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Reinterpretation of the Spectra of Hydrated Co^{++}: An ab Initio Study

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The absorption spectrum of aqueous Co^{++} is reinterpreted in light of ab initio calculations. CAS-MCSCF and MCQDPT calculations yield the spectral states and their oscillator strengths, as well as the spin−orbit coupling between the quartet and doublet states of four-, five-, and six-coordinate Co^{++}−water complexes. Spectral states and oscillator strengths are also computed for these complexes with one water replaced by a hydroxide ion. The results of the calculations are compared with measured spectra obtained from room temperature and high temperature Co^{++} solutions. A completely symmetric six-coordinate octahedral metal−water complex will have zero oscillator strength because of its symmetry. We find, moreover, that the calculated oscillator strength remains very small ($\leq 10^{-6}$) even when the symmetry of this species is allowed to relax or when we distort the molecule asymmetrically. Therefore, the calculations suggest that the six-coordinate species can contribute little to the observed spectrum, even though it is the dominant form of Co^{++} in solution. On the other hand, the computed spectra of other aqueous coordination states of Co^{++} do show features of the observed spectra. We propose that the observed absorption spectra result from a mixture of thermodynamically disfavored but optically allowed species, with the largest contribution coming from the five-coordinate Co^{++}−water complex.

Introduction

The spectral properties of Co^{++} and Co^{++} complexes in solution and crystals have been studied for over 40 years, and their spectra have been thought to be basically well-understood.[1−3] The theoretical interpretation of these spectra has been based largely on the semiempirical crystal-field theory in which ligands bound to the metal are assumed to influence the spectral properties of the metal only though electrostatic effects. Although crystal-field calculations have been useful in understanding some of the crystal spectra, many questions remain regarding the observed spectrum of Co^{++} in aqueous solution, as discussed below. With the increase in computer speed and the fast quantum codes now available, it is possible to revisit the interpretation of the Co^{++} spectra using ab initio quantum methods.

The electronic spectrum of Co^{++} dissolved in water probes both the geometric structure of the water ligands and the electronic interaction between the metal dication and water. The spectrum of Co^{++} dissolved in water shows two broad absorption peaks: one peak at about 8000 cm^{-1} and a structured peak around 20000 cm^{-1}, which can be deconvoluted into two peaks at 19400 and 21550 cm^{-1} (see e.g., refs 1−3). The visible absorption peak (∼20000 cm^{-1}) is assigned to the atomic d−d electronic transitions, $^4T_{lg}(F)$ to $4T_{lg}(P)$,[3] with the degenerate atomic states split by the crystal field of the first shell ligands.[3] This band may also be split by spin−orbit coupling between the doublet and quartet states.[2] The coordination number of Co^{++} in aqueous solution has been determined from X-ray[4] scattering experiments to be six. The solution spectra, in fact, resemble the absorption spectra in crystals known to have six-coordinate hydrate clusters.[2] It seemed natural then to assign the electronic spectra of Co^{++} in solution to a six-coordinate first-shell cluster. However, the observed intensities must be analyzed carefully because the selection rules for the T_h symmetry associated with an octahedral arrangement of ligands predict zero oscillator strengths for perfect symmetry and suggest very small values generally for six-coordinate species.[3]

It has usually been assumed that the intensity of the spectrum of hydrated Co^{++} arises from vibronic excitations. This view is based upon analysis of the temperature dependence of the crystal spectra of hexahydrate cations.[2] However, it is unclear how relevant the crystal data are to the solution spectra. The recently solved crystal structure of aqueous Co^{++} has C_2 symmetry with the waters rotated from T_h symmetry to form H-bonds with the sulfate counterions.[5] The fields produced by these counter-ions further lowers the symmetry from T_h. That the visible spectrum of Co^{++} in crystals and in solution are similar is not surprising since what one is observing in both cases are d−d transitions of the cobalt ion that result from a lowering of symmetry. The spectra are broad in all cases so that specific features that might distinguish the spectra are hard to ascertain. Vibronic excitations lead to modest distortions from octahedral symmetry. These distortions would lead to a broadening of the spectral peaks but not a splitting as large as 2000 cm^{-1}. Moreover, when the dependence of the spectra of the cobalt solution on temperature was studied,[6,7] the startling conclusion, from the rapid increase in the oscillator strength (by a factor of 5^6), was that at least one additional species was contributing to the spectra. This species was suggested to be the four-coordinate Co^{++} complex.

A fundamental assumption that is normally made in interpreting the spectra of Co^{++} is that the first shell binding around the cation dominates the electronic properties and that this shell consists of six waters. However, the temperature dependent behavior of the spectrum of aqueous Co^{++} suggests that we do not have a clear understanding of either the thermodynamic or dynamical behavior of the structure of water around the cation. For example, can transient species of Co^{++} complexes that arise when first shell waters exchange contribute to the observed spectrum? High-pressure NMR experiments[8] and theoretical

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studies[9] suggest that the exchange of waters occurs through a dissociative process. Therefore, during ligand exchange, a five-coordinate complex would form. On the basis of the computer modeling study of ligand substitution around a metal ion[10] it has been predicted that this five-coordinate complex will persist long enough to equilibrate to its lowest energy conformation.[11] Another issue is whether water in the first shell can ionize. The pKa of water bound to Co^{++} is 9.82 at room temperature and decreases rapidly with increasing temperature to a value of 6.10 at 473 K.[12] In summary, although the X-ray and NMR data show that the dominant coordination number for these cations is six, the temperature dependence of the spectrum and the exchange properties suggest that even at room temperature there may be small populations of other first shell structures. This would be important for assignment of the electronic spectra, because the six-coordinate clusters are known to have low oscillator strength. Small populations of five or four-coordinate first-shell clusters, or clusters where a water is deprotonated, may contribute substantially to the electronic spectra if their transitions have larger oscillator strength than the six-coordinated clusters. This paper examines the possibility that such alternative structures contribute to the observed spectrum of aqueous Co^{++}.

