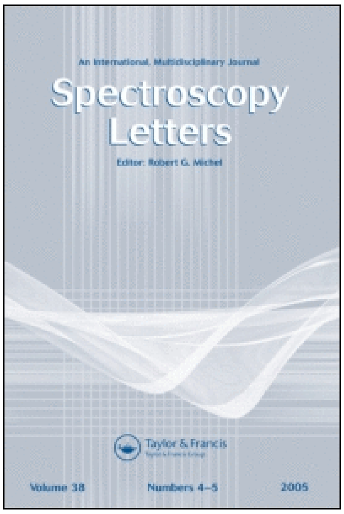

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Complex Compounds of Copper(II) Chromate and Dichromate With 2-(2'-Pyridyl)Imidazole. II. ESR Spectra and Magnetic Studies

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COMPLEX COMPOUNDS OF COPPER(II) CHROMATE AND DICHROMATE WITH 2-(2`- PYRIDYL)IMIDAZOLE.

II. ESR SPECTRA AND MAGNETIC STUDIES

KEY WORDS: Copper (II) chromate complexes, coordination of the chromate ion, ESR spectroscopy and magnetic data

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ABSTRACT

The mononuclear and dinuclear copper (II) chromate and dichromate complexes with 2-(2`-pyridyl)imidazole were synthesized and characterized. The EPR data and the magnetic studies revealed the dimeric structure for some of the compounds as well as elongated tetragonal and rhombic tetragonal octahedron around copper ion.

INTRODUCTION

In our previous paper [1, Part I] we have presented the synthesis, UV/Vis/NIR, IR/FIR spectra and conductometric data of novel copper(II) chromate complexes with 2-(2'-pyridyl)imidazole (pyim). It was found that all the complexes exibit the coordination of the anion forming $[CuN_xO_{6-x}]$ chromophore around the copper anion. The coordination of the CrO_4^{2-} ion to copper ion seems to be a promising feature in light of known toxic and genotoxic nature of this anion [1-6]. This part describes the results of the magnetic and ESR studies of copper(II) chromate complexes with pyim.

EXPERIMENTAL

The complexes have been obtained according to the procedure described previously [1].

The EPR measurements were made on a EPR- SE-X/25A/B as well as on Bruker ER 200 E-SRC, X - band spectrometers. The powder - state and DMF solutions EPR spectra were recorded at room and liquid nitrogen temperatures. DPPH was used as an external standard.

The magnetic measurements were made by the Faraday method in the temperature range 80 - 300 K, using a sensitive Sartorius M-25D electrobalance. The calibrant employed was $HgCo(NCS)_4$, with the magnetic susceptibility assumed to be $16.44 \cdot 10^{-6}$ cm^3 g^{-1}. The corrections for diamagnetism of the costituent atoms were calculated using the Pascal constants. The value $60 \cdot 10^{-6}$ cm^3 mol^{-1} was used as the temperature - independent paramagnetism of copper(II) ion. The effective magnetic moment was calculated per copper ion from the equation $\mu = 2.83\sqrt{\chi_{Cu} \cdot T}$ B.M.

RESULTS AND DISCUSSION

The experimental magnetic susceptibility vs. temperature and the magnetic moment vs. temperature for all complexes are plotted in Figure 1. Table 1 presents some magnetic data for the complexes. These data are consistent with

