CRYSTAL FIELD PARAMETERS OF SOME Co(II) AND Ni(II) COMPOUNDS

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Using the method of diffuse reflection spectrophotometry the optical spectra for several crystal compounds of Co(II) and Ni(II) are investigated. In these substances the Co^{2+} - and Ni^{2+}-ions are in octahedral surroudnings of two kinds: $M(OH_2)_6$ and MO_6. The interpretation of the recorded spectra is given and the values of the crystal field parameter 10 Dq are determined. These calculated values are used for some general considerations of crystal field spectra.

INTRODUCTION

The paper presents the results of investigation of the optical spectra by the method of diffuse reflection spectrophotometry. Two groups of Co(II) and Ni(II) compounds are examined. Firstly, the hexametylene-tetramine compounds , their crystals containing several H_2O - molecules per one stoichiometric unit. In these compounds the Co^{2+} - and Ni^{2+}-ions are surrounded by the H_2O - coordination octahedrons. For the purpose of comparison, the spectra of some other substances with similar cationic coordination are recorded. Secondly, the spectra of some mixed phosphates of Co and Ni with Ba and Sr and the spectra of Co-and Ni-borate are recorded also. In these substances the transition metal ions are in octahedral surroudning formed by oxygen atoms from the PO_4^{3-} and Bo_3^{3-}-ions. On the whole 13 pairs of Co(II) and Ni(II) crystal field spectra are recorded. In addition, the spectra of three mixed phosphates of Co(II) with Sr and Pb are recorded.

All these spectra are interpreted by the Tanabe-Sugano method [1]. The assignation of electronic transitions in observed spectra and the calculation of the corresponding transition energies enabled the determination of the values of the crystal field parameter 10 Dq. These obtained values are used for the deduction of certain conclusions about the influence the second coordination sphere and the whole crystal structure on the crystal (ligand) field strength, and about the meaning of some empirical relations established in this field of spectroscopy.

INVESTIGATED SUBSTANCES

Complex hexametylene-tetramine compounds. Following complex compounds with the formulae $MCl_2.2(HMT).10H_2O$, $MBr_2.2(HMT).10H_2O$, $MI_2.2(HMT).9H_2O$, $M(NO_3)_2.2(HMT).10H_2O$ and $MSO_4.1,5(HMT).10H_2O$, with M=Co, Ni are investigated. Crystal structures of these substances are not determined. On the basis of the investigation of optical spectra, magnetic properties and data of thermal analysis it is established that in these substances the octahedral $M(OH_2)_6^{2+}$-ions are existing [2,3].

Hydrated salts. The spectra of $MSO_4.7H_2O$, $M(NO_3)_2.6H_2O$ and $MCl_2.6H_2O$ are recorded. Crystal structures of these compounds are known. In the crystals of $NiSO_4.7H_2O$ [4] and of the isomorphous compound $CoSO_4.7H_2O$ [5] , the octahedral $[M(OH_2)_6]^{2+}$-ions are present also. It is valid also for $Ni(NO_3)_2.6H_2O$ [6] and for $Co(NO_3)_2.6H_2O$ [7] . In hydrated chlorides $NiCl_2.6H_2O$ [8] and $CoCl_2.6H_2O$ [9] the Ni^{2+} and Co^{2+} ions are in deformed octahedral surroudning of the type $[M(OH_2)_4Cl_2]$.

Hydrated acetates and oxalates. The spectra of $M(CH_3COO)_2.4H_2O$ and $M(C_2O_4).2H_2O$ are recorded. The crystal structures of these acetates are known [10]. In these substances the M^{2+} ions are surrounded by tetragonally deformed octahedra, which are formed from 4 H_2O molecules and two O-atoms from the carboxyl group of acetate ions. The crystal oxalates dihydrates of Ni [11] and Co [12] contain polymer chains in which M-atoms are surrounded by 4 O-atoms from the oxalate ions and 2 H_2O-molecules; this surrounding has the form of tetragonally deformed octahedron.

Mixed phospates. The spectra of $BaM_2(PO_4)_2$, $SrM_2(PO_4)_2$ and of $Sr_2Co(PO_4)_2$, $PbCo_2(PO_4)_2$ and $Pb_2Co(PO_4)_2$ are recorded. The crystal structure of $BaNi_2(PO_4)_2$ is determined [13] . Our investigation showed that $BaCo_2(PO_4)_2$ [14] , $SrCo_2(PO_4)_2$ and $SrNi_2(PO_4)_2$ [15] are isomorphous with this compound. In the crystals of these phosphates the M^{2+}-ions are coordinated with 6 O-atoms from the PO_4^{3-}-ions octahedrally arranged. The crystal structures of other phosphates are not determined, but from our investigation of their physical properties if follows that the M^{2+}-ions are present in corresponding crystal in the surroundning of the same kind.