This study examines the electronic spectra of hydrates of the divalent cobalt cation with ab initio methods. Although a number of studies have examined the ground state conformations and energetics of transition metal hexahydrates,[9,13,14] there has been no comparable study of the electronic spectra. Here, the spectra of four-, five-, and six-coordinate hydrates of cobalt are calculated using multireference methods to insure the proper spin and symmetry behavior for all states. This paper focuses on determining the origin, width, and splitting of the absorption bands, and their relative intensities. We restrict our consideration to the limiting behavior for low salt concentration. At higher concentrations, ion−ion interactions will affect the shell structure.[4]

Methods

Energy-gradient optimized structures are obtained at the restricted, open-shell Hartree−Fock (ROHF3) level for all model systems with the GAMESS code.[15] The active space for the MCSCF was chosen to represent the minimum number of orbitals necessary to occupy the d orbitals. Effective core potentials (ECP) were used to replace all the core electrons.[16] The 3s, 3p, and 3d orbitals are retained for the all-electron calculations. The CEP-31G basis was used with the default polarization basis in GAMESS.[16] Comparisons of DZP with smaller DZ bases were done and showed that, for the same geometries, the excitation energies were only slightly altered. However, all CAS-MCSCF and optimizations were done with the DZP basis set. The six-coordinate $Co^{++}(H_2O)_6$ structure was optimized both without constraints and also constrained to T_h symmetry. The four- and five-coordinate structures were optimized without constraints. Calculations were also done for systems in which one water is replaced by a hydroxide. These structures were also optimized without any constraints.

The excitation energies were first calculated at the CAS-MCSCF level using a minimum active space to include all d orbitals. The calculated atomic excitation energies were too large relative to the experiment[17] so the second-order perturbation correction to the multi-reference energies was considered[18] (MCQDPT). In this method, the second-order perturbation is applied to all matrix elements of an effective Hamiltonian. This perturbation will reproduce the energies of the CAS-MCSCF to first-order and yield second-order energies for all the states considered in the CAS-MCSCF by diagonalizing the matrix of the perturbed Hamiltonian. This correction correlates the 3s, 3p, and 3d electrons and greatly improves the agreement of the calculation with experimental atomic excitation energies as seen in Table 1. Because the CAS-MCSCF results show that the water ligands do not bind with significant covalent (charge transfer) interactions, the active space can be limited to the d orbitals for the complex as well. Oscillator strengths for the transitions are calculated using the length (dipole) form from the CAS-MCSCF orbitals. The active space for the hydroxide complexes was expanded to include the p orbitals of the hydroxide oxygen to include charge transfer effects from the hydroxide.

TABLE 1: Calculated and Experimental Excitation Energies for Isolated Co^{++}

state	exptl[17]	CAS-MCSCF	MCQDPT
^4F	780	0	0
^4P	15 345	18 785	15 222
^2G	17 323	18 852	17 930

Both the quartet and doublet states were calculated at the CAS-MCSCF and MCQDPT level. In addition, the spin−orbit interactions were determined for all states including the coupling between the spin states at the CAS-MCSCF level. The TZV basis set was used for these calculations since the ECPs could not be used in computing the spin−orbit interactions. The TZV and DZP energies agree very well (see Table 2). The spin−orbit method in GAMESS simplifies the Hamiltonian by considering only the dominant one-electron atomic terms.[15] However, this is appropriate for these systems since there is little charge transfer and covalent bonding between the metal and water ligands. The oscillator strengths for the hydroxide complexes are probably less accurate due to charge transfer from the hydroxide to the metal. Still, they are useful in interpreting the data. The two electron spin−orbit terms, which essentially shield the nucleus, are neglected and the one-electron spin−orbit integrals are evaluated by setting the effective nuclear charge for the cobalt to 15.3.[19] This value was derived by fitting the ground state splitting of the free ion. The spin−orbit coupling constant of the free Co^{++} ion is 180 cm^{-1}.[20] Interactions between the spin states are calculated to be weak unless the MCSCF state energies are within this value. Relative to the small spin−orbit interaction energies, the energetics of the two spin systems cannot be that accurately calculated. However, the present calculations do provide the splitting and relative excitation energies due to the ligands as well as the magnitude of the spin−orbit coupling between individual doublet and quartet states. This allows the discussion of the absorption spectra to consider all spin states for the cobalt system.

In order to evaluate the relative stabilities of the four-, five-, and six-coordinate Co^{++}−water complexes, we calculated the energies of these complexes, as well as that of a water molecule. These calculations were done in vacuo and with the polarizable continuum method (PCM) water model,[21] with the same basis set as described above.

Results

The six-coordinate cobalt complex is represented by four types of model structures: an octahedral complex constrained to have T_h symmetry, an octahedral complex optimized without constraints, a series of distorted complexes, in which an axial water is moved away from its equilibrium position in increments of 0.05 Å, and a complex with five waters and one hydroxide.

