Kinetics and Mechanism of the Reduction of Hydroxylamine-*O*-sulfonic Acid by the Hexaaquochromium(II) Ion

Andreja Bakac,* Joan L. Simunic, and James H. Espenson*

The title reaction takes place with a 2:1 [Cr^{2+}]:[HSA] stoichiometry (HSA = hydroxylamine-*O*-sulfonic acid) and yields $CrNH_3^{3+}$, Cr^{3+}, and $CrSO_4^+$ as the main products. The kinetics conform to the rate law $-d[HSA]/dt = -d[Cr^{2+}]/2(dt) = k_{obs}[Cr^{2+}][HSA]$, where $k_{obs} = kK_a/(K_a + [H^+])$. At 25 °C and 1.0 M ionic strength ($HClO_4$ + $LiClO_4$) the parameter k has the value of 20.5 ± 0.3 M^{-1} s^{-1} when K_a is set at the value (6.8 ± 0.8) × 10^{-2} M, as determined by pH titration. In the proposed mechanism, Cr^{2+} attacks at the nitrogen end of the anion, $NH_2OSO_3^-$, to form $CrNH_3^{3+}$ and $SO_4^{•-}$. The sulfate radical anion then oxidizes rapidly the second mole of Cr^{2+} to yield Cr^{3+} and some $CrSO_4^+$. In solutions containing Br^-, $SO_4^{•-}$ oxidizes it to $Br_2^{•-}$. The latter reacts with Cr^{2+} to yield $CrBr^{2+}$.
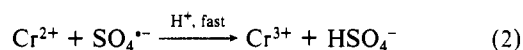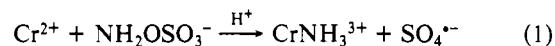
Introduction

The reduction of hydroxylamine by Cr^{2+} occurs in two one-electron steps.[1,2] By use of oxygen-18-labeled hydroxylamine it was demonstrated that the attack by Cr^{2+} takes place at the oxygen of NH_3OH^+. The amino radical formed then either oxidizes a second equivalent of Cr^{2+} or is trapped by a suitable trapping agent, such as 1,3-butadiene.[1] No $CrNH_3^{3+}$ was observed in this reaction. Similar results are obtained when hydroxylamine reacts with other oxidizable metals, such as Ti(III)[3–5] or V(III).[6,7]

Hydroxylamine-*O*-sulfonic acid, HSA, is an efficient amination reagent[8] for aromatic substrates in the presence of Ti(III), Fe(II), and Cu(I). Similarly, the redox chain decomposition of HSA, catalyzed by Fe^{2+}, leads to selective functionalization of heteroaromatic bases.[9,10] As with the hydroxylamine reactions,[1–7] the formation of the amino radical has been proposed[9,10] as the first step in these reactions. Subsequent rapid steps then yield the observed products.

The reactivity of hydroxylamine relative to HSA in nucleophilic substitution reactions has been examined by using cob(I)alamin.[11] Both reactions yielded aquocob(II)alamin as the sole product. The reaction takes place much more readily with HSA ($k > 2 \times 10^4$ M^{-1} s^{-1}) than with NH_3OH^+ ($k = 4.1$ M^{-1} s^{-1}). It was proposed that the reactions proceed by nucleophilic attack at oxygen of hydroxylamine and at nitrogen of HSA. The initially formed cob(III)alamin then reacts rapidly with cob(I)alamin to give the observed cobalt(II) product. The exceptionally high nucleophilic reactivity of HSA is thought[11] to be related to the fact that OSO_3H^- is an extremely good leaving group.

We have now studied the reaction of HSA with Cr^{2+}. This reaction is expected to take place in one-electron steps, as in the case of hydroxylamine. The site of the initial attack by Cr^{2+} is by no means obvious, but it should be possible to distinguish between the two possibilities on the basis of the products formed. If Cr^{2+} attacks at the nitrogen, then $CrNH_3^{3+}$ and Cr^{3+} should be the main products:

$$Cr^{2+} + NH_2OSO_3^- \xrightarrow{H^+} CrNH_3^{3+} + SO_4^{•-} \qquad (1)$$

$$Cr^{2+} + SO_4^{•-} \xrightarrow[]{H^+, \text{ fast}} Cr^{3+} + HSO_4^- \qquad (2)$$

