An ab Initio Calculation of the Bonding, Excited States, and g Value of Tetrachlorocobaltate(II), $(CoCl_4)^{2-}$

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Abstract: An all-electron ab initio SCF-MO calculation of the $^4A_2$ ground state of the $(CoCl_4)^{2-}$ ion is described for T_d symmetry. Both of the metal's 3d t_2 and e MO's have approximately the same (~5%) degree of covalency, and the main contribution to the Co–Cl covalent bonding arises in an a_1 MO which comprises considerable metal s character. The ground state wavefunction has been used to calculate the g value for the complex and excellent agreement with experiment obtained. Configuration interaction calculations have been performed in order to describe the low lying $^4T_2$, $^4T_1$(F), and $^4T_1$(P) states. The calculated transition energies and their oscillator strengths are found to be sensitive to the configurations included but, with quite a small expansion, good agreement with experimental data is obtained. The results of these calculations are compared with earlier semiempirical estimates of the covalency in this complex.

Accurate ab initio MO calculations can now be performed[1] for transition metal complexes and the resulting wavefunctions used to calculate the magnitudes of such properties as g values, transition energies, and oscillator strengths without recourse to any adjustable parameters. We here present the results of an ab initio study of the $(CoCl_4)^{2-}$ ion as part of an evaluation of the improvement in the understanding of the electronic structure of d-transition metal complexes afforded by this theoretical approach. $(CoCl_4)^{2-}$ was chosen for this study since not only do abundant accurate structural,[2,3] spectral,[4-9] and magnetic[7,10] data exist for this ion, but also it has been subject to much previous[8-12] theoretical discussion. The results obtained represent the first ab initio calculation of a g value for a d-transition metal complex and allow an assessment of the use which has previously been made of paramagnetic resonance studies to interpret the bonding in this complex. Configuration interaction (CI) calculations have been performed to interpret the $^4T_2$, $^4T_1$(F), and $^4T_1$(P) excited states, and the various contributions to the energies and intensities of the electronic transitions from the ground to these excited states are considered.

Computational Details

An all-electron ab initio SCF-MO calculation of the $^4A_2$ ground state of $(CoCl_4)^{2-}$ was performed in a basis of gaussian-type functions (GTF) by the restricted Hartree-Fock (RHF) method. The core atomic orbitals and chlorine 3s orbitals were represented by Slater-type orbitals (STO) with best atom exponents,[13] each fitted by three GTF's.[14] The chlorine 3p[15] and cobalt 3d orbitals[16] were double ζ STO's each fitted by two and three GTF's, respectively. The cobalt 4s and 4p orbitals were each represented by a single GTF with exponent 0.32. This basis is thus of near double ζ quality with 187 primitive GTF's. The calculation was performed using a value of 2.252 Å for the Co–Cl bond length as identified[2] for the $(CoCl_4)^{2-}$ ions of Cs_3CoCl_5 and assuming T_d symmetry, although a small distortion to D_{2d} symmetry is present for these ions in the Cs_3CoCl_5 lattice. Table I lists the energy and a Mulliken population analysis of the valence MO's for the electronic ground state of $(CoCl_4)^{2-}$. It should be noted that we have used the six d-type gaussian functions d_{x^2}, d_{y^2}, d_{z^2}, d_{xy}, d_{xz}, and d_{yz}, in our calculations so that in addition to the five true d atomic orbitals, a sixth s-type function will be generated of a_1 symmetry. This accounts for the "3d" population of the a_1 MO's of Table I, which should be regarded as s-type contributions. The observed deviation of the g value of $(CoCl_4)^{2-}$ from the free-electron value may be interpreted in terms of the admixture of the low-lying $^4T_2$ state into the ground state by spin-orbit coupling. If we write the spin-orbit Hamiltonian ($\mathcal{H}_{so}$) as (1),[17] where the summation is over all the electrons (i) and nuclei (N) with effective charge Z_N

$$\mathcal{H}_{so} = \sum_{i,N} (Z_N/r_{N,i}^3)\, l_{N,i} \cdot S_i \qquad (1)$$

then the isotropic g value is given by (2)