TABLE 2: Comparison of the CAS-MCSCF Transition States Calculated with DZP and TZV Basis Sets. The Fully Optimized (with DZP) Six- and Four-Coordinated Geometries Were Used

	six-coordinate				five-coordinate				four-coordinate			
	quartet		doublet		quartet		doublet		quartet		doublet	
state	DZP	TZV	DZP	TZV	DZP	TZV	DZP	TZV	DZP	TZV	DZP	TZV
1												
2	286	264	16 581	16 817	1 130	1 066	16 809	17 027	2 929	2 879	20 406	20538
3	286	264	16 584	16 819	1 155	1 113	18 631	18 773	2 954	2 897	20 483	20612
4	5 007	4 970	20 206	20 377	2 749	2 691	19 642	19 852	3 370	3 307	20 687	20 829
5	5 071	5 009	20 326	20 490	4 112	4 043	20 243	20 392	5 216	5 121	20 754	20 890
6	5 072	5 010	20 326	20 490	6 410	6 308	20 318	20 456	5 442	5 344	20 800	20 931
7	10 841	10 751	20 420	20 577	8 690	8 552	20 638	20 825	5 644	5 539	21 350	21 460
8	22 521	22 602	20 422	20 579	21 300	21 313	20 986	21 084	21 791	21 874	22 284	22 368
9	22 523	22 604	20 480	20 648	21 313	21 384	21 262	21 353	21 812	21 914	22 308	22 387
10	22 628	22 768	23 425	23 517	23 907	24 072	22 187	22 289	22 442	22 529	22 456	22 534

TABLE 3: MCQDPT Calculated Transition State Energies and Oscillator Strengths ($\times 10^{-4}$, 0 is $< 10^{-6}$) for the Six-Coordinate Co^{++} complexes. Transition Energies Are in Wavenumbers

			$(H_2O)_6$ fully optimized						
state	$(H_2O)_6$ t_h	OSC STR	quartet	doublet	OSC STR	$(H_2O)_6$ distorted	OSC STR	$(H_2O)_5$ OH^-	OSC STR
1									
2	0	0	361	14 024	0	302	0	659	0.01
3	0	0	361	14 028	0	460	0	2 043	0.05
4	5 297	0	6 682	19 356	0	5 857	0	5 919	0.01
5	5 297	0	6 784	19 361	0	6 436	0	6 820	0.01
6	5 297	0	6 785	19 640	0	6 661	0	8 460	0.06
7	11 400	0	14 150	19 901	0	13 269	0	14 185	0.07
8	19 200	0	20 441	20 261	0	19 663	0.01	17 448	0.10
9	19 200	0	20 444	20 268	0	19 898	0	22 481	0.03
10	19 200	0	20 526	23 941	0	20 842	0	23 751	0.49

The calculated Co−O distance of the complex constrained to T_h symmetry is about 0.1 Å larger than a previous calculation of 2.143 Å[14] and the X-ray value of 2.1 Å.[4] However, when the constraint on the water ligands is lifted, the Co−O bond distance shortens to 2.156 Å. Excitation energies were obtained for both the T_h symmetric structure and the fully optimized structure to probe the variation of the excitation energies with bond distance and modest rotations of the water ligands. The calculated energy levels of the symmetric complex show a triply degenerate state at 19200 cm^{-1}, but this state has no oscillator strength. Relaxing the octahedral constraint results in only a slight splitting of this state (by less than 100 cm^{-1}) and shift to about 20500 cm^{-1}. Even with this break in symmetry, the oscillator strength remains very low ($<10^{-6}$, see Table 3). To further break the symmetry of this complex, distortions were made as described above. These distortions cause the visible T state to split. Only in the case of a distortion of 0.15 Å, however, did any of these states reach an oscillator strength of $\geq 10^{-6}$. In this case the state was split by 1179 cm^{-1} and had an oscillator strength of only 10^{-6}. In the totally symmetric structure there are no states near 8000 cm^{-1}. When the complex is allowed to relax, the states at 5297 cm^{-1} split and shift to about 6800 cm^{-1}. It is possible that these states are within the errors of our calculations to be the observed 8000 cm^{-1} peak.

The doublet transition energies are calculated for the fully optimized quartet geometry and are found to overlap the quartet states (see Table 3).

The ^4F ground state of Co^{++} is split into three molecular states by an octahedral field; a ground $^4T_{1g}$ state and excited $^4T_{2g}$ and $^4A_2$ states. In the relaxed structure, however, the rotations of the waters cause these states to split. The triply degenerate ground state is split into a lower A state and a slightly higher E state. The ground state is additionally split by the spin−orbit interaction into six Kramers doublets with a combined difference in energy of 1110 cm^{-1} from the highest to the lowest state (see Figure 1). Note that the energies in Figure 1 refer to the TZV calculations (see Table 2), not the MCQDPT energy in Table 3. The excited T state, which arises from the atomic P state, is also slightly split into a lower E state and a higher A state, and is additionally split by the spin−orbit interaction into six Kramer doublets. This splitting spans a range of about 1200 cm^{-1}.

Substitution of one water by a hydroxide provides a conformation that is very distorted from the T_h symmetry. Electrostatic forces alone would yield a linear hydroxyl bond, but as shown in Figure 2, the Co−O−H angle is about 131° in the lowest energy structure, due to covalent or dative bonding and internal hydrogen bonding. The hydroxide oxygen forms hydrogen bonds with two waters with O−H distances of 2.04 and 1.98 Å. These hydrogen bonds cause the HO−Co−OH$_2$ angle to distort to 76° from 90°. The calculated spectrum of this structure gives an indication of the splitting of the degenerate transition as well as of the oscillator strengths to be expected from six-coordinate structures with complete C_1 symmetry. For this distorted complex, there is a large splitting in the visible absorption peak of over 6000 cm^{-1}. There is also a peak around 8460 cm^{-1}. All the calculated peaks have substantial oscillator strength. The calculated excited state energies and oscillator strengths for these structures are shown in Table 3 and Figure 3.

