oxonium perchlorate complex with essentially no contamination by Ib.[13]

The procedure outlined below can be modified in several ways. The oxonium complex can be precipitated first followed by the lead complex. Mercury(II) or thalium(I) perchlorate can be used instead of the lead(II) perchlorate. Only one isomer need be precipitated from solution as either the lead or oxonium complex; after the excess Pb^{2+} or OH_3^+ is removed, the other isomer can be obtained by concentrating the aqueous solution and then extracting with *n*-hexane. *None of the perchlorate complexes described in this paper could be detonated using either heat or percussion*; notwithstanding, the perchlorate complexes were handled with due care.

Experimental Section

The isomer mixture of dicyclohexyl-18-crown-6 (10.0 g)[14] was added to 1.0 l. of distilled water at 60°C. After the cyclic ether melted, the mixture was allowed to cool to room temperature with vigorous stirring. The dissolution took 10–20 hr. A solution of lead perchlorate, prepared by dissolving 14.4 g of lead carbonate (J. T. Baker) in a mixture of 14.8 g of 70% perchloric acid (Mallinckrodt) and 15 ml of water, was then added to the cyclic ether solution which was stirred for an additional 60 min to complete crystallization. The resulting lead perchlorate complex of Ib was filtered to yield 9.7 g of the colorless crystals.

The filtrate, containing mostly isomer Ia, was treated with hydrogen sulfide gas (Matheson) until the precipitation of lead sulfide was complete. The solid PbS was filtered off, and enough 70% perchloric acid (about 45 ml) was added to the filtrate to start the precipitation of the oxonium perchlorate complex of isomer Ia. The solution was stirred for 15 min and an additional 15 ml of 70% perchloric acid was added to ensure complete precipitation of the solid. The mixture was stirred for an additional 1 hr and then filtered to yield 6.4 g of the colorless crystals of the oxonium perchlorate complex.

Pure Ia and Ib were isolated as follows. The lead perchlorate complex was dissolved in 60 ml of reagent *N*,*N*-dimethylformamide (Eastman). Water (60 ml) was added to this solution and hydrogen sulfide gas was bubbled through it until precipitation of lead sulfide was completed. Immediately thereafter, 60 ml of acetone (Eastman) was added, the PbS was filtered off, and the solvents were removed from the filtrate under vacuum. To the resulting viscous oil was added 60 ml of water, and this mixture was extracted with three 250-ml portions of *n*-hexane (Matheson Coleman and Bell). The combined *n*-hexane extracts were dried over anhydrous magnesium sulfate (Mallinckrodt) and filtered. The *n*-hexane was removed under vacuum, and the solid was recrystallized from *n*-hexane. The yield was 3.9 g (39%) of colorless crystals of Ib, mp 83–84°C (high-melting polymorph).

The oxonium perchlorate complex was dissolved in 50 ml of acetone and then 150 ml of water was added. This solution was extracted with *n*-hexane and treated exactly as above. The product was recrystallized from *n*-hexane or diethyl ether (Mallinckrodt) to yield 4.4 g (44%) of colorless crystals of Ia, mp 61–62°C.

Registry No. Ia, 15128-65-1; Ib, 15128-66-2; $[PbIb][ClO_4]_2$, 56468-35-0; $[OH_3Ia][ClO_4]$, 39671-97-1.

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Correspondence

Reconciliation of Apparently Contradictory Assignments of Charge-Transfer Transitions in Acidopentacyanocobaltate(III) and Acidopentaamminecobalt(III) Complexes. Inferences about Photoprocesses and Charge-Transfer Energetics[1]

AIC50046V

Sir:

In a recent report to this journal Miskowski and Gray[2] have commented that the lowest energy absorption bands assigned as charge transfer to metal (CTTM) transitions in acidopentacyanocobaltate(III) complexes occur at energies only 2–4 kK greater than the corresponding CTTM transitions of acidopentaaminecobalt(III) complexes. On casual consideration this observation seems to belie the common experience that pentacyanocobaltates are much more difficult to reduce than the corresponding pentaammines. More careful considerations demonstrate that concern with the similarity of energies of transitions assigned as CTTM in these families of complexes is well founded. (1) Straightforward application of the semiemperical expression (1) which Jorgensen[3-5] has

$$\tilde{\nu}_{\max} = 30(\chi_L - \chi_M) + 10Dq + \delta_{SP} + aB \qquad (1)$$

proposed to correlate the energies of CTTM transitions suggests that similar transitions in $Co(CN)_5X^{3-}$ and $Co(NH_3)_5X^{2+}$ complexes should differ by approximately 7 kK.[6,7] (2) The minimum excitation energy required to generate redox products is given by (2). The only large difference in the

$$Co^{III}L_5(N_3^-) \xrightarrow[H_2O]{\Delta H^\circ{}_1} \{Co^{III}L_5OH_2,N_3^-\} \xrightarrow{\Delta H^\circ{}_{IP'}} \{Co^{II}L_5,\cdot N_3\} \qquad (2)$$

overall energetics of the cyano and ammine complexes must arise from the different contributions of the $Co(CN)_5OH_2^{2-}$–$Co(CN)_5^{3-}$ and $Co(NH_3)_5OH_2^{3+}$–$Co(NH_3)_5^{2+}$ couples; the respective enthalpy contributions can be estimated to be 20.5[8] and about 10 kK mol^{-1}.[9] (3) Many of the acidopentacyanocobaltates have been shown to exhibit photoredox behavior following CTTM excitation.[10,11] In the course of some of our studies,[10,12] originally stimulated by Basolo and coworkers' discovery[13] of a photochemical process involving nitrene intermediates, we have made some observations on photoredox processes in $Co(CN)_5N_3^{3-}$. We have found the threshold energy for significant photoredox behavior to be about 7 kK greater for $Co(CN)_5N_3^-$ (Figure 4[14]) than for $Co(NH_3)_5N_3^{2+}$.[15] Thus these three different lines of consideration seem to substantiate the expectation of considerably different energies for CTTM transitions in pentaammine and pentacyano complexes of cobalt(III). Yet the absorption features in question are very similar in both families of complexes,[2] and the observation of appreciable photoredox (forming $Co^{II}L_5$ and $\cdot X$) upon irradiation of these absorption

Scheme I

$$\begin{tikzcd}
\{Co^{II}L_5(\cdot X)\}^* \arrow[r, "\Delta H_{BE} + \Delta H_{FC}"] & \{Co^{II}L_5, \cdot X\} \\
Co^{III}L_5(X^-) \arrow[u, "h\nu"] \arrow[r, "\Delta H^{\ddagger}"] & \{Co^{III}L_5, X^-\} \arrow[u, "\Delta H^{\circ}_{IP}"]
\end{tikzcd}$$

