

process, the β ring passes through the double bond plane at the transition state and edge interchange, but no interchange of pairs of diastereotopic groups takes place. The second process having $\Delta G_c^\ddagger = 14.2 \text{ kcal mol}^{-1}$ interchanges these groups, and it could be either a $[\beta]$ - or a $[\beta, \beta']$ -ring flip.

Although the identity of the barriers calculated for both rings of **2** and **3** can be accounted for by successive ($[\beta]$, $[\beta']$) one-ring flips, the two one-ring flips are expected to have different ΔG_c^\ddagger 's since the β - and β' -mesityl rings are in diastereomeric environments. Moreover, the substantial change in the environment of the β ring in **2** and **3** changes the barrier, but still a single barrier is obtained for both rings in each substrate. Consequently, the two-ring flip is the threshold mechanism for both **2** and **3**.¹⁶

The shift in the rotational mechanism from a one-ring flip in **1** to a two-ring flip in **2** and **3** is rationalized by steric effects. The alkyl group should increase the ΔG_c^\ddagger of the $[\beta']$ -ring flip by hindering the passage of the β ring through the double-bond plane. Concurrently, the ΔG_c^\ddagger value for the two-ring flip is lowered by increasing the torsional angle of the β ring and thus raising the ground-state energy, therefore shifting the threshold mechanism. The higher barrier for **2** compared with **3** is consistent with this explanation.

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Registry No. 1, 54288-04-9; 2, 89959-15-9; 3, 89959-16-0; *t*-BuLi, 594-19-4; dimesitylketene, 87871-33-8.

(15) The zero-ring flip route does not exchange diastereotopic groups (cf. Table II) and hence cannot be monitored by NMR. It can be safely excluded as the threshold mechanism since its transition state, where the two rings pass through the reference plane, is so overcrowded that its ΔG^\ddagger should be much higher than that for the one-ring flip. Moreover, this route and the set of "nonflip" rotational mechanisms (i.e., rotation of one or two rings by π radians while the nonrotating rings remain fixed) were excluded in the closely related trimesitylvinyl system substituted with a prochiral group.^{3b}

(16) The different solvent used with **2** and **3** should have negligible effect on ΔG_c^\ddagger .^{3b}

Hydrogen Oxide Bridged Dimers of Metal Ions in Solution

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It was recently postulated that some metal ions may exist in aqueous solution as dinuclear species bridged by hydrogen oxide ligands.^{1,2} Such species were discovered in the *crystalline state* and are formed by a strong and symmetric hydrogen bond between an aqua ligand of one metal atom and a hydroxo ligand of another metal atom. The O...O separation in the H_3O_2 ligand is 2.44–2.52 Å. If species such as $[\text{M}(\text{H}_3\text{O}_2)\text{M}]^{(2n-1)+}$ do indeed exist in equilibrium with the hydrolyzed mononuclear species $\text{M}_{\text{aq}}^{n+}$ and $\text{MOH}^{(n-1)+}$, the current view on hydrolysis of metal ions in solution³ may have to be modified. However, to date such hydrogen oxide

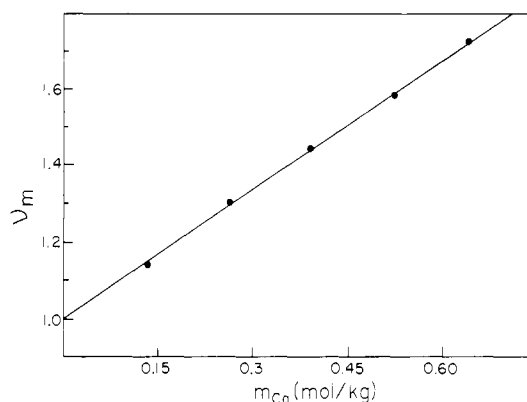
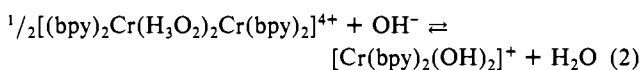
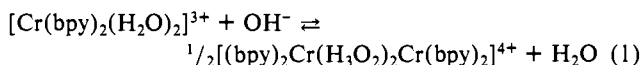


