THEORETICAL TREATMENT OF BINUCLEAR COMPLEX COMPOUNDS

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The energy levels and transitions of the $[(NH_3)_4Co(OH)_2Co(NH_3)_4]^{4-}$ and of the $[(NH_3)_3Co(OH)_3Co(NH_3)_3]^{3-}$ binuclear complex ions are calculated by the LCAO-MO method using the half-empirical approximation of WOLFSBERG and HELMHOLTZ.

The theory of complex compounds has been developed by several authors [1—3] and more recently in [4]. A distinguished group of complexes is represented by the complexes having two or several ions in their centres. In the Institute of General and Physical Chemistry of the University of Szeged the binuclear complex compounds were investigated, hence, their theoretical treatment had to be developed as well.

As a matter of fact, in this paper the binuclear complex compounds $[(NH_3)_4Co(OH)_2Co(NH_3)_4]^{4-}$ (denoted by K_1) and $[NH_3)_3Co(OH)_3Co(NH_3)_3]^{3-}$ (in the following K_2) are theoretically investigated in detail. The central ions are surrounded by ligands with bi-octahedral symmetry. The two octahedra have in the case of K_1 a common edge and in the case of K_2 a common face. In fact, the common edges and faces are somewhat contracted, nevertheless, the bi-octahedral symmetry is not disturbed in this way. The Co ions are in the centres of the octahedra the OH ion along the common edge and along the common face, respectively, furthermore, the NH_3 molecules are on the other vertices of the octahedra (Fig. 1 and Fig. 2).

The direction of the atomic orbitals of the ligands are denoted on the figures by vectors and the different atoms are labelled by arabic numerals. The ligands may be regarded as electric dipols where owing to the electrostatic attraction of the positive charged central ions the centre of negative charges, *i. e.* the O and N atoms, is nearer to the Co ions than the centre of the positive charges.

For the sake of simplicity, let us suppose that (*i*) the H atoms of the ligands do not take part in the formation of the complex, therefore, their influences can be neglected; (*ii*) this is the reason that also the electrons in the closed shells of the Co atoms are not taken into consideration at the fornation of molecular orbitals (MO-s). In fact, we take into account: five $3d$, one $4s$ and three $4p$ atomic orbitals of the Co atoms, the three $2p$ orbitals of the OH ions and O atoms, respectively, finally, the $2p\sigma$ orbitals of the N atoms of the ammonia molecules along the N-Co bounding axes. Owing to the supposition (*i*) the $2p\pi$ orbitals of N atoms can be

neglected. In the course of the calculation we have observed that in the case of K_1 the $2p\pi$ orbitals of the O atoms which are orthogonal to the Co-O bounding axes do not take port in the bounding, therefore, these atomic orbitals as well as the corresponding two electrons can also be neglected. As a matter of fact, we have
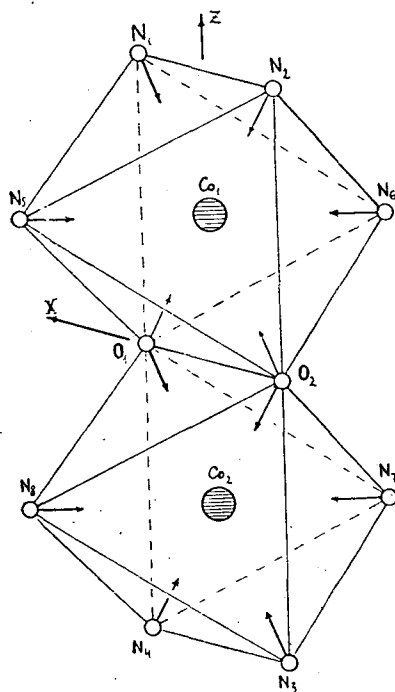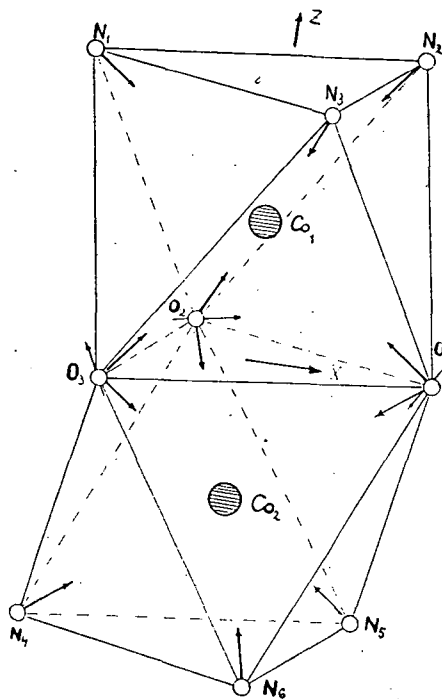

Fig. 1   Fig. 2

in the case of K_1 30 atomic orbitals and 36 electrons and in the case of K_2 33 atomic orbitals and 42 electrons, respectively.