Two five-coordinate structures are considered, $Co^{++}(H_2O)_5$ and $Co^{++}(H_2O)_4OH^-$. These complexes were optimized without constraints (see Figure 4). The pentahydrate complex has a distorted trigonal bipyramid (tbp) conformation. Internal H-bonds appear to cause the distortion. As a result, instead of the equivalent equatorial and axial Co−O bonds, four different values are found here, and only the two equatorial values are equivalent. The Co−O distances are 2.173, 2.085 (×2), 2.109, and 2.119 Å. Our results are consistent with a previous study[9] which found the tbp to be slightly lower in energy than the

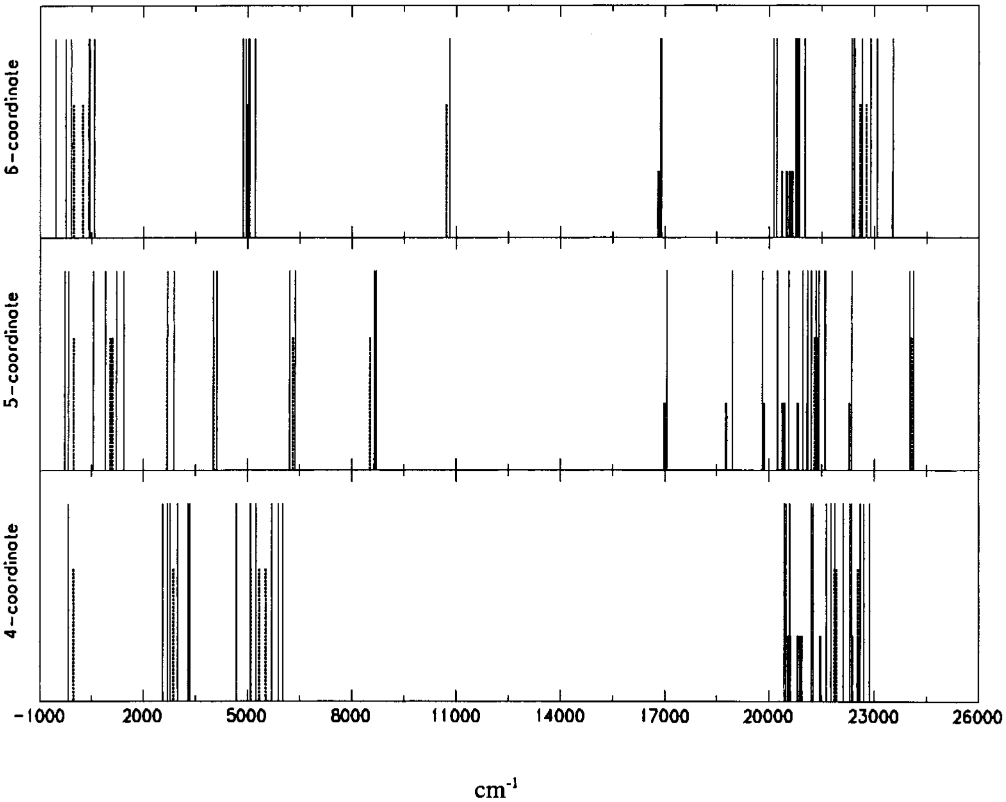

Figure 1. Calculated positions of spin−orbit peaks of Co^{++} hydrates. The tall thin lines are the spin−orbit states; the medium height, thick dots are the quartet states; and the small thick lines represent the doublet states.

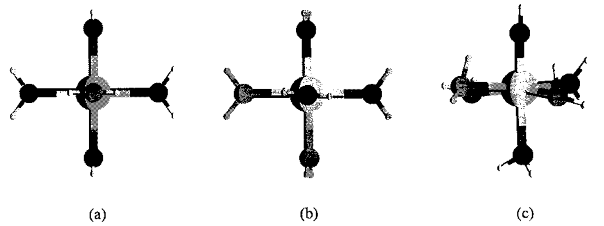

Figure 2. Structures for the six-coordinate Co^{++} complexes. (a) T_h symmetry (2.229). (b) Fully optimized (2.156). (c) Hydroxyl structure (OH^- 1.938, H_2O: 2.174, 2.177, 2.246, 2.196). Distances, in angstroms, between the Co^{++} and the water oxygen are given in parentheses. This figure is generated with Molden.[26]

square pyramidal (sqp) conformation when the geometry is constrained to be either tbp or sqp.

The dissociation energy of a single water may be computed as the energy of this five-coordinate complex plus the energy of a free water minus the energy of the six-coordinate complex. The result, calculated at the CAS-MCSCF level, is 120.2 kJ/mol, which is in good agreement with the value of 116.5 kJ/mol for the HF cluster bond energy calculated by Akesson et al.[9] This dissociation energy falls to 46.3 kJ/mol when the calculations are performed with the PCM water model.

The calculated absorption peaks for the five-coordinate complexes all have oscillator strength (see Table 3 and Figure 3). The hydrated complexes show a splitting of about 3000 cm^{-1} for the visible absorption peak and a peak at 8193 cm^{-1} (Table 4). The spin−orbit calculations indicate substantial mixing between the quartet and doublet states in the visible region (see Figure 1).

The hydroxide complex is highly distorted, much like the six-coordinate hydroxide structure. The oxygen of the hydroxide forms a single hydrogen bond with an O−H distance of 1.94 Å and an $HO-Co-OH_2$ angle of 75°. The splitting of the $^4T_{1g}(F)$ to $^4T_{1g}(P)$ transition is around 6000 cm^{-1} as in the six-coordinate hydroxide complex, and there is a state at 9067 cm^{-1} which may contribute to the observed 8000 cm^{-1} peak (Table 4 and Figure 3).