Figure 1. The dependence of ν_m , the apparent number of calcium ions per formula weight of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, on the molality m , in a saturated solution of barium nitrate at 25 °C.

bridged species were only reported in crystals.^{1,2}

Recently, the existence of dinuclear H_3O_2 -bridged species was reported in crystals of the iodide salt of *cis*-bis(bipyridine)hydroxo-aquachromium(III).² This salt was prepared by neutralizing the solution of $[\text{Cr}(\text{bpy})_2(\text{H}_2\text{O})_2](\text{NO}_3)_3 \cdot 1/2\text{H}_2\text{O}^4$ with 1 equiv of NaOH and crystallization by the addition of KI. The two chromium atoms of the tetrapositive ion $[(\text{bpy})_2\text{Cr}(\text{H}_3\text{O}_2)_2\text{Cr}(\text{bpy})_2]^{4+}$ are bridged by two $\mu\text{-H}_3\text{O}_2$ ligands. We now report the first evidence for dinuclear species of this type in *aqueous solution*.

Deprotonation of a $[\text{Cr}(\text{bpy})_2(\text{H}_2\text{O})_2]^{3+}$ ion by 1 equiv of OH^- was expected to yield a hydroxo-aqua ion⁴ $[\text{Cr}(\text{bpy})_2\text{H}_2\text{O}(\text{OH})]^{2+}$. It is now claimed that the main product of this reaction, in concentrated solution, is the dinuclear bis($\mu\text{-H}_3\text{O}_2$) bridged ion rather than the mononuclear hydroxo-aqua ion (reaction 1).



If more than one OH^- per chromium atom is used, the dihydroxo ion is formed by reaction 2. Evidence for dimerization of the hydroxo-aqua ion is based on the *decrease* of the number of chromium particles in reaction 1⁵ and its increase in reaction 2. The number, ν , of discrete chromium particles per diaqua ion should decrease from $\nu = 1$ to $\nu = 1/2$ as the diaqua ion is titrated with 1 mol of OH^- and then rise again to $\nu = 1$ as a second mole of OH^- is added. ν may be determined by measuring a colligative property of the solution. A most suitable method for ionic solutes is three-phase vapor tensiometry, TPVT.^{6,7} The three-phase solvent system consists of a saturated solution of an electrolyte in water, in equilibrium with the crystalline phase of that electrolyte and with water vapor. An isobaric temperature difference (ΔT_p) is established when the pure solvent is equilibrated with a solution of a foreign solute in the same solvent, at constant pressure. The *apparent number*, ν_m , of free particles per formula of solute depends on the molality of the solute (m), the three-phase ebullioscopic constant K_e , and (ΔT_p)⁸

$$\nu_m = (\Delta T_p) / K_e m \quad (3)$$

The apparent particle number ν_m depends linearly on m .

$$\nu_m = \nu + Nm \quad (4)$$

ν , the true number of free particles per formula of solute, is

(4) (a) Inskeep, R. J.; Bjerrum, J. *Acta Chem. Scand.* **1961**, *15*, 62–68. (b) Inskeep, J. R.; Benson, M. J. *Inorg. Nucl. Chem.* **1961**, *20*, 290–294.

(5) The possibility that the dinuclear bis(μ -hydroxo) ion $[(\text{dpy})_2\text{Cr}(\text{OH})_2\text{Cr}(\text{dpy})_2]^{4+}$ was formed in solution under the experimental condition used in this work (several hours at 25 °C) was checked and ruled out.

(6) (a) Magyar, B. *Helv. Chim. Acta* **1965**, *48*, 1259. (b) *Ibid.* **1968**, *51*, 194–204; (c) *Structure Bond.* (Berlin) **1973**, *14*, 111–140.

(7) Magyar, B.; Schwarzenbach, G. *Acta Chem. Scand., Ser. A* **1978**, *A32*, 943–955.

(8) In practice, the steady-state temperature difference (ΔT_s), which is proportional to (ΔT_p), is measured.⁷

(1) (a) Bino, A.; Gibson, D. *J. Am. Chem. Soc.* **1981**, *103*, 6741–6742; (b) *Ibid.* **1982**, *104*, 4383–4388; (c) *Inorg. Chem.* **1984**, *24*, 109–115.

