Toward a Theory of the Spectral and Magnetic Properties of Transition Metal Ions Occupying Low-Symmetry Sites in Metalloproteins. Application of the Angular Overlap Model to Distorted Tetrahedral $CoCl_4^{2-}$ Ions

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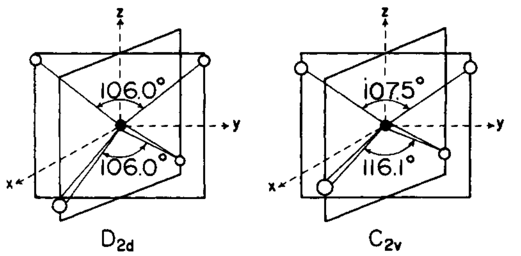
Abstract: The angular overlap model (AOM) is applied to the calculation of the spectral and magnetic properties of two distorted tetrahedral tetrachlorocobaltate(II) anions. The ligand-field calculation is carried out in the weak-field approximation and includes spin-orbit coupling. The calculational procedure is completely general and is applicable to complexes of any (or no) symmetry and any electronic configuration. The quantities calculated (energy levels, zero-field splittings, g values, principal molecular magnetic susceptibilities) for both complexes, which differ only in the angular distribution of the chloride ligands, agree satisfactorily with experiment using only four parameters (AOM σ parameter, spin-orbit coupling constant, orbital reduction factor, and Racah B parameter). The potential usefulness of these methods in treating low-symmetry transition metal complexes and metalloenzymes is stressed.

Chromophoric, paramagnetic reporter ions native to metalloenzymes or substituted for naturally occurring colorless, diamagnetic metal ions provide a unique and valuable means to probe structure-function relationships.[1,2] Studies of enzymatically active cobalt(II)-substituted zinc metalloenzymes have been particularly fruitful,[3] since a wide variety of physical methods, e.g., electronic spectroscopy,[4] electron paramagnetic resonance (EPR),[5-9] circular dichroism,[10] magnetic circular dichroism,[11-15] and fluorescence quenching,[16,17] are available to probe the environment of cobalt(II). In contrast to the coordination chemistry of monodentate ligands, where coordination geometries are often closely approximated by regular polyhedra of high symmetry, e.g., O_h and T_d, metal ion sites in metalloproteins can be expected to exhibit little or no symmetry and be highly distorted from any idealized structure. The zinc atom site in carboxypeptidase A is one of the better characterized examples, wherein the zinc atom is coordinated to two nitrogen atoms and two oxygen atoms in a geometry best described as a highly distorted tetrahedron.[18] Most attempts to characterize the cobalt(II) site in enzymes have depended on semiquantitative comparisons between spectroscopic and magnetic resonance results obtained on enzyme systems and those obtained on model complexes of known stereochemistry.

Thus far no attempt has been made to apply theory to interpret, in a detailed manner, the electronic and magnetic properties of transition metal ions in low-symmetry sites either of enzymes or model systems. Phenomenological ligand-field theory, which is so successful in high-symmetry cases, becomes less and less satisfactory as the symmetry is lowered. This is because more and more physically meaningless phenomenological parameters are needed to describe the experimental observables. While satisfactory fits may be achieved, such procedures amount to little more than a redistribution of unknowns from the experimental observables to phenomenological parameters lacking in physical meaning. For instance, the single ligand-field parameter, Δ or 10 Dq, necessary to describe d-orbital splitting in O_h or T_d symmetry is replaced by three, say, Dq, Ds, and Dt, in D_{2d} symmetry, by five, say, A_{20}, A_{22}, A_{40}, A_{42}, and A_{44}, in C_{2v} symmetry, and by even more than this when the symmetry is lower still.[19] Since parameters of this type are purely phenomenological and possess neither physical interpretability nor transferability from one system to another, there is little point to considering them when attempting to understand in a detailed and fundamental way the spectral and magnetic properties of low-symmetry transition metal complexes.

