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PHYSICAL PROPERTIES AND CRYSTAL FIELD OF COMPLEX Fe(II) AND Fe(III) CYANIDES WITH IONS OF 3d-TRANSITION METALS

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This paper presents results of the investigation of complex Fe(II) and Fe(III) cyanides of the type:

$$M_2[Fe(CN)_6] \quad \text{and} \quad M_3[Fe(CN)_6]_2$$

where M = Mn, Fe, Co, Ni, Cu. The optical reflection spectra are plotted and the magnetic susceptibility measured. This paper gives the analysis of the experimental data.

INTRODUCTION

Complex cyanides of transition metals are very interesting substances owing to their magnetic /1/ and dielectric characteristics /2/ and owing to their chemical properties /3/ and possibilities of applications /4/. Due to complex effects of strong crystal field in them, there is no reliable interpretation of properties of complex cyanides based on the knowledge of their electronic structure /4/ although the beginnings of their investigation date as far as 250 years ago /3/. The theory of crystal field based on the theory of purely ionic interactions /5/ only partly explains these substances while covalent bond effects /6,7/ have not as yet been considered in the formulation of complete theory of these substances.

The most extensively investigated among the complex cyanides are $K_4[Fe(CN)_6]$ and $K_3[Fe(CN)_6]$ /1,2,3,8,9/. These which have been investigated to a certain extent only are: Fe(II) and Fe(III) complex cyanides with alkaline and 3d metals /3,10/, while there is only a few data on the investigation of Fe(II) and Fe(III) compounds with 3d metals but without alkaline metals and water /3/.

This paper presents results of investigation of one of the mentioned groups of complex cyanides.

EXPERIMENT

By the procedure described in /11/ the synthesis of Fe(II) and Fe(III) - cyanide acid is performed. It is followed by synthetizing of appropriate complex salts with M^{2+}-ions: Mn, Fe, Co, Ni, Cu as well as with Fe^{3+}-ions , 12 substances in all (Table 1 and 2). For the sake of control of the synthesis performed and the measurement data processing the Fe(III) cyanide with Zn was synthetized.

All these substances crystallize with water due to their specific crystal structure /1,3/. The thermograms were plotted by the DTA method in order to determine the temperatures of anhydration and to eliminate crystalline water.

Experimental investigation of these substances was performed by plotting the optical spectra in the range from 360 to 950 nm by the method of optical reflection spectrophotometry taking $BaSO_4$ as a standard as well as by measuring magnetic susceptibility by Faraday method. The investigations were performed on powder samples.

MEASUREMENT RESULTS

Tables 1, and 2. and Figs. 1-3 show the experimental data obtained. Tables 1. and 2. present the values of effective magnetic moments (in terms of Bohr magnetons) calculated on the basis of magnetic susceptibilities measured. Corrections for diamagnetic contribution of atoms and CN-group were performed according to /12/. The contribution of CN-group was investigated on magnetic susceptibility of freshly prepared $H_4[Fe(CN)_6]$ and $Zn_3[Fe(CN)_6]_2$. Testing yields $\chi_{CN} = -18.10^{-6}$ in accordance with /12/.

Table 1. Magnetic moments of ions in complex Fe(II) cyanides

ion	formulae	effective magnetic moment (μ_B)
Mn^{2+}	$Mn_2[Fe(CN)_6]$	7,7
Fe^{3+}	$Fe_4[Fe(CN)_6]_3$	11,3
Fe^{2+}	$Fe_2[Fe(CN)_6]$	6,9
Co^{2+}	$Co_2[Fe(CN)_6]$	5,5
Ni^{2+}	$Ni_2[Fe(CN)_6]$	4,0
Cu^{2+}	$Cu_2[Fe(CN)_6]$	2,5

