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OPTICAL REFLECTION SPECTRA AND MAGNETIC SUSCEPTIBILITY OF COMPLEX COMPOUNDS OF TRANSITION METALS SALTS WITH UROTROPINE

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A group of several complex compounds of inorganic salts of transition 3d-metals with urotropine (hexametylene - tetramine, HMT) of a general formula $MX_a.b(HMT)nH_2O$ has been synthetyzed. In the general formulae M = Cr, Mn, Fe, Co, Ni, Cu, X = Cl, Br, J, No_3, SO_4, a=1-3, b=1-2 and $n \leq 10$. The optical reflection spectra between 360 and 950 nm have been recorded and magnetic susceptibility of these substances are investigated.

INTRODUCTION

In the aqueous solution the inorganic salts of transition 3d-metal ions form with urotropine $C_6N_4H_{12}$ (hexametylene-tetramine, HMT) the additive complex compounds which were described in the literature relatively long time ago (1910. -11, /1/). These substances are investigated from the point of view of their application /2/. During heating, a partial decomposition of these substances occurs at a certain temperature followed by a characteristic shange in colour. Due to these properties, they are used as indicators for temperature control.

These substances are very few investigated although they have been known and widely used for a long time. The crystal structure of any of these substances is not known. Moreover, some autors disagree in their opinion on the chemical composition of these substances /3-8/. Partial investigations performed with the aim of determination of chemical composition and the temperature of desintegration, i.e. the nature of the process that causes a change of colour during desintegration, are performed for Co, Ni and partly for Mn compounds. These investigations have shown that the composition of the substances just mentioned is $MX_a.2(HMT).nH_2O$ with $8 \leq n \leq 10$, where M represents metal ion, X_a=Cl, Br, I, No_3 SO_4(a=1-2). Besides, ions of metals are in an octahedral coordination, in the form of complex ions $[M(OH_2)_6]^{2+}$. This conclusion is in agreement with the information on the crystal structure of complex compounds of Ca and Mg bromides which are the only ones so far investigated /1/.

The presence of $M(OH_2)_6$ ions makes these substances interesting because, in principle, it provides a possibility for the investigation of ions spectra in H_2O coordination which is similar to that performed for hydrated sulphates of transition metals /9/ (and partly, /10/). Because of the difference in the type of crystal lattice a different effect of crystal field on 3d-ion spectra could have been expected. That is the reason for which the investigations of these substances were performed.

EXPERIMENT

Synthesis of HMT complex compounds with 22 different initial substances of transition metal salts ranging from Cr to Cu (Table 1) was performed by the well-known procedure /4,6,7/. The attempts to synthetize similar substances with Fe^{2+} ions were not successful due to a quick spontaneous oxidation of $Fe^{2+} \rightarrow Fe^{3+}$. The identification of the substances obtained was done by application of various physical methods /11/. Table 1. shows that a cetain number of substances synthetized crystalizes without water or with a smaller number of water molecules, meaning that in these substances the transition metal ions are in a different coordination from the above mentioned one.

Investigations presented in this paper deal with the optical spectra plotted by means of the optical reflection spectrophotometry method in the range of 360 - 950 nm taking $BaSO_4$ as a standard, and with the magnetic susceptibility measurements performed by Faraday method.

Table 1.

The investigated complex compounds and magnetic moments of transition ions

No	3d-ion	Initial Substance	Complex Compound	Magnetic Moment (μ_B)	Mean Value
1	Cr^{3+}	$Cr(NO_3)_3$	$Cr(OH)_3.(HMT).2H_2O$	4,76	4,78
2		$CrCl_3$	$CrCl_3.3(HMT).2H_2O$	4,80	
3	Fe^{3+}	$FeCl_3$	$FeCl_3.3(HMT).2H_2O$	5,97	5,97
4		$Fe(SO_4)_3$	$Fe_2(SO_4)_3.1(HMT)$	1,8	1,8
5	Mn^{2+}	$MnCl_2$	$MnCl_2.2(HMT).10H_2O$	5,99	5,99
6		$MnBr_2$	$MnBr_2.2(HMT).10H_2O$	5,98	
7		$Mn(NO_3)_2$	$Mn(NO_3)_2.2(HMT).10H_2O$	5,92	
8		$MnSo_4$	$MnSo_4.1,5(HMT).10H_2O$	5,92	

