

# SEMI-EMPIRICAL MOLECULAR ORBITAL CALCULATIONS OF BINUCLEAR COBALT COMPLEXES

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In this paper the energy levels, molecular orbitals, orbital and bond overlap 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 HELMHOLTZ.

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  $[(\text{NH}_3)_3\text{Co}(\text{OH})_3\text{Co}(\text{NH}_3)_3]^{3+}$  ( $K_2$ ) are theoretically investigated by a simple semiempirical LCAO-MO method. In these complexes the central cobalt ions are surrounded by ligands of approximately "bi-octahedral" symmetry ( $D_{2h}$  and  $D_{3h}$ ). The two octahedra have in the case of  $K_1$  a common edge and in the case of  $K_2$  a common face. The Co ions are in the centres of the octahedra, the OH ions are along the common edge ( $K_1$ ) and along the common face ( $K_2$ ), and the  $\text{NH}_3$  molecules are on the other vertices of the octahedra. If we disregard the distortions of the octahedra on the basis of Pauling's ions radii [1] we obtain 1,88 Å, 1,92 Å and 2,66 Å for the bond distances of Co-O, Co-N and Co-Co bonds, respectively.

## Computational details

In the calculations we neglect the influences of the H atoms on the complex compounds and we do not take into account the electrons in the closed shells of Co, O and N atoms, taking into account only the six valence electrons of the Co ions, the four valence electrons of the OH ions and the two valence electrons of the  $\text{NH}_3$  molecules (36 electrons for each of both complexes). For the LCAO-MO treatment of complex ions we take into account the five  $3d$ , one  $4s$  and three  $4p$  atomic orbitals of Co atoms, the three  $2p$  orbitals of O atoms and one  $2p$  orbital of N atoms. The  $2p$  and  $3d$  atomic orbitals are represented by SLATER type orbitals, and the radial wave function of  $4s$ ,  $4p$  orbitals is approximated by

$$\psi_{\text{approx}} = \sum_{k=1}^4 c_k r^k e^{-\alpha r}$$

where  $\alpha=2.60$  and

$$c_1 = -0.047\ 530\ 507$$

$$c_2 = 0.360\ 145\ 640$$

$$c_3 = 0.728\ 294\ 860$$

$$c_4 = -0.041\ 616\ 865$$

The coefficients  $c_k$  are calculated from the equation

$$\int (\psi - \psi_{\text{approx}})^2 d\tau = \min.$$

where  $\psi$  is a SLATER type  $4s$ ,  $4p$  radial wave function.

The energy levels and molecular orbitals have been calculated by means of group theoretical considerations, which give

$$\Gamma_1 = 7A_{1g} + 7B_{1u} + 4B_{2g} + 4B_{3u} + 4B_{2u} + 3B_{3g} + 2B_{1g} + A_{1u}$$

$$\Gamma_2 = 6E' + 5E'' + 5A'_1 + 5A'_2 + A'_2$$

reducible representations for the complexes. The bases of the irreducible representations are presented in Table I.

The group overlap integrals  $S_{ij}$  have been calculated exactly, the group integrals

Table I ( $K_1$ )