Table 2. Magnetic moments of ions in complex Fe(III) cyanides

ion	formulae	effective magnetic moment (μ_B)
Mn^{2+}	$Mn_3[Fe(CN)_6]_2$	10,2
Fe^{3+}	$Fe[Fe(CN)_6]$	6,1
Fe^{2+}	$Fe_3[Fe(CN)_6]_2$	8,9
Co^{2+}	$Co_3[Fe(CN)_6]_2$	7,1
Ni^{2+}	$Ni_3[Fe(CN)_6]_2$	5,9
Cu^{2+}	$Cu_3[Fe(CN)_6]_2$	4,1

Figs. 1-3 show the optical reflection spectra of all substances. Dependence of relative reflectance (arbitrary units) on wave number $^1/_\lambda$ is shown. Fig. 1. presents spectra of Fe^{3+}-ferrocyanide (1), Fe^{2+}-ferrocyanide (2) and Fe^{3+}-ferricyanide (3). Since the spectrum of Fe^{2+}-ferrocyanide is identical with that of Fe^{3+}-ferrocyanide, it is not separately shown. The similarity of Fe^{2+}-ferrocyanide with that of Fe^{3+}-ferrocyanide can also be noticed. These facts indicate that $Fe^{2+} \rightarrow Fe^{3+}$ oxidation is possible as shown in /13/. At the same time, according to /14-16/ ferrocyanide complex, in small extent, forms in

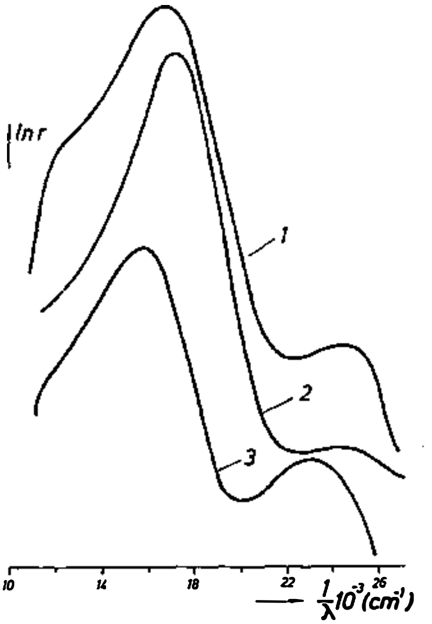

Fig. 1.

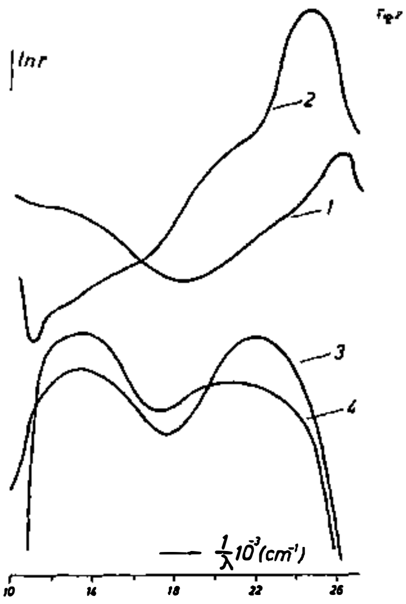

Fig. 2.

in time in Fe^{3+}ferricyanide which changes the original spectrum of this substance, but Fig. 1. shows that spectra 1. and 3. differ to a great extent.

Fig. 3.

Note that the above mentioned characteristics of plotted spectra related to the oxidation of Fe^{2+} are not in accordance with the results obtained by magnetic susceptibility measurement. This effect can probably be accounted for by the fact that the oxidation takes place on grain surface layers only, and that reflection spectrophotometry registers these changes, while the bulk properties, such as magnetic susceptibility, are affected only to a small extent.

Fig. 2. shows spectra of Co^{2+}-ferrocyanide (1), Co^{2+}-ferricyanide (2), Ni^{2+}-ferro cyanide (3) and Ni^{3+}-ferricyanide (4). In Fig. 3 spectra of Mn^{2+}-ferrocyanide (1), Mn^{2+}-ferricyanide (2) and Cu^{2+}-ferrocianide (3) and Cu^{2+}-ferricyanide (4) are shown.