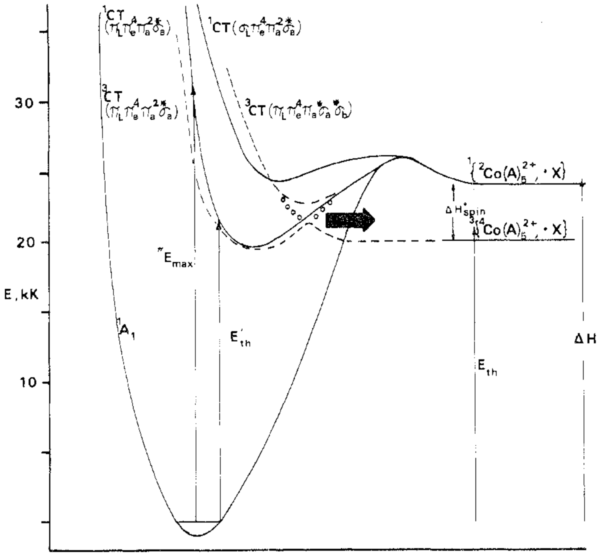

Figure 1. Qualitative representation of potential energy manifolds for the ground state and the lowest energy CTTM excited states of $Co^{III}(NH_3)_5(X^-)$ complexes (A = NH_3). Terms and symbols are described in the text; electronic configurations in parentheses refer to the donor ligand orbital (π_L or σ_L) and the metal ion configurations from Table I, with $^*\sigma_a$ and $^*\sigma_b$ for $^*\sigma(d_{z^2})$ and $^*\sigma(d_{x^2-y^2})$. Note that population of the $^3CT(\pi_L\pi_e{}^4\pi_a{}^*\sigma_a{}^*\sigma_b)$ state would require a two-electron transition from the ground state. The triplet manifolds are indicated by dashed lines and the region of strong interaction and possibly forbidden crossing is indicated by the open circles. The involvement of the $^3CT(\pi_L\pi_e{}^4\pi_a{}^*\sigma_a{}^*\sigma_b)$ state was suggested by Dr. V. M. Miskowski. Numerical values of parameters used in this figure are those reported in ref 9 for $Co(NH_3)_5Br^{2+}$. The heavy arrow represents the postulated predominant redox pathway.

features is at least qualitatively in accord with these assignments.

There is one outstanding difference between these two families of complexes: while the metallo fragment resulting from redox decomposition of $Co(CN)_5X^{3-}$, low-spin $Co(CN)_5{}^{3-}$, correlates with the spin-allowed optical transition, the ground state of the redox product from $Co(NH_3)_5X^{2+}$, a high-spin cobalt(II) complex, does not.[9,16] We believe this difference in chemistry can adequately account for the anomalies noted above.

The spin-conservative cycle in Scheme I[17] has been used effectively in discussions of the photoredox chemistry of acidopentaamminecobalt(III) complexes.[9] The qualitative relationships of these energy terms are illustrated in Figure 1, where, with $Co(NH_3)_5Br^{2+}$ as a specific example, experimental energies are entered for the absorption maximum, E_{max}, and the threshold for absorption, E'_{th}, in the lowest energy charge-transfer to metal transition, $^1CT(\pi)$, in $Co(NH_3)_5Br^{2+}$; the numerical value for the calculated enthalpy of formation of radical-pair species containing low-spin (doublet) $Co(NH_3)_5{}^{2+}$ and a ·Br radical, $\Delta H^{\circ}_c = \Delta H^{\ddagger} + \Delta H_{IP}$, has been discussed elsewhere;[9] also discussed previously is the reorganizational barrier, E_{reorg}, to recombination of the radical-pair species (estimated to be of the order of 2 kK).[9,18] Thus the $^1CT(\pi)$ state should be weakly "bound" with respect to dissociation into low-spin cobalt(II) products; we would

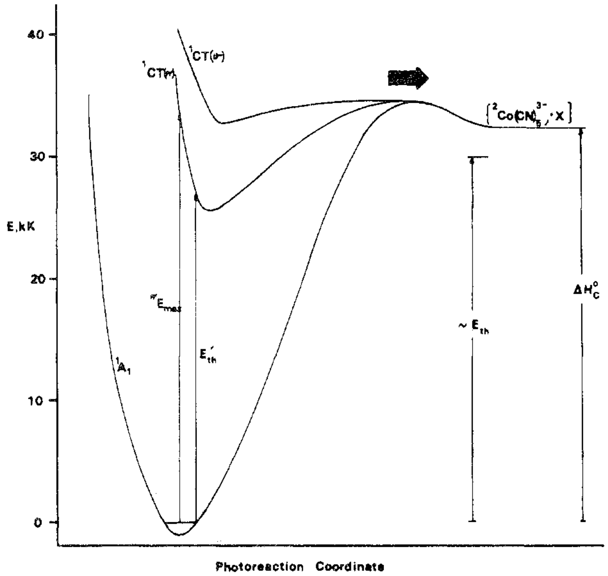

Figure 2. Qualitative representation of potential energy manifolds for the ground state and the lowest energy CTTM excited states of $Co^{III}(CN^-)_5(X^-)$ complexes. Terms and symbols are described in the text. Numerical values of parameters are based on $Co(CN)_5Br^{3-}$ according to data in ref 2, except for E_{th} which is based on the difference in threshold energies for photoredox decomposition found for $Co(NH_3)_5N_3{}^{2+}$ and $Co(CN)_5N_3{}^{3-}$ as described in the text. The heavy arrow indicates the postulated predominant redox pathway.

