

SEMI-EMPIRICAL MOLECULAR ORBITAL CALCULATIONS OF BINUCLEAR COBALT COMPLEXES, II

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In this paper the energy levels, molecular orbitals, orbital populations and transitions of the $[(\text{NH}_3)_4\text{Co}(\text{OH})_2\text{Co}(\text{NH}_3)_4]^{4+}$ and of the $[(\text{NH}_3)_3\text{Co}(\text{OH})_3\text{Co}(\text{NH}_3)_3]^{3+}$ binuclear complex ions are calculated by the LCAO-MO method using the half-empirical formula of Wolfsberg and Helmholz [1].

Introduction

In a previous paper [2] we investigated theoretically the binuclear complex compounds $[(\text{NH}_3)_4\text{Co}(\text{OH})_2\text{Co}(\text{NH}_3)_4]^{4+}$ (denoted in the following by K_1) and $[(\text{NH}_3)_3\text{Co}(\text{OH})_3\text{Co}(\text{NH}_3)_3]^{3+}$ (K_2), and we calculated the energy levels, molecular orbitals, orbital and bond overlap populations and transitions of these complex ions by a simple semi-empirical LCAO—MO method. In these calculations we neglected not only the influences of the H atoms and the electrons in closed shells on the complex compounds but the interactions between ligands OH and NH_3 , too.

In the present paper because of undoubted importance of the bridges we take into account besides metal-metal interactions the interactions between ligands OH but we neglect the interactions between NH_3 . The method of the calculations and the geometries of the complex ions are the same as in the paper [2]. The computations were performed on the MINSZK—22 computer of the Attila József University.

Results and discussion

The energy values of the MO's are summarized in Table I. These energies differ from the energies in [2] only a little (0.1—0.2 eV) with the exception of the symmetry A'_2 (K_2) where the difference is 0.8 eV. In the ground state of the complexes the highest filled MO of K_1 is $2b_{2u}$ (−8.557 eV), that of K_2 is $3e''$ (−9.207 eV), the lowest empty MO-s are $1b_{1g}$ and $3e'$, respectively, as in [2].

The wavenumbers of the allowed electron transitions were calculated by means of Bohr's frequency rule the most important wavenumbers of which are summarized in Table II. In this table we give the wavenumbers of those transitions which were also taken into account in the paper [2]. The difference between the two sets of wavenumbers is not too high except the transition $2b_{1g} \leftrightarrow 2b_{3u}$ where the difference is 4500 cm^{-1} .

Table I

K_1							
A_{1g}	B_{1u}	B_{2g}	B_{3u}	B_{2u}	B_{3g}	B_{1g}	A_{1u}
- 0.272	+ 59.191	+ 3.963	- 3.364	- 1.705	+ 1.881	- 8.550	- 9.343
- 5.998	- 1.418	- 6.014	- 7.122	- 8.557	- 9.110	- 11.843	
- 6.902	- 5.908	- 12.245	- 11.757	- 12.360	- 14.136		
- 9.281	- 8.335	- 14.719	- 14.752	- 14.111			
- 12.736	- 12.181						
- 14.886	- 14.794						
- 15.334	- 15.209						

K_2				
A'_1	A'_2	A''_2	E'	E''
+ 1.215	- 11.308	+ 48.986	- 2.985	+ 2.389
- 5.533		- 0.315	- 6.779	- 5.946
- 9.465		- 8.483	- 8.760	- 9.207
- 12.745		- 11.961	- 11.784	- 12.312
- 15.194		- 14.924	- 12.365	- 14.679
			- 14.679	

Table II

K_1		K_2	
7 633	26 859	5 688	24 399
13 353	27 214	5 842	26 311
17 420	38 090	7 923	36 541
20 647	39 172	19 590	40 382
25 835	46 336	20 558	47 103
25 875	46 465	21 672	48 531

Table III

atom	orbital	K_1	K_2
Co	$3d_{xy}$	1.2258	0.9688
	$3d_{xz}$	0.6419	0.7988
	$3d_{yz}$	1.9939	0.7988
	$3d_{x^2-y^2}$	0.7952	0.9688
	$3d_{z^2}$	0.8305	0.9057
	$4s$	0.5541	0.7610
	$4p_x$	0.1560	0.1679
	$4p_y$	0.2257	0.1679
	$4p_z$	0.1785	0.2638
O	$2p_x$	1.4997	1.5513
	$2p_y$	1.4997	1.5513
	$2p_z$	1.6935	1.6525
N	$2p_z$	1.6866	1.6885

The orbital populations [3] of the complexes are also similar in the two calculations (Table III.) and the resultant electron configurations of Co atoms according to the present calculations are

$$(3d)^{5.5} (4s)^{0.6} (4p)^{0.6} \text{ for } K_1 \text{ and } (3d)^{4.4} (4s)^{0.8} (4p)^{0.6} \text{ for } K_2.$$

The calculation shows that we obtain reasonable results for polinuclear complex compounds if we disregard the interactions between the ligands of the complexes.

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References

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ПОЛУЭМПИРИЧЕСКИЕ ВЫЧИСЛЕНИЯ НА ДВУХЪЯДЕРНЫХ КОМПЛЕКСАХ КОБАЛЬТА МЕТОДОМ МОЛЕКУЛЯРНЫХ ОРБИТ II.

В. Мараз

В данной работе рассчитаны энергии, молекулярные орбиты, орбитальные популяции и электронные переходы с помощью метода ЛКАО-МО с использованием полуэмпирической формулы Вольфсберга — Гельмгольца.