platinum complexes, and the Pt–NO_2 bond lengths imply that there is significant $Pt(d_{xy}) \rightarrow NO_2(\pi^*)$ back-bonding in the complexes. This result is also implicit in the RR results, in that the long observed progressions in the X–Pt^{IV}–X axial symmetric stretching mode on irradiation into the intervalence band are accompanied by other weaker progressions involving not only the X–Pt^{IV}–X equatorial symmetric stretching mode but also the symmetric NO_2 stretching and bending modes. The $Pt^{II} \rightarrow Pt^{IV}$ intervalence band, although axial, clearly has far reaching, though small, consequential effects on the equatorial bonds, presumably on account of both the π-acceptor nature of the nitro group as well as the anionic nature

of the linear-chain, factors which apparently also give rise[10] to the observed low $4f_{7/2}$ and $4f_{9/2}$ Pt binding energies in the complexes.

High-Pressure Oxygen-17 Fourier Transform Nuclear Magnetic Resonance Spectroscopy. Mechanism of Water Exchange on Iron(III) in Acidic Aqueous Solution

THOMAS W. SWADDLE* and ANDRÉ E. MERBACH*

The rate of exchange of water between iron(III) perchlorate and bulk acidic aqueous solution has been determined as a function of pressure (0.1–240 MPa) at 382.8 K by oxygen-17 NMR line-broadening measurements. The pseudo-first-order rate coefficient k is given by $k = k_1{}^\circ \exp(-P\Delta V_1^*/RT) + k_2{}^\circ [H^+]^{-1} \exp(-P\Delta V_2^*/RT)$, where $k_1{}^\circ$ (representing exchange on $Fe(H_2O)_6{}^{3+}$) = 6.8×10^4 s^{-1}, $\Delta V_1^* = -5.4$ cm^3 mol^{-1}, $k_2{}^\circ = 11.4 \times 10^4$ mol kg^{-1} s^{-1}, and $\Delta V_2^* = +7.8$ cm^3 mol^{-1} for ionic strength 6.0 mol kg^{-1} ($HClO_4/NaClO_4$). Optical measurements gave a temperature-independent volume of acid ionization for $Fe(H_2O)_6{}^{3+}$ of $+0.8$ cm^3 mol^{-1}, so that the volume of activation ΔV_{OH}^* for water exchange on $Fe(H_2O)_5OH^{2+}$ is $+7.0$ cm^3 mol^{-1}. These data are consistent with dissociative activation for substitution in $Fe(H_2O)_5OH^{2+}$ but associative activation in $Fe(H_2O)_6{}^{3+}$.

Introduction

In 1974, one of us pointed out[1] that the pattern of rates of substitution of water by other ligands in aqueous Fe-$(H_2O)_5OH^{2+}$ and $Fe(H_2O)_6{}^{3+}$ was consistent with dissociative activation in the former case, as was then considered to be quite general for "labile" octahedral complexes, but *associative* in the latter. Subsequently, other workers have drawn similar mechanistic conclusions on the basis of kinetic studies at both high[2-4] and atmospheric[5,6] pressures. In particular, the recent NMR study by Grant and Jordan[6] has provided a key piece of evidence favoring this mechanistic assignment, viz., the rate of exchange of solvent water with $Fe(H_2O)_6{}^{3+}$ and with Fe-$(H_2O)_5OH^{2+}$.

In this paper, we report our confirmation of the findings of Grant and Jordan[6] and an extension of their atmospheric-pressure study to high pressures (to 240 MPa) since, as we have argued elsewhere,[1,7-9] pressure effects can provide useful criteria of mechanism in solvent exchange reactions.

Experimental Section

Iron(III) perchlorate ($Fe(ClO_4)_3 \cdot nH_2O$, Fluka AG) was analyzed as received and then used without further treatment; the Mn content was shown to be not more than 3 μg/g, and the Fe content corresponded to a formula weight of 495.12 (i.e., $n \approx 8$). The solid was kept in a closed container inside a desiccator, and stock solutions were prepared by weight by dissolution of samples of the solid, weighed in closed capsules together with $NaClO_4 \cdot H_2O$ (Merck), in appropriate amounts of 69.1% $HClO_4$ (Merck) and distilled water. Solutions for ^{17}O NMR studies at high pressure were prepared by mixing weighed amounts of the stock solutions with multiply redistilled ^{17}O-enriched water (Yeda, normalized in ^1H, 25.5 atom % ^{17}O, 33.1 atom % ^{18}O) to yield a $H_2{}^{17}O$/(total water) ratio of about 1:10 and an ionic strength