Table I. Products of the Reaction of Cr^{2+} with HSA in the Presence of Different Anions

| product | % yield[a] | | |
	0.1 M $HClO_4$	0.1 M $HClO_4$ + 0.1 M NaBr	0.05 M H_2SO_4
$CrNH_3^{3+}$	48	47	40
Cr^{3+}	31	15	28
$CrSO_4^+$	13		22
$CrNH_2OSO_3^{2+b}$	(7)[c]		(10)[c]
$CrBr^{2+}$		38	

[a] The total isolated yield was ~90%; Initial concentrations were 0.020 M Cr^{2+}, 0.010 M HSA, and 0.10 M $HClO_4$. [b] Identified on the basis of the 2+ charge and the visible spectrum; see text. [c] Calculated by assuming $\epsilon_{550} = 20$ M^{-1} cm^{-1}.

If the attack takes place at the oxygen, then $CrOSO_3^+$ and Cr^{3+} should be formed:

$$Cr^{2+} + NH_2OSO_3^- \xrightarrow{H^+} CrOSO_3^+ + NH_3^{•+} \qquad (3)$$

$$Cr^{2+} + NH_3^{•+} \xrightarrow[H^+]{\text{fast}} Cr^{3+} + NH_4^+ \qquad (4)$$

Such a straightforward distinction between the two reaction paths is believed possible because the reactions of Cr^{2+} with both inorganic radicals, $SO_4^{•-}$ and $NH_3^{•+}$, are reported to yield the unsubstituted chromium(III) product exclusively.[1,12]

Equations 1 and 3 are written in terms of the anion, $NH_2OSO_3^-$, because this happens to be the reactive form, as determined in this study.

Results

Stoichiometry and Products. The stoichiometry was determined by spectrophotometric titration at 400 and 560 nm, the wavelengths of the greatest absorbance changes. The ratio [Cr^{2+}]:[HSA] = 1.92 ± 0.01 was obtained irrespective of the wavelength, acidity (0.1–1.0 M) and the order of addition of the reagents.

The reaction yields $CrNH_3^{3+}$, Cr^{3+}, and $CrSO_4^+$ as main products (Table I). In addition, a 2+ charged species was eluted from the column immediately after $CrSO_4^+$. The red species has maxima at 550 and 416 nm of approximately equal intensity, suggestive of a Cr(III)–N bond. In fact, the positions of the two λ_{max} values are intermediate between those for $CrNH_3^{3+}$[13] and $CrSO_4^+$.[12] This species probably contains coordinated HSA, the most reasonable candidate being $CrNH_2OSO_3^{2+}$. Its yield in Table I was calculated by assuming a molar absorptivity of 20 M^{-1} cm^{-1} at 550 nm.

Small amounts of the more highly charged species, probably $Cr_2(OH)_2^{4+}$ and/or Cr_2NH^{4+}, were also observed, but they were not quantified. The recovery of the chromium in the form of the complexes bearing 1+, 2+, and 3+ charges was usually ≥90%, indicating that any reaction pathway yielding the more highly charged products is at best a minor one.
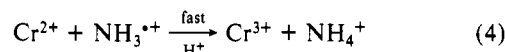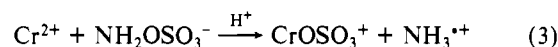
(1) Schmidt, W.; Swinehart, J. H.; Taube, H. *Inorg. Chem.* **1968**, 7, 1984.
(2) Jones, P. A.; Monk, C. B. *J. Chem. Soc. A* **1971**, 971.
(3) Albisetti, C. J.; Coffman, D. D.; Hoover, F. W.; Jenner, E. L.; Mochel, W. E. *J. Am. Chem. Soc.* **1959**, 81, 1489.
(4) Davis, P.; Evans, M. G.; Higginson, W. C. E. *J. Chem. Soc.* **1951**, 2563.
(5) Lingane, P. J.; Christie, J. H. *J. Electroanal. Chem.* **1967**, 13, 227.
(6) Varaprasad, D. V. P. R.; Mahadevan, V. *React. Kinet. Catal. Lett.* **1982**, 21, 473.
(7) Tomat, R.; Rigo, A. *J. Electroanal. Chem. Interfacial Electrochem.* **1974**, 50, 345.
(8) For reviews see: (a) Sosnovsky, G.; Rawlinson, D. J. *Adv. Free-Radical Chem.* **1972**, 4, 203; (b) Minisci, F. *Synthesis* **1973**, 1.
(9) (a) Minisci, F.; Galli, R. *Tetrahedron Lett.* **1965**, 1679; (b) Minisci, F.; Galli, R.; Cecere, M. *Ibid.* **1965**, 4663.
(10) Citterio, A.; Gentile, A.; Minisci, F.; Sarravalle, M.; Ventura, S. *J. Chem. Soc., Chem. Commun.* **1983**, 916.
(11) Balasubramanian, P. N.; Gould, E. S. *Inorg. Chem.* **1984**, 23, 824.