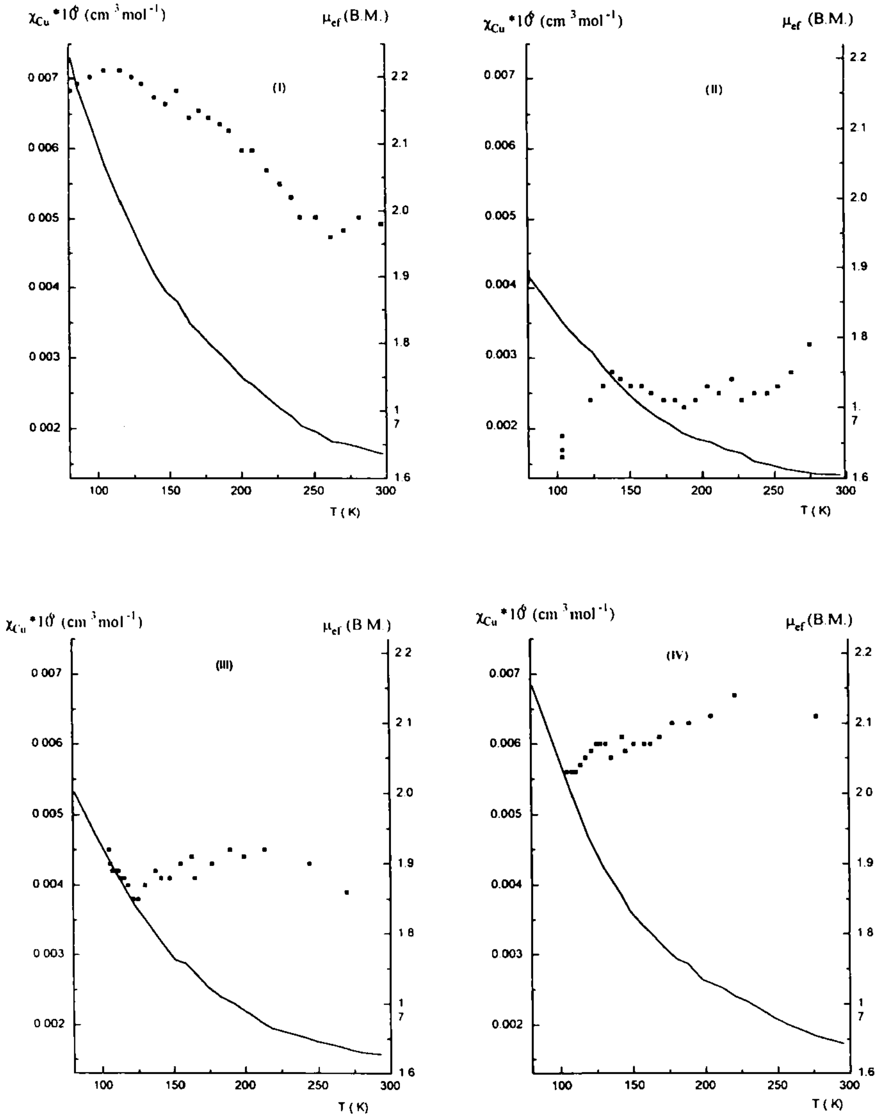


FIGURE 1

The magnetic susceptibility and moments vs. temperature changes for copper(II) chromate complexes with 2-(2'-pyridyl)imidazole.

TABLE 1

The magnetic data for the studied complexes

compound	χ_{mol} (m^3 mol^{-1})		μ_{eff} (B.M.)		Θ (K)
	81 K	295 K	81 K	295 K	
I $[CuLCrO_4 (H_2O)_2]_2$	730	165	2.18	1.98	32.9
II $[CuL_2CrO_4]_2 \cdot 2H_2O$	408	135	1.63	1.79	-10.3
III $CuL_3CrO_4 \cdot 2H_2O$	532	157	1.86	1.92	0.3
IV $Cu_2L_3Cr_2O_7SO_4 \cdot 4H_2O$	684	174	2.11	2.03	12.9

paramagnetic with partly ferromagnetic properties for **I** and **IV** whereas **III** is a paramagnetic with the magnetic moments slightly higher than „spin only" values. The behaviour of II is typical for the antiferromagnetically coupled compounds as it was found e.g. for the dimers with the imidazole bridge between two copper ions [8].

The powder EPR spectra were studied to known the triplet state for dimeric copper(II) complexes (Table 2, Fig.2). Since **I** and **II** contains two spin-coupled, axially symmetric copper(II) centers, both $\Delta M_s = 1$ and $\Delta M_s = 2$ transitions are expected. It seems interesting to calcilate the zero-field splittings, parameter D and compare the averaged g-value with that of the susceptibility measurements.

The powder spectra of **I** and **II** were analyzed using the Wasserman, Snyder and Yager method [9] and spin Hamiltonian for S=1:

$$H = \beta HgS + DS_z^2 + E(S_x^2 - S_y^2) - 2 / 3\ D$$

$H_\perp$(where resonance for an isolated doublet species occurs) = $(g_0/g_\perp)^2 H_0(H_0 \pm D')$; $H_0 = h\nu / g_e\beta$; $D' = D / g_e\beta$; ν - resonance frequency in GHz; D, D' - the separation of the upper triplet state from singlet ground state.