I of 6.0 m (m = mol kg^{-1}); the apparent molecular weight of water in these solutions was therefore 18.56. Preliminary studies at atmospheric pressure were made with similar electrolyte concentrations but an $H_2{}^{17}O$/(total water) ratio of 1:25. All surfaces with which the solutions would come in contact were first cleaned with $K_2S_2O_8$/concentrated H_2SO_4, rinsed thoroughly with distilled water, and air-dried at 110 °C; great care was taken at all stages to avoid contamination with oxidizable matter (cf. precautions advocated by Grant and Jordan[6]).

NMR measurements were made with a Bruker WP-60 spectrometer (8.13 MHz ^{17}O) in the ^{19}F lock mode. Preliminary variable-temperature studies were made at ~0.1 MPa with the solution sample sealed in vacuo in a 9-mm sphere fitting inside a 10-mm NMR tube. High-pressure studies (0.1–240 MPa, 382.8 K) were made with the use of an assembly, similar to that described elsewhere for ^{13}C studies but with the coil wound and tuned appropriately for ^{17}O resonance, in which the sample was contained in a glass tube (2.0-mm i.d.) fitted with a collapsible Teflon® outer tube closed with a Vespel® plug; thus, the sample was in contact with borosilicate glass, polytetrafluoroethylene, and polyimide resin during the NMR experiments. The temperature was controlled with circulating oil to ±0.1 K and monitored with an internal Pt resistance thermometer (referred to

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DIN 43760; precision ±0.1 K, accuracy ±1.0 K after all corrections[13]). Pressure was transmitted with octane and measured with a calibrated Heise Bourdon gauge (±1%).

NMR spectra were recorded with pulse lengths of 14 and 4 μs in the variable-temperature and variable-pressure studies, respectively; the high-pressure spectra of the iron(III) solutions were collected (usually 2000 scans) over a 10-kHz sweep width and $(2 + 2)k$ memory size with use of quadrature detection. Transverse ^{17}O relaxation times T_2 were obtained by computing the half-height line width $\Delta\nu$ in a least-squares fit of the Fourier transformed and phased spectra to a Lorentzian curve; $T_2 = (\pi\Delta\nu)^{-1}$. The standard deviation in T_2 was typically 0.5% in both variable-temperature and variable-pressure experiments.

The effect of pressure on the optical spectrum of iron(III) perchlorate (0.01–0.02 m) in 1.0 m aqueous $HClO_4$ (for which compression data are available[14]) was studied at 295 K with a Franck-type optical cell,[15] in which the optical path length is fixed and compression corrections are necessary, and at 371 K with an Aminco 41-11551 optical cell with the solution contained in a leNoble-Schlott cell,[16] for which the number of solute molecules in the light path is independent of pressure. In either case, the pressure was transmitted with water and measured with a Heise Bourdon gauge calibrated against a deadweight balance (±1%). The cell temperature was controlled (±0.2 K) by circulating oil through a jacket and measured inside the cell body with calibrated thermistors. Following precedent,[17-19] the concentration of $(H_2O)_5FeOH^{2+}$ was taken as being proportional to the absorbance at 340 nm, with the transparent region around 500 nm used as the baseline reference.

Results

Preliminary experiments at 0.1 MPa showed that the ^{17}O line width of water in 6.0 m (H,Na)ClO₄ solutions was independent of the H^+/Na^+ ratio and only slightly (~4 Hz) broader than that reported for relatively dilute acidic perchlorate solutions[6,20] under the conditions of interest (370–397 K, 0.3–6.0 m H^+). In the high-pressure NMR probe at 382.8 K, the apparent line width of the (H,Na)ClO₄ solutions at 0.1 MPa ranged only from 20 to 22 Hz over the entire series of experiments, with negligible (+1.0 ± 0.4 Hz/GPa) pressure dependence up to 240 MPa at least.