(12) Pennington, D. E.; Haim, A. *J. Am. Chem. Soc.* **1968**, 90, 3700.
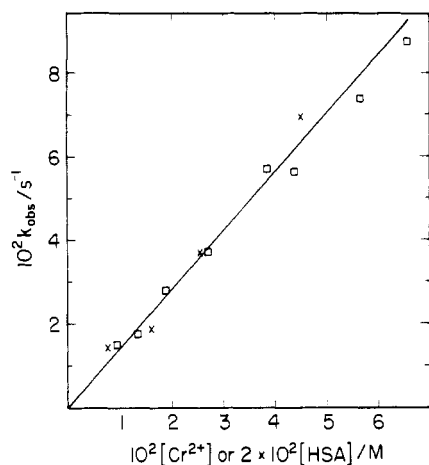(13) Ardon, M.; Mayer, B. E. *J. Chem. Soc.* **1962**, 2816.

Figure 1. Plot of k_{obs} against the concentration of excess reagent, Cr^{2+} (crosses) or HSA (squares) at 0.85 M $HClO_4$. The concentration of HSA was multiplied by 2 to account for the reaction stoichiometry.

When the reaction was run in the presence of 0.10 M NaBr, a scavenger for $SO_4^{\bullet-}$, large amounts of $CrBr^{2+}$ were produced (Table I). On the other hand, the addition of 1,3-butadiene, a scavenger for $\bullet NH_2$, had no significant effect on the nature of the chromium products. In the presence of 0.05 M sulfate, the amount of $CrSO_4^+$ increased somewhat.

All the kinetic experiments were conducted under pseudo-first-order conditions by using either Cr^{2+} or HSA in a large excess over the other reagent. The kinetics were monitored at 560 and 400 nm. The data obeyed a first-order rate expression precisely under both sets of conditions, yielding the pseudo-first-order rate constants k_{obs}. A plot of k_{obs} against the concentration of excess reagent at constant $[H^+]$ is shown in Figure 1. The concentration of HSA was multiplied by 2 to account for the reaction stoichiometry. The plot is linear with a zero intercept, confirming that the rate law of eq 5 applies. From Figure 1 the value of k' is 1.40 ± 0.05 M^{-1} s^{-1} at 25 °C in 0.85 M $HClO_4$.

$$-d[HSA]/dt = -d[Cr^{2+}]/2dt = k'[Cr^{2+}][HSA]_T \quad (5)$$

The effect of the acidity on the kinetics was investigated in the range 0.080–0.94 M $HClO_4$. The observed rate constant increases as the concentration of H^+ decreases, indicating that the anion $NH_2OSO_3^-$ reacts with Cr^{2+} more rapidly than the neutral, zwitterionic[14] HSA. The kinetic data were fitted to eq 6, where

$$k' = kK_a/(K_a + [H^+]) \quad (6)$$

K_a stands for the acidity constant of HSA. The calculations yielded $k = 24.1 \pm 2.6$ M^{-1} s^{-1} and $K_a = (5.4 \pm 0.8) \times 10^{-2}$ M. This K_a is somewhat higher than the expected value of ~0.01 –0.02 M. The estimate is based on the reported value at 45 °C ($K_a = 0.033$ M) and the assumption that the temperature effect on the K_a of HSA and hydroxylammonium ion ($\Delta H° = 9.3$ kcal/mol)[15] is similar.

We have therefore determined directly the acidity constant for HSA. The value obtained, 0.068 ± 0.008 M at 25 °C in 1.0 M $LiClO_4$, is consistent with that calculated from the kinetic data. Equation 6 thus fully describes the kinetics of the HSA–Cr^{2+} reaction. In particular, there is no acid-independent term, indicating that the anion $NH_2OSO_3^-$ is the only reactive form of HSA. With K_a fixed at 0.068 M, the kinetic data yield $k = 20.5 \pm 0.3$ M^{-1} s^{-1}. A plot of k' against $(K_a + [H^+])^{-1}$, with $K_a = 0.068$, is shown in Figure 2.

