OPTICAL REFLECTION SPECTRA AND CRYSTAL FIELD OF Co (II) AND Ni (II) COORDINATION COMPOUNDS WITH MELAMINE

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Abstract

This paper presents the results of the investigation of two not previously investigated coordination compounds $CoCl_2 \cdot 2MA$ and $NiCl_2 \cdot 2MA$, where MA denotes melamine, $C_3N_3(NH_2)_3$. The optical reflection spectra and magnetic susceptibility of these substances are investigated.

INTRODUCTION

Melamine (MA) is 2, 4, 6 triamino – 1, 3, 5 triazine of formula $C_3H_3(NH_2)_3$. The crystal structure of this heterocyclic amine is determined [1]. The different amines, e.g. hexametylen-tetramine [2], form the coordination compounds with the transition metal inorganic salts. The possibility of existence of the compounds of this type in the case melamine is examined in our laboratory. This paper presents the first results obtained durring the investigation of the coordination compounds $CoCl_2 \cdot 2MA$ and $NiCl_2 \cdot 2MA$.

EXPERIMENTAL

The synthesis of these compounds is accomplished by mixing the corresponding chloride and melamine in the stoichiometric proportion and heating till 220°C. The results of the chemical analysis confirms the assumed composition on the obtained products. The method of x-ray diffractometry shows that both substances form pure crystalline phases and that these compounds are isostructural (in preparation for publication).

The synthetized compounds are examined by the method of the diffuse reflectance spectrophotometry. The corresponding spectra in the Fig. 1. and 2. are shown. Additional investigations by the magnetic susceptibility measurement are performed. The dependence of the magnetic susceptibility from the temperature by the force method (at B = 0,6 T) is determined.

RESULTS AND DISCUSSION

The first examination of the obtained spectra shows that the Co (II) and Ni (II) ions in the corresponding compounds have the tetrahedral surrounding (e.g. [3]). The interpretation of these spectra is realised by the application of three different graphic methods, which are proposed by Tanabe and Sugano [4], Berkes [5] and König and Kremer [6]. These methods are based on the different approximative calculation of the electronic structure of the d^n-ions in the crystal field of the cubic or other symmetry. The results of such spectrum analysis are given in the Table 1. The wave numbers of the electronic transitions evaluated by the use of the three different method are in relatively good agreement, which corresponds to the accuracy or better to the spectral resolution of the spectra recorded at the room temperature [3, 7].

The transition given in the Table 1. are marked with the arrows in the Fig. 1. and 2. The shorter arrows correspond to the twofold forbidden transitions [3].

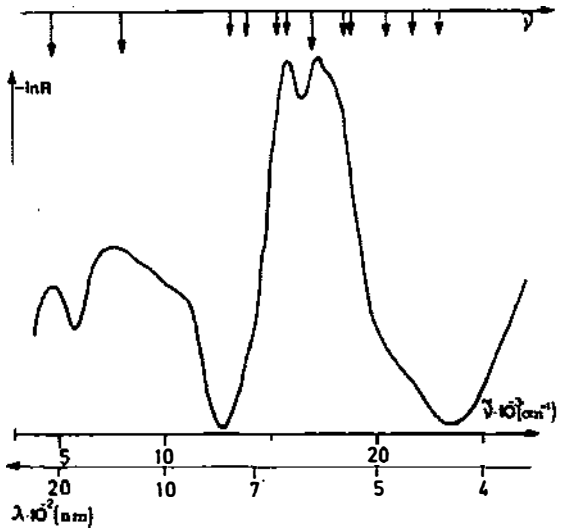

Fig. 1. The optical spectrum of the $CoCl_2 \cdot 2MA$

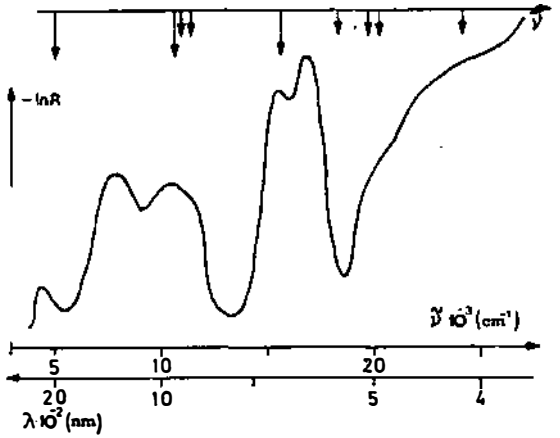

Fig. 2. The optical spectrum of the $NiCP_2 \cdot 2MA$

Finally, the values of the crystal field parameter 10 Dq given in the Table 1. are relatively high, which shows that the Co (II) and Ni (II) ions are surrounded by the N-atoms from the MA-molecules.