The reduced water relaxation time T_{2r} for solutions of iron(III) perchlorate in 6.0 m (H,Na)ClO₄ was obtained from the relationship

$$T_{2r}^{-1} = (P_m'T_{2p})^{-1} = (T_2^{-1} - T_{2s}^{-1})/P_m' \qquad (1)$$

where P_m' is the molar ratio of water coordinated to iron(III) (assumed to be 6 molecules per ion) to free water, T_{2p} is the contribution to the observed T_2 arising from the presence of the paramagnetic ion, and T_{2s} is the contribution due to the pure solvent. Preliminary variable-temperature experiments gave T_{2r} values in good agreement with those of Grant and Jordan[6] (see below). In particular, the results were quantitatively consistent on repetition of the experimental cycle up to 397 K on the same (or different) samples; i.e., the time dependence of $H_2^{17}O$ line widths reported by Judkins[21] and Dodgen et al.[22] for certain acidic iron(III) solutions was sought for but not observed. It was confirmed that T_{2r}^{-1} is a linear

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Table I. Compositions of Solutions Used in Variable-Pressure Experiments

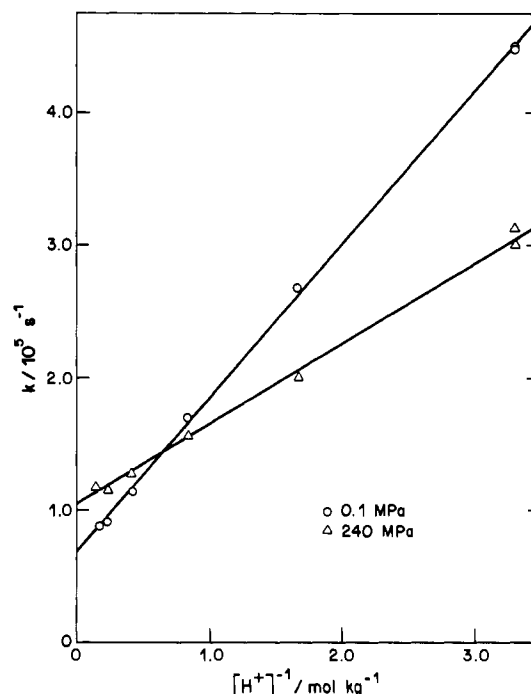| [HClO₄]/mol kg⁻¹	5.97₈	4.19₆	2.39₅	1.19₉	0.601	0.300
[NaClO₄]/mol kg⁻¹		1.80	3.59	4.80	5.41	5.70
[Fe(ClO₄)₃]/mmol kg⁻¹	14.76	13.41	14.53	11.94	7.92	5.02
$10^3 P_m'$	1.646	1.494	1.621	1.330	0.889	0.560

Figure 1. Dependence of the total water-exchange rate coefficient k upon the hydrogen ion concentration.

function of $[H^+]^{-1}$ at 370–397 K over the range 0.3–6.0 m $HClO_4$ at ionic strength 6.0 m, and so, accepting that only inner-sphere aqua exchange contributes significantly to T_{2r} under these conditions,[6] we can write eq 2 where k_1 is the rate

$$T_{2r}^{-1} = k = k_1 + k_2[H^+]^{-1} \qquad (2)$$

coefficient for exchange of an aqua ligand on $Fe(H_2O)_6^{3+}$ with bulk solvent and $k_2 = k_{OH}K_a$ in which K_a is the equilibrium quotient for reaction 3 and k_{OH} is the rate coefficient for aqua

$$Fe(H_2O)_6^{3+} \rightleftharpoons Fe(H_2O)_5OH^{2+} + H^+ \qquad (3)$$
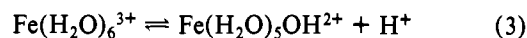
exchange on $Fe(H_2O)_5OH^{2+}$. All six oxygens in $Fe(H_2O)_5OH^{2+}$ were assumed to contribute equally to the observed k_2 value.[23]

Variable-pressure line-broadening measurements were made at 382.8 K (which, coincidentally, lies just below the 110 °C reproducibility ceiling found by Dodgen et al.[22]) and an ionic strength of 6.0 m; solution compositions are listed in Table I. Spectra were taken at 40-MPa intervals, first with rising pressure, 0.1–240 MPa, and then 220–20 MPa with decreasing pressure; final measurements of k at 0.1 MPa agreed within ±2% at worst with the initial values. In duplicate runs, values of k were reproducible to within ±1% on the average. Figure 1 shows that eq 2 represents the data accurately at both extremes of the pressure range; the representation at intermediate pressures was at least as good as this. From linear least-