The present paper represents the initial stage of our search for a satisfactory theoretical framework and computational methodology to handle this problem. In order to be useful, any such theory must have the following characteristics: (1) It must invoke a minimum number of adjustable parameters; (2) these parameters should be based on a realistic model and possess some degree of physical interpretability; (3) ideally, the parameters should be transferable from system to system; (4) the method should be independent of symmetry and applicable to systems of any (or no) symmetry; and (5) as many observables as possible should be interpretable within the same theoretical framework. To this end we have explored the application of the angular overlap model (AOM)[20-22] to the interpretation of the spectral and magnetic properties of low-symmetry cobalt(II) complexes. The AOM was chosen since it is based on a realistic model for covalent bonding in complexes and the parameters, characteristic of individual metal ion-ligand atom pairs, may have some degree of transferability. This transferability feature is an important one which will ultimately determine the general utility of the proposed calculational method, particularly in the usual case where more than one type of ligand is involved. However, since the present paper is concerned with a single metal ion and a single ligand species, the question of transferability of AOM parameters is deferred to future studies. Cobalt(II) was chosen as our initial object of study, since it has a many-electron (d^7) configuration which illustrates the generality of our procedure. It also is of particular interest, owing to the accumulating quantity of spectroscopic data on cobalt(II)-substituted zinc metalloenzymes. Before attempting an analysis of specific biological systems or models we felt it advisable to calibrate the capability of the method on well-characterized species of known structure, for which a reasonable amount of experimental data is available.

The tetrachlorocobaltate(II) ion, $CoCl_4^{2-}$, exists in a variety of salts and double salts. In the cases of Cs_3CoCl_5 and Cs_2CoCl_4, the solid-state structures are known[23,24] and the electronic spectra,[25,26] EPR spectra,[27] and magnetic susceptibility anisotropy[28,29] have been investigated in one or both cases. The structures of the complex anions present in these



D_{2d}
1

C_{2v}
2

Figure 1. Structures of $CoCl_4^{2-}$ anions in Cs_3CoCl_5 (**1**) and Cs_2CoCl_4 (**2**).

two substances are illustrated in Figure 1. The $CoCl_4^{2-}$ ion in Cs_3CoCl_5 (structure **1**) has D_{2d} crystallographic symmetry and the coordination geometry is that of a tetrahedron slightly elongated along the tetragonal (S_4) axis such that this axis bisects Cl-Co-Cl angles of 106.0°. The complex anion in Cs_2CoCl_4 possesses C_s crystallographic symmetry, but has very nearly C_{2v} symmetry with the C_2 axis bisecting Cl-Co-Cl angles of 116.1 and 107.5°, as shown in Figure 1, structure **2**. The very slightly idealized[30] geometry shown was used in the calculations.

We consider that the $CoCl_4^{2-}$ ions represented by structures **1** and **2** constitute a favorable case for testing the AOM. They possess but a single type of cylindrically symmetric (monatomic) ligand and differ essentially only in the angular disposition of their ligand atoms. It was our intention to determine, given the known geometric structures, how few adjustable parameters are necessary to describe the energy levels, zero-filled splittings, *g* values, and susceptibility tensor components of $CoCl_4^{2-}$ in *both* Cs_3CoCl_5 and Cs_2CoCl_4. At the very least a single ligand-field AOM parameter (e_σ), spin-orbit coupling constant (λ), orbital reduction factor (k), and Racah parameter (B) would be necessary in our formalism. These four alone, it turns out, serve quite adequately.