	Co	O	N
$A_{1g}$	$d_{z^2}(1) + d_{z^2}(2)$ $d_{x^2-y^2}(1) + d_{x^2-y^2}(2)$ $s(1) + s(2)$ $p_z(1) + p_z(2)$	$p_x(1) + p_y(1) + p_x(2) + p_y(2)$	$p_z(1) + p_z(2) + p_z(3) + p_z(4)$ $p_z(5) + p_z(6) + p_z(7) + p_z(8)$
$A_{1u}$	$d_{xy}(1) + d_{xy}(2)$		
$B_{1g}$	$d_{xy}(1) - d_{xy}(2)$	$p_z(1) + p_z(2)$	
$B_{1u}$	$d_{z^2}(1) - d_{z^2}(2)$ $d_{x^2-y^2}(1) - d_{x^2-y^2}(2)$ $s(1) - s(2)$ $p_z(1) - p_z(2)$	$-p_x(1) + p_y(1) - p_x(2) + p_y(2)$	$p_z(1) + p_z(2) - p_z(3) - p_z(4)$ $p_z(5) + p_z(6) - p_z(7) - p_z(8)$
$B_{2g}$	$d_{xz}(1) - d_{xz}(2)$ $p_x(1) - p_x(2)$	$-p_x(1) + p_y(1) + p_x(2) - p_y(2)$	$p_z(1) - p_z(2) + p_z(3) - p_z(4)$
$B_{2u}$	$d_{yz}(1) - d_{yz}(2)$ $p_y(1) - p_y(2)$	$p_z(1) - p_z(2)$	$p_z(5) - p_z(6) - p_z(7) + p_z(8)$
$B_{3g}$	$d_{yz}(1) + d_{yz}(2)$ $p_y(1) + p_y(2)$		$p_z(5) - p_z(6) + p_z(7) - p_z(8)$
$B_{3u}$	$d_{xz}(1) + d_{xz}(2)$ $p_x(1) + p_x(2)$	$p_x(1) + p_y(1) - p_x(2) - p_y(2)$	$p_z(1) - p_z(2) - p_z(3) + p_z(4)$

Table I ( $K_2$ )

	Co	O	N
$A'_1$	$d_{z^2}(1)+d_{z^2}(2)$ $s(1)+s(2)$ $p_z(1)+p_z(2)$	$p_x(1)+p_y(1)+p_x(2)+$ $+p_y(2)+p_x(3)+p_y(3)$	$p_z(1)+p_z(2)+p_z(3)+$ $+p_z(4)+p_z(5)+p_z(6)$
$A'_2$		$p_z(1)+p_z(2)+p_z(3)$	
$A''_2$	$d_{z^2}(1)-d_{z^2}(2)$ $s(1)-s(2)$ $p_z(1)-p_z(2)$	$p_x(1)+p_x(2)+p_x(3)-$ $-p_y(1)-p_y(2)-p_y(3)$	$p_z(1)+p_z(2)+p_z(3)-$ $-p_z(4)-p_z(5)-p_z(6)$
$E'$	$d_{x^2-y^2}(1)+d_{x^2-y^2}(2)$ $d_{xz}(1)+d_{xz}(2)$ $p_x(1)+p_x(2)$	$-2p_x(1)-2p_y(1)+p_x(2)+$ $+p_y(2)+p_x(3)+p_y(3)$ $p_x(3)-p_z(2)$	$p_z(2)+p_z(3)+p_z(5)+$ $+p_z(6)-2p_z(1)-2p_z(4)$
	$d_{xy}(1)-d_{xy}(2)$ $d_{yz}(2)-d_{yz}(1)$ $p_y(2)-p_y(1)$	$p_x(2)+p_y(2)-p_x(3)-p_y(3)$ $p_z(2)+p_z(3)-2p_z(1)$	$p_z(3)+p_z(6)-p_z(2)-p_z(5)$
$E''$	$d_{xy}(1)+d_{xy}(2)$ $d_{yz}(1)+d_{yz}(2)$ $p_y(1)+p_y(2)$	$p_x(2)+p_y(3)-p_y(2)-p_x(3)$	$p_z(2)+p_z(6)-p_z(3)-p_z(5)$
	$d_{x^2-y^2}(2)-d_{x^2-y^2}(1)$ $d_{xz}(1)-d_{xz}(2)$ $p_x(1)-p_x(2)$	$2p_x(1)-2p_y(1)-$ $-p_x(2)-p_x(3)+p_y(2)+p_y(3)$	$p_z(2)+p_z(3)-p_z(5)-$ $-p_z(6)-2p_z(1)+2p_z(4)$

$H_{ij}$  ( $i \neq j$ ) have been determined by the approximation formula of WOLFSBERG and HELMHOLTZ [2]

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

where the empirical factor  $F_x$  was chosen to be 2.20 for  $\sigma$  bonds and 2.62 for  $\pi$  bonds [3]. The integrals  $H_{ii}$  were substituted by the ionization potentials: in the case of Co ions for 4s orbitals -7.84 eV, for 4p orbitals -4.08 eV, for 3d orbitals -9.38 eV [4], in the case of  $\text{NH}_3$  molecules for 2p orbitals -13.81 eV and in the case of OH for 2p $\sigma$  orbitals -11.24 eV and for 2p $\pi$  orbitals -10.54 eV [5], respectively.