(2) Ardon, M.; Bino, A. *J. Am. Chem. Soc.* **1983**, *105*, 7747–7748.

(3) Burgess, J.; "Metal Ions in Aqueous Solutions"; Wiley: New York, 1978; pp 259–309.

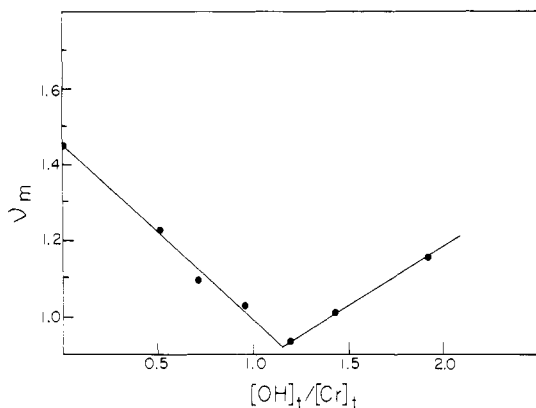
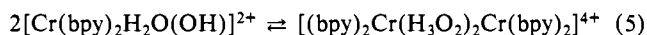


Figure 2. TPVT titration of a solution of $[\text{Cr}(\text{bpy})_2(\text{H}_2\text{O})_2](\text{NO}_3)_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ in a saturated solution of barium nitrate at 25 °C. Molality of total chromium species in mol Cr per 1 kg water = 0.24*m*.

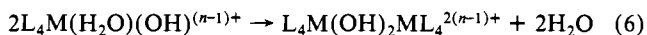
determined by linear extrapolation to $m = 0$. The validity of (4) was confirmed experimentally in over 40 solute-solvent systems,⁶ using solutes with known ν . The precision of ν determinations is ± 0.05 .

The solute used in this work was $[\text{Cr}(\text{bpy})_2(\text{H}_2\text{O})_2](\text{NO}_3)_3 \cdot \frac{1}{2}\text{H}_2\text{O}$. A saturated solution of barium nitrate was used as solvent. The validity of the linear relationship (4) in this solvent was confirmed with a standard dipositive solute ion ($\nu = 1$), Ca^{2+} . The salt used was $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Figure 1). The bis(bipyridine)diaquachromic salt was used for investigating the dimerization of the hydroxo-aqua ion. A weighed sample of $[\text{Cr}(\text{bpy})_2(\text{H}_2\text{O})_2](\text{NO}_3)_3 \cdot \frac{1}{2}\text{H}_2\text{O}^4$ was dissolved in the saturated barium nitrate solution and neutralized *stepwise* by the addition of weighed portions of $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$. ν_m was determined after the addition of each portion of barium hydroxide. Since both the nitrate counterion of the chromic species and the barium ion added in the form of barium hydroxide were common to solute and solvent, they did not affect ν_m , which was exclusively dependent on the chromic species. If dimerization of $[\text{Cr}(\text{dpy})_2\text{H}_2\text{O}(\text{OH})]^{2+}$ occurred, the initial ν_m of the diaqua salt solution should be reduced by the addition of barium hydroxide and reach its minimum value after 1 equiv of barium hydroxide was added. The results, presented in Figure 2, confirm this expectation. Addition of more than 1 equiv of OH^- converts the dinuclear hydroxo-aqua ion to the mononuclear dihydroxo ion and raises ν_m as expected. However, dimerization is not complete at a molality of 0.24*m* (formula weights of the diaqua salt), since ν_m is not reduced to 50% of its initial value, but only to ~64% (from 1.45 to 0.92). This indicates that an equilibrium is established in solution between the mononuclear and the dinuclear hydroxo-aqua ions:

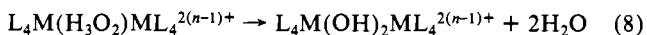
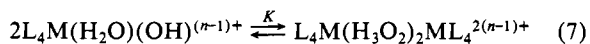


Dilution of the solution should favor dissociation of the dimer, hence an increase in ν_m . Two ν_m determinations, at $m_2 = 0.202$ and $m_3 = 0.114$, confirm this conclusion. The corresponding values ν_{m_2} and ν_{m_3} are 1.074 and 1.108, respectively.

