COMMENTS

Comment on “Reinterpretation of the Spectra of Hydrated Co^{++}: An ab Initio Study” (*J. Phys. Chem. A* 1998, *102,* 6525)

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Gilson and Krauss[1] have recently revisited the problem of the interpretation of the visible/near-infrared spectrum of the hydrated Co^{2+} ion using ab initio calculations. As Lever[2] has noted, complete analysis of the visible band occurring around 20 000 cm^{-1}, customarily assigned to the $^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$ transition of the $(H_2O)_6Co^{2+}$ species, is particularly difficult because of multiple structure attributable to the admixture of spin-forbidden transitions to the ^2G and ^2H states as well as vibrational and low-symmetry components. There has been little change in the standard ligand-field interpretation of the spectrum since the classic work of Holmes and McClure[3] published in 1957; thus, reconsideration of the problem using modern computational methods is timely and welcome.

Gilson and Krauss[1] correctly point out that the selection rules for *d*−*d* transitions in $(H_2O)_6Co^{2+}$ in strict T_h symmetry imply zero oscillator strength. In the standard model of this and other octahedral metal−ion complexes, the observed (weak) oscillator strength is gained mainly by vibronic coupling that destroys the center of symmetry. Gilson and Krauss[1] present an alternative interpretation, viz., that at near-ambient temperatures “the dominant optically allowed species is the five-coordinate complex”, since their calculations indicate that the oscillator strength for $(H_2O)_5Co^{2+}$ is at least 10^3-fold greater than for $(H_2O)_6Co^{2+}$. The predicted wavenumbers of the absorption maxima of the putative $(H_2O)_5Co^{2+}$ are also said[1] to provide a better fit of the observed spectrum.[3] The hexaaqua ion, however, is the only cobalt(II) species detectable in EXAFS and X-ray diffraction studies of aqueous solutions with noncomplexing counterions and of solid hexahydrate salts,[4] so that $(H_2O)_5Co^{2+}$ cannot constitute more than a very small fraction of the total Co in these environments. In addition, Gilson and Krauss[1] propose that the species $(H_2O)_5CoOH^+$ is a major contributor to the high-temperature aqueous spectrum of Co^{2+}(aq) measured in our laboratories some 20 years ago.[5] These proposals can be tested experimentally, as described below, and we find that both can be rejected.

It has been shown[6] that the “absolute” molar volumes V^0_{abs} of ions M^{z+}(aq) in aqueous solution (based on $V^0_{abs}(H^+) = -5.4$ cm^3 mol^{-1}) at 298 K are given to within the experimental uncertainty by eq 1 , in which r is the Shannon ionic radius[7] in picometers and n is the primary coordination number in $(H_2O)_nM^{z+}$. Equation 1 is a reliable empirical relation that confirms, for example, that there is a change in primary

$$V^0_{abs}/\text{cm}^3\ \text{mol}^{-1} = 2.523 \times 10^{-6}(r + 238.7)^3 - 18.07n - 417.5z^2/(r + 238.7) \quad (1)$$

coordination number of M^{3+}(aq) from 9 to 8 as one crosses the lanthanide series from La to Lu and that this is associated with an increase of 12−13 cm^3 mol^{-1} in the normalized V^0_{abs}.[6] It has further been shown[8] that eq 1 can be used to calculate the molar volume change ΔV^0 for the processes

$$M^{z+}(\text{aq},n\text{-coordinate}) \rightarrow M^{z+}(\text{aq},(n-1)\text{-coordinate}) \quad (2)$$

and so, if ΔV^0 is sensibly constant over a range of hydrostatic pressure P, the dependence of the equilibrium constant K for process (2) on P can be calculated from eq 3. For Co^{2+}(aq)

$$\ln(K_P/K_0) = -P\Delta V^0/RT \quad (3)$$

going from six- to five-coordination, $\Delta V = +12._5$ cm^3 mol^{-1}.[8] If we assume for argument’s sake that the molar absorbance ϵ of Co^{2+}(aq) is due *entirely* to a species $(H_2O)_5Co^{2+}$ comprising less than (say) 1% of the total Co^{2+} in solution, then the concentration of $(H_2O)_5Co^{2+}$ will be directly proportional to the observed ϵ, and so

$$\ln(\epsilon_P/\epsilon_0) = -12.5P/RT \quad (4)$$

if P is in MPa and ϵ_P is independent of pressure. Values of ϵ_P/ϵ_0 calculated on this basis are listed in the second column of Table 1 and show that pressures of a few hundred megapascals will cause a dramatic reduction in ϵ if the 20 000 cm^{-1} band is due, either in entirety or even in part, to the minor species $(H_2O)_5Co^{2+}$.

We have therefore measured the effect of pressures up to 300 MPa on the 20 000 cm^{-1} band of aqueous Co^{2+}(aq) in acidic perchlorate and trifluorosulfonate media at 295.1 ± 0.2 K, using a Cary 5E spectrophotometer with fiber optics accessory and the pressure apparatus described elsewhere.[9] The pressurizing fluid was distilled water. Because the samples were enclosed in a le Noble-Schlott “pillbox” cell in which the optical path length b contracted freely under increasing pressure, only a small compressional correction to absorbance A_P at pressure P for the volume swept out by the inner cell wall (inner and outer radii r_i and r_o, respectively; length l) was necessary:[9,10]

$$\epsilon_P = A_P/[\text{Co}][(b_0 - l) + (r_i/r_o)^2 l + (V_0/V_P)\{1 - (r_i/r_o)^2\}l] \quad (5)$$

Here, V_0 and V_P are the specific volumes of water at ambient (effectively zero) pressure and pressure P, respectively.

