

LFMO TREATMENT OF BINUCLEAR COBALT COMPLEXES

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In this paper the energy levels and electron transitions of the $[(\text{NH}_3)_4\text{Co}(\text{OH})_2\text{Co}(\text{NH}_3)_4]^{4+}$ and $[(\text{NH}_3)_3\text{Co}(\text{OH})_3\text{Co}(\text{NH}_3)_3]^{3+}$ binuclear complex ions are calculated by the LFMO method (ligand field method combined with LCAO-MO method).

Introduction

As well known, the ligand field (LF) method (BETHE [1], VAN VLECK [2]) is a fairly good approximation for the interpretation of some important properties of complex compounds having only one central metal ion. As known, this method treats the ligands as point charges or point electric dipoles and considers the electrons of the central metal ions as if they were subjected to an electric field originating from the surrounding atoms or molecules.

Since the first application of the LF method [2] many authors dealt with this method and employed it to calculate the electronic structure, transitions, magnetic properties etc. of such complexes, and several excellent books have been published on this topic. (ILSE and HARTMANN [3], BALLHAUSEN [4], JØRGENSEN [5], GRIFFITH [6], ORGEL [7], MOFFITT [8], LIEHR [9], TANABE and SUGANO [10], KISS [11], GILDE and BÁN [12] etc.)

It is evident that the LF method cannot be applied in itself in the case of polynuclear complexes, but the basic idea of the method is applicable in this case, too, if we combine this method with other methods, for example the LCAO-MO method. In the following we call this method LFMO method and we treat the binuclear complex ions $[(\text{NH}_3)_4\text{Co}(\text{OH})_2\text{Co}(\text{NH}_3)_4]^{4+}$ and $[(\text{NH}_3)_3\text{Co}(\text{OH})_3\text{Co}(\text{NH}_3)_3]^{3+}$ (denoted in the following by K_1 and K_2 , respectively) by this method.

Geometries and method of calculation

We assume that the geometry of the complex ions K_1 and K_2 is "bi-octahedral": the two octahedra have in the case of K_1 a common edge and in the case of K_2 a common face, and on the basis of Pauling's ions radii [13] we take the nuclear distance Co—O to be 1.88 Å, Co—N 1.92 Å and Co—Co 2.66 Å for both complexes. The symmetry of these systems is $D_{2h}(K_1)$ and $D_{3h}(K_2)$.

In the present paper we treat these complex ions by the LFMO method: (1) because of the undoubted importance of the bridges we treat the compounds $\text{Co}(\text{OH})_2\text{Co}$ and $\text{Co}(\text{OH})_3\text{Co}$ by the LCAO-MO method (zeroth order problems), (2) then, we take into account the NH_3 molecules as point electric dipoles (having 1.48 Debye dipole moment) setting up an electrostatic field around the central compounds. After K. Jørgensen [5] we call this field "ligand field".

Zeroth order problems

In the LCAO—MO treatment of $\text{Co}(\text{OH})_2\text{Co}$ and $\text{Co}(\text{OH})_3\text{Co}$ we neglect the influences of the H atoms on the compounds and we do not take into account the electrons in the closed shells of Co and O atoms. We take into account only the six valence electrons of the Co ions and the four valence electrons of the OH ions (20 electrons for K_1 and 24 electrons for K_2). For the calculation of MO-s we take into account the five 3d, one 4s and three 4p atomic orbitals of Co atoms and the three 2p orbitals of O atoms and we represent these atomic orbitals by Slater type orbitals.

Table I (K_1)

	Co	O
A_{1g}	$d_{z^2}(1) + d_{z^2}(2)$ $d_{x^2-y^2}(1) + d_{x^2-y^2}(2)$ $s(1) + s(2)$ $p_z(1) + p_z(2)$	$p_x(1) + p_y(1) + p_x(2) + p_y(2)$
A_{1u}	$d_{xy}(1) + d_{xy}(2)$	
B_{1g}	$d_{xy}(1) - d_{xy}(2)$	$p_z(1) + p_z(2)$
B_{1u}	$d_{z^2}(1) - d_{z^2}(2)$ $d_{x^2-y^2}(1) - d_{x^2-y^2}(2)$ $s(1) - s(2)$ $p_z(1) - p_z(2)$	$-p_x(1) + p_y(1) - p_x(2) + p_y(2)$
B_{2g}	$d_{xz}(1) - d_{xz}(2)$ $p_x(1) - p_x(2)$	$-p_x(1) + p_y(1) + p_x(2) - p_y(2)$
B_{2u}	$d_{yz}(1) - d_{yz}(2)$ $p_y(1) - p_y(2)$	$p_z(1) - p_z(2)$
B_{3g}	$d_{yz}(1) + d_{yz}(2)$ $p_y(1) + p_y(2)$	
B_{3u}	$d_{xz}(1) + d_{xz}(2)$ $p_x(1) + p_x(2)$	$p_x(1) + p_y(1) - p_x(2) - p_y(2)$