9	Co^{2+}	$CoCl_2$	$CoCl_2.2(HMT).10H_2O$	4,88	5,02
10		$CoBr_2$	$CoBr_2.2(HMT).10H_2O$	5,oo	
11		CoI_2	$CoI_2.2(HMT) . 9H_2O$	5,o2	
12		$Co(NO_3)_2$	$Co(NO_3).2(HMT).10H_2O$	5,12	
13		$CoSO_4$	$CoCo_4.1,5(HMT).10H_2O$	5,10	
14	Ni^{2+}	$NiCl_2$	$NiCl_2.2(HMT).10H_2O$	3,22	3,22
15		$NiBr_2$	$NiBr_2.2(HMT).10H_2O$	3,24	
16		NiI_2	$NiI_2.2(HMT).9 H_2O$	3,24	
17		$Ni(NO_3)_2$	$Ni(NO_3)_2.2(HMT).10H_2O$	3,19	
18		$NiSo_4$	$NiSo_4.1,5(HMT).10H_2O$	3,21	
19	Cu^{2+}	$CuCl_2$	$CuCl_2.(HMT)$	2,20	2,54
20		$CuBr_2$	$CuBr_2.(HMT).2H_2O$	2,60	
21		$Cu(NO_3)_2$	$Cu(NO_3)_2.(HMT)$	2,68	
22		$CuSO_4$	$CuSO_4.(HMT)$	2,68	

MEASUREMENT RESULTS

Figs. 1 - 3, show a selection of optical reflection spectra indicating the dependence of the relative reflectance (arbitrary units) on

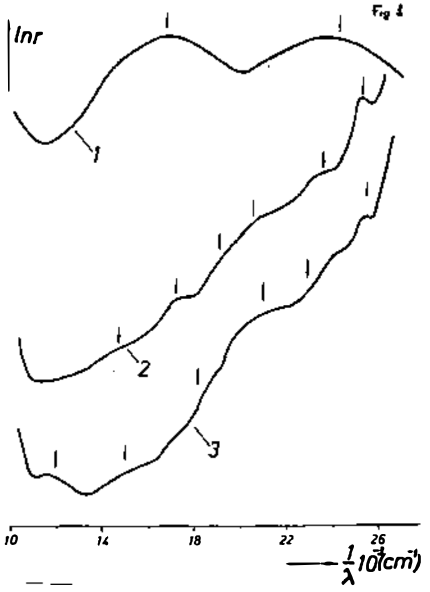

Fig. 1.

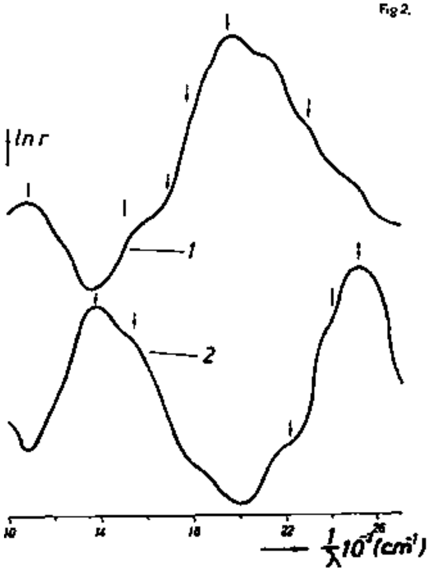

Fig. 2.

the wave number $1/\lambda$. Fig. 1. presents the graphs of $CrCl_3$ (1), $MnCl_2$ (2) and $FeCl_3$ (3) complex compounds. The spectra of $Cr(OH)_3$ complex compound and the spectra of others compounds with Mn-ion are identical with those given by curves 1, and 2. This is not true for the spectrum of $Fe_2(SO_4)_3$ compound which is not given in this paper. Fig. 2. shows spectra of $CoCl_2$(1) and $NiCl_2$(2) complex compounds. The spectra of other substances with Co^{2+} and Ni^{2+} ions are identical with the given ones. Finally, Fig. 3. shows spectra of $CuBr_2$ (1), $CuCl_2$(2), $Cu(NO_3)_2$(3) and $CuSo_4$(4) complex compounds.