Baseline corrections were established separately at the selected pressures with blank solutions in the pillbox cell, using the small molar absorbance at 400 nm (0.30 L mol^{-1} cm^{-1} at 295 K and 0.1 MPa) as a reference point. The maximum molar absorbances ϵ_{max}, together with the corresponding wavenumbers ν_{max} and bandwidths $\delta\nu_{1/2}$ at half-height, are listed as functions of pressure in Table 1.

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TABLE 1: Effects of Pressure on the 20 000 cm^{-1} Band of Co(ClO$_4$)$_2$ in 0.1 mol L^{-1} Aqueous HClO$_4$ at 295 K

pressure/MPa	ϵ_P/ϵ_0(calc)	$\nu_{max}/10^3$ cm^{-1}	$\delta\nu_{1/2}$/cm^{-1}	ϵ_{max}/L mol^{-1} cm^{-1}
0	1	19.55	3750	4.74
100	0.60	19.59	3770	4.71
200	0.36	19.65	3750	4.64
300	0.22	19.63	3750	4.66

Table 1 shows that there is a barely discernible blue shift with increasing pressure (attributable to shortening Co−O bond lengths), that the bandwidth is independent of pressure, and that ϵ decreases by only about 2% over the range 0−300 MPa—an insignificant amount, given the uncertainty of about 1% in ϵ originating mainly in the baseline correction. A parallel study of the spectrum of Co(CF$_3$SO$_3$)$_2$ in 0.1 mol L^{-1} aqueous CF$_3$SO$_3$H gave precisely the same results, within experimental uncertainty. Comparison of the second and fifth columns of Table 1 shows that there can be no significant contribution to the band intensity from $(H_2O)_5Co^{2+}$ at near-ambient temperatures. This conclusion is supported by the observation of Holmes and McClure[3] that the oscillator strength of the 20 000 cm^{-1} band is roughly similar in solid salts and aqueous solutions of $(H_2O)_6Co^{2+}$; it is difficult to see how reproducible minor amounts of a pentacoordinate ion could be present in the solid hydrates, in which an equilibrium involving it and solvent water (process (2)) is not possible.

With regard to the high-temperature aqueous spectrum of Co^{2+}(aq), Gilson and Krauss are justified in expecting the hydrolytic equilibrium (6) to become increasingly significant

$$(H_2O)_6Co^{2+} \rightleftharpoons (H_2O)_5CoOH^+ + H^+ \qquad (6)$$

as the temperature increases toward the critical point *in the absence of added acid*.[11] In addition, one can anticipate an increased tendency to complexation of Co^{2+}(aq) by the counterion. Swaddle and Fabes[5] therefore took pains to show that spectra of $Co^{2+}/H^+/HSO_4^-$ solutions up to 610 K remained *identical* when [H$^+$] and [HSO$_4^-$] were simultaneously increased from 0.1 to 0.5 mol L^{-1}.[12] At such high acidities, reaction 6 will be either suppressed completely (as is evidently the case) or will exhibit a dependence on [H$^+$]. Thus, neither the hydrolyzed species $(H_2O)_5CoOH^+$ nor any Co sulfato complexes contributed to the observed visible spectra of the solutions.

There remains, however, room for debate regarding the origin of the feature with a maximum near 18 000 cm^{-1} that emerges in the high-temperature (>500 K) spectrum of $Co^{2+}/H^+/HSO_4^-$ solutions.[5] Difference spectra[5] show that this is a new feature that appears *in addition to*, but overlapping, the familiar 20 000 cm^{-1} band, which, as argued above, is truly attributable to $(H_2O)_6Co^{2+}$. Swaddle and Fabes[5] attributed the additional feature to the presence of minor amounts of $(H_2O)_4Co^{2+}$, on the grounds that its absorbance maximum appeared at the position relative to the $(H_2O)_6Co^{2+}$ peak that would be expected from naïve ligand-field concepts[13] and by analogy with the tetranitratocobalt(II) ion in which Co^{2+} is known to be tetrahedrally coordinated with oxygen atoms.[14] Furthermore, the absorbance due to the putative tetrahedral species was inversely related to the *square* of the solvent water concentration (density), rather than the first power as would be anticipated for $(H_2O)_5Co^{2+}$. The chemistry of cobalt(II) in general shows a striking tendency toward the formation of tetrahedral complexes, presumably reflecting symmetrical occupancy of the t$_2$ and e orbitals of the high-spin d^7 configuration under T_d ligand field splitting. Thus, while the high-temperature 18 000 cm^{-1} band may indeed be due to minor amounts of $(H_2O)_5Co^{2+}$, the original proposal that it is caused by tetrahedral $(H_2O)_4Co^{2+}$ remains both tenable and attractive. The inferred transient involvement of five-coordinate Co^{2+} in the transition state of solvent exchange on aqueous $(H_2O)_6Co^{2+}$ at near-ambient temperatures is not relevant to the present case, as the water exchange mechanism is believed to be of the dissociative *interchange* type in which the lifetime of five-coordinate Co^{2+} is extremely short and hence its concentration is undetectably small.[4,15]

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Supporting Information Available: Spectra of Co^{2+}(aq) in acidic aqueous perchlorate and trifluoromethanesulfonate media, at ambient pressure and 300 MPa. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

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