NDDO/CI Calculations of the Electronic Spectra of Cobalt(III) Ammine Complexes

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(Received October 12, 1989; revised January 16, 1990)

Abstract

A NDDO method capable of calculating configuration interaction for transition-metal compounds is applied to mixed ligand complexes $[Co(NH_3)_5L]^{n+}$ ($L = Cl^-$, OH^-, H_2O, CN^-, NH_3). The parameters used are discussed. The calculated transition energies are in fairly good agreement with experimental data.

Introduction

Photochemical reactions of cobalt(III) mixed ligand complexes are of permanent interest because of certain open questions concerning the role of the various excited electronic states as sources of photoredox, photosubstitution and isomerization reactions, respectively [1–3]. The prediction and interpretation of the reaction pathways require detailed knowledge about the structure of the absorption spectra and the relative order of the excited electronic states.

In previous papers Zerner *et al.* [4–7] and Baranowski *et al.* [8, 9] have published semiempirical all-valence ZDO-SCF calculations (INDO, CNDO) which describe the bonding properties and electronic spectra of selected transition-metal compounds. The calculated transition energies are in reasonable agreement with data obtained experimentally. However, the relatively high number of adjusted parameters leads to problems in applying these methods to different metal systems.

For organic molecules it has been shown [10, 11] that the NDDO method, originally proposed by Pople and Beveridge [12] is able to yield qualitatively better results than CNDO or INDO methods because of consideration of two-center two-electron integrals in the NDDO formalism.

The NDDO/CI calculations of the electronic spectra of cobalt(III) ammine mixed ligand complexes which we have performed are reported here.

Methodology

The NDDO/CI program used in our calculations is based on a version that includes d-symmetry orbitals as published by Nieke and Reinhold recently [13]. The following parameters have been taken into account: the orbital exponents ξ_μ (μ = 4s, 4p, 3d), the resonance parameters β_μ and the valence state ionization potentials I_μ which are estimated from atomic spectroscopy. The $\xi_{4s,4p}$ and β_μ values are as used by Clack *et al.* [14]. Configuration dependent ionization potentials of the central metal were chosen according to Ballhausen and Gray [15] (Co: $I_s = -7.31$ eV; $I_p = -3.84$ eV; $I_d = -9.42$ eV). I_μ values for main group elements were taken from Pople and Beveridge [12].

Results and Discussion

In agreement with Zerner *et al.* [6] our results confirm that the ξ_{3d} orbital exponent strongly influences the energy of electronic transitions (Table 1). In our calculations the cobalt ξ_{3d} exponent was adjusted to give good agreement between the calculated and observed long-wavelength ligand-field (LF) band of the hexaamminecobalt(III) complex (ξ_{3d} = 3.12). It was found, however, that the variation of

TABLE 1. Dependence of the energies of ligand-field transitions on ξ_{3d} orbital exponent for $[Co(NH_3)_6]^{3+}$

ξ_{3d}	$^1A_1-^1T_1$		$^1A_1-^1T_2$	
	E (eV)	$\tilde{\nu} \times 10^{-3}$ (cm^{-1})	E (eV)	$\tilde{\nu} \times 10^{-3}$ (cm^{-1})
2.84	3.65	29.44	4.55	36.7
2.90	3.39	27.34	4.32	34.84
3.00	3.0	24.2	3.98	32.1
3.12	2.6	20.97	3.62	29.2
3.20	2.36	19.04	3.42	27.58
3.30	2.08	16.78	3.18	25.65

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0020-1693/90/$3.50

this parameter has only a small influence on the difference between $^1A_1$–$^1T_1$ and $^1A_1$–$^1T_2$ transitions as well as on the difference between LF- and LMCT-transitions in the mixed-ligand complexes discussed here. The results are not very sensitive towards variation of β_{3d}, so that in accordance with INDO/S results a change of 20% in the value of β_{3d} (Co) does not significantly alter the calculated electronic spectra. As proposed by Clack *et al.* [14] $\beta_{3d} = -28.0$ eV has been used.

Whereas most INDO and CNDO calculations of the electronic spectra include special approximation formulas to estimate the two-center coulomb integrals, in our NDDO/CI version the $\gamma_{\mu\nu}$ are calculated exactly from atomic orbitals. The same procedure has been applied for the determination of the one-center coulomb integrals.