From these atomic orbitals we can easily construct symmetry adapted functions transforming according to the irreducible representations of D_{2h} and D_{3h} using group theoretical considerations. The reducible representations are

$$\Gamma_1 = 5A_{1g} + 5B_{1u} + 3B_{2g} + 3B_{2u} + 3B_{3u} + 2B_{3g} + 2B_{1g} + A_{1u}$$

$$\Gamma_2 = 5E' + 4E'' + 4A_1' + 4A_2'' + A_2'$$

The symmetry adapted functions are presented in Table I.

Table I (K_2)

	Co	O
A_1'	$d_{z^2}(1) + d_{z^2}(2)$ $s(1) + s(2)$ $p_z(1) + p_z(2)$	$p_x(1) + p_y(1) + p_x(2) +$ $+ p_y(2) + p_x(3) + p_y(3)$
A_2'		$p_z(1) + p_z(2) + p_z(3)$
A_2''	$d_{z^2}(1) - d_{z^2}(2)$ $s(1) - s(2)$ $p_z(1) - p_z(2)$	$p_x(1) + p_x(2) + p_x(3) -$ $- p_y(1) - p_y(2) - p_y(3)$
E'	$d_{x^2-y^2}(1) + d_{x^2-y^2}(2)$ $d_{xz}(1) + d_{xz}(2)$ $p_x(1) + p_x(2)$	$-2p_x(1) - 2p_y(1) + p_x(2) +$ $+ p_y(2) + p_x(3) + p_y(3)$ $p_z(3) - p_z(2)$
	$d_{xy}(1) - d_{xy}(2)$ $d_{yz}(2) - d_{yz}(1)$ $p_y(2) - p_y(1)$	$p_x(2) + p_y(2) - p_x(3) - p_y(3)$ $p_z(2) + p_z(3) - 2p_z(1)$
E''	$d_{xy}(1) + d_{xy}(2)$ $d_{yz}(1) + d_{yz}(2)$ $p_y(1) + p_y(2)$	$p_x(2) + p_y(3) - p_y(2) - p_x(3)$
	$d_{x^2-y^2}(2) - d_{x^2-y^2}(1)$ $d_{xz}(1) - d_{xz}(2)$ $p_x(1) - p_x(2)$	$2p_x(1) - 2p_y(1) -$ $- p_x(2) - p_x(3) + p_y(2) + p_y(3)$

For the secular equations we calculated the group overlap integrals S_{ij} exactly, while the group integrals H_{ij} ($i \neq j$) have been determined by the approximation formula of WOLFSBERG and HELMHOLZ [14]

$$H_{ij} = 0,5KS_{ij}(H_{ii} + H_{jj})$$

where the empirical factor K was chosen to be 2.20 for σ bonds and 2.62 for π bonds [15]. The integrals H_{ii} were substituted by ionization potentials: in the case of Co, for 4s orbitals -7.84 eV, for 4p orbitals -4.08 eV, for 3d orbitals -9.38 eV [16] and in the case of O, for $2p\sigma$ orbitals -11.24 eV and for $2p\pi$ orbitals -10.54 eV [17].

The energy values (in eV) and the LCAO coefficients of the normalized MO-s are summarized in Table II.

Table II (K_1)