### Results and discussion

The energy values of the MO's are summarized in Table II. The 36 electrons occupy these energy levels according to Pauli's principle. In the ground state of the complexes the highest filled MO of  $K_1$  is  $2b_{2u}$  (-8.357 eV), that of  $K_2$  is  $3e''$  (-9.208 eV). The lowest empty MO's are  $1b_{1g}$  and  $3e'$ , respectively. On the basis

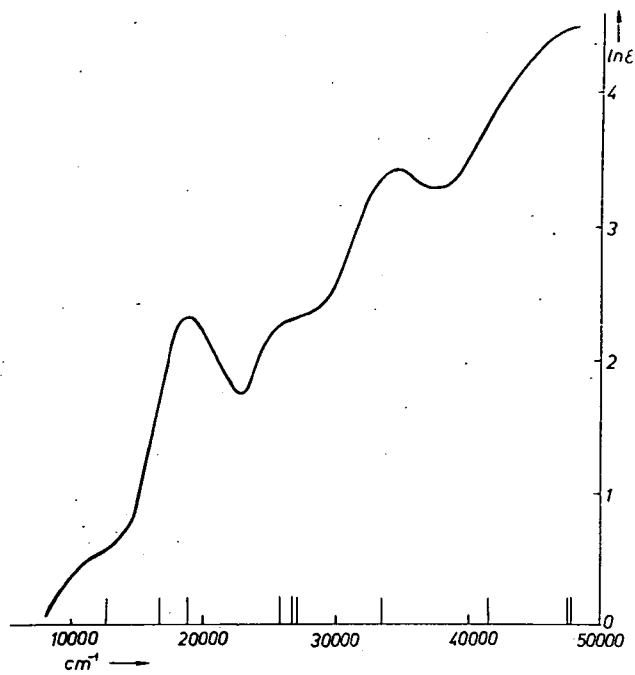


Fig. 1

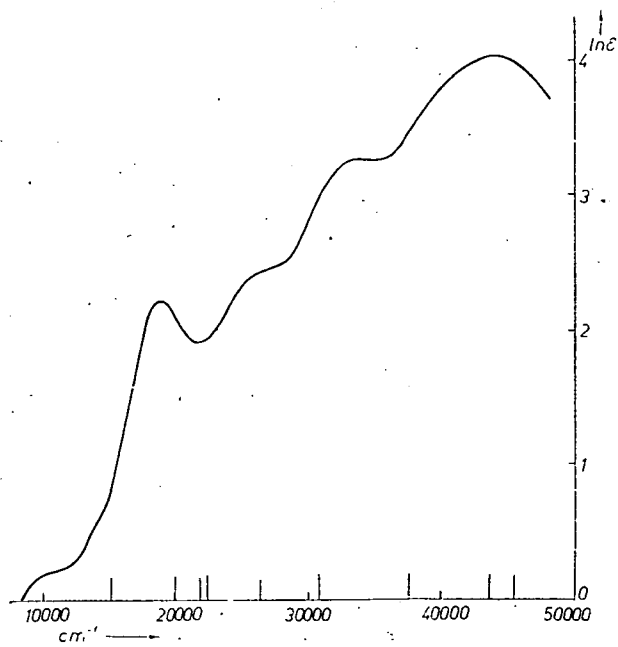


Fig. 2

of Bohr's frequency rule the allowed electron transitions can be easily calculated with respect to the selection rules summarized in Table III. The most important transitions (in  $\text{cm}^{-1}$ ) are given in Table IV, and are indicated in Figs. 1 and 2, which show the experimental absorption spectra of the complexes [6]. The figures show that the agreement between the experimental and theoretical results is fairly good.