Methodology

The calculation was carried out in the weak-field approximation in a completely general and symmetry-independent manner. The weak-field formulation was used, since the spin-orbit coupling perturbation necessary to the calculation of magnetic properties may be conveniently included in this framework. The basis set was comprised of the ^4F and ^4P terms of the d^7 (three vacancy) configuration and consisted of 40 basis functions of the type $|L,M_L,S,M_S\rangle$: $|3,3,3/2,3/2\rangle$, ... $|3,-3,3/2,-3/2\rangle$, $|1,1,3/2,3/2\rangle$, ... $|1,-1,3/2,-3/2\rangle$. A 40 × 40 perturbation matrix was computed with the ligand field (AOM) $\mathbf{V}_{AO}$ and spin-orbit coupling $\lambda k\mathbf{L}\cdot\mathbf{S}$ perturbations applied simultaneously, where λ is the many-electron spin-orbit coupling constant and k is the orbital reduction factor, both taken as isotropic in the present calculation. The quantity $15B$ was added to the 12 diagonal elements of the excited $^4P(L = 1)$ state, where B is the Racah parameter. Since the ligand-field perturbation does not affect spin variables, the ligand-field problem reduces to one of computing elements of a 10 × 10 matrix of the type $\langle L,M_L|\mathbf{V}_{AO}|L',M_L'\rangle$. These are readily evaluated by writing the $|L,M_L\rangle$ functions in their Slater determinantal form. Thus the required matrix elements are given in terms of one-electron matrix elements of the type $\langle m_l|\mathbf{V}_{AO}|m_l'\rangle$.[31] Matrix elements of the latter type comprise a Hermitian matrix in the basis: $|m_l\rangle = |2\rangle, |1\rangle, |0\rangle, |-1\rangle, |-2\rangle$. Diagonalization of this 5 × 5 matrix yields, of course, the five one-electron d-orbital energies.

According to the AOM, if we consider first of all only a σ interaction, the matrix elements between the *real* d orbitals $d_i = d_{z^2}, d_{yz}, d_{xz}, d_{xy}$, and $d_{x^2-y^2}$ are given by

$$\langle d_i|\mathbf{V}_{AO}|d_j\rangle = \sum_{k=1}^{N} e_\sigma(k)S(d_i, \sigma_k)S(d_j, \sigma_k') \tag{1}$$

where the sum is taken over the N ligands, $e_\sigma(k)$ is an adjustable energy parameter denoting the strength of the metal-ligand σ interaction, $S(d_i, \sigma_k)$ represents the angular part of the overlap integral between the real d orbital d_i, and a σ function, σ_k on the kth ligand. Given a particular coordination geometry the values of $S(d_i, \sigma_k)$ are fixed, since they depend only on the angular (spherical harmonic) properties of the individual d orbitals and the angular distribution of ligand atoms. The AOM may be generalized to include π- and δ-type interactions as well.[21] For cylindrically symmetric ligands a π-type interaction introduces an additional energy parameter $e_\pi(k)$ for each kind of ligand.

Schaffer has described the analytical form of $S(d_i, \sigma_k)$ integrals and has outlined an elaborate matrix algebraic method for the computation of the one-electron matrix elements, $\langle d_i|\mathbf{V}_{AO}|d_j\rangle$. His procedure is readily adapted for machine computation. Further details of the method and a listing of the computer program used by us can be found elsewhere.[32] The many-electron part of the present calculation involves the complex d-orbital basis denoted by the column vector $\mathbf{m}_l$, which is related to the real d-orbital basis $\mathbf{d}$ by the unitary transformation T.

$$\mathbf{d} = T\mathbf{m}_l \tag{2}$$

Thus the required 5 × 5 matrix $\mathbf{V}_{AO}^{complex}$ may be obtained from $\mathbf{V}_{AO}^{real}$ by the similarity transformation

$$\mathbf{V}_{AO}^{complex} = T^{-1}\mathbf{V}_{AO}^{real}T \tag{3}$$

The eigenvalues of the 40 × 40 perturbation matrix in the $|L,M_L,S,M_S\rangle$ basis occur in pairs (Kramers doublets). Magnetic properties (molecular susceptibilities and g values) were calculated by evaluating matrix elements of the Zeeman operator $k\mathbf{L}_\alpha + 2\mathbf{S}_\alpha$, $\alpha = x, y$, or z, between the eigenfunctions resulting from diagonalization of the 40 × 40 matrix. The principal molecular susceptibilities were calculated using the Van Vleck equation, including both first- and second-order Zeeman contributions.[33] The g values are defined by the equation: $h\nu = g_\alpha\beta H$, where ν is the spectrometer frequency, β is the Bohr magneton, and H is the magnetic field strength in gauss.

