{III}L_5(X^-)$, ΔH^+; a solvent cage "trapped" radical-pair species $\{Co^{II}L_5,\cdot X\}$.
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Coordination Number of Molybdenum(VI) in Monomeric Molybdic Acid

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Sir:

When it was definitely established by direct spectrophotometric determination that the two successive ionization constants of monomeric molybdic acid are very nearly equal,[1] the suggestion[1,2] that this was due to an increase in the coordination of Mo(VI) from four to six in the first step of the protonation of the molybdate ion according to the equilibria

$$MoO_4^{2-} + H^+ + 2H_2O \rightleftharpoons MoO(OH)_5^- \quad (1)$$

$$MoO(OH)_5^- + H^+ \rightleftharpoons Mo(OH)_6 \quad (2)$$

was tentatively rationalized[1] in terms of an abnormally low protonation constant for reaction 1 due to a considerable decrease in entropy accompanying the immobilization of two molecules of water in this step. The above formulation has been accepted by several authors[3-6] in discussions of Mo(VI) equilibria in acidified molybdate solutions.

Table I. Thermodynamic Quantities for Protonation Reactions 3 and 4

Medium^a (temp range)	Protonation	ΔH, kJ mol^{-1}	ΔS, J mol^{-1} K^{-1}	log K (25°C)
1.0 *M* NaCl	First	22.5 ± 0.9	143 ± 3	3.47 ± 0.07
(15–35°C)	Second	−46.5 ± 1.4	−85 ± 4	3.74 ± 0.07
0.1 *M* NaCl	First	20 ± 5	140 ± 17	3.74 ± 0.07
(10–40°C)	Second	−49 ± 8	−92 ± 25	3.77 ± 0.07

^{a} Enthalpy and entropy values for 1 *M* NaCl were computed from 990 individual absorption measurements and those for 0.1 *M* NaCl from only 280.

However, in a recent dilatometric study of isopolymolybdate equilibria,[7] preliminary computer analysis of the volume changes accompanying the acidification of molybdate in terms of published stability constants[8] indicated a considerable negative volume change for the second protonation. This result cast doubt on the above formulation since a strong decrease in apparent molar volume is held to be associated with an increase in the coordination of the central atom by the addition of water molecules.[9,10] It was therefore decided to extend our previous spectrophotometric investigation of the protonation of molybdate at high dilution in order to test by more direct evidence whether the following alternative formulation of the successive protonation reactions was not perhaps more acceptable

$$MoO_4^{2-} + H^+ \overset{K_1}{\rightleftharpoons} HMoO_4^- \quad (3)$$

$$HMoO_4^- + H^+ + 2H_2O \overset{K_2}{\rightleftharpoons} Mo(OH)_6 \quad (4)$$

In this formulation the first protonation constant would be regarded as "normal" while the second would be abnormally high. This would require a high negative enthalpy change for reaction 4 to more than outweigh the expected negative entropy change associated with the increase in coordination of the central atom.

The thermodynamic quantities given in Table I were computed from uv absorption values for 5×10^{-5} *M* Mo(VI) solutions measured at ten different wavelengths in the range 215–235 nm as a function of both pH and temperature (10–40°C) assuming molar absorptivities, ΔH, and ΔS to be constant over this temperature range. These results strongly support formulations 3 and 4, with the expansion of the coordination sphere of Mo(VI) occurring during the second protonation step rather than during the first, in accordance with predictions based on Coulomb interaction calculations by Chojnacki.[11]

The relatively small value of ΔH and the considerable positive value of ΔS for the first protonation are compatible with corresponding values for similar protonations without change in coordination number

	ΔH, kJ mol^{-1}	ΔS, J mol^{-1} K^{-1}	Ref
$CrO_4^{2-} + H^+ \rightleftharpoons HCrO_4^-$	5.4	142	12
$HPO_4^{2-} + H^+ \rightleftharpoons H_2PO_4^-$	−5.0	130	13
$HAsO_4^{2-} + H^+ \rightleftharpoons H_2AsO_4^-$	−3.2	119	14

whereas the thermodynamic constants for the second protonation appear reasonable only if the considerable negative enthalpy and entropy change is associated with the expansion of coordination number. For an analogous expansion of coordination number in the reaction

$$IO_4^- + 2H_2O \rightleftharpoons H_4IO_6^-$$

the values[15] $\Delta H = -62$ kJ mol^{-1} and $\Delta S = -236$ J mol^{-1} K^{-1} have been reported.