Table II

$K_1$							
$A_{1g}$	$B_{1u}$	$B_{2g}$	$B_{3u}$	$B_{2u}$	$B_{3g}$	$B_{1g}$	$A_{1u}$
-0.259	+59.168	+3.940	-3.373	-1.561	+1.881	-8.344	-9.343
-6.004	-1.417	-6.021	-7.211	-8.357	-9.110	-11.374	
-6.766	-5.905	-12.264	-11.919	-11.927	-14.136		
-9.275	-8.328	-14.718	-14.754	-14.107			
-12.622	-12.160						
-14.883	-14.794						
-15.331	-15.207						

$K_2$				
$A'_1$	$A'_2$	$A''_2$	$E'$	$E''$
+1.158	-10.54	+49.096	-2.886	+2.375
-5.772		-0.315	-6.723	-5.953
-9.470		-8.472	-8.670	-9.208
-12.881		-11.920	-11.368	-12.328
-15.199		-14.923	-12.185	-14.679
			-14.678	

Table III

$K_1$		
$A_{1g} \leftrightarrow B_{1u}$	$A_{1u} \leftrightarrow B_{2g}$	$B_{1g} \leftrightarrow B_{2u}$
$A_{1g} \leftrightarrow B_{2u}$	$A_{1u} \leftrightarrow B_{3g}$	$B_{2u} \leftrightarrow B_{3g}$
$A_{1g} \leftrightarrow B_{3u}$	$B_{2g} \leftrightarrow B_{3u}$	$B_{1u} \leftrightarrow B_{3g}$
$A_{1u} \leftrightarrow B_{1g}$	$B_{1g} \leftrightarrow B_{3u}$	$B_{1u} \leftrightarrow B_{2g}$

$K_2$		
$A'_1 \leftrightarrow A''_2$	$E' \leftrightarrow E'$	$A'_2 \leftrightarrow E'$
$A'_1 \leftrightarrow E'$	$E' \leftrightarrow E''$	$A''_2 \leftrightarrow E''$
	$E'' \leftrightarrow E''$	

Table IV

$K_1$		$K_2$	
7 641	27 190	5 938	22 164
12 840	33 588	6 455	26 262
16 653	41 572	8 052	30 797
18 988	47 583	15 088	37 477
25 857	47 616	20 050	43 690
26 803	47 720	21 768	45 150

Table V ( $K_1$ )

MO	energy (eV)	Co			O	N
		3d	4s	4p	2p	2p
1b <sub>3u</sub>	-3.373	22	0	38	10	30
3b <sub>1u</sub>	-5.905	44	1	3	16	36
2a <sub>1g</sub>	-6.004	41	12	7	2	38
2b <sub>2g</sub>	-6.021	40	0	7	24	30
3a <sub>1g</sub>	-6.766	21	18	7	33	20
2b <sub>3u</sub>	-7.211	34	0	18	34	14
4b <sub>1u</sub>	-8.328	57	4	2	25	12
1b <sub>1g</sub>	-8.344	59	0	0	41	0
2b <sub>2u</sub>	-8.357	50	0	10	32	8
2b <sub>3g</sub>	-9.110	89	0	5	0	6
4a <sub>1g</sub>	-9.275	62	9	7	12	10
a <sub>1u</sub>	-9.343	100	0	0	0	0
2b <sub>1g</sub>	-11.374	39	0	0	60	0
3b <sub>2u</sub>	-11.919	15	0	4	58	24
3b <sub>2u</sub>	-11.928	32	0	8	45	14
5b <sub>1u</sub>	-12.160	23	5	3	51	18
3b <sub>2g</sub>	-12.264	14	0	11	60	16
5a <sub>1g</sub>	-12.622	18	7	8	48	20
4b <sub>2u</sub>	-14.107	2	0	10	4	84
3b <sub>3g</sub>	-14.136	0	0	12	0	88
4b <sub>2g</sub>	-14.718	19	0	5	8	68
4b <sub>3u</sub>	-14.753	20	0	4	11	66
6b <sub>1u</sub>	-14.794	15	9	4	8	64
6a <sub>1g</sub>	-14.883	19	7	2	7	66
7b <sub>1u</sub>	-15.207	19	12	0	1	68
7a <sub>1g</sub>	-15.331	12	15	2	3	68