Results and Discussion

It was our intention to test the ability of the AOM to reproduce, reasonably well, the spectral and magnetic properties of two complexes (**1** and **2**), which differ only in the angular distribution of identical ligands using but a single set of parameters. The calculated ground-state magnetic properties are compared with experiment in Table I, while the observed and calculated excited-state energy levels are set out in Table II. These results were obtained using a σ-only model and only four parameters, which had the following values: e_σ, 2300 cm^{-1}; B, 740 cm^{-1}; λ, -172 cm^{-1}; and k, 0.92. Our object was not to obtain *exact* agreement between observed and calculated quantities, but rather to see how many observables could be fit *reasonably* well with how few adjustable parameters. Owing to the fact that the electronic spectra of these complexes are complicated by vibronic effects, it is felt that the magnetic properties (Table I) provide a more stringent test of theory. In obtaining the fits shown, λ was kept fixed at the free ion value and e_σ was adjusted so that the calculated range of energy levels (including spin-orbit coupling) corresponded to observed absorptions arising from the split ^4F state of the free ion. The Racah parameter B was likewise adjusted to match the levels arising from the ^4P state of the free ion. The value of the orbital reduction factor k was then adjusted to achieve a match to the ground-state magnetic properties. The angular distribution of ligand atoms was, of course, kept fixed at the positions observed in the solid state (Figure 1). The quality of the fit obtained for the magnetic properties is quite satisfying in the sense that, although four parameters are involved, there was no opportunity to achieve agreement should a qualitatively incorrect fit have been found initially, e.g., if $\chi_\parallel$ had been calculated to be less than $\chi_\perp$ for Cs_3CoCl_5. The values of e_σ and B were determined by the electronic spectral results (the calculated magnetic properties are insensitive to the value of B in any case); λ was kept fixed at the free ion value, so k was the only remaining adjustable parameter. The value that it assumed is not an unreasonable one, especially considering the multitude of factors which determine this quantity.[34] It is an

Table I. Comparison of Calculated[a] and Observed Ground-State Magnetic Properties of the $CoCl_4^{2-}$ Anion in Cs_3CoCl_5 and Cs_2CoCl_4

	Cs_3CoCl_5		Cs_2CoCl_4	
Quantity	Calcd	Obsd	Calcd	Obsd
Zero-field splitting $2D$, cm^{-1}	−7.2	−8.6[b]	6.3	~6[c]
M_S[d]	$\pm\frac{3}{2}$,[e] $\pm\frac{1}{2}$[f]	$\pm\frac{1}{2}$[f]	$\pm\frac{1}{2}$,[e] $\pm\frac{3}{2}$[f]	
g_x	0.01, 4.64	4.60[b]	5.81, 1.08	
g_y			3.39, 1.31	
g_z	7.10, 2.38	2.40[b]	2.12, 6.74	
χ_x[g]	9 536	9 351[h]	10 017	9 955[h,i]
χ_y			9 804	
χ_z	10 144	10 116[h]	9 412	9 207[h]
μ_{eff}	4.67	4.64	4.67	
χ_x(TIP)	504		474	
χ_y(TIP)			309	
χ_z(TIP)	293		526	

[a] Calculated using the AOM with the parameters as described in the text. [b] Reference 27. [c] Estimated from the splitting of a band near 17300 cm^{-1}, ref 25. [d] Approximate spin-state quantum members. [e] Lower lying level. [f] Higher lying level. [g] Susceptibility including TIP contribution given in VVk mol^{-1} at 280 K, 1 VVk = 10^{-6} cgs. [h] Reference 28. [i] Treated experimentally as having axial symmetry.

