ABSORPTION SPECTRA OF INORGANIC COÖRDINATION COMPLEXES II. BANDS ASSIGNED TO SYMMETRY FORBIDDEN ELECTRONIC TRANSITIONS IN THE ABSORPTION SPECTRA OF COMPLEX CYANIDS OF SOME TRANSITION METALS

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In the present paper the possibilities of the appearance of symmetry forbidden electronic transitions – combined simultaneously with corresponding vibrational transitions – in the absorption spectra of octahedral and planar square complex cyanids of some transition metals are given by means of the group theory. Low-intensity bands occuring in the spectra of complex cyanids of the Cr^{3+}, Mn^{3+}, Co^{3+}, Fe^{3+} and Ni^{2+} ions could be interpreted in this manner.

I. Introduction

In the previous works of GILDE and BÁN 5, BÁN 1 and GILDE 4 using the LCAO-MO approximation the allowed electronic transitions between the orbitals of the central ion and of the ligands were discussed. The high-intensity bands in the spectra of complex cyanids are due to such excitations. However, symmetry forbidden transitions are to be taken into consideration as interpreting the low-intensity bands occuring in the region of the bands »b» [8]. (In the spectroscopy the term »forbidden transition» is generally applied to transitions associated with a spectrum of relatively low but not vanishing intensity.)

The symmetry forbidden transitions may be allowed in three different ways: (i) asymmetric distortions intervene in the molecule ceasing the center of symmetry, (ii) the actual symmetry of the molecule changes (e.g. $O_h \rightarrow D_{4h}$), (iii) the forbidden electronic transition in question combines with a vibrational transition of corresponding symmetry (Dissolution of Prohibitory Rules). Although, it there can be supposed some asymmetric distortions and a change of the actual symmetry of the molecule in solution, nevertheless, the consideration of these circumstances is hardly feasible. On the contrary, the dissolution of the prohibitory rules is easy to follow by the methods[1)] of group theory [12]. To point out the possibilities of the appearance of symmetry forbidden electronic transitions combined wirth vibrational transitions it is necessary to know the symmetry types of the normal vibrations of the complex cyanids considered. These are given by the direct sums [2], [3] as follow:

$$O_h: \Gamma_{vib} = 2A_{1g} + 2E_g + T_{1g} + 4T_{2g} + 2T_{2u} \quad (1)$$

D_{4h}: $\Gamma_{vib.}$ $2A_{1g}+A_{2g}+2A_{2u}+2B_{1g}+2B_{2g}+2B_{2u}+E_g+4E_u$. (2)

The vibrational transitions can be slassified in the following way: (a) Fundamental vibrations (0-1 vibrational transitions of the molecule). These transitions occur when one vibration is excited from the nonvibrating state to a state with one quantum of vibration. (b) Overtone vibrations (0-2, 0-3,... vibrational transitions). These transitions occur where one vibration is excited by one or more quanta. (c) Combination vibrations. Such transitions occur where more than one vibration is excited by one or more quanta. Thogh the nearer infrared region is generally associated with vibrational transitions of types above mentioned there is really no sharp line separating these transitions from the electronic ones. Thus one can reckon with the appearance of vibrational transitions simultaneously with electronic ones, viz., with superpositions of vibrational transitions on electronic ones. Vibrational transitions of type 0-1 are the most intense transitions. Therefore, above all these vibrational transitions can make forbidden electronic transitions allowed for radiation polarized in different directions. Overtone and combination vibrations generally have a very low intensity, nevertheless, it is assumed that these transitions can also increase the transition probability of an electronic transition. Further on, the symmetry types of the vibrational transitions, which can make the forbidden electronic transitions to be allowed, will be considered only. The vibrational transitions of A_{1g} symmetry are omitted both for symmetry O_h and D_{4h} because these transitions will not change the symmetry of an electronic transition.

2. Dissolution of prohibitory rules

The Table I and II give the dissolution of the prohibitory rules in the case of O_h and D_{4h} symmetry, respectively. It is seen that e.g., a forbidden electronic transition of type $T_{1u} \rightarrow T_{2u}$ (O_h) can be allowed by a vibrational transition of species T_{1u} or T_{2u}. On the other hand, e.g., an electronic transition of type $A_{2g} \rightarrow A_{1g}$ (D_{4h}), polarized in the direction x and y, can occur if it combines with an allowed vibrational transition of species E_u.

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1) Forbidden electronic transition between two states A and B will be allowed by electric dipole radiation if the direct product $\chi_A \cdot \chi_{\vec{r}} \rightarrow \chi_V \chi_B$ contains in its reduced form the totally symmetric representation of the group of the molecule (χ_A, χ_B, $\chi_{\vec{r}}$ and χ_V are the characters of the irreducible representations of the states A and B, of the electric vector and of one of the normal vibrations of the molecule, respectively). Then

$$\chi_A \chi_{\vec{r}} \rightarrow \chi_V \chi_B = \sum_i a_i \Gamma_i \qquad (3)$$

Here, if

$a_{A_{1g}} = 0$ the transition is forbidden,

$a_{A_{1g}} \neq 0$ the transition is allowed.