It was suggested² that a hydrogen oxide bridged dimer of an aqua ion may be the reactive intermediate in olation reactions such as



which is believed to proceed by



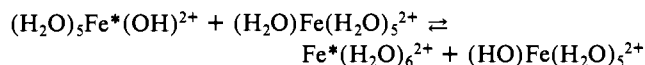
This mechanism is supported by the evidence, reported here, for a monomer-dimer equilibrium in aqueous solution. The olation of *cis*- $[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})(\text{OH})]^{2-}$, which was investigated by Grant and Hamm,⁹ is a first-order reaction at chromium concentration

(9) Grant, D. M.; Hamm, A. E. *J. Am. Chem. Soc.* 1956, 78, 3006-3009.

>0.01 M. Its order increases at lower concentrations. A monomer-dimer equilibrium explains the kinetics of this reaction. The equilibrium constant K should be higher for the negative oxalato complex ion than for the positively charged bipyridine complex.

The existence of hydrogen oxide bridges between metal ions in concentrated aqueous solutions is not unexpected, if one considers the bond energy of the hydrogen bond that links the hydroxide and water ligands of that bridge. The energy of this short symmetrical bond, with an internuclear O-O distance of 2.44 Å, was estimated to be over 100 kJ/mol.^{10,11} The alternative weak and unsymmetrical H bond that may be formed between an OH ligand and an H_2O solvent molecule has an O-O distance of 2.75 Å.¹² This distance equals the O-O separation in the solvent itself (2.76 Å in ice¹³), and the hydrogen bond energies of these bonds are probably similar (21 kJ/mol¹³).

Over 30 years ago, an H atom transfer mechanism was proposed by Silverman and Dodson,¹⁴ as an alternative to an outer-sphere mechanism in reactions such as



In view of the results reported here, this mechanism seems to merit serious reconsideration. Although the equilibrium concentration of the $[\text{Fe}(\text{H}_3\text{O}_2)\text{Fe}]^{4+}$ dimer is probably low in dilute aqueous solutions, it could, nevertheless, constitute a plausible intermediate in the exchange reaction.

Work is in progress on a precise determination of the equilibrium constant of reaction 5 and on reactions of similar hydroxo-aqua ions such as $\text{Cr}(\text{H}_2\text{O})_5\text{OH}^{2+}$.

Registry No. $[\text{Cr}(\text{bpy})_2(\text{H}_2\text{O})_2](\text{NO}_3)_3$, 59186-33-3; $[\text{Cr}(\text{bpy})_2\text{H}_2\text{O}(\text{OH})]^{2+}$, 57651-38-4; $[\text{Cr}(\text{bpy})_2(\text{OH})_2]^{2+}$, 47514-01-2.

(10) Roos, B. O.; Kramer, W. P.; Dierksen, G. H. F. *Theor. Chim. Acta* 1976, 42, 77-82.

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(13) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Interscience: New York, 1980.

(14) Silverman, J.; Dodson, R. W. *J. Phys. Chem.* 1952, 56, 866.

Stepwise Metal-Assisted Oxidative Decarboxylation of Vanadium(V) Ethylenebis(*o*-hydroxyphenyl)glycine). Isolation of a Possible Intermediate

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We have previously examined the chelate chemistry of ethylenebis(*o*-hydroxyphenyl)glycine (EHPG) with a variety of metals.³ Vanadium complexes of this ligand have proved to be especially interesting, and we report here a novel metal-assisted, stepwise, oxidative decarboxylation of the ligand to yield ultimately vanadyl *N,N'*-disalicylideneethylenediamine (SALEN).

A dark blue complex, **1**, can be isolated from a solution of EHPG and vanadyl ion in aqueous ethanol solution. This complex has been characterized by the appropriate techniques⁴ as V^{VO} .

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(3) (a) Patch, M. G.; Simolo, K. P.; Carrano, C. J. *Inorg. Chem.* 1982, 21, 2972. (b) Patch, M. G.; Simolo, K. P.; Carrano, C. J. *Ibid.* 1983, 22, 2630.

(4) All compounds were characterized by elemental analysis, ¹H and ¹³C NMR, infrared, and UV-visible spectrophotometry, and where appropriate mass spectrometry.