Table II. Energy Levels of $CoCl_4^{2-}$ in Cs_3CoCl_5 and Cs_2CoCl_4

	Cs_3CoCl_5 (D_{2d}) calcd		Cs_2CoCl_4 (C_{2v}) calcd		
Parentage[a] in T_d symmetry	Orbital state energies, cm^{-1}	Kramers doublet energies, cm^{-1}	Orbital state energies, cm^{-1}	Kramers doublet energies, cm^{-1}	Observed range of band maxima, cm^{-1}
$^4T_2(^4P)$	14 973 (^4E)	15 434	15 003 ($^4B_1$)	15 438	16 330–14 490[b]
	14 825 ($^4B_2$)	15 237	14 982 ($^4A_1$)	15 252	
		15 171	14 765 ($^4B_2$)	15 162	
		14 866		14 886	
		14 795		14 762	
		14 772		14 730	
$^4T_2(^4F)$	5 423 ($^4B_2$)	5 990	5 763 ($^4B_2$)	6 179	6 410-4 845[b]
	5 288 (^4E)	5 911	5 248 ($^4A_1$)	6 130	
		5 833	4 996 ($^4B_1$)	5 666	
		5 351		5 341	
		5 282		5 137	
		4 910		4 845	
$^4T_1(^4F)$	3 175 (^4E)	3 411	3 256 ($^4A_2$)	3 443	3 330-2 825[c]
	2 807 ($^4A_2$)	3 366	3 013 ($^4B_2$)	3 389	
		3 281	2 840 ($^4B_1$)	3 170	
		3 030		2 972	
		2 884		2 879	
		2 744		2 763	
$^4A_1(^4F)$	0 ($^4A_1$)	7.2	0 ($^4A_1$)	6.2	8.6,[d] ~ 6[e]
		0		0	

[a] See ref 35 for a discussion of the symmetry labels. [b] Reference 26. [c] Reference 27. [d] Zero-field splitting measurement for Cs_3CoCl_5 from ref 27. [e] Measurement on Cs_2CoCl_4, ref 25.

attribute of a successful theory that it predict accurately as many observables as possible with the fewest adjustable parameters. In the present case the AOM passes this test remarkably well. Were the complexes under consideration to be treated using the phenomenological theory, a total of eight ligand-field parameters (three for **1** and five for **2**) would have been required, whereas the present analysis employs but a single parameter, e_σ, common to both.

It is commonly accepted that the lone electron pairs on halide ligands exert an antibonding influence on metal d orbitals of proper symmetry to overlap with them. For this reason we explored the effect of including a non-zero e_π parameter in the AOM calculations to see if agreement with experiment could still be obtained. It was found that agreement with the observed magnetic properties of the same quality as illustrated in Table I for the σ-only model could be obtained for an indefinite number of different (e_σ, e_π) pair values. The appropriate value of e_σ depends, of course, on the value of e_π employed. For instance, a good fit to the magnetic properties was obtained for $e_\sigma = 5700$ and $e_\pi = 2425$ cm^{-1}. Including a non-zero e_π parameter gave equally satisfactory results for the energy levels, with the only noticeable change from the σ-only model being a slightly greater spread in the overall splitting of the levels arising from the ^4P state of the free ion, perhaps in slightly better agreement with experiment. The general problem of parameter choice in calculations of this sort, particularly in cases for which less experimental data is available, is currently under investigation and clearly requires the detailed analysis of a statistically significant number of examples. Since in the present case, the simpler σ-only model appears adequately to describe the known experimental data, no further consideration will be made here of π-type parameters. Only an analysis of further, more complex systems involving other ligands and complexes of other metal ions will indicate whether or not e_π parameters will in general be important.