(23) Grant and Jordan[6] assumed that the hydroxo ligand does not contribute to the exchangeable ^{17}O and applied a factor of $^5/_6$ to the rate coefficients accordingly; this was allowed for in making our comparison of results. Arguably, a statistical factor of $^1/_6$ should be applied if the hydroxo ligand activates the trans aqua specifically, but there is no direct evidence for this. These considerations do not affect the calculation of either volumes or enthalpies of activation.
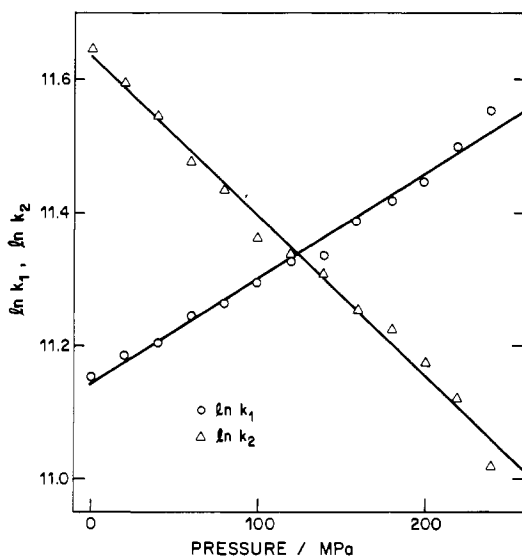
Figure 2. Pressure dependence of the rate coefficients for the acid-independent (k_1) and inversely acid-dependent (k_2) water-exchange pathways.

squares fits of the variable-acidity data at each pressure P, corresponding values of k_1 $(k_1{}^P)$ and k_2 $(k_2{}^P)$ were obtained, and it was found that $\ln k_1{}^P$ and $\ln k_2{}^P$ are linear functions of P within the experimental uncertainty (Figure 2; eq 4 and 5), i.e., that the corresponding volumes of activation $\Delta V_1{}^*$ and

$$\ln k_1{}^P = \ln k_1{}^\circ - P\Delta V_1{}^*/RT \qquad (4)$$

$$\ln k_2{}^P = \ln k_2{}^\circ - P\Delta V_2{}^*/RT \qquad (5)$$

$\Delta V_2{}^*$ are independent of pressure, as is usual for simple solvent exchange reactions.[1,9,20,24,25]

Least-squares fits of k_1 and, independently, k_2 data to eq 4 and 5 gave $\Delta V_1{}^* = -5.0 \pm 0.2$ cm^3 mol^{-1}, $\Delta V_2{}^* = +7.6 \pm 0.3$ cm^3 mol^{-1}, $k_1{}^\circ = k_1$ at zero (effectively, atmospheric) pressure $= (6.9 \pm 0.1) \times 10^4$ s^{-1}, and $k_2{}^\circ = (11.3 \pm 0.1) \times 10^4$ mol kg^{-1} s^{-1}, the uncertainties being standard deviations.

Combination of eq 2, 4, and 5 into eq 6 allowed all the

$$k = k_1{}^\circ \exp(-P\Delta V_1{}^*/RT) + k_2{}^\circ [\mathrm{H^+}]^{-1} \exp(-P\Delta V_2{}^*/RT) \qquad (6)$$

available data to be fitted simultaneously, with use of a non-linear least-squares computer program, giving $\Delta V_1{}^* = -5.4 \pm 0.4$ cm^3 mol^{-1}, $\Delta V_2{}^* = +7.8 \pm 0.2$ cm^3 mol^{-1}, $k_1{}^\circ = (6.8 \pm 0.1) \times 10^4$ s^{-1}, and $k_2{}^\circ = (11.4 \pm 0.1) \times 10^4$ mol kg^{-1} s^{-1}. Taking logarithms of both sides of eq 6 and fitting $\ln k$ values, with or without data editing based on various assumptions, gave $\Delta V_1{}^* = -5.6$ to -5.7 and $\Delta V_2{}^* = +8.0$ to $+8.3$ cm^3 mol^{-1}; this procedure would be preferable if the uncertainty in k were a constant percentage of k, but in fact the larger $T_2{}^{-1}$ values are less susceptible to errors from the T_{2s} correction. The set of parameters obtained by fitting k directly has been adopted as final and was used to calculate the curves in Figure 3, which shows that the experimental data are satisfactorily represented by these parameters despite the compounding of the errors.