From the measured magnetic susceptibilities the values of effective magnetic moments of 3d-ions are calculated. The results are given in Table 1.

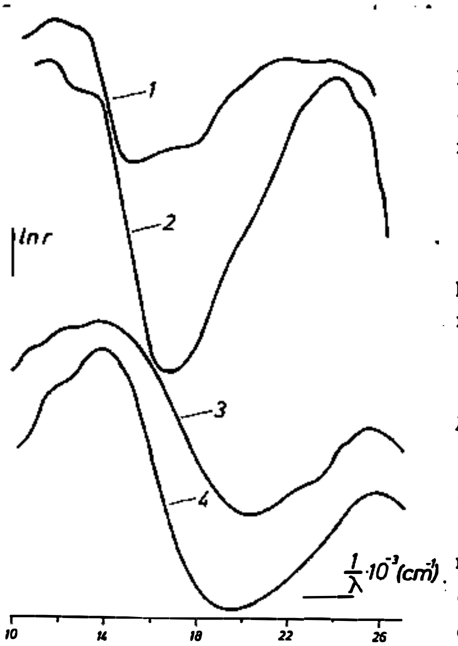

Fig. 3.

ANALYSIS OF RESULTS

The vlues of magnetic moments of 3d-ions for all substances except this at N° 4, lie above those for pure spin moments /1/, what means that in the corresponding coordinations there is only a partial quenching of orbital moments. The exception from this is a magnetic moment of Fe^{3+}-ion in N° 4 which corresponds to $\mu = 1,73\ \mu_B$ i.e. s = 1/2, indicating that in this case Fe^{3+} ion is in a strong crystal field /12/. This can be expected if the absence of H_2O molecule is taken into consideration. That means that N - atoms from HMT /13/ probably belong to the Fe^{3+} ion coordination.

The analysis of spectra obtained is not simple due to the broadness of the bands corresponding to individual transitions and the mutual overlapping which significantly affects the determination of the maxima positions. Better separation is achieved only at the very low temperatures /14/. That is the reason why each of such analysis can be a source of errors. The problem is particularly complex in the case of the spectrum of Mn^{2+} ion having weak, spin forbidden transitions and for the spectrum and of Fe^{3+} ion where such bands are superposed on the intensive band of the charge transfer spectra /13,14/.

The investigation of the spectra obtained is performed by means of Tanabe - Sugano method /14/, and yields the following interpretation:

Cr^{3+} ion spectrum (Fig. 1.1). The spectrum has the bands which may be ascribed to the transitions

$1/\lambda$ = 16 900 cm^{-1} $\quad {}^4A_{2g} \to {}^4T_{2g}$
24 400 cm^{-1} $\quad {}^4T_{1g}$.

In this case we obtain B' = 761 cm^{-1}, for the Racah parameter B. When compared with the value for free ion, B_o = 918 cm^{-1} /14/, we obtain $\beta = B'/B_o$ = 0,82. Finally, crystal field parameter Δ = 10Dq equals to Δ = 17070 cm^{-1}.

Mn^{2+} ion spectrum (Fig. 1. 2. In this case we obtain

14 700 cm^{-1} $\quad {}^6A_{1g} \to {}^4T_{1g}$, $\quad$ 20 500 cm^{-1} $\quad {}^6A_{1g} \to {}^4A_{1g}, {}^4E_g$,
17 100 cm^{-1} $\quad {}^4T_{2g}$, $\quad$ 23 500 cm^{-1} $\quad {}^2A_{2g}, {}^2T_{1g}$,
19 000 cm^{-1} $\quad {}^2T_{2g}$, $\quad$ 25 200 cm^{-1} $\quad {}^4E_g$.