In Table V the atomic orbital percentage of occupied and of some empty molecular orbitals are listed, and in Table VI the total gross populations on atoms [7] are summarized. Table VII shows the subtotal overlap populations between atoms.

According to these results the first and the second bands arise from Co-O bonding orbitals 2b<sub>2u</sub>, 2b<sub>3g</sub>, 3e'' in both complexes and the remaining two bands are assigned according to our calculations to the MO's 2b<sub>1g</sub>, 3b<sub>3u</sub>, 4a<sub>1g</sub>, a'<sub>2</sub>, 4e' respectively, which are mainly of Co-O bonding character and correlate with O orbitals in origin. The orbital and bond overlap populations are similar in both complexes, but in the case of K<sub>1</sub> the orbital population on Co 3d orbital is higher than in the case of K<sub>2</sub> and the overlap population between Co atoms in the case of K<sub>1</sub> is less than that of K<sub>2</sub>. The electron charge densities on Co atoms are also higher in K<sub>1</sub> than in K<sub>2</sub>. According to our calculations, the resultant electron configurations of Co atoms are

$$(3d)^{5.5}(4s)^{0.6}(4p)^{0.6} \text{ for } K_1 \text{ and } (3d)^{4.6}(4s)^{0.8}(4p)^{0.6} \text{ for } K_2.$$

\* \* \*

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Table V ( $K_2$ )

MO	energy (eV)	Co			O	N
		3d	4s	4p	2p	2p
$2a_1'$	-5.772	16	17	6	41	20
$7e''$	-5.953	43	0	7	24	26
$2e''$	-5.953	46	0	7	22	24
$8e'$	-6.723	25	0	5	42	18
$2e'$	-6.723	34	0	4	42	20
$3a_2'$	-8.472	52	4	1	31	12
$9e'$	-8.670	48	0	13	30	8
$3e'$	-8.670	49	0	13	29	10
$3e''$	-9.208	84	0	1	10	6
$8e''$	-9.208	82	0	1	11	6
$3a_1'$	-9.470	44	26	10	6	14
$a_2'$	-11.24	0	0	0	100	0
$4e'$	-11.368	13	0	4	70	14
$10e'$	-11.368	13	0	4	71	12
$4a_2'$	-11.920	12	8	2	64	14
$5e'$	-12.185	24	0	6	56	14
$11e'$	-12.185	25	0	6	56	12
$4e''$	-12.328	20	0	9	53	18
$9e''$	-12.328	19	0	8	55	18
$4a_1'$	-12.881	14	5	8	50	22
$6e'$	-14.678	22	0	3	10	66
$12e'$	-14.678	24	0	3	10	62
$5e''$	-14.679	24	0	4	10	62
$10e''$	-14.679	22	0	4	10	64
$5a_2'$	-14.923	4	13	5	14	70
$5a_1'$	-15.199	7	16	4	12	62

Table VI

	Co	O	N
$K_1$	6.673	4.574	1.688 and 1.692
$K_2$	5.906	4.684	1.689

Table VII

	Co-Co	Co-O	Co-N
$K_1$	0.178	0.387	0.277 and 0.278
$K_2$	0.327	0.369	0.273

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ПОЛУЭМПИРИЧЕСКИЕ ВЫЧИСЛЕНИЯ НА ДВУЯДЕРНЫХ КОМПЛЕКСАХ  
КОБАЛТА МЕТОДОМ МОЛЕКУЛЯРНЫХ ОРБИТ

*В. Мараз*

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