The activation parameters published by Grant and Jordan[6,23] give $k_1 = 6.3 \times 10^4$ s^{-1} and $k_2 = 6.1 \times 10^4$ mol dm^{-3} s^{-1} for 382.8 K, $P = 0.1$ MPa, and ionic strength 6.0 mol dm^{-3}. The agreement with our $k_1{}^\circ$ value is close, while the discrepancy in $k_2{}^\circ$ arises partly from the different choice of concentration scale but mainly from an apparent overestimate of the ionic

strength dependence of K_a at high I values and temperatures in Grant and Jordan's adaptation of the results of Matijević et al.[19] (which covered the range $0.1 \geq I \geq 2.67$ mol dm^{-3} and 298–353 K only; see also comments below on the hydrolysis reaction). In fact, values of k calculated from our parameters were within $\sim 5\%$ of values interpolated from the raw data of Grant and Jordan[6] at their highest ionic strength (4 mol dm^{-3}), and within the range of values observed by Dodgen et al.[22] for 1.5 m HClO$_4$ at ~ 383 K.

The volume change ΔV_a accompanying reaction 3 was determined by observing the effect of pressure on the optical absorbance A due to Fe(H$_2$O)$_5$OH^{2+} under conditions for which the concentration of this ion was small compared to that of Fe(H$_2$O)$_6{}^{3+}$ and for which hydrolytic polymerization could be neglected[17–19,26,27] (1.05 m HClO$_4$, with [Fe(total)] = 0.0235 m for measurements using the Franck cell at 295 K and 0.0134 m for measurements with the leNoble–Schlott cell up to 371 K). It was assumed, reasonably,[28] that a molar absorbance ϵ, compression corrected if necessary, due to nonligand field electronic transitions of transition-metal complexes is not significantly affected by the small changes in solution density involved here. Taking K_a at 294 K to be 1.17×10^{-3} mol L^{-1} and $\epsilon_{\mathrm{FeOH}} = 920$ for Fe(H$_2$O)$_5$OH^{2+},[17–19,26,27] measurements at 340 nm, 294 K, and 0.1 MPa gave a molar absorbance ϵ_{Fe} for Fe(H$_2$O)$_6{}^{3+}$ of 2.9 ± 0.1 L mol^{-1} cm^{-1}, in excellent agreement with the high-acidity study of Milburn and Vosburgh.[17] This was large enough to contribute significantly to A at [H$^+$] ≈ 1.0 m, especially at about 300 K, and consequently K_a had to be derived as a function of pressure or temperature with use of the full eq 7, in which b is the optical path length.

$$K_a = [A - b\epsilon_{\mathrm{Fe}}[\mathrm{Fe(total)}]][\mathrm{H^+}]/b\epsilon_{\mathrm{FeOH}}[\mathrm{Fe(total)}] \qquad (7)$$

In fact, A was only slightly decreased by increasing the pressure, after the relatively large initial increase due to compressional heating had decayed away, and the readings were stable enough to permit reproduction within the experimental error over the compressional and decompressional parts of the pressure cycle (which was repeated twice). Least-squares fits of the results to eq 7 gave $\Delta V_a = +1.1 \pm 1.1$ cm^3 mol^{-1} at 295 K over a 0.1–125 MPa range and $+0.8 \pm 0.1$ cm^3 mol^{-1} at 371 K over the range 0.1–250 MPa. The first value is very uncertain because ϵ_{Fe} contributes a major fraction of A and serves only to show that ΔV_a is not significantly temperature dependent. The possibility of a significant ionic strength dependence of ΔV_a can be disregarded since K_a itself is not very sensitive to I at high I values, and in any case our value of ΔV_a lies in the middle of the range $(+3.0,^3 +1.6,^4$ and -1.2^{29} cm^3 mol$^{-1})$ reported by others for iron(III) hydrolysis at various ionic strengths and near-ambient temperatures.

This study was not primarily designed to produce precise values of K_a as a function of temperature, but ancillary experiments using an optical cell described elsewhere[28] gave $10^3 K_a = 1.2$, 5.24, 13.5, 24.8, and 35.7 m for temperatures of 295.3, 329.6, 349.2, 366.1, and 371.4 K, respectively, at ~ 1 MPa and $I = 1.1$ m. These data give $\Delta H = 40.3 \pm 1.8$ kJ mol^{-1} and $\Delta S = 80 \pm 5$ J K^{-1} mol^{-1} if ΔC_p is assumed to be 0; these parameters are slightly lower than (but in reasonable agreement with) the more likely values listed in Sylva's review[18] and somewhat larger than $\Delta H = 33.5$ and $\Delta S = 58$ from Grant and Jordan's analysis[6] of the data of Matijević et al. At the temperature of our NMR experiments under pressure (382.8 K), our parameters predict a K_a value some