ANALYSIS OF MEASUREMENT RESULTS

Values of magnetic moments in terms of stoechiometric units for complex Fe(II) cyanides with Co, Ni, Cu and Fe^{2+}-ion, determined on the basis of magnetic susceptibility measured, correspond to values calculated according to the relation

$$\mathcal{M}_{eff} = \mu_B \left[2 \mathcal{M}_w^2 (M) \right]^{1/2} \quad (1)$$

where $\mathcal{M}_w$ (M) is magnetic moment of a divalent ion in a weak crystal field (maximal spin). Contribution of Fe^{2+} from the ferrocyanide complex equals zero, showing that this ion is in the strong crystal field. Magnetic moment of $Fe_4[Fe(CN)_6]_3$ corresponds to the value calculated in a way similar to (1).

However, magnetic moment of Mn^{2+}-ferrocyanide corresponds to the value calculated according to the relation

$$\mathcal{M}_{eff} = \mu_B \left[\mathcal{M}_w^2(\mathrm{Mn}) + \frac{1}{2}\left(\mathcal{M}_w^2(\mathrm{Mn}) + \mathcal{M}_w^2(\mathrm{Fe}) \right) + \frac{1}{2} \mathcal{M}_s^2(\mathrm{Mn}) \right]^{1/2} \tag{2}$$

where $\mathcal{M}_W(\mathrm{Mn})$ and $\mathcal{M}_W(\mathrm{Fe})$ are the magnetic moments of Mn^{2+} and Fe^{2+}-ions in a weak crystal field, while $\mathcal{M}_S(\mathrm{Mn})$ is the magnetic moment for Mn^{2+} ion in a strong crystal field.

Magnetic moments in terms of stoechiometric units of Fe(III) complex cyanide are determined on the basis of measured susceptibility values and correspond to the relation:

$$\mathcal{M}_{eff} = \mu_B \left[3\mathcal{M}_w^2(\mathrm{M}) + 2\mathcal{M}_s^2(\mathrm{Fe}) \right]^{1/2} \tag{3}$$

for all substances with Mn^{2+}- ions. The similar is valid for complex ferricyanide with Fe^{3+}-ion.

Relation (2) can be explained as the effect of partial redistribution of Mn^{2+} and Fe^{2+}-ions over cationic positions corresponding to weak (N - coordination) and strong (C - coordination) crystal field, which is caused by heating during anhydration. Due to the equality of magnetic moments of Mn^{2+} and Fe^{3+} it is not possible to determine, within the limits of the measurement error, if the same phenomena exist in the corresponding ferricyanide what is, in fact, quite possible if the oxidation potentials of Mn^{2+} and Fe^{2+}-ions /17/ are taken into consideration.

The problem of analysis of the reflection spectra recorded is a much more complex one. To support this, it is enough to say that even the spectra of $K_4[Fe(CN)_6]$ and $K_3[Fe(CN)_6]$ that have been investigated for a long time are not yet satisfactorily interpreted. Beside the previously mentioned reasons relating to the condition of contemporary theory, we should also mention that the spectral bands corresponding to the Fe-ion crystal field spectra are very weak and, in addition, superposed to the strong bands of charge transfer spectra /5/. A review of spectra shown in Figs. 1-3 shows that these spectra, observed individually, yield very few information in contrast with the spectra of 3d-ions in a weak crystal field /5/. At the same time, we may notice that the spectra plotted have characteristic bands that change with the nature of ions. That means that the spectra of this type enable differentiation of ion contribution in C-, i.e. N - coordination of complex cyanides. Magnetic measurements on the other hand show that, except in the case of Mn^{2+} ions, M - ions are in a weak crystal field. The following phase in interpretation of the spectra should be based on comparison, in a broader spectral region, of these spectra with those of isolated complexes having M-N bonds. This type of investigations should, in a way, be analogous to the investigation of transition metals oxides spectra /18/ although the case of complex cyanides is a much more complex one.

CONCLUSION

The investigation of complex cyanides has yielded additional information on magnetic properties of these substances. It has given new data on their electronic spectra and pointed out a possible way for their interpretation.

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