ELECTRONIC STRUCTURE OF Cr (III) HEXACYANIDE COMPLEX ION BY THE LCAO METHOD

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The energy levels and transitions of the Cr(III) hexacyanide complex ion were calculated. Only the 3d, 4s and 4p atomic orbitals of the central Cr^{3+} ion and only the 2p atomic orbitals of the C atoms of the cyanide groups were taken into consideration. By means of the O_h symmetry of the complex ion and the empiric data ($R = 2,00$ A, ionisation energies), the MO method was employed in its LCAO form. We can range the calculated transitions into four groups consisting of transitions close to each other. These groups of transitions are in good agreement with the observed spectrum of the ion the difference being not more than 3 per cent.

§ 1. *Introduction*

The theory of complex compounds was started by the investigations of WERNER [14] and MAGNUS [8]. The further elaboration of the theory was only rendered possible by quantum mechanics. SIDGWICK [11] initiated the first step in this direction by assuming the presence of covalent bonds between the central ion of the complexes and the groups in the coordination zone. As a next step was the determination of the eigenfunctions of valence (concerning different coordination numbers and symmetries) by PAULING [10] and KIMBALL [4] applying the "Valence Structure Theory" of valence eigenfunctions. Afterwards BETHE [1] tried to make use of this theory in his "Crystal Field Theory" for crystals of similar symmetry as well as ILSE and HARTMANN [3] for the calculation of the Ti^{3+} octahedral complexes. ILSE and HARTMANN applied the perturbation method so that their investigation as a foundation of the quantum mechanical treatment of the electrostatic complexes can be regarded.

WOLFSBERG and HELMHOLZ [16] were the first to make calculations for complexes of crystalline state with covalent bond. In the case of experimental study and its immediate heuristical interpretation of the light absorption of complex compounds KISS and his co-workers [5] reached outstanding results. Recently KISS explained the light absorption of the electrovalent and covalent complexes [6] by the "Term Split Theory" based upon the results of quantum mechanics. The present investigation aims at the quantum mechanical interpretation of his results referring to covalent complexes.

§ 2. *Contributions to the model of the complex*

The Cr (III) hexacyanide ion consists of a Cr^{3+} ion and six cyanide ions so that the nucleus of the complex being the Cr^{3+} ion is surrounded by six cyanide groups with octahedral symmetry (Fig. 1).

It is assumed that between the central ion and the groups of the coordination zone covalent bonds exist. These bonds are the molecular orbitals composed from the atomic orbitals of the nucleus and the groups. Taking into account the octahedral symmetry of the complex considered usually the well-known d^2sp^3-hybridization of the Cr^{3+} ion orbitals is used, in accordance with KIMBALL's theory of coordination. Molecular orbitals with octahedral symmetry can be, however, composed by d^3 atomic orbitals too, relating to the T_{2g} irreducible representation of the O_h group. In the following a special mixture of both the above mentioned hybridization will be used. It is namely supposed that the central Cr^{3+} ion contributes to the molecular orbitals with five $3d$, one $4s$ and three $4p$ orbitals on which, in the case of the free ion, three $3d$ electrons are present, furthermore the other electrons of the Cr^{3+} ion $(1s^2, 2s^2, 2p^6, 3s^2, 3p^6)$ belong to the closed shells. The groups have a nega-

Fig. 1[1]

tive charge and they are localized in the complex so that the C atom is nearer to the ion than the N atom [12]. Each group[2] contributes with three $2p$ orbitals of the C atom to the common MO system being orthogonal to each other and showing a maximum value in the direction of edges of an orthogonal trihedron, the edges of which run parallel to the axes of a Cartesian coordinate system which is determined by the axes of the octahedron. On these atomic orbitals of the cyanide groups we have to take into account
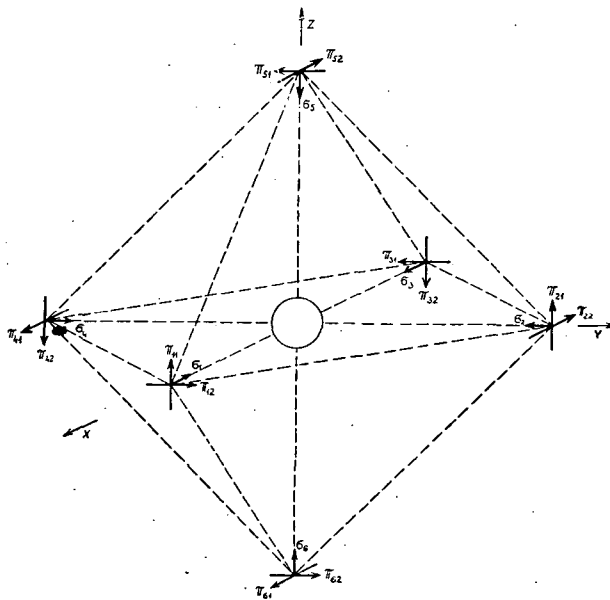
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[1] In the vertices of the octahedron there are six CN^-. σ_i indicates the orientation of the maximum distribution for one of the $2p$ orbitals of the group which is on the i-th vertex, π_{i1} and π_{i2} mark the orientations of the other two orbitals which are perpendicular to the former.