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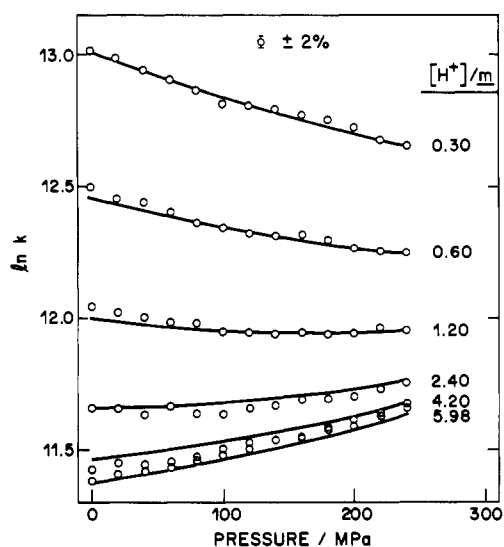(29) Stranks, D. R.; Vanderhoek, N. *Inorg. Chem.* **1976**, *15*, 2645.

Figure 3. Pressure dependence of the total water-exchange rate coefficient k at various acidities. Curves are those calculated from eq 6 with the parameters given in the Abstract.

70% larger than is given by the Grant–Jordan–Matijević formula[6] at $I \approx 1.0$ mol L^{-1} and would account for the apparent discrepancy noted above between our measurements of k_2 and the values calculated from the parameters of Grant and Jordan.[6] There is, however, a clear need for a detailed investigation of iron(III) hydrolysis equilibria from ambient temperature to 400 K and beyond.

Discussion

The effect of pressure on the ^{17}O line width of acidified water at 383 K is a barely discernible broadening (~ 1 Hz GPa^{-1} in $\Delta \nu$ or $(\partial \ln T_{2s}/\partial P)_T \approx -0.05 \pm 0.02$ GPa^{-1}), which is negligible for our present purpose. By contrast, a previous study at 298 K showed a definite sharpening of the H$_2^{17}$O line with increasing pressure $((\partial \ln T_{2s}/\partial P)_T \approx +0.4$ GPa$^{-1})$.[24] The latter effect is attributable to the disruption of the hydrogen-bonded water structure at 298 K by applied pressure,[24] in which case the observation at 383 K reflects the expected reduction in the degree of structuring of water as the temperature is raised. Presumably, definite pressure broadening of the H$_2^{17}$O line would become evident, and water would increasingly resemble a "normal" liquid (cf. acetonitrile[30,31]) in this respect, if the temperature were raised beyond 383 K.

The iron(III) water-exchange system provides an interesting example of a reaction proceeding by two parallel pathways of comparable importance which have opposite pressure dependences, so that under certain conditions (e.g., [H$^+$] = 1.2 m, in Figure 3), one observes first a deceleration and then an acceleration of the reaction with increasing pressure as the pathway with the positive volume of activation is progressively "squeezed out". Fortunately, these two water-exchange pathways comprise the *only* two mechanisms contributing significantly to T_{2r} (eq 2 and Figure 1) under our experimental conditions, and their volumes of activation are independent of pressure to within the experimental uncertainty, so that the line-broadening data are cleanly reducible according to eq 4–6 (Figures 2 and 3).

Since $\Delta V_2^* = +7.8 \pm 0.2$ and $\Delta V_a = +0.8 \pm 0.1$ cm^3 mol^{-1}, the volume of activation ΔV_{OH}^* for water exchange on (H$_2$O)$_5$FeOH^{2+} is $+7.0 \pm 0.3$ cm^3 mol^{-1}. This effectively is the same as the volumes of activation observed for the exchange of water on Ni(H$_2$O)$_6^{2+}$ ($+7.2$)[24,25] and Co(H$_2$O)$_6^{2+}$

($+6.1$),[25] where there is ample evidence of dissociative activation in substitution, and is close to those ($+8$ to $+9$ cm^3 mol^{-1})[32] measured for the replacement of water in Co(CN)$_5$OH$_2^{2-}$ in various substitution reactions, which constitute the best documented cases of the limiting type of dissociative mechanism (D, or S$_N$1 lim).[33,34] Furthermore, simple considerations[8,35] indicate that the limiting value of the volume of activation for dissociative water exchange should indeed be about $+9$ cm^3 mol^{-1}. Thus, we can safely conclude that solvent exchange of aqueous Fe(H$_2$O)$_5$OH^{2+}, like the anation of this species,[1–6] is dissociatively activated, and this is confirmed by the closeness of ΔV_{OH}^* to the corresponding parameters for anation of Fe(H$_2$O)$_5$OH^{2+} by Cl$^-$ ($+7._8$)[2] and NCS$^-$ ($+7._1$ cm^3 mol^{-1}).[3]

