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Response to "Comment on 'Reinterpretation of the Spectra of Hydrated Co^{++}: An ab Initio Study'"

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Until recently, the spectrum of aqueous Co(II) at room temperature had been attributed to the six-coordinate cobalt complex $Co(H_2O)_6^{2+}$. This interpretation was based on the similarity of the aqueous spectrum to the spectrum of crystalline $CoSO_4 \cdot 7H_2O$[1] and on X-ray scattering data showing that the coordination number of cobalt in solution is six.[2] However, there are problems with this assignment. A six-coordinate complex in solution would have high symmetry for which electronic transitions are forbidden. The crystal chromophore has C_2 symmetry[3] for which electronic transitions are allowed. The break in high symmetry in the crystal is due to the arrangement of the second shell counterions that create a large field around the cobalt. In contrast, any absorbance associated with the highly symmetric 6-coordinate Co(II) complex in solution would need to arise from vibronic coupling. However, the temperature dependence of the solution spectrum is not in accord with the predicted behavior for the vibronically allowed mechanism, suggesting the presence of an additional Co(II) species that is present at low concentration and thus is not detected in the X-ray scattering experiment.[4] On the basis of ab initio quantum calculations, we proposed that the spectrum of the aqueous Co(II) results, at least in part, from a small amount of the pentaaquacobalt(II) complex.[5] Since the calculated oscillator strength of the five-coordinate species is at least 1000 times greater than that of the six-coordinate, only a small amount of the five-coordinate species in solution is needed to dominate the observed spectrum. We also presented calculations[5] suggesting that the high-temperature spectrum[4] may be due, in part, to a negative ion bound in the first shell of the cobalt. In contrast, the experimentalists interpreted the data to indicate the presence of a four-coordinate, tetraaquacobalt(II) complex whose concentration increased with temperature.[4]

Fedorchuk and Swaddle (see Comment) disagree with our interpretations. They predict a large pressure dependence in the spectrum of a solution of cobalt perchlorate and cobalt trifluoromethanesulfonate would occur if the five-coordinate species contributed substantially to the spectrum, but they observe only a minor effect. They also conclude that it is not possible for an anion to be bound to the cobalt in the high-temperature experiment. Finally, they maintain that the minor species in the solution is the tetraaquacobalt(II) complex. We will address each of these issues below and conclude that our original proposals are still valid.

The first issue we address is what cobalt complexes are contributing to the room-temperature spectrum of aqueous cobalt(II). Swaddle and Fabes[4] have found that the hexaaqua species is in equilibrium with a minor species with an ΔH of 17 kJ/mol. They assigned the minor species as tetraaqua on the basis of ligand-field concepts (which we addressed in our paper[5]) and a spectrum of tetranitratocobalt(II). Our reasons for suggesting the five-coordinate species were provided in detail earlier,[5] and a summary is given here. (1) Theoretical calculations of the absorption spectrum of the tetraaqua species and for a model of the asymmetric vibration that lowers the symmetry of the hexaaqua species do not show sufficient splitting in the upper degenerate level to account for the observed splitting in the measured spectrum. (2) The calculations indicate that the energy cost of forming the four-coordinate species is about twice that of forming the five-coordinate complex, favoring a higher concentration of the five-coordinate species. (3) The spectrum that is calculated for the pentaaqua species captures the features of the measured spectrum for both oscillator strength and energy splitting. (4) The spectrum of tetranitratocobalt(II) shows one absorption peak at 18 500 cm^{-1} with no higher energy bands[6] and therefore does not resemble the spectra reported by Swaddle and Fabes either at room or higher temperatures. On the basis of these considerations, we identified the minor species that has been shown to exist by Swaddle and Fabes as five-coordinate.