Discussion

The $CrNH_3^{3+}$ accounts for approximately half of the chromium products recovered. This is consistent with the attack of Cr^{2+} at the nitrogen of SA⁻, as shown in eq 1. The sulfate radical anion,
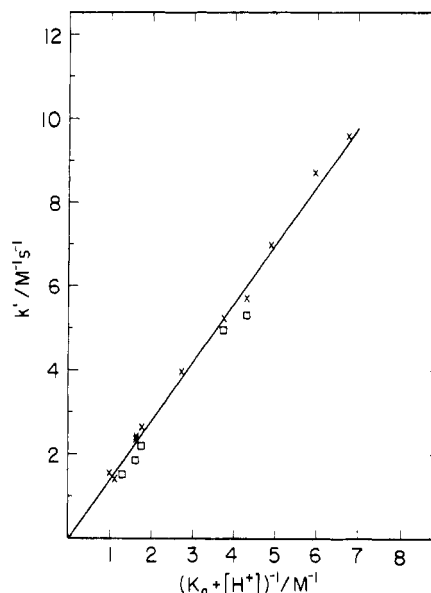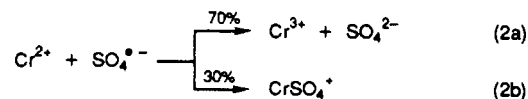
(14) Candlin, J. P.; Wilkins, R. G. *J. Am. Chem. Soc.* **1965**, *87*, 1490.
(15) Lumme, P.; Lahermo, P.; Tummavuori, J. *Acta. Chem. Scand.* **1965**, *19*, 2175.

Figure 2. Plot of k' against $(K_a + [H^+])^{-1}$, where $K_a = 0.068$ M. The data were obtained by using either Cr^{2+} (crosses) or HSA (squares) in excess.

also produced in reaction 1, should oxidize the second molecule of Cr^{2+} to Cr^{3+} (eq 2).[12] As expected, large amounts of Cr^{3+} were produced, although the yield was smaller than that of $CrNH_3^{3+}$, indicating that eqs 1 and 2 are not sufficient to describe the reaction. The "missing" chromium(III) appears largely as $CrSO_4^+$. The simplest explanation of these results is that the reaction of Cr^{2+} with $SO_4^{\bullet-}$ proceeds by two parallel pathways to yield both Cr^{3+} and $CrSO_4^+$ (eq 2a,b). However, in a study of the reaction
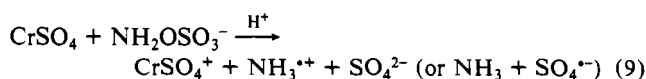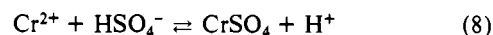
$$Cr^{2+} + SO_4^{\bullet-} \underset{30\%}{\overset{70\%}{\longrightarrow}} \begin{cases} Cr^{3+} + SO_4^{2-} & (2a) \\ CrSO_4^+ & (2b) \end{cases}$$

of Cr^{2+} with $S_2O_8^{2-}$, Pennington and Haim[12] concluded that reaction 2a provides the exclusive pathway for the reaction of Cr^{2+} with $SO_4^{\bullet-}$. The work[12] was done carefully, but the reaction of eq 2 could not be studied independently of the first step of the Cr^{2+}–$S_2O_8^{2-}$ reaction. It is thus possible that minor amounts of $CrSO_4^+$ from reaction 2b could escape detection in the presence of the large amounts of $CrSO_4^+$ produced in the first step of the reaction (eq 7). The yield of $CrSO_4^+$ obtained in this work does, however, seem larger than the experimental error in ref 12.

$$Cr^{2+} + S_2O_8^{2-} \rightarrow CrSO_4^+ + SO_4^{\bullet-} \quad (7)$$
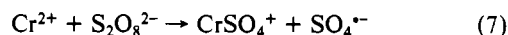
Another possibility is that the reaction of Cr^{2+} with SA⁻ proceeds in part by eqs 1 and 2 and in part by eqs 3 and 4. In that case, the formation of both $CrNH_3^{3+}$ and $CrSO_4^+$, in addition to Cr^{3+}, would be expected. This explanation seems less likely, because it would require that the yield of Cr^{3+} be equal to the sum of the yields of $CrNH_3^{3+}$ and $CrSO_4^+$, contrary to our finding that $[CrNH_3^{3+}] \simeq [Cr^{3+}] + [CrSO_4^+]$.