Two four-coordinate structures are also considered, $Co^{++}(H_2O)_4$ and $Co^{++}(H_2O)_3OH^-$. For the tetrahydrate complex the Co−O distances differ by small amounts due to differences in the local hydrogen bonding: the Co−O distances are 2.050, 2.044, 2.048, and 2.048 Å. The calculated quartet spectrum of this complex shows only an 800 cm^{-1} split in the visible absorption peak, and there are also states around 6800 cm^{-1} (Table 4). All the quartet peaks have oscillator strength, with the visible peak having large oscillator strength. Even when spin-orbit coupling is considered, however, the visible absorption band broadens by less than 1500 cm^{-1} (Figure 1).

The computed dissociation energy of two waters from the six-coordinate complex to form the four-coordinate complex is 205.8 kJ/mol in vacuo and 84.1 kJ/mol with the PCM water model.

The four-coordinate hydroxyl structure exhibits the bent hydroxyl bond that was found for the five and six-coordinate hydroxyl complexes. The hydroxide oxygen forms one hydrogen bond of length 2.50 Å, and an $HO-Co-OH_2$ angle of 89°. As with the five- and six-coordinate hydroxide spectra, the four-coordinate spectrum shows a splitting of over 6000 cm^{-1} for the visible absorption peak and states near 6700 and 9300 cm^{-1}.

Discussion

As discussed in the Introduction, many features of the spectra of aqueous Co^{++} are not consistent with a six-coordinate structure. It is of particular concern that the six-coordinate complex is not expected to have any oscillator strength. Even though some oscillator strength can arise from asymmetrical vibrational modes, these modes would lead to a single broad

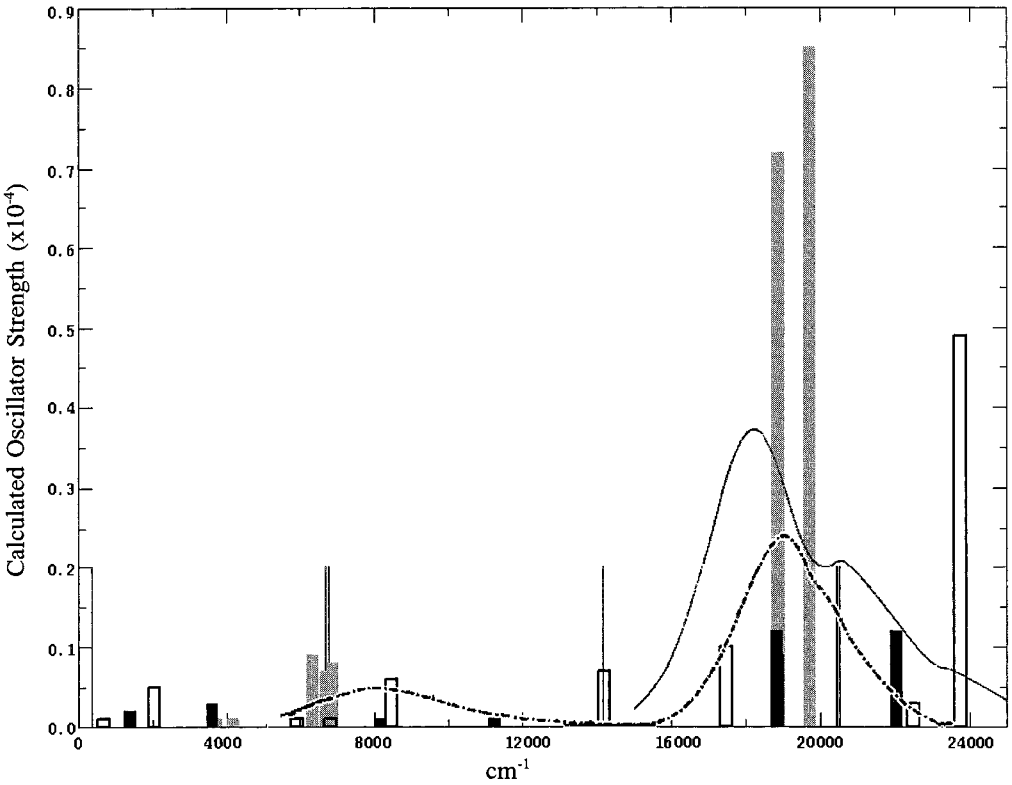

Figure 3. Calculated spectra for the six-, five- four- and six-coordinate hydroxide Co^{++} complex. The six-coordinate peaks are given oscillator strength so their positions relative to the other complexes can be illustrated. Thin black lines Co^{++}(H$_2$O)$_6$, Black bars Co^{++}(H$_2$O)$_5$, grey bars Co^{++}(H$_2$O)$_4$, and empty bars Co^{++}(H$_2$O)$_4$OH$^-$. No peaks are completely hidden. The dashed line is the experimentally determined room temperature spectrum,[3] and the solid line is the high temperature spectrum.[6] The experimental spectra shown here are not to scale. They are displayed solely to show line positions.

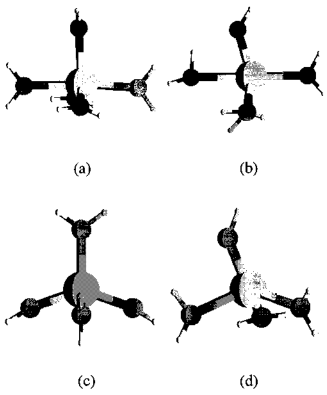

Figure 4. Structures for the five and four-coordinate Co^{++} complexes. All structures are optimized without constraints. (a) (H$_2$O)$_5$ (2.173, 2.119, 2.109, 2.085) (×2). (b) (H$_2$O)$_4$OH$^-$ (OH$^-$ 1.874, 2.123, 2.111, 2.319, 2.157). (c) (H$_2$O)$_4$ (2.050, 2.048 (×2), 2.044). (d) (H$_2$O)$_3$OH$^-$ (OH$^-$ 1.835, 2.103, 2.102, 2.090). Distances, in angstroms, between Co^{++} and the water oxygen are given in parentheses. This figure is generated with Molden.[26]

peak, not to a peak which is split by more than 2000 cm^{-1}, as is observed in the visible absorption band. The temperature dependence of the oscillator strength also indicates that asymmetric vibrational modes are not enough to account for the observed peaks.[6] Finally, the large width of the experimental absorption peak indicates that there may be more than one species contributing to the spectrum. The present ab initio calculations allow these data to be reexamined and alternate explanations to be proposed. It is worth noting at the outset that we do not expect these calculations to yield the exact spectra of Co^{++} in aqueous solution. Rather we focus on the relative positions of the calculated states, the splittings of the T states, and their relative oscillator strengths. The following sections consider the spectra of each coordination complex.