[2] The groups may be regarded as an electric 'dipole where, owing to the electrostatic attraction of the positive charged central ion, the centre of the negative charges is nearer to the centre of the complex than the centre of the positive charges.

four electrons involving even the electron which produces the negative charge of. the cyanide group. So twenty-seven electrons must be placed on the molecular orbitals formed by the twenty-seven atomic orbitals.

§ 3. Method of the Calculation

The energies of the electrons are calculated by means of the LCAO version of the MO method (see *e. g.* [9]), for the extensive simplification of which group theoretical considerations are used [13], [15]. The twenty-seven atomic orbitals mentioned above span the space of the twenty-seven dimensional reducible representation of the O_h group. The characters of this reducible representation were obtained with the help of the mentioned functions by studying their behaviours under the symmetry operations of the O_h group. Using the character system of the O_h group (see *e. g.* [2]) and characters obtained in this manner (Table I), the reducible representations have the form:

$$\Gamma_\sigma = \Gamma_{d^2sp^3} = A_{1g} + E_g + T_{1u}$$
$$\Gamma_\pi = T_{1g} + T_{1u} + T_{2g} + T_{2u}$$
$$\Gamma_{d^3} = T_{2g} \tag{1}$$
$$\Gamma = 2A_{1g} + 2E_g + T_{1g} + 3T_{1u} + 2T_{2g} + T_{2u}.$$

In order to attain the breaking down achieved in this manner instead of the atomic orbitals new linear combinations (Table II) were introduced

Table I.

O_h		E	$8C_3$	$3C_2$	$6C_2$	$6C_4$	i	$8iC_3$	$3iC_2$	$6iC_2$	$6iC_4$
	A_{1g}	1	1	1	1	1	1	1	1	1	1
	A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1
	A_{2g}	1	1	1	−1	−1	1	1	1	−1	−1
	A_{2u}	1	1	1	−1	−1	−1	−1	−1	1	1
	E_g	2	−1	2	0	0	2	−1	2	0	0
	E_u	2	−1	2	0	0	−2	1	−2	0	0
	T_{1g}	3	0	−1	−1	1	3	0	−1	−1	1
x, y, z	T_{1u}	3	0	−1	−1	1	−3	0	1	1	−1
	T_{2g}	3	0	−1	1	−1	3	0	−1	1	−1
	T_{2u}	3	0	−1	1	−1	−3	0	1	−1	1
	χ_σ	6	0	2	0	2	0	0	4	2	0
	χ_π	12	0	−4	0	0	0	0	0	0	0
	χ_{d^3}	3	0	−1	1	−1	3	0	−1	1	−1
	$\chi_{d^2sp^3}$	6	0	2	0	2	0	0	4	2	0
	χ	27	0	−1	1	3	3	0	7	5	−1

Table II.