We also consider the possibility that the source of $CrSO_4^+$ is the sulfate-catalyzed reaction of Cr^{2+} with SA⁻ (eqs 8 and 9),

$$Cr^{2+} + HSO_4^- \rightleftharpoons CrSO_4 + H^+ \quad (8)$$

$$CrSO_4 + NH_2OSO_3^- \xrightarrow{H^+}$$
$$CrSO_4^+ + NH_3^{\bullet+} + SO_4^{2-} \text{ (or } NH_3 + SO_4^{\bullet-}) \quad (9)$$
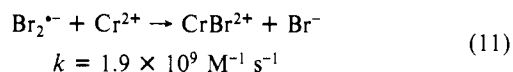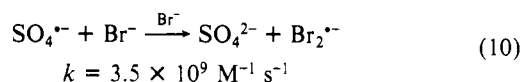
analogous to that observed with hydroxylammonium ion.[1] Although we cannot completely rule out the existence of such a pathway, it must be quite inefficient under our conditions. In a typical experiment in Table I, the concentration of the free sulfate in solution varies from zero at the beginning of the run to 0.01 M at the end, and the reaction produces 13% $CrSO_4^+$. In the presence of added 0.05 M sulfate, which is 10 times more than the average concentration produced by the reaction, this yield
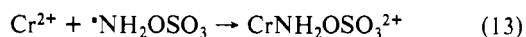
increases only to 22%. Thus in the experiments with no added sulfate the reaction sequence shown in eqs 8 and 9 can account for only a small fraction of the $CrSO_4^+$ found.

The proposed reaction scheme is strongly supported by the results of the trapping experiments with Br^-. The sulfate radical anion reacts rapidly with Br^- to yield $Br_2^{\bullet-}$ (eq 10).[16] The

$$SO_4^{\bullet-} + Br^- \xrightarrow{Br^-} SO_4^{2-} + Br_2^{\bullet-} \tag{10}$$
$$k = 3.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$$

$$Br_2^{\bullet-} + Cr^{2+} \rightarrow CrBr^{2+} + Br^- \tag{11}$$
$$k = 1.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$$

reduction of $Br_2^{\bullet-}$ by Cr^{2+} (eq 11) yields $CrBr^{2+}$,[17] which can be easily identified by its visible spectrum. The formation of large amounts of $CrBr^{2+}$ in the reaction of HSA with Cr^{2+} in the presence of free bromide is thus a strong indiciation that $SO_4^{\bullet-}$ was produced in the reaction.[12]

The species that we assigned the composition $CrNH_2OSO_3^{2+}$ is a minor product. The most obvious route to it, namely reactions 12 and 13, can probably be ruled out on the basis of the spec-

$$SO_4^{\bullet-} + NH_2OSO_3H \rightarrow HSO_4^- + {}^{\bullet}NH_2OSO_3 \tag{12}$$

$$Cr^{2+} + {}^{\bullet}NH_2OSO_3 \rightarrow CrNH_2OSO_3^{2+} \tag{13}$$

trophotometric titrations, which yielded the same stoichiometric ratio of 1.92, irrespective of the order of addition of the two reactants. The sequence of reactions 1, 12, and 13 should have a 1:1 stoichiometry, and it should contribute to the overall reaction most significantly when HSA is present in excess, i.e., in the early stages of titrations with Cr^{2+}. No deviations from linearity were ever observed in any of the titrations.[18] Although the experimental stoichiometric ratio is not precisely 2.0, the deviation is too small to have any mechanistic significance.

It is possible that small amounts of $Cr(NH_2OSO_3)^+$ exist in reaction solutions. Oxidation of this species by $SO_4^{\bullet-}$ or by HSA may account for the observed product.