symmetry	energy	c_1	c_2	c_3	c_4	c_5
A_{1g}	- 3.425	-0.059 138	-0.043 349	0.284 836	1.052 616	0.398 073
	- 8.208	0.665 666	0.235 770	0.522 180	0.168 007	-0.631 554
	- 9.441	-0.292 055	0.954 304	0.014 894	-0.006 985	0.057 616
	- 9.799	-0.603 264	-0.177 328	0.783 875	-0.048 049	-0.177 026
	-13.040	0.347 462	0.048 320	0.371 078	-0.119 734	0.704 611
A_{1u}	- 9.343	1				
B_{1g}	- 8.550	0.902 097	0.515 110			
	-11.843	-0.439 903	0.861 377			
B_{1u}	+40.640	-0.289 141	-0.086 190	-0.146 637	0.143 289	-0.523 670
	- 5.466	-0.108 230	0.217 003	0.485 199	0.539 337	0.357 385
	- 8.237	-0.500 138	0.741 289	-0.201 041	-0.122 941	0.409 595
	- 9.054	0.837 761	0.519 545	-0.100 773	0.033 479	0.079 291
	-12.449	0.142 542	-0.382 249	-0.160 923	-0.006 404	0.811 277
B_{2g}	+ 2.701	-0.343 684	1.023 286	0.625 703		
	- 8.175	0.873 498	0.298 007	-0.390 963		
	-12.416	0.409 138	-0.130 174	0.799 262		
B_{2u}	- 3.810	-0.075 041	0.987 295	0.468 299		
	- 8.613	0.901 800	0.202 422	-0.459 036		
	-12.432	0.439 406	-0.183 982	0.792 978		
B_{3g}	- 1.899	-0.139 556	0.999 040			
	- 9.124	0.992 223	0.076 800			
B_{3u}	- 5.264	0.148 135	0.995 703	0.014 215		
	- 7.742	0.854 178	-0.113 340	0.671 425		
	-12.230	-0.528 837	0.018 591	0.762 123		

Table II (K_2)

symmetry	energy	c_1	c_2	c_3	c_4	c_5
A'_1	- 2.470	-0.155 695	0.167 135	0.102 850	0.573 758	
	- 7.467	0.612 587	0.618 890	0.329 762	-0.617 880	
	- 9.763	0.695 179	-0.737 786	0.043 971	0.120 595	
	-13.155	0.375 006	0.394 784	-0.128 670	0.644 253	
A'_2	-11.308	1				
A'_2	+47.702	0.290 326	1.559 748	-1.492 805	-0.650 839	
	- 5.394	-0.121 404	0.491 707	0.561 751	-0.329 839	
	- 8.730	0.962 781	0.056 223	0.094 860	0.224 506	
	-12.121	-0.214 054	0.229 541	0.010 192	0.875 835	
E'	- 4.082	-0.127 224	-0.043 830	0.980 326	0.070 714	0.435 881
	- 7.772	0.150 743	0.861 337	0.162 714	-0.508 971	-0.331 774
	- 8.942	0.920 663	-0.178 292	0.155 195	0.267 924	-0.264 276
	-11.957	0.318 428	-0.121 420	-0.125 037	-0.629 115	0.623 291
	-12.491	0.137 834	0.487 715	-0.112 449	0.541 911	0.537 618
E''	+ 1.622	-0.147 161	-0.307 561	1.003 708	-0.570 871	
	- 7.856	0.544 901	0.663 596	0.304 040	0.455 551	
	- 9.250	0.775 610	-0.627 044	-0.031 295	0.044 362	
	-12.554	-0.306 432	-0.328 974	0.106 686	0.782 210	

Ligand field potentials.

The electrostatic potential of the ligand fields can be written in the form

$$\Phi(\vec{r}) = - \sum_{i=1}^n \bar{p}_i \text{grad} |\vec{r} - \vec{r}_i|^{-1},$$

where n is the number of the point dipoles, \vec{r}_i and \bar{p}_i is the position vector and the dipole moment of the i -th dipole. By means of the well known formula [18]

$$\frac{1}{r_{12}} = \sum_{l=0}^{\infty} \sum_{m=-l}^l \frac{4\pi}{2l+1} \frac{r_{<}^l}{r_{>}^{l+1}} Y_{lm}(\vartheta_1, \varphi_1) Y_{lm}^*(\vartheta_2, \varphi_2),$$

where $r_{<}$ is the lower and $r_{>}$ is the higher of r_1 and r_2 , the ligand field potentials can be expressed in terms of spherical harmonics. Because of the approximations applied in the calculations it will be convenient to expand Φ in the form

$$\Phi = - \sum_{l=0}^{\infty} \sum_{m=-l}^l \frac{4\pi}{2l+1} \left\{ \sum_{(1)} \bar{p}_i \text{grad} \left[\frac{r_{<}^l}{r_{>}^{l+1}} Y_{lm}(\vartheta, \varphi) Y_{lm}^*(\vartheta_i, \varphi_i) \right] + \sum_{(2)} \bar{p}_j \text{grad} \left[\frac{r_{<}^l}{r_{>}^{l+1}} Y_{lm}(\vartheta', \varphi') Y_{lm}^*(\vartheta_j', \varphi_j') \right] \right\},$$