This finding, that expansion of coordination number of Mo(VI) by the uptake of water molecules from the solution occurs only when the negative charge on the monomeric molybdate has been reduced to less than 1, is helpful in formulating a readily visualized interpretation of the observation that the heptameric species $Mo_7O_{24}^{6-}$ appears to be the first predominant condensed species to appear on acidification of molybdates at moderate concentrations in aqueous media.

By analogy with the enthalpy-driven reaction

$$2HCrO_4^- \rightleftharpoons Cr_2O_7^{2-} + 2H_2O$$

(where $\Delta H = -19.7$ kJ mol^{-1} and $\Delta S = -36.8$ J mol^{-1} K^{-1} [16]) the initial appearance of $HMoO_4^-$ should lead to the equilibrium

$$2HMoO_4^- \rightleftharpoons Mo_2O_7^{2-} + H_2O$$

However, since the second protonation constant for the monomeric species is relatively large, the octahedral neutral species $Mo(OH)_6$ simultaneously appears in concentrations less than that of $HMoO_4^-$ only by a factor $K_2[H^+]$. The decrease in enthalpy associated with the condensation of $Mo(OH)_6$ with $HMoO_4^-$ with the elimination of water to a complex in which the neutral central octahedron is joined to the tetrahedral MoO_4^- group by a common corner should, by reason of coulombic effects, be much greater than that in the competing formation of the dimeric $Mo_2O_7^{2-}$, even for the successive similar coordination of up to a maximum of six tetrahedral groups around the central octahedron. This places the reactions

$$Mo(OH)_6 + xHMoO_4^- \rightleftharpoons [MoO_x(OH)_{6-x}(MoO_3)_x]^{x-} + xH_2O$$

(where x can vary from 1 to a maximum of 6) in a strongly competitive position relative to the condensation of two $HMoO_4^-$ anions. In these condensation products, with one or more tetrahedral groups linked by a shared corner to the central neutral octahedral group, the peripheral tetrahedral groups retain their charge of 1− and are therefore not expected to expand to an octahedral form by addition of water molecules from the solution because of the large negative entropy involved. When, however, six tetrahedra have been accommodated, and not before, all of these peripheral tetrahedra can, without the immobilization of any free water molecules and the attendant entropy decrease, expand to octahedra simply by folding at the common corners to share octahedral edges (one each with the central octahedron and two with neighboring ligands as in the $Mo_7O_{24}^{6-}$ structure found in solid paramolybdates) with the considerable decrease in enthalpy associated with the formation of additional Mo–O bonds. This negative enthalpy change, together with the abundance of $HMoO_4^-$ relative to $Mo(OH)_6$ up to pH ~5, can be expected to stabilize the heptameric $Mo_7O_{24}^{6-}$ sufficiently to account for the nonobservance of intermediate condensation products[8,17,18] with the peripheral Mo(VI) atoms still tetrahedrally coordinated and is in accord with the observed high negative enthalpy change[19] for this condensation reaction.

Registry No. $Mo(OH)_6$, 13597-71-2; Mo, 7439-98-7.

Supplementary Material Available. Equations used to compute the thermodynamic constants and Table II, a listing of composite observed and calculated molar absorption coefficients at various −log [H$^+$] values in 1.0 *M* NaCl at 15, 25, and 35°C, will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Business Office, Books and Journals Division, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.50 for microfiche, referring to code number AIC503430-12-75.

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