$$g = 2.0023 + 4\,\frac{\left\langle {}^4T_2 \middle| \sum_{i,N} (Z_N/r_{N,i}^3)\, l_{zi} S_{zi} \middle| {}^4A_2 \right\rangle \langle {}^4A_2 | l_z | {}^4T_2 \rangle}{E({}^4A_2) - E({}^4T_2)} \qquad (2)$$

where we have taken $m_s = 1/2$ components of the $^4A_2$ and $^4T_2$ states. In terms of the half-filled t_2 and doubly occupied e MO's of mainly metal 3d character, (2) reduces to (3)

$$g = 2.0023 - (2/3) \times \frac{\left\langle e(x^2-y^2) \middle| \sum_N (Z_N/r_N^3)\, l_z \middle| t_2(xy) \right\rangle \langle t_2(xy) | l_z | e(x^2-y^2) \rangle}{E({}^4A_2) - E({}^4T_2)} \qquad (3)$$

If we assume that the wavefunction for the $^4T_2$ state may be accurately represented by the orbital excitation e → t_2, the integrals of (3) may be evaluated exactly using the form of the t_2 and e MO's obtained from the RHF calculation. The integrals involving the operators l_z and l_z/r^3 were computed in terms of the corresponding integrals over r and r/r^3 by an analysis similar to that described by Ito and I'Haya.[18]

Table I. Valence Orbital Characteristics for the Ground State of the $(CoCl_4)^{2-}$ Ion

Orbital[a]	Energy, au	Orbital character, %					Co–Cl overlap population (per electron)
		Cobalt			Chlorine		
		3d	4s	4p	3s	3p	
$10t_2$	0.1019	96				4	−0.02
$2t_1$	−0.0862					99	0.0
3e	−0.0984	3				96	−0.01
$9t_2$	−0.1123	2				97	0.0
$8t_2$	−0.1409	2		3		93	0.0
$8a_1$	−0.1809	15	−9		2	90	0.09
2e	−0.3505	97				3	0.01
$7t_2$	−0.6837	1		1	98		0.0
$7a_1$	−0.6959	12	−8		96	1	0.01

[a] The orbital numbering includes the core orbitals.

Table II. Calculated Excited States of $(CoCl_4)^{2-}$

CI expansion	State	Transition energy, cm^{-1}	Oscillator strength
CI1	$^4T_2$	12800	0
	$^4T_1$	20800	1×10^{-7}
	$^4T_1$	34700	2×10^{-7}
CI2	$^4T_2$	3460	0
	$^4T_1$	14500	2×10^{-4}
	$^4T_1$	31900	2×10^{-4}
CI3	$^4T_2$	3450	0
	$^4T_1$	6100	7×10^{-5}
	$^4T_1$	21600	5×10^{-4}

A number of CI calculations were performed using the computed MO's of the $^4A_2$ state to study the low lying excited states of $(CoCl_4)^{2-}$. The smallest expansion included the configurations $(2e^3 10t_2^4)$ and $(2e^2 10t_2^5)$ which correlate with the ^4F and ^4P states, respectively, of the free cobalt(II) ion. This calculation is designated CI1. A larger calculation (CI2) included the configurations of CI1, together with the additional single excitations $(3e, 2t_1, 10t_2) \rightarrow (11t_2\ (4p), 9a_1\ (4s))$ and $(2e \ldots 2t_1) \rightarrow 10t_2$ (see Table I). This latter calculation includes the lowest lying single excitations which are usually the most important in CI calculations. A third CI calculation (CI3) included the configurations from CI2, together with the doubly excited configurations $(3e^2 10t_2^5)$ and $(2e^3 3e^3 10t_2^5)$. All of these CI calculations were performed using the bonded functions of Reeves,[19] CI3 including 153 such functions.

All calculations were performed using the ATMOL system of programs on the CDC 7600 computer of the University of Manchester Regional Computing Center.