In order to calculate the spectra of each complex, the molecular orbitals of the ground states obtained by an SCF calculation have been analysed and at least 105 configurations were taken into account. Transition moments and oscillator strengths have been evaluated for each transition by using the dipole length operator.

Calculated and observed spectroscopic data of the cobalt complexes are summarized in Table 2.

TABLE 2. Calculated and experimental electronic spectra of selected Co(III) ammine complexes $[Co(NH_3)_5L]^{n+}$

L	Type	Calculated			Experimental		Reference
		E (eV)	f	$\bar{\nu} \times 10^{-3}$ (cm^{-1})	E (log ϵ) (eV)	$\bar{\nu} \times 10^{-3}$ (cm^{-1})	
NH_3 $n = 3$	$xy \to x^2-y^2$ $d_\pi \to z^2$	*2.61*	0	21.05	2.63 (1.75)	21.21	16
	$d_\pi \to z^2$ $d_\pi \to x^2-y^2$	3.61	0	29.12	3.66 (1.66)	29.52	
Cl $n = 2$	$xy \to x^2-y^2$	2.26	10^{-5}	18.23	2.32 (1.71)	18.71	17
	$d_\pi \to x^2-y^2$	2.55	10^{-6}	20.57	2.65 (1.08)	21.37	
	$d_\pi \to z^2$	3.33	3×10^{-5}	26.86	3.41 (1.72)	27.50	
	$xy \to z^2$	4.03	10^{-6}	32.5			
	$Cl_\pi \to z^2$	4.90	2×10^{-3}	39.52	4.60 (2.65)	37.1	
	$Cl_\sigma \to z^2$	5.60	10^{-2}	45.17	5.43 (4.31)	43.8	
	$Cl_\sigma \to z^2$	6.43	0.39	51.86			
OH $n = 2$	$d_\pi \to z^2$	2.42	5×10^{-5}	19.52	2.45 (1.83)	19.76	18
	$xy \to z^2$	2.53	10^{-6}	20.38			
	$d_\pi \to x^2-y^2$	3.36	3×10^{-5}	27.09	3.33 (1.80)	26.86	
	$O_\pi \to z^2$	5.70	4×10^{-3}	45.97	~5.58 (4.15)	~45.0	
	$O_\sigma \to z^2$	11.40	7×10^{-2}	91.95			
H_2O $n = 3$	$d_\pi \to z^2$	2.47	10^{-5}	19.91	2.53 (1.67)	20.4	18
	$xy \to z^2$	2.56	10^{-6}	20.62			
	$d_\pi \to x^2-y^2$ $d_\pi \to z^2$	3.52	6×10^{-5}	28.39	3.59 (1.65)	28.98	
	$O_\pi \to z^2$	6.70	10^{-3}	54.04			
	$O_\sigma \to z^2$	12.4	5×10^{-2}	100			
CN $n = 2$	$d_\pi \to z^2$	2.71	10^{-5}	21.86	2.81 (1.74)	22.66	19
	$xy \to z^2$	2.87	10^{-5}	23.15			
	$d_\pi \to x^2-y^2$	3.97	10^{-5}	32.02	3.79 (1.72)	30.57	
trans-$[Co(NH_3)_4Cl_2]^+$							
	$xy \to x^2-y^2$	2.08	0	16.78	1.98 (1.63)	15.97	20
	$d_\pi \to x^2-y^2$	2.48	0	20.0	2.6 (1.38)	20.97	
	$d_\pi \to z^2$	3.24	0	26.13	3.1 (1.54)	25.0	
	$xy \to z^2$	4.1	0	33.07			
	$Cl_\pi \to z^2$	4.62	6×10^{-4}	37.26	4.2 (2.86)	32.95	
	$Cl_\pi \to z^2$ $Cl_\pi \to x^2-y^2$	5.5	10^{-3}	44.36			
	$Cl_\sigma \to z^2$	5.6	4×10^{-2}	45.17	4.89 (4.39)	39.44	

Although the ξ_{3d} exponent has been adjusted to the energy of the observed low-energy LF-transition ($^1A_1$–$^1T_1$), the higher energy d–d band ($^1A_1$–$^1T_2$) could be calculated with remarkable accuracy. However, the weak spin-forbidden $^1A_1$–$^3T_1$ absorption band which appears at 13 000 cm^{-1} [16] has been obtained at higher wavenumbers ($\tilde{\nu} \sim 17\,000$ cm^{-1}).