estimate a net binding energy of the order of 5 kK. Since the threshold energy for photoredox decomposition, E_{th}, of acidopentaamminecobalt(III) complexes has been found to be generally a few kilokaisers less than ($\Delta H^{\circ}_c + E_{reorg}$),[9,18] it seems likely that the photoredox chemistry derives from the sequential relaxation of the $^1CT(\pi)$ state vibrationally and electronically, probably through intermediate states of transient existence and high-spin multiplicity, to form radical-pair products containing high-spin (quartet) $Co(NH_3)_5{}^{2+}$. Experimental quantities, with $Co(CN)_5Br^{3-}$ taken as the example, have been similarly used to construct Figure 2 illustrating the relationships of these energy quantities for acidopentacyanocobaltates. For this family of complexes the $^1CT(\pi)$ state should appear less photosensitive with $E_{th} \sim (\Delta H^{\circ}_c + E_{reorg}) > E'_{th}$.[19] If the differences in threshold energies for photoredox behavior are generally the same between $Co(NH_3)_5X^{2+}$ and $Co(CN)_5X^{3-}$ complexes as we find for $Co(NH_3)_5N_3{}^{2+}$ and $Co(CN)_5N_3{}^{3-}$ (~7 kK), then $E_{th} > E'_{th}$ for the cyano complexes as expected; obviously, accurate estimates of E_{th} in simple halopentacyanocobaltate(III) complexes would be very useful.

Thus we infer that the spectroscopic assignments of Miskowski and Gray are not in conflict with either the photochemical observations or the inferences drawn from (2). We have drawn Figure 2 to represent somewhat greater binding of $^1CT(\pi)$ in $Co(CN)_5X^{3-}$ than in $Co(NH_3)_5X^{2+}$; this is an expected consequence of significant $Co(d\pi) \rightarrow CN(^*\pi)$ back-bonding, since such back-bonding should slightly increase the apparent electronegativity of the metal. It is also apparent that back-bonding (Co→CN) of such significance as assumed by Gray and coworkers[2,20] would render $10Dq$ an inappropriate estimate of the energy of the d_{z^2} orbital on cobalt and further limit the utility of (1) in correlating CTTM spectra of $Co(CN)_5X^{3-}$ and $Co(NH_3)_5X^{2+}$ complexes.

The above analysis of the interesting contrasts in charge-transfer spectroscopy and the photochemistry of ammine and cyano complexes of cobalt(III) suggests a scheme of classification of coordination complexes according to their CTTM spectroscopy and photoredox chemistry. We would

Table I. Metal Ion Electronic Configurations in CTTM Excited States and in Ground States of Photoproducts for Several Classes of Simple Complexes[b]

Class and example	Formal d-electronic confign of CTTM excited state and correlated metallo products[a]: Confign	Metallo fragment[c]	Ground-state d-electronic configurn of metallo products
I, $Ru(NH_3)_5X^{2+}$	(a) $\pi_e^4\pi_a^2$	$Ru(NH_3)_5^{2+}$	$\pi_e^4\pi_a^2$
	(b) $\pi_e^4\pi_a{}^*\sigma(d_{z^2})$	$^*Ru(NH_3)_5^{2+}$	
I′, $Co(CN)_5X^{3-}$	(a) $\pi_e^4\pi_z^2{}^*\sigma(d_{z^2})$	$Co(CN)_5^{3-}$	$\pi_e^4\pi_a^2{}^*\sigma(d_{z^2})$
	(b) $\pi_e^4\pi_a^2{}^*\sigma(d_{x^2-y^2})$	$^*Co(CN)_5^{3-}$	
II, $Co(NH_3)_5X^{2+}$	(a) $\pi_e^4\pi_a^2{}^*\sigma(d_{x^2-y^2})$	$^*Co(NH_3)_5^{2+}$	$\pi_e^4\pi_a{}^*\sigma(d_{z^2}){}^*\sigma(d_{x^2-y^2})$
	(b) $\pi_e^4\pi_a^2{}^*\sigma(d_{x^2-y^2})$	$^*Co(NH_3)_5^{2+}$	
III, $Cr(NH_3)_5X^{2+}$	(a) $\pi_e^3\pi_a$	$^*Cr(NH_3)_5^{2+}$	$\pi_e^2\pi_a{}^*\sigma(d_{z^2})$
	(b) $\pi_e^2\pi_a{}^*\sigma(d_{z^2})$	$Cr(NH_3)_5^{2+}$	