Thus it can be stated which normal vibrations of the molecule will make the forbidden transition in question allowed in any direction.

3. Assignments

The low-intensity bands, in the spectra of some complex cyanids, assigned to forbidden electronic transitions and the observed [7], [8], [9], [10] and calculated wavelengths (in mμ) are given in the Table III. The calculated wavelengths and the assignments are determined on the basis of the term-systems given in works [1], [4], [5]. The transitions of the Table III are forbidden transitions between the 3d orbitals of the central ion and between the orbitals of the central ion and of the ligands. It can be seen that the agreement between the observed and calculated positions of the bands is satisfactory. It is interesting that the bands occuring at $\lambda_{max} > 1000$ mμ belong to the same excitation ($1t_{1u} \rightarrow t_{2u}$) for all the octahedral complex cyanids examined. The progressive shift of the absorption maxima of these complexes to shorter wavelengths /from $Cr(CN)_6^{3-}$ to $Co(CN)_6^{3-}$/ can also well be interpreted.

The bands [2] given in the Table III, according to the theory of KISS [7], [8], [9], 10, are bands «b», thus on this basis they are also to be assigned to forbidden transitions. The assigments above verify in all, the statements of his theory concerning to the spectra of these compounds.

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[2] Considering that these low-intensity bands in most cases could be assigned to allowed transitions in the previous works [1], [4], [5] it may be the real situation that such a band observed is the envelope of several allowed and forbidden transitions.

Table I[a] (O_h symmetry)

Forbidden transition	Allowed by
$A_{1g} \leftrightarrow A_{1g}$; $A_{2g} \leftrightarrow A_{2u}$	$T_{1g}(x,y,z)$
$A_{1g} \rightarrow A_{1g}$; $A_{1u} \rightarrow A_{1u}$ $A_{2g} \rightarrow A_{2g}$; $A_{2u} \rightarrow A_{2u}$	$T_{1u}(x,y,z)$
$A_{1g} \leftrightarrow A_{2u}$; $A_{1u} \leftrightarrow A_{2g}$	$T_{2g}(x,y,z)$
$A_{1g} \leftrightarrow A_{2g}$; $A_{1u} \leftrightarrow A_{2u}$	$T_{2u}(x,y,z)$
$E_g \leftrightarrow A_{1u}, A_{2u}, E_u$ $E_u \leftrightarrow A_{1g}, A_{2g}$	$T_{1g}(x,y,z)$ and $T_{2g}(x,y,z)$
$A_{1g} \leftrightarrow T_{2u}$; $A_{1u} \leftrightarrow T_{2g}$ $A_{2g} \leftrightarrow T_{1u}$; $A_{2u} \leftrightarrow T_{1g}$	$E_g(x,y,z)$, $T_{1g}(x,y,z)$ and $T_{2g}(x,y,z)$
$E_g, T_{1g}, T_{2g} \leftrightarrow A_{1g}, A_{2g}, E_g, T_{1g}, T_{2g}$ $E_u, T_{1u}, T_{2u} \leftrightarrow A_{1u}, A_{2u}, E_u, T_{1u}, T_{2u}$	$T_{1u}(x,y,z)$ and $T_{2u}(x,y,z)$

[a] x, y, z, in brackets indicate the directions of polarizations.

Table II[a] (D_{4h} symmetry)

Forbidden transition	Allowed by
$A_{1g} \longleftrightarrow A_{2u}$; $A_{1u} \longleftrightarrow A_{2g}$ $B_{1g} \longleftrightarrow B_{2u}$; $B_{1u} \longleftrightarrow B_{2g}$ $E_g \longleftrightarrow E_u$	$E_g(x,y)$
$E_g \longleftrightarrow A_{1u}, A_{2u}, B_{1u}, B_{2u}$ $E_u \longleftrightarrow A_{1g}, A_{2g}, B_{1g}, B_{2g}$	$E_g(z)$
$A_{1g}, B_{1g} \longleftrightarrow A_{2g}, B_{2g}$; $A_{1u}, B_{1u} \longleftrightarrow A_{2u}, B_{2u}$	$E_u(x,y)$
$A_{1g} \longleftrightarrow A_{1u}$; $A_{2g} \longleftrightarrow A_{2u}$ $B_{1g} \longleftrightarrow B_{1u}$; $B_{2g} \longleftrightarrow B_{2u}$	$E_g(x,y)$ and $A_{2g}(z)$
$A_{1g} \longrightarrow A_{1g}$; $A_{1u} \longrightarrow A_{1u}$ $A_{2g} \longrightarrow A_{2g}$; $A_{2u} \longrightarrow A_{2u}$ $B_{1g} \longrightarrow B_{1g}$; $B_{1u} \longrightarrow B_{1u}$ $B_{2g} \longrightarrow B_{2g}$; $B_{2u} \longrightarrow B_{2u}$	$E_u(x,y)$ and $A_{2u}(z)$
$A_{1g} \longleftrightarrow B_{2u}$; $A_{1u} \longleftrightarrow B_{2g}$ $A_{2g} \longleftrightarrow B_{1u}$; $A_{2u} \longleftrightarrow B_{1g}$	$E_g(x,y)$ and $B_{1g}(z)$
$A_{1g} \longleftrightarrow B_{1u}$; $A_{1u} \longleftrightarrow B_{1g}$ $A_{2g} \longleftrightarrow B_{2u}$; $A_{2u} \longleftrightarrow B_{2g}$	$E_g(x,y)$ and $B_{2g}(z)$
$A_{1g} \longleftrightarrow B_{1g}$; $A_{1u} \longleftrightarrow B_{1u}$ $A_{2g} \longleftrightarrow B_{2g}$; $A_{2u} \longleftrightarrow B_{2u}$	$E_u(x,y)$ and $B_{2u}(z)$
$E_g \longleftrightarrow A_{1g}, A_{2g}, B_{1g}, B_{2g}$ $E_u \longleftrightarrow A_{1u}, A_{2u}, B_{1u}, B_{2u}$	$A_{2u}(x,y)$, $B_{2u}(x,y)$ and $E_u(z)$
$E_g \longrightarrow E_g$; $E_u \longrightarrow E_u$	$E_u(x,y)$, $A_{2u}(z)$ and $B_{2u}(z)$