At that B' = 720 cm^{-1} given β = 0,82 for B_o = 860 cm^{-1} and Δ =7560 cm^{-1}.

Fe^{3+} ion spectrum (Fig. 1. 3). In this case we obtain

12 000 cm^{-1} $\quad {}^6A_{1g} \to {}^4T_{1g}$, $\quad$ 21 000 cm^{-1} $\quad {}^6A_{1g} \to {}^4A_{1g}, {}^4E_g$,
15 000 cm^{-1} $\quad {}^4T_{2g}$, $\quad$ 22 900 cm^{-1} $\quad {}^2A_{2g}, {}^4T_{1g}$,
18 200 cm^{-1} $\quad {}^2T_{2g}$, $\quad$ 25 500 cm^{-1} $\quad {}^4E_g$.

In this case we obtain B' = 570 cm^{-1}, thus, β =0,56 for B_o=1015 cm^{-1} and Δ = 7250 cm^{-1}.

Co^{2+} -ion spectrum (Fig. 2. 1). For this spectrum

10 950 cm^{-1} $\quad {}^4T_{1g} \to {}^2E_g$, $\quad$ 17 800 cm^{-1} $\quad {}^4T_{1g} \to {}^2T_{1g}$
15 050 cm^{-1} $\quad {}^4A_{2g}$, $\quad$ 19 600 cm^{-1} $\quad {}^4T_{1g}$
17 000 cm^{-1} $\quad {}^4T_{2g}$, $\quad$ 23 100 cm^{-1} $\quad {}^2A_{1g}$.

In this case we obtain B' = 890 cm^{-1}, thus, β = 0,92 for B_o= 971 cm^{-1} and Δ = 7890 cm^{-1}.

Ni^{2+} -ion spectrum (Fig. 2. 2). For this spectrum

13 600 cm^{-1} $\quad {}^3A_{2g} \to {}^3T_{2g}$, $\quad$ 23 900 cm^{-1} $\quad {}^3A_{2g} \to {}^1A_{1g}$
15 300 cm^{-1} $\quad {}^1T_{2g}$, $\quad$ 24 950 cm^{-1} $\quad {}^3T_{1g}$
22 100 cm^{-1} $\quad {}^1T_{2g}$,

These data correspond to B' = 880 cm^{-1}, giving β = 0,86 for B_o=1030 cm^{-1} and Δ = 7930 cm^{-1}.

The agreement between the values obtained for transition energies and the spectra can be determined by the relative position of arrows and the corresponding bands in the spectra. The values of the coeficient should correspond to the degree of ionic character of the bond M-O (i.e. M-Cl, for Fe^{3+}-ion due to a small number of H_2O molecules, N°3 substance, Table 1) and is in considerable good agreement with the expected values /13/. The values obtained for Δ are systematically lower than those given in /9/ what can be expected considering the change in crystal lattice nature. The exception is observed for Fe^{3+}-ion which is much less in value; however, that can be probably explained by the presence of Cl^- in the coordination of this ion.

Fe^{3+}-ion spectrum from $Fe_2(SO_4)_3$ compound is not given in this paper. Comparison of this spectrum with those of Fe^{3+}-ions as given by other authors (e.g. /15/) shows that the spectrum corresponds to the one given by $/Fe(CN)_6/^{3+}$ ion, and corresponding to the case of a strong crystal field. This conclusion is in agreement with the data obtained in magnetic measurements. All the previous interpretation of Fe^{3+}-ion spectrum in the strong crystal field have shown to be unreliable so we had no support for the interpretation of this spectrum.

Cu^{2+}-ion spectrum (Fig. 3) in the visible region yields one band of crystal field (low $1/\lambda$) and one band of charge transfer spectrum; and due to that, no quantitative estimates of the crystal field are possible on the basis of these measurements. It is evident that the crystal field band has several maxima what is explained by the deformation of octahedral coordination /13,14/. The unidentified maxima shown in Figs. 1. and 2. /13/ can be explained in a similar way.

CONCLUSION

The investigation of the complex compounds of salts of transition metals with HMT has enabled the compillation of the new data on 3d-ions in a weak crystal field.

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