Results

The data presented in Table I show clearly that the half-filled MO $10t_2$ is predominantly (96%) metal character and is slightly Co-Cl antibonding. The other mainly metal valence MO, 2e is at much lower energy than $10t_2$ and is slightly Co-Cl bonding in nature. The remaining valence MO's are predominantly chlorine in character, although $8a_1$ has considerable cobalt s component and provides by far the largest bonding contribution to the Co-Cl bonds. The calculated configuration of the cobalt atom obtained by a Mulliken population analysis of the RHF wavefunction for the $^4A_2$ state is $3d^{6.97}4s^{0.29}4p^{0.51}$, and the formal charges on the atoms of $(CoCl_4)^{2-}$ are estimated to be $Co^{1.36+}$ and $Cl^{0.84-}$.

The results of the CI calculations are shown in Table II. These are to be compared with the experimental transition energies, $^4A_2 \rightarrow {}^4T_2$, $^4T_1(F)$, and $^4T_1(P)$ of 3000,[7] 5500, and 15000 cm^{-1},[8] respectively. The first absorption is observed to be very weak,[7] and the second and third peaks have oscillator strengths of ca. 7×10^{-4} and 6×10^{-3}, respectively.[4] The results from CI1 are in complete disagreement with such data, only the order of the excited states being predicted. Thus the "d-d" transition energies and intensities cannot be interpreted in terms of states arising from the metal $3d^7$ configuration alone. The introduction of single excitations CI2 yields an improvement; the energy of the $^4T_2$ state is now in good agreement with experiment but those of the $^4T_1$ states are too high and both are predicted to be of equal intensity. The introduction of the additional doubly excited configurations, $(3e^2 10t_2^5)$ and $(2e^3 3e^3 10t_2^5)$ (CI3), yields calculated excitation energies which are now in quite good agreement with the experimental values for all three "d-d" transitions. Furthermore, the oscillator strength of the $^4A_2 \rightarrow {}^4T_1(P)$ transition is predicted to be an order of magnitude greater than the $^4A_2 \rightarrow {}^4T_1(F)$ one, in agreement with experiment, although both these calculated oscillator strengths are still an order of magnitude too low.

To calculate the value for the effective nuclear charge at the cobalt atom needed in (3), a configuration of $3d^7$ was taken and Slater's rules used, giving $Z_{Co} = 6.9$. The values of the one-electron integrals of (3) were then calculated to be those shown in (4) and (5).

$$\langle e(x^2 - y^2)|l_z|r_{Co}{}^3|t_2(xy)\rangle = -i9.76 \text{ au} \tag{4}$$

$$\langle e(x^2 - y^2)|l_z|t_2(xy)\rangle = -i1.89 \text{ au} \tag{5}$$

The integrals involving $l_z/r_{Cl}{}^3$ were calculated to be only ca. 0.1% of that involving $l_z/r_{Co}{}^3$ so that the former have been neglected in the calculations reported here. Using the values of (4) and (5) in equation 3, together with a value for the $^4A_2 \rightarrow {}^4T_2$ transition energy of 3000 cm^{-1} gave an isotropic g value of 2.33. This result is in excellent agreement with the reported[7] experimental data for Cs_3CoCl_5; $g_\parallel = 2.40$ and $g_\perp = 2.30$, giving $\bar{g} = 2.33$.

Discussion

The results described here include the first ab initio calculation of a g value for a d-transition metal complex and they show that, with a wavefunction of near double ζ quality, excellent correlation between theory and experiment in this and other respects is obtained.