However, Fedorchuk and Swaddle have argued that the weak pressure dependence of the spectrum provides evidence that the five-coordinate species is not an important contributor to the spectrum under ambient conditions. Increasing the pressure drives the equilibrium between 6-coordinate and 5-coordinate cobalt toward the species with the smaller partial molar volume and the extent of the shift in equilibrium depends on the difference in the partial molar volumes of the two species. In a previous study,[7] Swaddle estimated the volume difference between $(H_2O)_6Co^{2+}$ and $(H_2O)_5Co^{2+}$ to be 12.5 cm/mol. On the basis of this number they proposed that there should be a 4.5-fold change in absorption intensity as pressure is increased from 0 to 300 MPa. One of the key components of the semiempirical model that led to this estimated volume change, however, is that the radius of the complex increases markedly with the number of bound waters. Given this model, one would predict an even larger change (21-fold) in absorption intensity with pressure if the minor absorbing species were four-coordinate, as claimed by Swaddle and Fabes in their discussion of the temperature dependence of the spectrum.[4] Because of the large oscillator strength of the tetraaqua complex,[8] even if only 0.08% of the Co(II) in solution at room temperature and pressure were in the tetraaqua form, as proposed by Swaddle and Fabes, a marked pressure dependence should be observed. The weak dependence of the spectrum upon pressure thus indicates either that the model they have used to estimate partial molar volumes is inaccurate or that neither the tetra- or pentaaquacobalt(II) complexes contribute to the room-temperature spectrum.

Estimating molar volume changes is not an easy task. Qualitatively, the five-coordinate complex is smaller than the six and electrostriction effects on the surrounding solvent will be greater for the five-coordinate complex. However, the volume of the water molecule released from the six-coordinate complex into the bulk solvent will be larger than its volume in the complex, also due to electrostriction. To estimate the net volume change on going from the 6- to the 5-coordinate complex, we calculated the molecular volumes of the in vacuo optimized structure of $(H_2O)_6Co^{2+}$, $(H_2O)_5Co^{2+}$, and water as determined previously[5] with the program UHBD,[9−11] and obtained values of 163, 139, and 21 Å^3, respectively. Thus, the volume

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difference between the six-coordinate complex and the five-coordinate complex + water is −3 Å^3/molecule, corresponding to a molar volume change of −2 cm^3/mol. This calculation is only an estimate since neither the volume of the released water nor electrostriction effects are fully taken into account. Nonetheless, this value is much smaller than the estimate of Fedorchuk and Swaddle and is more consistent with the observed small pressure effect. We therefore conclude that the pressure study does not rule out and possibly supports the existence of $(H_2O)_5Co^{2+}$ in solution.

Finally, Fedorchuk and Swaddle state that since Co(II) tends to form four-coordinate complexes it is "both tenable and attractive" that the minor species in solution is $(H_2O)_4Co^{2+}$. In fact, however, Co(II) is very adaptable, forming complexes of various coordination numbers, including, in particular, an abundance of five-coordinate Co(II) complexes (see, e.g., refs 8 and 12).

The second issue to be addressed is the mechanism by which an increase in temperature affects the spectrum. As temperature increases, higher energy bands appear in the spectrum. Our calculations indicate that these bands cannot be accounted for by the hexa-, penta-, or tetraaquacobalt complexes. However, the high-temperature spectrum agrees well with that calculated for Co(II) with a bound negative ion and to the *measured* spectra of cobalt(II) perchlorate in alcohol,[13] where significant ion-pairing is expected to occur. In particular, calculations of the spectra of $(H_2O)_nCoOH^+$ indicate that ion-pairing will cause a red shift in the lower energy band, a blue shift in the higher energy band, the appearance of a third band at even higher energy, and an increase in overall intensity.[5] This is precisely what is observed experimentally as the temperature is increased.[4] Moreover, the degree of ion-pairing is expected to increase with higher temperature because of the decreasing dielectric constant of the aqueous solvent. The dielectric constant of water at 625 K and 25 MPa is 15, far lower than the value of 80 at room temperature and pressure.[14−16] The attractive forces between Co(II) and the negative ions in solution will be far larger under these conditions than under ambient conditions. One can see experimental evidence of increased ion-pairing of Co(II) with perchlorate in mixed water/1-propanol solvents as the dielectric constant is reduced by increasing the mole fraction of propanol.[13] As the mole fraction of propanol approaches 1.0 and the dielectric constant of the solvent approaches 20, the spectrum shows changes similar to those observed in the high-temperature studies of Co(II).

An obvious candidate for the anion that pairs with Co(II) at high temperature is HSO_4^-, since this is present at 0.5 M concentration in the experiments. It is also possible that hydroxide plays a role, despite the high concentration of sulfuric acid, since the affinity of Co(II) for hydroxide rises steeply with increasing temperature,[14] even in the relatively low range of 298−473 K.

In conclusion, the most straightforward interpretation of the spectral data for aqueous Co(II) is that, at room temperature, intensity arises from a small concentration of the pentaaqua species $(H_2O)_5Co^{2+}$, and at higher temperatures, additional intensity arises from ion-pairing between Co(II) and a solution anion.

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