	d^3	d^2sp^3	$2p\sigma$	$2p\pi$
A_{1g}		s	$1/\sqrt{6}\,(\sigma_1+\sigma_2+\sigma_3+\sigma_4+\sigma_5+\sigma_6)$	
E_g		$d_{x^2-y^2}$ d_{z^2}	$1/2\,(\sigma_1+\sigma_3-\sigma_2-\sigma_4)$ $1/\sqrt{12}\,(2\sigma_5+2\sigma_6-\sigma_1-\sigma_2-\sigma_3-\sigma_4)$	
T_{1g}				$-1/2\,(\pi_{21}+\pi_{42}+\pi_{51}+\pi_{62})$ $1/2\,(\pi_{11}+\pi_{32}+\pi_{52}+\pi_{61})$ $-1/2\,(\pi_{12}+\pi_{22}+\pi_{31}+\pi_{41})$
T_{1u}		p_x p_y p_z	$1/\sqrt{2}\,(\sigma_1-\sigma_3)$ $1/\sqrt{2}\,(\sigma_2-\sigma_4)$ $1/\sqrt{2}\,(\sigma_5-\sigma_6)$	$-1/2\,(\pi_{22}-\pi_{41}+\pi_{52}-\pi_{61})$ $1/2\,(\pi_{12}-\pi_{31}-\pi_{51}+\pi_{62})$ $1/2\,(\pi_{11}+\pi_{21}-\pi_{32}-\pi_{42})$
T_{2g}	d_{yz} d_{xz} d_{xy}			$1/2\,(\pi_{21}+\pi_{42}-\pi_{51}-\pi_{62})$ $1/2\,(\pi_{11}+\pi_{32}-\pi_{52}-\pi_{61})$ $1/2\,(\pi_{12}-\pi_{22}+\pi_{31}-\pi_{41})$
T_{2u}				$-1/2\,(\pi_{22}-\pi_{41}-\pi_{52}+\pi_{61})$ $-1/2\,(\pi_{12}-\pi_{31}+\pi_{51}-\pi_{62})$ $1/2\,(\pi_{11}-\pi_{21}-\pi_{32}+\pi_{42})$

which span the subspaces of the space of the twenty-seven dimensional reducible representation being invariant under the operations of the O_h group.

In this way it was achieved that the secular equation having originally the form:

$$|H_{ij}-E\cdot S_{ij}|=0 \qquad (2)$$

where

$$i,j=1,2,\ldots,27$$

may be broken up into a product including the following determinants: two of the first order belonging to the T_{1g} and T_{2u} representations, three of the second order belonging to the A_{1g}, E_g and T_{2g} representations and one of the third order belonging to the T_{1u} irreducible representation. The roots belonging to the A, E and T representations are one, two and threefold degenerate, respectively.

The integrals occuring in the secular determinant were determined by approximate methods. The so-called group overlap integrals may be expressed by the atomic overlap integrals. A new method[3] was elaborated for the calculation of the atomic integrals assuming that the distance between the central ion and the C atom of the cyanide group is 2,00 A. The integral type H_{ii} was substituted by the suitable ionisation potentials (see Fig. 2 Column 1). The H_{ij} integrals were determined with the formula of WOLFSBERG and HELMHOLZ [16]:

$$H_{ij} = F \cdot S_{ij} \frac{H_{ii} + H_{jj}}{2} \qquad (3)$$

where F is an empiric factor which was chosen as 2,5 for σ bonds and as 3 for π bonds. The energy values obtained in this way are to be found in Table III.

Table III.

Number[4]	Symmetry	Energies in eV
1	E_g	—11,4130
2	A_{1g}	—9,5927
3	T_{1u}	—8,7000
4	T_{1u}	—8,1219
5	T_{2g}	—7,8288
6	T_{1g} T_{2u}	—7,8000
7	T_{2g}	—7,5101
8	A_{1g}	—5,2039
9	T_{1u}	—3,2030
10	E_g	—0,1688

Table IV.

A_{1g}	$\longleftrightarrow$	T_{1u}
E_g	$\longleftrightarrow$	T_{1u}
E_g	$\longleftrightarrow$	T_{2u}
T_{1g}	$\longleftrightarrow$	T_{1u}
T_{1g}	$\longleftrightarrow$	T_{2u}
T_{1u}	$\longleftrightarrow$	T_{2g}
T_{2g}	$\longleftrightarrow$	T_{2u}

§ 4. *Selection rules*

For the interpretation of the spectrum the knowledge of the selection rules is needed. Transition between two states which are characterized by the functions ψ_1 and ψ_2 is possible if the integral $\int \psi_1 \xi \psi_2 \, d\tau$, where ξ is one of the coordinates, is different from zero. With simple group theoretical considerations can be decided if this integral is zero or not. In Table IV a summary of the allowed transitions is given.

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[3] The publication of this work will follow at a later date.
[4] The energy values are numbered according to Fig. 2.

§ 5. *Interpretation of the spectrum*

The transitions denoted on Fig. 2 in cm^{-1} are to be found in Table V where the experimental values are also presented.

It can be registered immediately that the difference between the calcu-lated and observed transitions obtained by the experimental absorption curve at disposal [7] ranges from 5000 cm^{-1} to 50 000 cm^{-1} does not exceed 3 per cent. Our results are surprisingly good and all the more so because the na--

Table V.