The $\Delta M_s = 2$ forbidden transitions occur at 1743.1 and 1647.8 for **I** and **II** complexes, respectively. They are faint and blurred on decreasing temperature.

TABLE 2

The powder EPR data for the complexes (at 80 K)

compound	observed transitions (G)	Assignment of transitions			D (cm^{-1})	ν (GHz)
I $[CuLCrO_4\cdot(H_2O)_2]_2$	1743.1 $\Delta M_s = \pm 2$	2684.5 $H_{\perp 1}$	3152.2 H_x	3219.7 $H_{\perp 2}$	0,055	9.2415
II $[CuL_2CrO_4]_2\cdot 2H_2O$	1647.8 $\Delta M_s = \pm 2$		3135 $H_{\perp 1}$	3195 $H_{\perp 2}$	0.006	9.3274
III $CuL_3CrO_4\cdot 2H_2O$		2750 H_1	2908 H_2	3238.5 H_3		9.3285
IV $Cu_2L_3Cr_2O_7SO_4\cdot 4H_2O$			2970.4 $H_{\parallel}$	3238.5 $H_{\perp}$		9.3283

Only for **I** the forbidden transition line was enough clear both in room and liquid nitrogen temperatures. The line at g ~ 4 indicate the presence of the exchange and dipole - dipole interactions between the dimers centers. At room temperature I complex is paramagnetic with powder EPR spectrum characteristic of the triplet state while at low temperature the compound is diamagnetic (Fig.2). The signals of 2684.5 and 3219.1 Gs (for **I**) and 3184.9 and 3247.5 Gs (for **II**) are assigned to the low - field perpendicular transitions $H_{\perp 1}$ and high-field $H_{\perp 2}$ respectively.

The line of 3152.2 Gs (for **I**) are associated with high-field parallel transitions H_{z2}. According to the described assignments we have determined the zero-field splitting parameter D for studied complexes (Table2). The direct dipole - dipole coupling energy between the two interacting electrons may be estimated by assuming that they act as if they were each localized on their corresponding nuclei. Under these, as well as the spin - orbit interaction, with an anisotropic