Both one-electron and two-electron[11] reactions of HSA/SA^- take place by the initial attack at the nitrogen. Since the steric

crowding at this site does not seem dramatically different from that at the oxygens, the preference for nitrogen must be caused by electronic factors. As mentioned earlier,[11] the anion OSO_3H^- is an exceptionally good leaving group. This explains the unusually high reactivity of HSA in nucleophilic substitutions. For example, cob(I)alamin reacts with HSA >5 × 10³ times faster than with NH_3OH^+. However, the one-electron reductant Cr^{2+} reacts with $SA^- \sim 10^3$ times more rapidly than with NH_3OH^+ ($k = 0.014$ M^{-1} s^{-1}).[1] It is difficult to comment on the relative stabilities of the two radicals, $SO_4^{\bullet-}$ and $NH_2^{\bullet}/NH_3^{\bullet+}$, produced in these reactions. However, other factors, such as the one-electron-reduction potentials of the parent molecules, must play a crucial role in determining their reactivity toward Cr^{2+}. Our data suggest that $NH_2OSO_3^-$ is a more reactive one-electron oxidant than NH_3OH^+.

We have no new experimental results to offer concerning the reaction[9,10] of Fe^{2+} with HSA. In view of the aminations caused by this reaction, however, we suggest that either the mechanism for Fe^{2+} changes compared to that for Cr^{2+}, producing an active ${}^{\bullet}NH_2/{}^{\bullet}NH_3^+$ radical, or the species $FeNH_3^{3+}$ (analogous to $CrNH_3^{3+}$) is itself an aminating agent. Of course the iron(II) mechanism may change even more drastically, and a two-electron process remains yet another possibility.

Experimental Section

Solutions of $Cr(ClO_4)_2$ were prepared by reduction of solutions of hexaaquochromium(III) over zinc amalgam. Hydroxylamine-*O*-sulfonic acid (Aldrich) was used as received.

Products were separated aerobically by ion-exchange chromatography using SP-Sephadex C-25 resin. The acidity of the eluent was increased in 0.1 M increments until all products bearing ≤3+ charge were removed from the column. The products Cr^{3+}, $CrNH_3^{3+}$, $CrBr^{2+}$, and $CrSO_4^+$ were identified by visible spectroscopy.[13,19]

The kinetics were monitored at 394 and 545 nm by use of a Cary 219 spectrophotometer. All kinetic experiments were conducted under pseudo-first-order conditions at 25.0 ± 0.2 °C. Anaerobic conditions were maintained throughout. Lithium perchlorate was used as the supporting electrolyte to maintain ionic strength at 1.0 M. Data were analyzed by standard procedures.

The acidity constant of HSA was determined by measuring the pH of solutions containing different concentrations of HSA (0.015–0.15 M) in 1.0 M $LiClO_4$. Some of the solutions were partly neutralized with a standard solution of NaOH. The electrode was standardized against solutions of 0.1 and 0.01 M $HClO_4$ in 1.0 M $LiClO_4$.

(16) Redpath, J. L.; Willson, R. L. *Int. J. Radiat. Biol. Relat. Stud. Phys., Chem. Med.* **1975**, *27*, 389.

(17) Laurence, G. S.; Thornton, A. T. *J. Chem. Soc., Dalton Trans.* **1974**, 1142.

(18) Note that reactions 12 and 13 would not affect the kinetics in the presence of excess HSA, despite the change in stoichiometry. This is due to the fact that for each rate-determining step 2 equiv of the limiting reagent, Cr^{2+}, would still be consumed.

(19) Taube, H.; Myers, H. *J. Am. Chem. Soc.* **1954**, *76*, 2103.

Contribution from the Laboratory of General and Inorganic Chemistry, Faculty of Technology, University of Zagreb, POB 177, 41000 Zagreb, Yugoslavia

Stability of Metal Ion Unsubstituted and Substituted Monocarboxylate Complexes in Aqueous Solutions

I. Filipović, M. Tkalčec, and B. S. Grabarić*

Summarized results obtained in this laboratory on the stability of 90 metal ion complexes with unsubstituted and substituted monocarboxylate ligands, published elsewhere, have been analyzed. The contribution of ligand basicity, chelating effect, and metal ion order of stability are quantitized in order to give better insight into the stability of this class of weak coordinative interactions between metal ion and ligands. The special value of this analysis lies in the fact that all systems have been investigated with at least two independent physicochemical methods using identical or close to identical experimental conditions such as $t = 25$ °C and $I = 2$ mol/L ($NaClO_4$), but the same procedure can be used for any class of coordination compounds if reliable data on their stability are available.

Introduction

The factors governing the stability of coordination compounds formed between a metal ion and organic ligands are quite complex. Despite the advances in theoretical chemistry, at the present time,

it is not possible to calculate the stability constants of a given compound from strictly theoretical considerations. Therefore, the correlation of the stability constants with respect to different metal ions and/or ligands with identical experimental conditions usually