where the first summation is extended over the dipoles near Co_1 , the second is extended over the dipoles near Co_2 and $\{r, \vartheta, \varphi\}$; $\{r_i, \vartheta_i, \varphi_i\}$ are coordinates referred to Co_1 as origin and $\{r', \vartheta', \varphi'\}$, $\{r_j', \vartheta_j', \varphi_j'\}$ are coordinates referred to Co_2 as origin. As the dipoles are all directed radially toward the corresponding central ion and all dipoles have the same extent (p) of dipole moment both members of the expression of Φ can be written in the form

$$\tilde{\Phi} = - \sum_{l=0}^{\infty} \sum_{m=-l}^l R_{lm}^<(r) Y_{lm}(\vartheta, \varphi)$$

where

$$R_{lm}^<(r) = \begin{cases} \frac{4\pi}{2l+1} l p r^{l-1} \sum_i r_i^{-l-1} Y_{lm}^*(\vartheta_i, \varphi_i) & \text{if } 0 \leq r \leq r_i \\ -\frac{4\pi}{2l+1} (l+1) p r^{-l-2} \sum_i r_i^l Y_{lm}^*(\vartheta_i, \varphi_i) & \text{if } r_i \leq r \leq \infty \end{cases}$$

In the case of K_1 and K_2 $r_i = r_0 = 1.92 \text{ \AA}$, and $\vartheta_1 = \vartheta_2 = 45^\circ$, $\vartheta_5 = \vartheta_6 = 90^\circ$, $\varphi_1 = 0$, $\varphi_2 = 180^\circ$, $\varphi_5 = -\varphi_6 = 90^\circ$ for K_1 , and $\vartheta_1 = \vartheta_2 = \vartheta_3 = 45^\circ$, $\varphi_1 = 180^\circ$, $\varphi_2 = -\varphi_3 = 60^\circ$ for K_2 . The potential energy of an electron in the ligand field is of course $V = -e\Phi$.

Energy levels and transitions

According to the perturbation theory, for the calculation of the energy levels in first order the matrix elements $\langle \psi | V | \psi \rangle$ must be calculated with the zeroth order MO-s. As these MO-s are built up from Co and O atomic orbitals, these matrix elements are multicentre integrals. In the calculations we neglected all the two- and

three-centre integrals and took into account only the single-centre integrals. (For this reason the potential Φ has been written in two terms.) With this approximation we get the values for the first order energies (in eV) summarized in Table III. The wavenumbers (in cm^{-1}) of the allowed electron transitions are presented in Table IV.

Table III*

K_1		K_2	
-5.787	-9.415	-2.104	-11.308
-6.194	-9.441	-2.220	-11.533
-6.828	-11.862	-6.592	-11.897
-7.190	-12.111	-7.368	-12.465
-7.798	-12.243	-7.769	-12.498
-8.315	-12.250	-8.182	-12.979
-8.629	-12.319	-9.038	
-8.830	-12.604	-9.420	
-9.111			

* In this table only the negative energies are summarized.

Table IV

K_1		K_2	
10 588	32 784	9 993	36 539
13 043	34 607	10 240	37 892
15 495	36 472	13 474	38 703
16 150	38 776	16 559	39 867
17 950	41 379	19 738	41 127
21 083	42 628	22 823	41 394
21 267	43 683	30 369	42 802
24 550	43 748	31 778	45 269
28 614	47 745	33 304	47 390
29 156	48 804	34 828	47 657
29 217	48 865		

Comparing these results with other calculations [19] and the experimental absorption spectra of the complexes [20] we can say that the results of the transitions are acceptable and they reproduce the main electronic bands of the complexes fairly well. However, this method is in consequence of his nature, incapable to reproduce many other properties, as for example the charge transfer states. These other properties can be interpreted with other methods as for example with the extended Wolfsberg—Helmholz method [21].

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ИССЛЕДОВАНИЯ ДВУХЪЯДЕРНЫХ КОМПЛЕКСОВ КОБАЛЬТА МЕТОДОМ ЛПМО

В. Мараз

В данной работе рассчитаны энергии состояний и электронных переходов двухъядерных комплексных молекул $[(\text{NH}_3)_4\text{Co}(\text{OH})_2\text{Co}(\text{NH}_3)_4]^{4+}$ и $[(\text{NH}_3)_5\text{Co}(\text{OH})_2\text{Co}(\text{NH}_3)_3]^{3+}$ с помощью метода ЛПМО (метод лигандного поля с ЛКАМО).