[a] Lowest energy CTTM excited state is listed first (a); the next lowest state, second (b). For simplicity only the X^- ligands are considered as electron donors and states differing only in the energies of donor orbitals are not distinguished. [b] The metal ion t_2 orbitals are considered largely nonbonding except in the cyano complexes (where M→CN back-bonding may be significant), the metal ion e orbitals are considered largely antibonding; owing to the C_{4v} microsymmetry we have distinguished the π_a (i.e., d_{xy}) from π_e (i.e., d_{xz} and d_{yz}) and the $^*\sigma(d_{z^2})$ from $^*\sigma(d_{x^2-y^2})$. [c] An asterisk indicates that the primary metallo product correlated with excited state dissociation would be electronically excited.

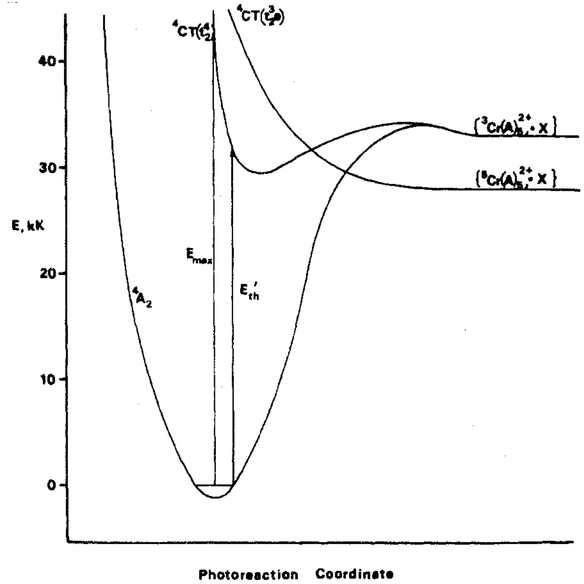

Figure 3. Qualitative representation of potential energy manifolds for the ground state and the lowest energy CTTM excited states of $Co^{III}(NH_3)_5(X^-)$ complexes ($A = NH_3$). Numerical values of parameters are based on the spectroscopy of $Cr(NH_3)_5Br^{2+}$ [M. Linhard and M. Weigel, *Z. Anorg. Allg. Chem.*, **266**, 49 (1951)]. Separation of triplet and quintet states of $Cr(NH_3)_5^{2+}$ has been taken to be 5 kK. For purposes of clarity only the lowest energy $X^-(\pi) \rightarrow Cr^{III}$ CTTM states have been represented. We currently have no estimates of the enthalpies of formation of the primary products and qualitative representations have been made by analogy with the cobalt analogs. Quantities in parentheses abbreviate the formal d-electronic configurations of chromium in the CTTM excited states; elaboration may be found in Table I.

suggest that three qualitatively distinct classes of behavior should be differentiated among simple coordination complexes.

Class I. Lowest CT(π and σ^{21}) excited states correlate smoothly with ground states of primary products. Higher energy CT excited states correlate with excited-state product species; characteristic energy relations $E'_{th} << \Delta H°_c < E_{th}$; example $Ru(NH_3)_5X^{2+}$.[9]

Class I′. This has the same general description as class I but more distorted excited states and moderated energy constraints; characteristic energy relations $E'_{th} < \Delta H°_c \leq E_{th}$; examples $Co(CN)_5X^{3-}$ and $Rh(NH_3)_5X^{2+}$.