Six-Coordinate Co^{++}−Water Complex. We begin by considering the spectra of the six-coordinate Co^{++} complex. For the unconstrained six-coordinate Co^{++} complex, the ground triply degenerate T state is only slightly split into a nondegenerate A ground state and a doubly degenerate E state that is higher in energy by 361 cm^{-1} (see Table 2). The excitation energy to the only slightly split ^{4}T(P) state at the MCQDPT level is in apparent good agreement with the largest experimental peak (about 20500 cm^{-1}). However, the oscillator strengths to the P states are so low ($<10^{-6}$) that they should not be experimentally detectable.

Oscillator strength can derive from asymmetric vibrational modes. In order to asses the level of distortions needed to yield an oscillator strength of $\geq 10^{-6}$, an axial water was moved from its equilibrium position in increments of 0.05 Å. It took a distortion of 0.15 Å to obtain an oscillator strength of 10^{-6} (see Results). Although, each of these distorted complexes will contribute little to the spectrum, in total they probably contribute an observable amount.

Doublet states are calculated on both sides of the 20500 cm^{-1} quartet state. The effect of the spin-orbit interaction on the doublet states is important because the high-energy shoulder of the visible absorption peak in Co^{++} crystals is often assigned to the doublet state.[22,23] It might therefore been assumed that this assignment holds true for the solution spectrum as well as for Co^{++} in proteins. In comparing our results with those obtained from crystal-field theory, we find the same ordering of the quartet states (^{4}T(F), ^{4}T(F), ^{4}A(F), ^{4}T(P)) and doublet states (^{2}E(G), ^{2}T(G), ^{2}T(G), ^{2}A(G)). However, the order of the quartet and doublet state relative to each other can differ from

TABLE 4: MCQDPT Calculated Quartet Transition State Energies and Oscillator Strengths ($\times 10^{-4}$) for the Five- and Four-Coordinate Co^{++} Complexes. Transition Energies Are in Wavenumbers

	five-coordinate				four-coordinate			
state	$(H_2O)_5$	OSC STR	$(H_2O)_4$ OH^-	OSC STR	$(H_2O)_4$	OSC STR	$(H_2O)_4$ OH^-	OSC STR
1								
2	1 389	0.02	2 024	0.01	3 667	0.00	2 268	0.01
3	1 607	0.00	3 301	0.00	3 712	0.01	4 484	0.01
4	3 607	0.03	5 160	0.00	4 175	0.01	5 580	0.03
5	5 095	0.00	6 441	0.01	6 347	0.09	6 429	0.01
6	8 193	0.01	9 067	0.16	6 703	0.07	6 869	0.06
7	11 248	0.01	10 631	0.14	6 892	0.08	9 262	0.05
8	18 850	0.12	17 583	0.43	18 866	0.72	16 882	0.17
9	18 872	0.09	21 974	0.42	18 900	0.72	21 408	0.35
10	22 031	0.12	23 530	0.01	19 707	0.85	23 506	0.16

the crystal-field results depending on the crystal-field parameters used to calculate the spectrum. As mentioned in the Introduction, it seems inappropriate to interpret the solution spectrum in the same manner as the crystal spectrum given the lowered symmetry of the Co^{++} center in the crystal and the strong fields around the Co^{++} due to the counter ions in the second shell. Still, it is interesting to investigate whether or not the high-energy shoulder of the visible peak can result from spin−orbit coupling between the quartet and doublet states.

Our calculations indicate that the spin-orbit coupling between the doublet and quartet states could produce broadening of the $^4T(P)$ state at both high and low energies (see Figure 1). The broadening at higher energies may be somewhat exaggerated in these calculations, because the TZV orbitals are used to calculated the coupling. The energy of the $^4T(P)$ state is closer to the highest doublet with the TZV basis set than in the corrected MCQDPT calculations. Nonetheless, the calculated splitting of 1200 cm^{-1} is only half that which is observed. Again, the oscillator strengths for the quartets are all zero, so there is no intensity from which the doublets can borrow. In summary, there is no evidence from these calculations that the high-energy shoulder of the visible absorption peak could result from the doublet state.

The calculated state near 6800 cm^{-1} may be within the error of the calculations to represent the observed 8000 cm^{-1} peak. However, in order for the calculated 6800 cm^{-1} peak to represent the 8000 cm^{-1} peak it would have to gain oscillator strength from asymmetric vibrations. Oscillator strength derived from distorted six-coordinate complexes probably does contribute to the observed spectrum. However, it is difficult to see how these contributions alone could cause a split in the visible absorption band, rather than a single broad band.

Four-Coordinate Co^{++}−Water Complex. Let us now consider the possibility that the absorption spectrum of aqueous Co^{++} is due to the four-coordinate species. Unconstrained optimization of the four-coordinate species produces small differences in the Co−O distances due to internal hydrogen-bonding effects. This small distortion from the tetrahedral symmetry does split the visible excited state into a lower E state at 18900 cm^{-1} and an A state about 800 cm^{-1} higher. This splitting could broaden the spectrum or produce a slight shoulder to higher energy, but not the shoulder observed at 21550 cm^{-1}. There are also states around 6800 cm^{-1} which may contribute to the 8000 cm^{-1} peak.