Table 1. REFLECTANCE SPECTRA OF $CoCl_2 \cdot 2MA$ AND $NiCl_2 \cdot 2MA$ (TRANSITION WAVE NUMBERS AND CRYSTAL FIELD PARAMETERS DETERMINED BY THE USE OF DIFFERENT METHODS)

$CoCl_2 \cdot 2MA$					$NiCl_2 \cdot 2MA$				
No.	TRANSITION				No.	TRANSITION			
	$^4A_2$ (F) →					$^3T_1$ (F) →			
1.	→ $^4T_2$ (F)	4530 cm^{-1}	4640 cm^{-1}	4660 cm^{-1}	1.	→ $^3T_2$ (F)	4980 cm^{-1}	4800 cm^{-1}	4980 cm^{-1}
2.	$^4T_1$ (F)	8020	7990	7960	2.	$^3A_2$ (F)	10300	10900	10600
3.	^2E (G)	15270	14220	13100	3.	$^1T_2$ (D)	11700	11100	10900
4.	$^2T_1$ (G)	15910	14900	13890	4.	^1E (D)	12100	11400	11300
5.	$^2A_1$ (G)	17990	17070	16240	5.	$^3T_1$ (P)	16000	15800	15700
6.	$^2T_2$ (G)	19523	17780	16780	6.	$^1T_2$ (G)	19200	18700	18300
7.	$^4T_1$ (P)	16950	16830	16900	7.	$^1A_1$ (G)	20300	20100	19600
8.	$^2T_2$ (H)	–	19470	18550	8.	$^1T_1$ (G)		20700	20200
9.	$^2T_1$ (P)	–	19980	18790	9.	^1E (G)	24300	23900	24100
10.	^2E (H)	–	21500	20480					
11.	$^2T_1$ (H)	–	22680	21800					
12.	^2E (D)	–	24200	23000					
	$^2T_2$ (D)								
	10 Dq	4640 cm^{-1}	4830 cm^{-1}	4580 cm^{-1}		10 Dq	6350 cm^{-1}	6400 cm^{-1}	6640 cm^{-1}
	B	749 cm^{-1}	736 cm^{-1}	728 cm^{-1}		B	907 cm^{-1}	907 cm^{-1}	910 cm^{-1}
	β	0,77	0,76	0,75		β	0,88	0,88	0,88

The magnetic measurement results show that examined coordination compounds are the Curie-Weiss paramagnets. The experimental values for the magnetic susceptibility after correction for the diamagnetic contribution [8] enable the calculation of the magnetic moments (μ) of the Co (II) and Ni (II) ions. This procedure gives

μ (Co) = 4,97 μ_B and μ (Ni) = 3,91 μ_B

(μ_B = Bohr magneton). These values show the considerable contribution of the orbital moments, i.e. the weak quenching of the orbital moments [8]., which is an indication for the exact symmetry of the N-coordination polyhedra in the given crystals.

REFERENCES

1. Hughes E. W., J. Am. Chem. Soc., 63, 1737 (1941).
2. Imanakunov B. I. and Lukina L. I., Vzaimodeistvie geksametilentetramina s neorganicheskami solyami i svoistva tverdykh faz, ILIM, Frunze, 1984.
3. Lever A. B. P., Inorganic Electronic Spectroscopy, Elsevier, Amsterdam, 1984.
4. Tanabe Y. and Sugano S., J. Phys. Soc., Japan, 9, 753, 766 (1954).
5. Berkes J. S., Energy Level Diagrams for Transition Metal Ions in Cubic Fields, Mater. Res. Labor. Pennsylvania Univer., Pennsylvania, 1968.
6. Konig E. and Kremer S., Ligand Field Energy Diagrams, Plenum Press, New York, 1977.
7. Sviridov D. T., Sviridova R. K. i Smirnov Yu. F., Opticheskie spektri ionov perekhodnykh metallov v kristallakh, „Nauka", Moskva, 1976.
8. Whitre R. M., Quantum Theory of Magnetism, Springer, Berlin, 1983.