Transition	cm^{-1}	Observed [5]
3 → 10	68821	band from
1 → 9	66230	43000 cm^{-1},
4 → 10	64158	probably maxi-
6 → 10	61561	mum > 50 000
2 → 9	51546	
5 → 9	37316	38000
6 → 9	37084	
1 → 6	29146	
3 → 8	28203	27000
4 → 8	23540	(22000)[6]
3 → 7	9599	
3 → 6	7260	probably maxi-
4 → 7	4935	mum < 10 000
4 → 6	2599	
6 → 7	2339	

ture of our calculations is very approximate as well as, although the empiric values used seem to be plausible, they can not be considered as the exact values of the physical quantities in question. The good results show that our model approximates the objective structure of the molecule well, furthermore, the used approximation can be regarded as fortunate one.

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[5] The data present the positions of the maxima of the absorption curve.

[6] Strong transparency between 10 000 cm^{-1} and 20 000 cm^{-1} was observed. The datum in the brackets denotes "shoulder".
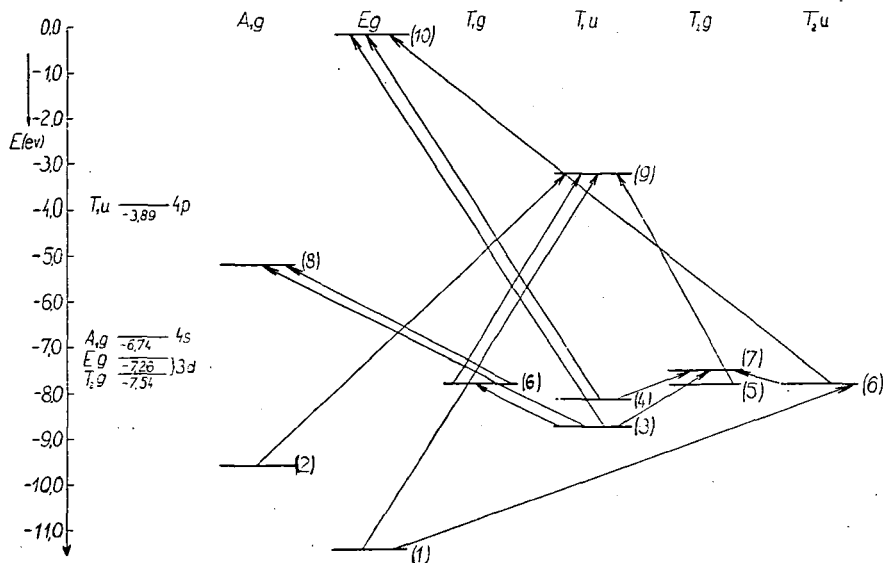
Fig. 2. The states 1, 2, 3, 4, 5 are completely and the states 6 partly
filled up in normal state.

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References

[1] *Bethe, H.:* Ann. Physik 5, 3, 133 (1929).
[2] *Hartmann, H.:* Theorie der Chemischen Bindung (Springer-Verlag, Berlin, 1954).
[3] *Ilse, F. E., H. Hartmann:* Z. physik. Chem. 197, 239 (1951).
[4] *Kimball, G.:* J. Chem. Phys. 8, 188 (1940).
[5] *Kiss, Á.:* Acta Univ. Szegediensis, Acta Chemica et Physica 3, 6 (1950).
[6] *Kiss, Á.:* Magyar Tud. Akad. Osztályközl. 6, 77 (1955); 7, 367 (1956).
[7] *Kiss, Á., J. Császár, L. Lehotai:* Magyar Tud. Akad. Osztályközl. (in press).
[8] *Magnus, H.:* Z. anorg. Chem. 124, 288 (1922).
[9] *Mulliken, R. S.:* J. Chim. Phys. 46, 497 (1949).
[10] *Pauling, L.:* The Nature of the Chemical Bond (Cornell University Press, New
York, 1939).
[11] *Sidgwick, N. V.:* J. Am. Chem. Soc. 53, 1367, 3225 (1931).
[12] *Syrkine, Y. K., M. E. Dyatkina:* Structure of Molecules and the Chemical Bond
(Butterworths Scientific Publications, London, 1950).
[13] *Van der Waerden, B. L.:* Die Gruppentheoretische Methode (Springer-Verlag,
Berlin, 1932)
[14] *Werner, A.:* Neuere Anschauungen auf dem Gebiete den anorganischen Chemie
(Friedr. Vieweg & Sohn Akt. Ges., Braunschweig, 1905).
[15] *Wigner, E.:* Gruppentheorie und ihre Anwendung (Friedr. Vieweg & Sohn Akt.
Ges., Braunschweig, 1931).
[16] *Wolfsberg, M., L. Helmholz:* J. Chem. Phys. 20, 837 (1952).