The ground state is orbitally non-degenerate and there is no first-order splitting. The lowering of the symmetry does, however, lead to two Kramers doublets split by 12 cm^{-1}. We calculate spin−orbit coupling between the doublet and quartet states in the visible region. However, this splitting would lead to a broadening of the absorption band of about 1600 cm^{-1}, and not the observed high energy shoulder (Figure 1). Our results agree with the crystal-field interpretation of tetrahedral Co^{++} crystals by Weakliem,[24] in that we calculate the same ordering of quartet and doublet states. There are some differences in the relative ordering of the quartet and doublet in the middle range of the spectrum, but these states are overlapping in energy and therefore difficult to assign. The relative intensities of the peaks that we calculate are also consistent with the crystal-field calculations.

As mentioned in the Introduction, it has been proposed that this four-coordinate complex contributes to the absorption spectrum to some extent at room temperature and to a larger extent at high temperature.[6] It is, however, energetically very unfavorable to dissociate two waters from the six-coordinate complex to form the four-coordinate complex in solution (see Results). Therefore, the concentration of the four-coordinate complex is expected to be extremely low.

On the other hand, the calculated oscillator strengths are very large relative to the five and six-coordinate complexes in the visible region and the positions of the visible peaks are in the observed region, so even a minor component of this species could contribute to the experimental spectrum.

Five-Coordinate Co^{++}−Water Complex. Next we consider the five-coordinate complexes. The calculated excitation energies show that the distorted trigonal bipyramid will split the degeneracy of the visible absorption peak into a lower E state at 18900 cm^{-1} and an A state about 3000 cm^{-1} higher in energy. Both these states have substantial oscillator strengths. The calculated spectrum shows the observed peak near 8000 cm^{-1} (at 8193 cm^{-1}), as well. The spin−orbit coupling calculation also shows that there are many possible states in the 18000−23000 cm^{-1} region. Inhomogeneous broadening effects also should be more pronounced for the five-coordinate species than either the four- or six-coordinate complexes, because a wider range of thermodynamically accessible geometries would be absorbing. This broadening would be consistent with the large breadth observed in the absorption bands. Because the oscillator strength of the five-coordinate complex is at least three orders of magnitude larger than the six-coordinate complex, even a small population of this species (∼0.1%) could contribute substantially to the observed absorption. Therefore this five-coordinate species matches the experimentally determined spectrum. But is this a plausible explanation of the data?

As mentioned in the Introduction, it is believed that ligand exchange for the six-coordinate Co^{++} complex occurs through a dissociative process. The five-coordinate species has been identified as essentially the transition state in the dissociative exchange process.[9] Thus, it seems likely that a small amount of the five-coordinate species is always present in solution. The five-coordinate population should also increase with temperature, as water exchange becomes more rapid. This increase in population would account for the marked increase in oscillator strength that is observed as a function of temperature.

The results from the PCM calculations also support this hypothesis, because the calculated energy cost of removing a single water molecule from the six-coordinate complex is only 46 kJ/mol. This is in contrast to the cost of 84 kJ/mol to form the four-coordinate complex. We propose, therefore, that the five-coordinate species is much more highly populated than the four-coordinate species in contrast to what has been previously proposed.[6] Perhaps the five-coordinate complex has not been considered to contribute to the absorption spectrum of aqueous cobalt because of the lack of crystal data on this species.

In summary it does seem possible that the five-coordinate could be the dominant optically allowed species in aqueous Co^{++} solutions. This complex most closely reproduces the features of the observed spectrum. The visible T state has oscillator strength and is split by more than 2000 cm^{-1}, but not by 6000 cm^{-1} as in the hydroxide-ion complexes and there are states near 8000 cm^{-1} with oscillator strength.

Hydroxide-Ion Complexes. We now consider the six-coordinate hydroxide structure. This is the only complex, other than the five-coordinate complex, where the computed spectrum shows a large splitting in the visible absorption peak, a band near 8000 cm^{-1}, and that has substantial oscillator strengths. The T state splitting of 6000 cm^{-1}, however, is much greater than the observed splitting at room temperature. As mention in the Introduction we considered these complexes because the pKa of water in the presence of Co(II) decreases markedly with temperature, to a value of 6.10 at 473 K putting the pKa of water in the possible pH range of the experiments.[12] If one plots their pKa versus temperature data, one finds that the pKa is still decreasing at 473 K, and thus is likely to be even lower at 625 K. In the high temperature study care was taken to avoid hydrolysis by acidifying the solution.[6] At very high temperatures, however, there is a clear band evident near 23500 cm^{-1} and a total splitting of about 5500 cm^{-1},[6] indicating that at these temperature there is at least one other species that is contributing to the spectrum. Clearly, the pH of this solution was very low and one would not expect at first that any hydroxide could form in such a solution. It is, however, difficult to ascertain exactly what are the pH and properties of a solution at 625 K and 25 MPa pressure. The critical point of pure water is very close to this temperature and pressure, and the dielectric constant of water at 625 K and 25 MPa is only 15 (as opposed to 80 under ambient conditions).[25] This fall in the dielectric constant destabilizes dissolved ions, particularly doubly charged ions. This helps to explain why increasing temperature pushes $Co^{++}(H_2O)_6$ toward $Co^{++}(H_2O)_5OH^-$: the former is doubly charged, the latter only singly. Since the oscillator strength of the six-coordinate hydroxide structure is relatively large at 23800 cm^{-1} we propose that a small amount of this complex may be forming at the higher temperatures thus accounting for the increased structure in the absorption spectrum.