Class II. Lowest CT(π and σ) excited states correlate with an excited state of the primary redox products. Ground state of the primary products does not correlate smoothly with any spectroscopic (or one electron) excited state; characteristic energy relations $E_{th} \leq E'_{th} < \Delta H°_c$; example $Co(NH_3)_5X^{2+}$.

Class III. Lowest CT(π and σ) excited states correlate with an excited state of the primary products. Ground state of the primary redox products correlates with a higher energy CT excited state; characteristic energy relations $E'_{th} \sim \Delta H°_c < E_{th}$; example $Cr(NH_3)_5X^{2+}$ (Figure 3).

Examples of these classes are elaborated in Figures 1–3 and Table I.

The charge-transfer spectroscopy and photoredox chemistry of chromium(III) warrant closer examination since there are a large number of possible CTTM excited states, some with symmetry species which suggest the crossing of their potential energy surfaces may be forbidden—a situation which could lead to photosensitivity[22] in a transition associated with very little excited-state distortion ($^4CT(t^4)$ in Figure 3). This is similar to Miskowski's suggested forbidden crossing in $Co(NH_3)_5X^{2+}$ (Figure 1), but with a single electron being excited in the $^4CT(t^4)$ state compared to two in the $^3CT(\pi_L\pi_e{}^4\pi_a{}^*\sigma_a{}^*\sigma_b)$ state of cobalt. These systems are being investigated further and we plan to make a detailed report elsewhere.

Details of experimental procedures may be found in the literature[19,23,24] and in the supplementary material.

Acknowledgment. We are grateful to Professor H. B. Gray for his useful and critical comments during the development of ideas contained in this paper and to Dr. V. M. Miskowski for providing provocative and insightful responses to some of our questions at several stages during the evolution of this paper.

Supplementary Material Available. Procedural and observational details (including quantum yield data in Table II and Figure 4 and $Co(NH_3)_5F^{2+}$ scavenging data in Figure 5) 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 papers in this issue may be obtained from the Business Office, Books and Journals Division, American Chemical Society, 1155 16th Street, N.W., Washington, D.C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number AIC50046V-12-75.

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(5) The terms in (1) are, transition frequency ($\bar{\nu}$), electronegativities of ligand (χ_L) and metal (χ_M), the d-orbital energy difference caused by ligand field splitting ($10Dq$), spin-pairing energy (δ_{SP}), and the Racah parameter (B). We have expressed all energies in kK ($=10^3$ cm^{-1}). In the discussion of differences in ν_{max} for $Co(CN)_5X^{3-}$ and for $Co(NH_3)_5X^{2+}$ we assumed δ_{SP}, B, and χ_M to have about the same values for both families of complexes.

(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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(16) We are indebted to Dr. V. M. Miskowski for his comments pertinent to this point.

(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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(19) Our estimates apparently result in a value of E_{th} which is about 4 kK less than ($\Delta H°_c + E_{reorg}$). However, the estimates of these quantities are each accurate to only 1 or 2 kK and there is an estimate of E_{th} for only one pentacyanocobaltate. Further along this line, we have previously demonstrated[9] for $Co(NH_3)_5X^{2+}$ complexes that E_{max} is equal to or only a few kilokaisers less than ($\Delta H°_c + \Delta H_{FC}$). Since the net excited-state binding energy only seems to be of the order of 5 kK in the pentaammines, this previously demonstrated correlation is not surprising. However, it is not unlikely that our estimates of ΔH_{FC} have underestimated the compression energy required to force the ground-state (cobalt(III)) nuclear coordinates onto axially distorted (low-spin) cobalt(II).

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(21) In this and similar contexts in this paper, the parenthetical π and/or σ refer to the symmetry of the donor orbitals on the halide or pseudohalide ligand.

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Received January 20, 1975

Coordination Number of Molybdenum(VI) in Monomeric Molybdic Acid

AIC503430

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

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

$$MoO(OH)_5^- + H^+ \rightleftharpoons Mo(OH)_6 \tag{2}$$

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

$$MoO_4^{2-} + H^+ \overset{K_1}{\rightleftharpoons} HMoO_4^- \tag{3}$$

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

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 pro-