Comparing the sequence of transition types of the calculated complexes, d–d transitions are generally obtained at low energies followed by CT transitions at higher energies in agreement with experimental observations. On the contrary, INDO calculations [21] give an opposite order of these transition types.

The relative order of the energy of the long-wavelength band in acidopentaamminecobalt(III) complexes $[Co(NH_3)_5L]^{n+}$ agrees with the position of the ligand L in the spectrochemical series: Cl < OH < H_2O < NH_3 < CN. The calculated $^1T_1$ splitting of $E = 0.29$ eV in $[Co(NH_3)_5Cl]^{2+}$ is reflected by the occurrence of two absorption bands ($^1A_1$–^1E and $^1A_1$–$^1A_2$) in the energy region around 20 000 cm^{-1}, whereas the stronger hydroxide ligand causes only a band broadening of the original $^1A_1$–$^1T_1$ absorption. On the other hand, the significant hypsochromic shift of the LF-transitions for $[Co(NH_3)_5CN]^{2+}$ confirms the unique position of cyanide in the spectrochemical series.

The calculated transition energies of lowest energy in the mixed ligand complexes are generally related to the $^1A_1$–^1E(a), $^1A_1$–$^1A_2$ and $^1A_1$–^1E(b) transitions in order of increasing energy (Table 2). Whereas the metal reduction bands $Cl^- \rightarrow Co(III)$ of the type $\pi \rightarrow z^2$ are observed at 33–37 × 10^3 cm^{-1}, the more intensive $\sigma \rightarrow z^2$ type transitions are found at higher energies. Our calculations are in good agreement with these experimental results. Therefore we see the possibility of applying our results to localize CT-transitions also in cases where spectroscopic measurements are uncertain (L = OH^-, H_2O).

The potential-surface diagram for the $^1A_1$, $^1T_1$, $^1T_2$ and $^3T_1$ electronic states in $[Co(NH_3)_6]^{3+}$ along the Co–N-coordinate is shown in Fig. 1. The general shapes of the calculated curves are similar to those reported by Zerner *et al.* [22], Wilson and Solomon [23] and those that might be inferred from ligand-field theory [24]. Bond lengthening results from the population of the antibonding e_g orbital in the excited LF-states. The calculated equilibrium distances are 203 ($^3T_1$), 204 ($^1T_1$) and 204 ($^1T_2$) pm, respectively. The 195 pm minimum for the ground state is in good agreement with crystallographic data [25]. The energetic position of the quintet T_2 term, which is of particular interest with respect to the discussion of LF-induced photoredox reactions of cobalt(III) complexes will be considered separately.

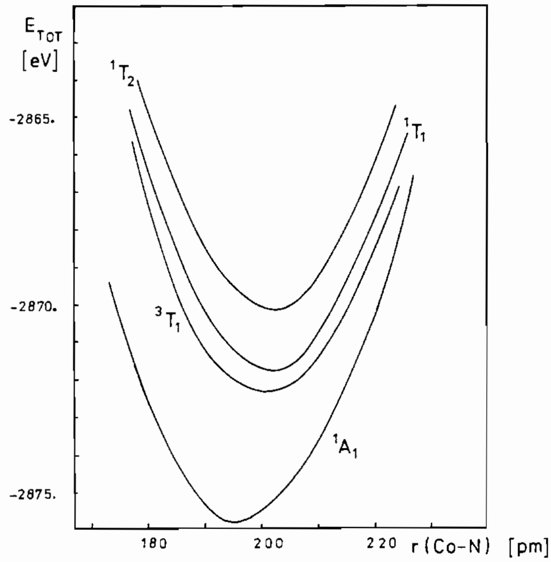

Fig. 1. Potential-surface diagram for the $^1A_1$, $^1T_1$, $^1T_2$ and $^3T_1$ electronic states in $[Co(NH_3)_6]^{3+}$.

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