Jesson[26] has presented an analysis of energy levels, zero-field splitting, and g values of Cs_3CoCl_5 in terms of phenomenological crystal-field theory. While he obtained reasonable fits to experiment for various sets of parameters, he states that the best fit was obtained for Δ, −2825; D_s, −180; and D_t, −83 cm^{-1}. In all cases he found D_t to be negative. The results of the present AOM calculation correspond to the following set of crystal-field parameters: Δ, −2810; D_s, 57; D_t, −42 cm^{-1}, and thus are entirely consistent with the phenomenological approach. It is important to realize that a *single* e_σ parameter and the observed solid-state structure uniquely determine the *three* crystal-field parameters. The present AOM calculations reproduce Jesson's finding that the first excited orbital triplet state of T_d splits in a field of D_{2d} symmetry such that the orbital singlet state ($^4A_2$ in our notation)[35] lies below the ^4E state (Table II). Significantly, this result is independent of any effort on our part to fit the magnetic data and would occur in the AOM for any value of e_σ, given the experimentally observed distortion from regular tetrahedral symmetry.

As the present calculation appears to correspond in some measure to reality, it is instructive to consider, briefly, some of the individual calculated quantities. Our program readily allows us to evaluate the temperature-independent contribution to the susceptibility (TIP), which is the second-order Zeeman contribution from levels which are not thermally populated. Values for this quantity and its anisotropy are given in Table I. It is interesting that estimates of this quantity for the tetrahalocobaltate(II) ions made some time ago were quite reasonable.[36]

One by-product of our calculation is the one-electron d-orbital splitting pattern. For structure 1 (D_{2d}) the relative d-orbital energies (cm^{-1}) are as follows: d_{xy}, 0; d_{z^2}, 17; $d_{x^2-y^2}$, 2807; d_{xz},d_{yz}, 3188 cm^{-1}. Our e_σ value corresponds to a Δ value of 3070 cm^{-1} for a regular tetrahedron. It should be pointed out that for a complex of D_{2d} symmetry the one-electron d-orbital splitting pattern uniquely determines the many-electron matrix elements.[37] As discussed in detail elsewhere,[37] the one-electron orbital energies could themselves have been employed as ligand-field parameters; however, for the present purposes the AOM is to be preferred, since but a single parameter (e_σ) is required rather than three orbital energies.

The $CoCl_4{}^{2-}$ ions, involving as they do but a single type of cylindrically symmetric ligand and showing small angular distortions from regular T_d symmetry, are prototypal of very slightly distorted tetrahedral complexes. We have, therefore, carried out calculations of the magnetic properties of such complexes as a function of distortion (elongation or compression along the S_4 axis of the tetrahedron), while retaining D_{2d} symmetry and using the parameter values (e_σ, k, λ, B) given earlier. The distortion is given in terms of the angle θ, the Cl–Co–Cl angle bisected by the S_4 axis of the tetrahedron or the principal C_2 axis in D_{2d} symmetry. The results for $\chi_\parallel$, $\chi_\perp$, and $\bar{\chi}$ are shown in Figure 2A. As to be expected from the foregoing results, elongation of the tetrahedron ($\theta < 109.47°$) results in $\chi_\parallel > \chi_\perp$, while compression results in the opposite. $\bar{\chi}$ is seen to be relatively unaffected by distortion over the range examined.