The energies of the electrons are calculated by means of the LCAO-MO method, for the extensive simplification of which group theoretical considerations are used [5]. The 30 and 33 atomic orbitals, respectively, mentioned above span the reducible representations of the groups considered. Using the character systems of the groups [6, 7] the reducible representations have the form:

(K_1) $\qquad \Gamma_1 = 7A_{1g} + 7B_{1u} + 4B_{2g} + 4B_{3u} + 3B_{2u} + 3B_{3g} + B_{1g} + A_{1u},$

(K_2) $\qquad\qquad \Gamma_2 = 6E' + 5E'' + 5A_1' + 5A_2'' + A_2'.$

The new basic functions spanning the irreducible subspaces can be found in Table I (K$_1$) and in Table II (K$_2$).

The secular equation having originally the form $|H_{ij} - ES_{ij}| = 0$ may be broken up into products corresponding in the case of K_1 to the decomposition (K_1)

and in the case of K_2 to the decomposition (K_2), respectively. For the calculation of the overlap integrals S_{ik} an approximation method [4] was used; in the case of Co-O bound the nuclear distance 1,88 Å, and in the case Co-N bound the nuclear distance 1,92 Å was taken into account [8]. The integrals of type H_{ii} were substituted by the ionisation potentials: in the case of the Co atom for $4s$ orbitals $-7{,}84$ eV, for $4p$ orbitals $-4{,}08$ eV, for $3d$ orbitals $-9{,}38$ eV [9], in the case of N for $2p\sigma$ orbitals $-13{,}81$ eV and in the case of O for $2p\sigma$ orbitals $-11{,}24$ eV [10], respectively. The integrals H_{ij} $(i \neq j)$ were determined by the approximation formula of WOLFSBERG and HELMHOLTZ [3]:

$$H_{ij} = F_x S_{ij} \frac{H_{ii} + H_{jj}}{2}$$

where the empirical factor F_x was chosen as 2,20 for σ bounds and 2,65 for π bounds [4]. The energy values are summarized in Table III.

Owing to PAULI's principle the electrons occupy the lowest energy levels, then due to the selection rules, summarized in Table IV, the allowed transitions in Table V can be calculated without any difficulties. The results obtained are in good agreement with those of the experiments [11].

Table I. (K_1)

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

Table II. (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'	$d_{x^2-y^2}(1) + d_{x^2-y^2}(2)$ $d_{xz}(1) + d_{xz}(2)$ $p_x(1) + p_x(2)$	$2p_x(1) + 2p_y(1) - p_x(2) -$ $- p_y(2) - p_x(3) - p_y(3)$ $p_z(2) - p_z(3)$	$2p_z(1) + 2p_z(4) - p_z(2) -$ $- p_z(3) - p_z(5) - p_z(6)$
	$d_{xy}(1) - d_{xy}(2)$ $d_{yz}(2) - d_{yz}(1)$ $p_y(2) - p_y(1)$	$p_x(2) + p_y(2) - p_x(3) - p_y(3)$ $p_z(2) + p_z(3) - 2p_z(1)$	$p_z(3) + p_z(6) - p_z(2) - p_z(5)$
E''	$d_{xy}(1) + d_{xy}(2)$ $d_{yz}(1) + d_{yz}(2)$ $p_y(1) + p_y(2)$	$p_x(2) + p_y(3) - p_y(2) - p_x(3)$	$p_z(2) + p_z(6) - p_z(3) - p_z(5)$
	$d_{x^2-y^2}(2) - d_{x^2-y^2}(1)$ $d_{xz}(1) - d_{xz}(2)$ $p_x(1) - p_x(2)$	$2p_y(1) - 2p_x(1) + p_x(2) +$ $+ p_x(3) - p_y(2) - p_y(3)$	$2p_z(1) - 2p_z(4) + p_z(5) +$ $+ p_z(6) - p_z(2) - p_z(3)$

Table III.