In contrast, ΔV_1^* for aqua exchange on Fe(H$_2$O)$_6^{3+}$ ($-5._4$ cm^3 mol^{-1}) is quite strongly negative and differs from the volumes of activation reported for the anation of this cation by Cl$^-$,[2] NCS$^-$,[3] and Br$^-$[4] ($-4._5$, ~ 0, and -8 cm^3 mol^{-1}, respectively, disregarding any initial ion pairing). These observations, like the relative rate data,[1,5,6] indicate associative activation for substitution in Fe(H$_2$O)$_6^{3+}$ itself.[7–9,35] The clear difference in sign between ΔV_{OH}^* and ΔV_1^* cannot be accommodated in terms of a differing response of the nonreacting ligands in a common activation process, as Langford has proposed when comparing some other solvent-exchange systems,[36] since the central ion and all but one of the ligands are the same in Fe(H$_2$O)$_6^{3+}$ and Fe(H$_2$O)$_5$OH^{2+}; the reason for the opposite effects of pressure on their water-exchange rates must surely be a difference in intimate reaction mechanism.

For aqua exchange on Mn(H$_2$O)$_6^{2+}$, ΔV_1^* is also $-5._4$ cm^3 mol^{-1},[25,37] although the exact equality with the Fe(H$_2$O)$_6^{3+}$ parameter is perhaps fortuitous. As pointed out elsewhere,[8] associative activation is to be anticipated in octahedral sextuplet Mn(II) complexes since the spherically symmetrical 3d^5 Mn^{2+} ion is known to adopt stable heptacoordination in complexes as familiar as Mn(EDTA)OH$_2^{2-}$. The smaller Fe^{3+} ion is similarly seven-coordinate in K[Fe(EDTA)OH$_2$]·H$_2$O,[38] and so the arguments for associative activation in both Mn(H$_2$O)$_6^{2+}$ and Fe(H$_2$O)$_6^{3+}$ are mutually supportive.

For aqua exchange on Cr(H$_2$O)$_6^{3+}$, however, ΔV_1^* is markedly more negative ($-9._3$ cm^3 mol$^{-1})$[39] than that for Fe(H$_2$O)$_6^{3+}$ or Mn(H$_2$O)$_6^{2+}$. It might naively be expected that the limiting value of ΔV_1^* for associative activation would be the negative of that for dissociative activation, in which case the Cr(H$_2$O)$_6^{3+}$ exchange represents particularly well-developed associative activation (perhaps because of vacation of a t$_{2g}$ orbital in the O_h complex by electronic excitation to assist in bonding to the incoming ligand, much as suggested by Spees et al.[40]). For aquation of Pt(dien)Cl$^+$ and Pt(dien)Br$^+$, which are considered to react by limiting associative mechanism, the volumes of activation are -10 and -9.5 cm^3 mol^{-1}, respectively.[41]

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Exchange Coupling in the Hydroxo-Bridged Chromium Dimer Di-μ-hydroxo-bis(ethylenediamine-*N*,*N'*-diacetato)dichromium(III) Tetrahydrate. Observations on the Effect of Structure on Superexchange Interactions

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The magnetic susceptibility of the hydroxo-bridged chromium dimer di-μ-hydroxo-bis(ethylenediamine-*N*,*N'*-diacetato)-dichromium(III) has been measured in the temperature range 3.0–79 K and the data fitted by the Van Vleck equation for pairs of exchange coupled $S = {}^3/_2$ ions including a biquadratic term to yield the parameters $J = -9.3$ cm^{-1}, $j = -0.2$ cm^{-1}, and $g = 1.96$. These magnetic data for [Cr$_2$(EDDA)$_2$(OH)$_2$]·4H$_2$O, the complex with the smallest ratio of ϕ, the angle at the bridging oxygen atom, to r, the chromium–bridge oxygen bond distance, confirm that a correlation between the singlet–triplet splitting and ϕ/r exists. The correlation is similar to that which has been observed for di-μ-ligand-bridged copper(II) systems. The dependence of the exchange coupling mechanism on structural features is discussed in terms of molecular orbital theory.