Notable features of the results (Table I) obtained for the ground state of $(CoCl_4)^{2-}$ include: (i) the small amount of Co-Cl covalent bonding involved; (ii) the approximately equal extent of the d-electron delocalization in the metal e and t_2 3d orbitals; and (iii) the insignificant extent to which the metal's 3d and 4p orbitals are mixed in this tetrahedral complex. The $2e-10t_2$ energy separation of 99279 cm^{-1} is not[20] taken to represent the conventional value of $10Dq$; indeed the data contained in Tables I and II show clearly that the order of the excited states for $[CoCl_4]^{2-}$ cannot be deduced simply from a consideration of the one-electron energies. Thus although there are 12 filled MO's with energy higher than that of the 2e orbital, the first excited state *is* calculated to be the $^4T_2$ state which arises primarily (90%) from the transition $2e \rightarrow 10t_2$. As shown by Basch et al.,[1] the electron repulsion correction to the transition energy is crucial. Such Coulomb integrals are significantly larger for the "d-d" than for the "charge-transfer" transitions and thus result in the former being at the lower energy. An examination of the eigenvectors obtained from the calculation CI3 reveals that the $^4T_1(P)$ and $^4T_1(F)$ states are composed mainly (~60%) of the $2e^3 10t_2^4$ and $2e^2 10t_2^5$ configurations respectively, in disagreement with simple crystal-field arguments. In addition, two points in particular mitigate against a free ion description of these $^4T_1$ excited states. Firstly, the inclusion of additional single excitations and other doubly excited configurations having no analogues in the free ion situation are necessary to obtain good excitation energies. Secondly, the predominant single excitation contributing to both $^4T_1$ states is $3e \rightarrow 10t_2$, and it is the participation of this Cl(3p) to Co(3d) charge transfer configuration to the $^4T_1(P)$ wavefunction which is primarily responsible for the considerable intensity of the $^4A_2 \rightarrow {}^4T_1(P)$ transition. Therefore, the common assumption[21] that d-d transitions in tetrahedral complexes derive their intensity from d-p mixing is not valid for $(CoCl_4)^{2-}$ (Table I), and the use[22] of experimental oscillator strengths to obtain estimates of metal-ligand covalency is probably an oversimplification. The calculated oscillator strengths for all the "d-d" transitions of $(CoCl_4)^{2-}$, whilst in reasonable agreement with the experimental data (Table II), are too low. However, these values were computed neglecting any considerations of dynamic contributions due to vibronic motions. As shown by Jaeger and Englman,[23] these latter effects are probably significant for $(CoCl_4)^{2-}$, and their inclusion may improve the agreement between the calculated and experimental oscillator strengths.

Measured g values of transition metal complexes which deviate from the free-electron value are usually interpreted in terms of the mixing of excited states into the ground state by spin-orbit coupling. Such deviations have frequently been used to make inferences concerning the bonding in particular complexes via models which in some way include, often as adjustable parameters, the degree of covalency of the complex.[22,24-26] However, to date these treatments have been somewhat inconclusive due to the rather drastic approximations that are commonly employed, such as the use of semiempirical wavefunctions at the Hückel level approximation, parameterization by the use of orbital reduction factors,[27] and data fitting by variation of the free-ion spin-orbit coupling parameter. Thus, although agreement between theory and experiment is often found with quite reasonable values for the chosen parameters, it is not clear to what extent such treatments yield reliable information about the electronic structure of the complex.

The results of the CI calculations (Table II) show that, for $(CoCl_4)^{2-}$, the $^4T_2$ state is mainly (90%) composed of the configuration $(2e^3 10t_2^4)$ so that the discussion of the g value of this ion in terms of an excited state represented by the simple $2e \rightarrow 10t_2$ orbital transition is valid. The value of the angular momentum integral (eq 5) which deviates from 2 by ca. 5% reflects the small degree of covalency in *both* the $10t_2$ and 2e MO's. Therefore it would appear that it is *not* a valid assumption to take the e MO to be pure cobalt 3d, and to use the measured g value to arrive at a value for the covalency of the t_2 MO.[22] In these calculations we have used a double ζ basis to represent the 3d atomic orbitals of cobalt so that the effective "size" of these 3d orbitals in the complex is determined by the self-consistent field procedure. It is this 3d-orbital "size" which will determine the magnitude of the integral involving l_z/r_{Co}^3 (eq 4) which is usually approximated in terms of an "effective" spin-orbit coupling parameter. Due to the flexibility of the wavefunctions used here, there is no need for such a parameter. It is of interest to estimate the value of this parameter, taking our calculated degrees of covalency for the 2e and $10t_2$ MO's. To fit the measured g value, we need ape of the spin-orbit coupling parameter λ of approximately -130 cm^{-1} which is reasonably close to the value of ca. -140 cm^{-1} estimated from spectral studies[6,8] and represents a reduction from the Co^{2+} free-ion value which is -172 cm^{-1}.[28]

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References and Notes

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