K_1							
A_{1g}	B_{1u}	B_{2g}	B_{3u}	B_{2u}	B_{3g}	B_{1g}	A_{1u}
$-\ 3{,}702$	$+\ 8{,}070$	$-\ 0{,}794$	$-\ 3{,}892$	$-\ 4{,}135$	$-\ 4{,}034$	$-9{,}38$	$-9{,}38$
$-\ 6{,}787$	$-\ 3{,}960$	$-\ 8{,}442$	$-\ 8{,}085$	$-\ 9{,}380$	$-\ 9{,}380$		
$-\ 8{,}813$	$-\ 7{,}862$	$-12{,}274$	$-11{,}569$	$-13{,}811$	$-13{,}811$		
$-\ 9{,}806$	$-\ 8{,}466$	$-14{,}197$	$-14{,}187$				
$-11{,}353$	$-11{,}261$						
$-13{,}977$	$-14{,}126$						
$-14{,}669$	$-16{,}769$						

K_2				
A_1'	A_2'	A_2''	E'	E''
$-\ 4{,}299$	$-10{,}54$	$+\ 8{,}001$	$-\ 4{,}113$	$-\ 3{,}987$
$-\ 8{,}295$		$-\ 6{,}063$	$-\ 9{,}086$	$-\ 9{,}084$
$-\ 9{,}616$		$-\ 9{,}467$	$-\ 9{,}38$	$-\ 9{,}38$
$-12{,}603$		$-11{,}402$	$-10{,}494$	$-11{,}622$
$-14{,}576$		$-14{,}725$	$-11{,}329$	$-14{,}121$
			$-14{,}079$	

Table IV.

$A_{1g} \longleftrightarrow B_{1u}$	$A_{1u} \longleftrightarrow B_{2g}$	$B_{1g} \longleftrightarrow B_{2u}$
$A_{1g} \longleftrightarrow B_{2u}$	$A_{1u} \longleftrightarrow B_{3g}$	$B_{2u} \longleftrightarrow B_{3g}$
$A_{1g} \longleftrightarrow B_{3u}$	$B_{2g} \longleftrightarrow B_{3u}$	$B_{1u} \longleftrightarrow B_{3g}$
$A_{1u} \longleftrightarrow B_{1g}$	$B_{1g} \longleftrightarrow B_{3u}$	$B_{1u} \longleftrightarrow B_{2g}$

K₂

$A_1' \longleftrightarrow A_2'$	$A_2' \longleftrightarrow E'$	$E' \longleftrightarrow E'$
	$A_2'' \longleftrightarrow E''$	
$A_1' \longleftrightarrow E'$	$E'' \longleftrightarrow E''$	$E' \longleftrightarrow E''$

Table V.

K₁

5 817	23 939	40 898	44 940
8 189	26 375	41 568	45 594
8 746	26 948	42 479	46 925
10 376	28 086	42 544	47 417
11 667	28 199	42 568	47 579
12 748	29 296	43 464	48 103
15 983	29 869	44 246	48 668
21 018	32 644	44 432	48 991
21 341	32 757	44 811	49 846
21 913	39 462	44 852	50 475

K₂

|			
8 754	18 113	40 285	44 214
9 456	20 461	40 301	44 295
11 360	20 477	40 624	44 400
11 376	24 479	40 640	44 852
11 731	25 068	40 995	45 513
17 742	26 762	41 697	46 667
17 895	28 376	42 496	49 983
18 097	28 667	43 512	51 484

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ТЕОРЕТИЧЕСКОЕ ИССЛЕДОВАНИЕ ДВУЯДЕРНЫХ КОМПЛЕКСНЫХ ИОНОВ

В. Мараз

Были рассчитаны электронные энергии двуядерных комплексных ионов

$$[(NH_3)_4Co(OH)_2Co(NH_3)_4]^{4-} \quad \text{и} \quad [(NH_3)_3Co(OH)_3Co(NH_3)_3]^{3-}$$
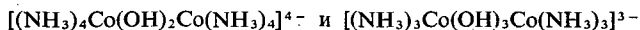
с помощью полуэмпирического метода МО-ЛКАО.