In D_{2d} symmetry under the action of spin-orbit coupling, the $^4A_2$ ground state of T_d splits into two Kramers doublets separated by a zero-field splitting of $2D$ in the usual spin-Hamiltonian notation. D is taken to be positive if the $M_S = \pm 1/2$ doublet lies below the $M_S = \pm 3/2$ doublet of the $S = 3/2$ state. The variation of D as a function of distortion angle θ is shown in Figure 2B. For $\theta < 109.47°$, the $M_S = \pm 3/2$ doublet lies lowest and the calculated g values for this level vary in the range: $g_\parallel(\pm 3/2) = 7.21$–$7.00$; $g_\perp(\pm 3/2) = 0.01$. Since for parallel polarized microwave radiation the selection rule is $\Delta M_S = \pm 1$ and for perpendicular polarized radiation g is too small to allow observation of a signal at reasonable field strengths, no transitions between components of the lowest Kramers doublet should be observed. Indeed, the EPR results obtained on Cs_3CoCl_5 were interpreted in this manner.[27] For the observable $M_S = \pm 1/2$ doublet, which becomes the ground level for $\theta > 109.47°$, the g values range as follows: $g_\parallel(\pm 1/2) = 2.42$–$2.29$ and $g_\perp(\pm 1/2) = 4.62$–4.73 as θ ranges from 102 to 116°. Thus, although the susceptibility anisotropy changes sign as the distortion angle θ passes through 109.47°, the g-tensor anisotropy of the EPR *observable* Kramers doublet is very little affected.

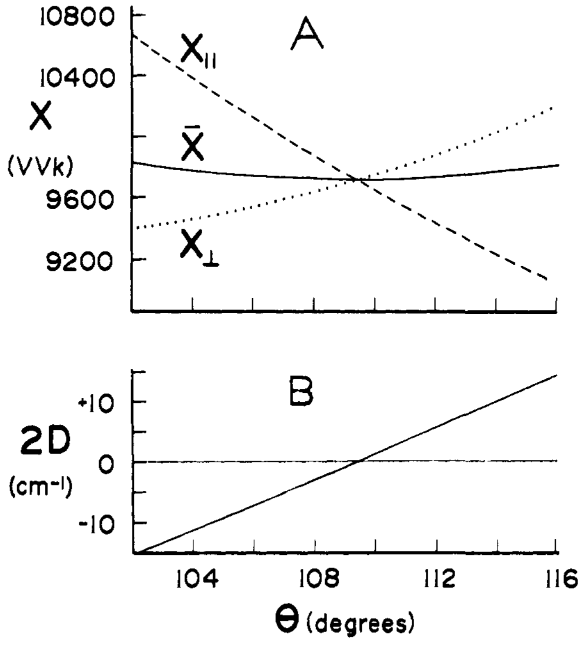


Figure 2. A. (Upper panel) Variation of calculated molecular susceptibilities with distortion angle θ; see text. B. (Lower panel) Variation of calculated zero-field splitting ($2D$) with distortion angle θ.

Conclusions

The AOM has been applied in the context of a completely general, symmetry-independent, weak-field approximation ligand-field calculation, including spin–orbit coupling. This model describes a reasonable number of experimental observables (energy levels, zero-field splittings, g values, and principal magnetic susceptibilities) for two different forms of the $CoCl_4{}^{2-}$ ion with a minimum number of adjustable parameters. The success of our theoretical approach suggests that calculations of this type may prove useful in analyzing in a detailed and fundamental way the electronic and magnetic properties of transition metal ions in low-symmetry complexes and metalloproteins. Application of these methods to systems of greater complexity and to other d-electron configurations is in progress in these laboratories.

Acknowledgment. This research was supported by the National Science Foundation through Grant MPS73-08550. We wish to thank H. D. (Skip) Knoble for his kind assistance with programming problems.

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(35) For consistency the coordinate system demanded by the C_{2v} point symmetry of structure **2** was retained throughout: $C_2 = z$ axis, $\sigma_v = xz$ plane, $\sigma_v' = yz$ plane. Using this coordinate system the ground ^4F and excited ^4P states of the cobalt(II) ion in a regular tetrahedral field split into the following levels in the order of increasing energy: $^4A_1(F)$, $^4T_1(F)$, $^4T_2(F)$, $^4T_2(P)$, rather than having the more common symmetry labels $^4A_2(F)$, $^4T_2(F)$, $^4T_1(F)$, $^4T_1(P)$, respectively, which apply when the x and y coordinates are rotated by $\pi/4$. The symmetry labels appropriate to D_{2d} symmetry in our coordinate system are indicated in Table II. The choice of coordinate system for T_d and D_{2d} symmetries is arbitrary; however, this is not true for C_{2v} symmetry. Failure to appreciate this point has resulted in the incorrect labeling of the energy levels of the C_{2v} complexes $M[(C_6H_5)_3P]_2Cl_2$, M = Co [C. Simo and S. Holt, *Inorg. Chem.*, 7, 2655 (1968)] and M = Ni [R. J. Fereday, B. J. Hathaway, and R. J. Dudley, *J. Chem. Soc. A*, 571 (1970)].