Finally, we calculate states that have oscillator strength from the four- and five-coordinate hydroxide-ion complexes in the range of 17000−23500 cm^{-1} and states around 8000 cm^{-1} (Table 4). It is difficult to speculate as to the extent that these species contribute to the observed spectrum since nothing is known about their pK_as.

Conclusion

This study indicates that, although the dominant species in solution is six-coordinate, this species alone cannot explain the features found in the observed spectrum. Our calculations suggest that the dominant optically allowed species is the five-coordinate complex, with possible contributions from the six-coordinate hydroxide complex, at least at high temperature, and perhaps the four-coordinate complex. The low oscillator strength of the six-coordinate complex makes it possible for even small amounts of other species to contribute significantly to the observed spectrum.

The spin-orbit coupling calculations also support this conclusion. There is no indication from these calculations that the large width of the visible absorption band, or the high-energy shoulder, could be caused by quartet−doublet mixing in the six-coordinate complex. For the six-coordinate complex, the splitting results from the diagonal quartet−quartet and doublet−doublet interactions. Although there are overlapping quartet−doublet states in the four-coordinate complex, the spin−orbit coupling calculations indicate that a broadening of at most 1600 cm^{-1} would be expected and not the formation of a high-energy shoulder. This splitting is caused by quartet−quartet and doublet−doublet mixing as well as quartet−doublet interactions. Similarly, broadening of the visible absorption peak of the five-coordinate complex caused by quartet−doublet mixing also appears to be possible. Broadening due to spin−orbit splitting, however, would be difficult to distinguish from inhomogeneous broadening.

Existing experimental data do not make clear whether the coordination states considered here are indeed sufficiently populated to yield the observed spectra. The five-coordinate complex is an intermediate in the exchange of water between the first and second hydration shell. This suggests that the absorption spectra can be used to probe the dynamics of the exchange mechanism. Finally, it is worth noting that these spectral and dynamical problems are not specific to Co^{++} but pertain to the transition metals in general.

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References and Notes

(1) Jorgensen, C. K. *Acta Chem. Scand.* **1964**, 1495.

(2) Holmes, O. G.; McClure, D. S. *J. Chem. Phys.* **1957**, *26*, 1686.

(3) Bertini, I.; Luchinat, C. In Advances in Inorganic Biochemistry; Eichorn, G. L., Marzilli, L. G., Eds.; Elsevier: New York, 1984, Vol. 6, 71−111.

(4) Magini, M.; Licheri, G.; Paschina, G.; Piccaluga, G.; Pinna, G. *X-ray Diffraction of Ions in Aqueous Solutions: Hydration and Complex Formation*; CRC Press: Boca Raton, FL, 1988.

(5) Cotton, F. A.; Daniels, L. M.; Murillo, C. A.; Quesada, J. F. *Inorg. Chem.* **1993**, *32*, 4861.

(6) Swaddle, T. W.; Fabes, L. *Can. J. Chem.* **1980**, *58*, 1418.

(7) Swift,T. J.; Connick, R. E. *J. Chem. Phys.* **1962**, *37*, 307.

(8) DuCommun,Y.; Newman, K. E.; Merbach, A. E. *Inorg. Chem.* **1980**, *19*, 3696.

(9) Akesson, R.; Pettersson, L. G. M.; Sandstrom, M.; Siegbahn, P. E. M.; Wahlgren, U. *J. Phys. Chem.* **1993**, *97*, 3765.

(10) Connick, R. E.; Alder, B. J. *J. Phys. Chem.* **1983**, *87*, 2764.

(11) Swaddle, T. W. *Comments Inorg. Chem.* **1991**, *12*, 237.

(12) Giasson, G.; Tewari, P. H. *Can. J. Chem.* **1978**, *56*, 435.

(13) Akesson, R.; Pettersson, L. G. M.; Sandstrom, M.; Wahlgren, U. *J. Phys. Chem.* **1992**, *96*, 150.

(14) Akesson, R.; Pettersson, L. G. M.; Sandstrom, M.; Siegbahn, P. E. M. *J. Phys. Chem.* **1992**, *96*, 10773.

(15) Schmidt, M. W.; Baldridge, K. K.; Boatz, J.A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. *J. Comput. Chem.* **1993**, *14*, 1347.

(16) Stevens, W. J.; Basch, H.; Krauss, M. *J. Chem. Phys.* **1984**, *81*, 6026.

(17) NBS atomic energy tables.

(18) Nakano, H. *J. Chem. Phys.* **1993**, *99*, 7983.

(19) Koseki, S.; Gordon, M. S.; Schmidt, M. W.; Matsunaga, N. *J. Phys. Chem.* **1995**, *99*, 12764.

(20) Abragam, A.; Pryce, M. H. L. *Proc. R. Soc. London* **1951**, *A206*, 175.

(21) Cammi, R.; Tomasi, J. *J. Comput. Chem.* **1995**, *16*, 1449.

(22) Reedijk, J.; Driessen, W. L.; Groeneveld, W. R. *Rec. Trav. Chim.* **1969**, *88*, 1095.

(23) Gailey, K. D.; Palmer, R. A. *Chem. Phys. Lett.* **1972**, *13*, 176.

(24) Weakliem, H. A. *J. Chem. Phys.* **1962**, *36*, 2117.

(25) Fernandez, D. P.; Goodwin, A. R. H.; Lemmon, E. W.; Levelt Sengers, J. M. H.; Williams, R. C. *J. Phys. Chem. Ref. Data* **1997**, *26*, 4, 1125.

(26) Schaftenaar, G. QCPE619, MOLDEN: A Portable Electron Density Program. *QCPE* **1992**, *12*, 3.