Introduction

Following an extensive study of the effects of structural variations and chemical functional groups on exchange coupling in di-μ-hydroxo-dichromium(III) complexes of the general formula [Cr$_2$L$_n$(OH)$_2$L'$_m$]$^{q\pm}$ (where L is a bidentate or tridentate ligand and L' = H$_2$O in complexes with tridentate ligands), Scaringe[1] observed that the singlet–triplet splitting was highly correlated with the function ϕ/r. Here ϕ is the angle at the bridging hydroxo oxygen atom and r is the chromium–bridging oxygen bond distance, or the average of the structural parameters ϕ and r, respectively, if they are crystallographically independent. The singlet–triplet splitting is given by $|\Delta E| = 2J - 6.5j$, where J is the bilinear exchange coupling constant and j is the biquadratic term from the Hamiltonian $\mathcal{H} = -2JS_1 \cdot S_2 - j(S_1 \cdot S_2)^2$ required for the analysis of the temperature variation of the magnetic susceptibility in most cases. Scaringe[1] provided an explanation for the correlation between structural and magnetic properties of these dimeric chromium complexes in terms of the molecular orbital formalism developed by Hoffmann and co-workers[2] and postulated that the minor deviations from the general trend between ΔE and ϕ/r were a result of other structural features, electronic effects, and intermolecular interactions. The data[3,4] for [Cr$_2$(glycine)$_4$(OH)$_2$] suggested that ΔE had reached a maximum at a ϕ/r value of ~50°/Å, and we were lead to speculate that ΔE should decrease with further decreases in ϕ/r in a manner similar to that which has now been established for uni- and di-μ-ligand-bridged copper(II) complexes.[5] The recent report[6] of the synthesis and crystal structure of di-μ-hydroxo-bis[(ethylenediamine-*N*,*N'*-diacetato)chromium(III)] tetrahydrate has provided an excellent opportunity to verify the anticipated decrease in ΔE below ϕ/r values of 50°/Å, since the chromium–bridging oxygen bond distance in this complex is 1.964 (3) Å and the Cr–O–Cr bridging angle is 97.6 (1)°, giving $\phi/r = 49.7$°/Å, the smallest value that has been observed in this series of complexes. We have now

prepared [Cr$_2$(EDDA)$_2$(OH)$_4$]·4H$_2$O by an alternate synthetic route and determined its magnetic properties. The results of our work are presented in this article.

Experimental Section

[Cr(EDDA)(acac)]·2H$_2$O. The crystalline product was prepared by Shepherd's modification[7] of the synthesis reported by Fuji.[8] CrCl$_3$·3H$_2$O (5.28 g) was powdered in a mortar and transferred to a 400-mL beaker. H$_2$EDDA (8.00 g) and 40 mL of H$_2$O were added, and the pH was adjusted to 3.5 with powdered (NH$_4$)$_2$CO$_3$. The solution was heated for 30 min at ca. 45 °C. Acetylacetone (Hacac) (2.00 g) was added to the solution, and the pH was adjusted to 7.0 with (NH$_4$)$_2$CO$_3$. The stirred solution was heated to 75 °C for 1 h, cooled to room temperature, and stored overnight (12 h) in a refrigerator at 4 °C. The solid crystals were collected by filtration and washed with CH$_3$OH which has been chilled in an ice-salt slush.

[Cr$_2$(EDDA)$_2$(OH)$_2$]·4H$_2$O. [Cr(EDDA)(acac)]·2H$_2$O (3.32 g, 9.19 × 10^{-3} mol) was dissolved in a solution of 10.0 mL of H$_2$O and 10.0 mL of 1.095 M HClO$_4$ in a 50-mL beaker. The sample was heated with constant stirring for 8 h at 80 °C with the volume being maintained between 10 and 20 mL. During the reaction, which involved distillation of Hacac into the vapor phase, samples showed a decreasing absorbance at 386 nm, with the band shifting to 390 nm, and almost no change in the absorbance band at 532 nm. Acetylacetone was also detectable by its characteristic odor until the later periods of heating. After 8 h, the solution was adjusted to pH 5.96 with 0.38 g of NaOH pellets. The color changed with a shift in the long-wavelength maximum from 549 to 557 nm. The solution was heated for 1 h at 80 °C, resulting in a reduction in the volume to 10 mL by evaporation. The solution was allowed to cool to room temperature overnight, after which time a purple-pink opalescent

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