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The Kinetics of Ligand Detachment from Labile Cobalt(II)–Amine Complexes in Aqueous Solution

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Received September 15, 1975

Abstract: The e_{aq}^- reduction of some Co(III)–amine complexes and the kinetics of ligand detachment of the resulting Co(II) complexes have been examined by pulse radiolysis with kinetic conductivity detection (time resolution ~1 μs). The halide ligands in $Co(NH_3)_5Cl^+$, $Co(en)_2Cl_2$, and $Co(trien)Cl_2$ are lost very rapidly (<1 μs). Similarly all but three NH_3 ligands from $Co(NH_3)_6^{2+}$ and other amine complexes are lost in <1 μs. The last three NH_3 ligands from all monodentate complexes are replaced by water with half lives of 11, 81, and 630 μs, independent of pH (3–4.5). Ethylenediamine ligands in $Co(en)_3^{2+}$ and $Co(en)_2Cl_2$ are detached in well-defined consecutive steps. The detachment rates of ethylenediamines are much slower than for ammonia ligands ($t_{1/2}$ = 0.5, 3, and 10 ms at pH 3.5) and are pH dependent. In $Co(trien)Cl_2$ the elimination of trien proceeds by a single observable pH-dependent step in the ms range. No detachment from $CoEDTA^-$ was observed as expected for stable complexes.

The alternating current (ac) kinetic conductivity technique has been coupled successfully with pulse radiolysis[2] and exploited in the study of charged free radicals over a wide pH range (2–12). This combination, referred to as "conductometric pulse radiolysis" (CPR), was subsequently demonstrated to be useful for studying the kinetics of ammonia detachment from some simple Co(II) ammine complexes[3] and was suggested as a powerful method for the study of the fast kinetics (time resolution of ~1 μs) of basic-ligand detechment from labile Co(II) complexes. More recently, CPR was successfully exploited in the study of ammonia detachment from Rh(II) complexes.[4] This technique can also be used to monitor intramolecular electron transfer processes[3] as in the case of (p-nitrobenzoate)$Co^{III}(NH_3)_5^{2+}$, where initial addition of an electron to the nitro group is followed by the intramolecular electron transfer to the metal center.[5]

We present here kinetic data concerning the detachment of ammonia and some polyamines from labile Co(II) complexes that are generated by rapid (τ < 1 μs) reduction of stable Co(III) complexes in aqueous solutions. These kinetic data provide also an insight into the mechanism of detachment of polydentates from Co(II) and all partially aquated intermediates. In addition, the significance of the participation of those intermediates in the chemical reactions can be assessed from their lifetimes and reactivities as in the case of the $Rh^{II}(NH_3)_4^{2+} + O_2 \rightarrow O_2Rh^{II}(NH_3)_4^{2+}$ reaction.[4]

Experimental Section

A 10-MHz ac conductivity cell with two pairs of platinum electrodes, one serving as a compensatory pair, was irradiated using 0.5 μs pulses of 1.6 MeV electrons from a Van de Graaff generator. The cell can be used for simultaneous conductivity and optical measurements with 1-μs resolution. Since the intermediates in the systems examined have very small absorbances, only induced conductivity changes were recorded. The associated optical and electronic equipment have been described elsewhere.[6] The ac kinetic conductivity cannot be used above 10^{-2} M ionic concentration, i.e., below pH 2.

The solutions were made up from ultrapure water generated by a millipore system. All chemicals were of highest commercial grade