[a] x, y and z, respectively, in brackets indicate the direktions of polarizations.

Symmetry	Complex	Transition	Polarized in	Allowed by	Wavelengths (in mu) Calc.	Obs.
O_h	$Cr(CN)_6^{3-}$	$(1t_{1u})^{-1}t_{2u}$		T_{1u}, T_{2u}	1377	1000 (1600)
		$(1a_{1g})^{-1}2t_{2g}$		T_{1u}, T_{2u}	595	556
		$(1t_{2g})^{-1}2a_{1g}$	xyz	T_{1u}, T_{2u}	472	438
		$(t_{1g})^{-1}2a_{1g}$		T_{1u}, T_{2u}	477	
		$(t_{2u})^{-1}2a_{1g}$		E_g, T_{1g}, T_{2g}		
O_h	$Mn(CN)_6^{3-}$	$(1t_{1u})^{-1}t_{2u}$		T_{1u}, T_{2u}	1362	1000 (1500)
		$(2t_{1u})^{-1}3t_{1u}$	xyz	T_{1u}, T_{2u}	357	380
		$(t_{2u})^{-1}3t_{1u}$		T_{1u}, T_{2u}		
O_h	$Co(CN)_6^{3-}$	$(1t_{1u})^{-1}t_{2u}$	xyz	T_{1u}, T_{2u}	1319	1000 (1350)
		$(1e_g)^{-2}t_{2g}$		T_{1u}, T_{2u}	411	400
O_h	$Fe(CN)_6^{3-}$	$(1t_{1u})^{-1}t_{2u}$	xyz	T_{1u}, T_{2u}	1319	1000
D_{4h}	$Ni(CN)_4^{2-}$	$(a_{2g})^{-1}2a_{1g}$	x,y	E_u	1033	1000
		$(b_{2u})^{-1}2a_{1g}$	x,y	E_g		
			z	B_{1g}		
		$(1e_g)^{-1}2e_g$	x,y	E_u	426	444
			z	B_{2u}		
			z	A_{2u}		
		$(b_{2u})^{-1}3a_{1g}$	x,y	E_g	421	
			z	B_{1g}		
		$(a_{2g})^{-1}3a_{1g}$	x,y	E_u		
		$(1e_g)^{-1}2b_{1g}$	x,y	A_{2u}	421	
			x,y	B_{2u}		
			z	E_u		
		$(a_{2g})^{-1}2b_{1g}$	x,y	E_u	415	

References

[1] Bán, M.I.: Acta Chim. Hung. (to be published).

[2] Bán, M. I.: Acta Chim. Hung. (to be published).

[3] Bán, M. I.: Unpublished calculations.

[4] Gilde, F. J.: This Issue.

[5] Gilde, F. J.: M. I. Bán: Acta Phys. Chem. Szeged 3, 42 (1957).

[6] Herzberg, G.: Infrared and Raman Spectra of Polyatomic Molecules (D. Van Nostrand, New York, 1945).

[7] Kiss, Á.: Magyar Tud. Akad. Kémiai Tud.Oszt.Közl. 7, 367 (1956).

[8] Kiss, Á.: Tagungsber. Chem.Ges.DDR. Hauptjahrestagung 1954. (Akad. Verlag, Berlin, 1955).

[9] Kiss, Á.: Z. anorg. allg. Chem. 282, 141 (1955).

[10] Kiss, Á.: J. Császár, L. Lehotai: Magyar Tud.Akad. Kémiai Tud.Oszt.Közl. 9, 281 (1957).

[11] Weissberger, A.: Technique of Organic Chemistry IX., Chemical Applications of Spectroscopy (Interscience Publishers, Inc., New York, 1956).

[12] Wigner, E.: Gruppentheorie und ihre Anwendung (Vieweg, Braunschweig, 1931).