Borates. The spectra of $M_3(BO_3)_2$ are recorded. In crystals of $Co_3(BO_3)_2$ [16] and $Ni_3(BO_3)_2$ [17] the M^{2+}-ions are in octahedral coordination, which is formed by 6 O-atoms from the Bo_3^{3-}-atoms.

REFLECTION SPECTRA

The recorded spectra are used for the determination of the values of the crystal field parameter 10 Dq. As already mentioned this is accomplished by the Tanabe-Sugano method (TSM). Detailed analysis of the contemporary meaning of this method is given in [18, 19] . The TSM is derived from the simplified crystal field theory, in which the second order interactions, e.g. spin-orbit soupling [18, 20] are neglected. Just for this reason the TSM is very suitable, since it reguires the introduction of a minimal number of parameters and does not demand any additional assumptions of the validity of values of different parameters obtained on the basis of other experiments. This is very important for the interpretation of optical electronic spectra obtained by the method of reflection spectrophotometry. Reflection spectra consist of a few spectral bands, which originates from the d-d transitions and which are not superposed on the charge-transfer spectral bands. In paper [21] the criterion for the accuracy of the test of a theoretical model is given. This accuracy depends on the difference between the number of the theoretical parameters and the number of spectral bands. For these reasons we have used the TSM for the interpretation of reflection spectra.

The calculation on the basis of the TSM are performed with the purpose to determine the best values of the parameters 10 Dq (and B[1]). It is necessary to remark that from the obove description of crystal structures of the examined substances it follows that for some of them the coordination polyhedra have deformed octahedron symmetry. We have adopted the so-called rule of average environenement [22], which holds for pseudo octahedral crystal fields [22] formed by similar ligands. This procedure offers a larger numbers of values of crystal field parameters for direct comparison.

It should be emphasized that the corectness of the adopted assumption is tested not only by comparison of the observed and calculated values of electron transition energy, but also by the use of ligand field diagrams calculated for deformed octahedral surroudnings (tetragonal and trigonal symmetry) and published not long time ago [19]. This test has been performed for all the examined compounds and it confirms that the assumed condition are fulfilled.

The values of 10 Dq calculated for the pairs of Co and Ni--compounds are given on table 1. The values are determined with an error less than 0,3%.

Table 1.Values of 10 Dq (cm^{-1}) for M^{2+} -compounds

Compound	ion	
	Co	Ni
oxalate	8400	8500
sulphate	8300	8350
nitrate	8080	8180
HMt-complex	7890	7930
acetate	7550	8090
chloride	7500	7800
$BaM_2(PO_4)_2$	7500	7600
$SrM_2(PO_4)_2$	6700	6980
borate	7200	7640

From the data given on this table it can be seen that for the five HMT complex compounds of M^{2+} only one value for 10 Dq is given. Identical values for different compounds can be explained by the fact that in these compounds there are identical first coordination surroudnings formed by the H_2O molecules, and almost identical second coordination surroudnings formed by HMT-globular molecules [2]. To our knowledge, similar effect has not been described in literature.

Secondly, from table 1. it follows that for the same surroudning the values 10 Dq for the Ni^{2+}-ion are always larger than the values fot the Co^{2+}-ion. These results differ from the data for $M(OH_2)_6^{2+}$ -complexes cited in the literature [19, 20] , although there are data which are in agreement with those given on table 1. [21].

On table 2. the values are given for the parameter 10 Dq for a few mixed Co phosphates. In all these compounds the Co^{2+}-ions are surrounded by the oxygen atom octahedra.

Table 2. Values of 10 Dq (cm^{-1}) for Co-phosphates

substance	$PbCo_2(PO_4)_2$	$SrCo_2(PO_4)_2$	$Pb_2Co(PO_4)_2$	$Sr_2Co(PO_4)_2$	$BaCo_2(PO_4)_2$
10 Dq	6100	6700	6940	7170	7500

The different values of 10 Dq in this case may be explained not only by the differences in the second coordination sphere but also by the differences in the first coordination sphere. The other cations present in these crystals have different ionic radii and electron cloud configurations, and even they are present in different quantities. This causes different relations of the PO_4^{3-}-ions with the Co^{2+} ions in the examined phosphates, and the mentioned differences in 10 Dq values.

FINAL REMARKS

The considerations given in connection with the obtained spectral data indicate that a more detailed investigation is necessary of the applicability of the empirically estabilished relations (spectrochemical and nephelauxetic series [18,22] , parameters f and g [22] and so on) to the crystals.

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