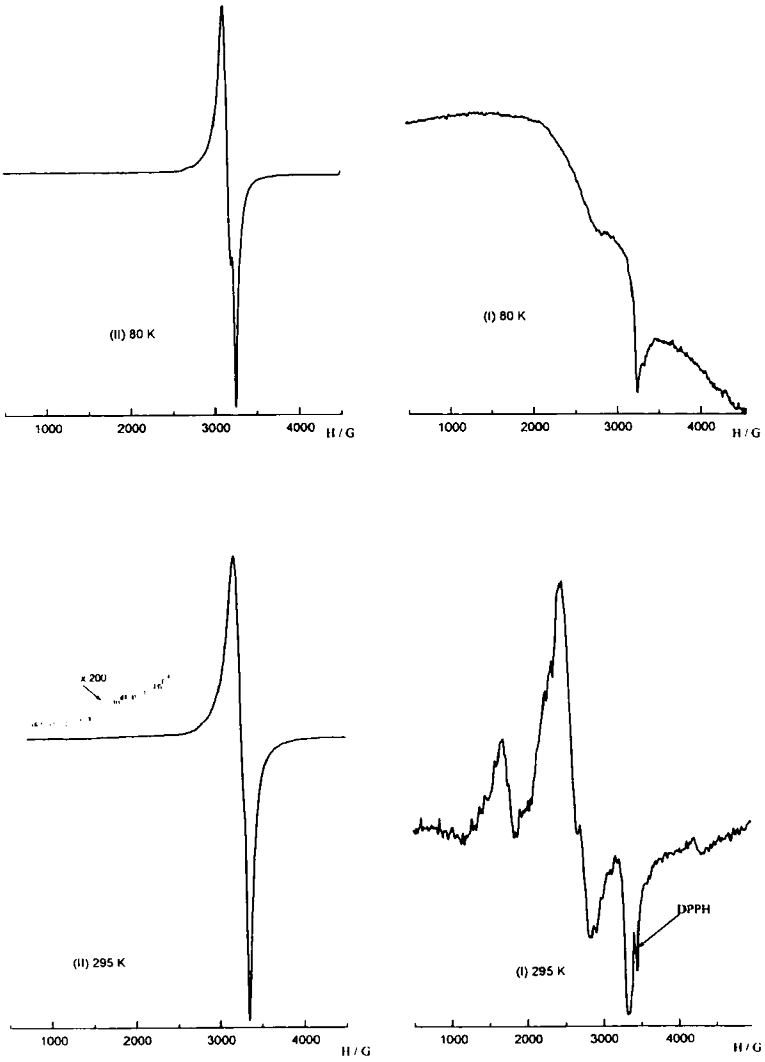


FIGURE 2

The powder EPR spectra of the copper(II) chromate complexes with 2-(2`-pyridyl)imidazole (**I** and **II**) at 80K and 295K temperature.

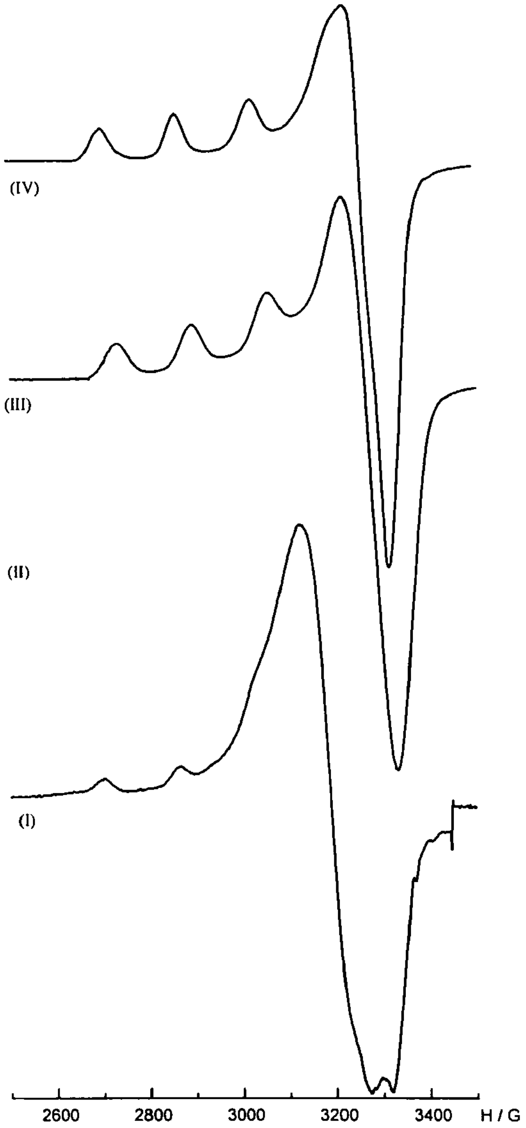


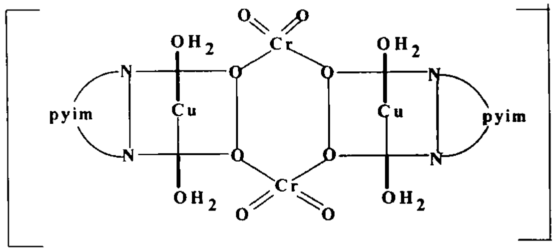
FIGURE 3

The solution EPR spectra of the copper chromate complexes with 2-(2'-pyridyl)imidazole.

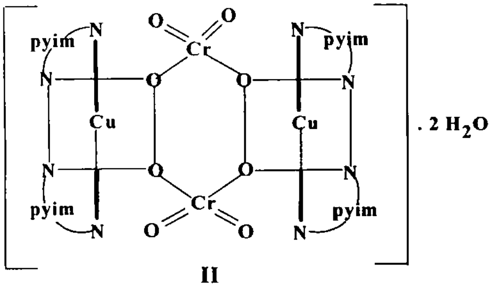
TABLE 3

The EPR data for the DMF solutions of the complexes

Compound	liquid (295 K)		frozen (80 K)	
	$A_0 (10^{-4} cm^{-1})$	g_0	$A_{\parallel} (10^{-4} cm^{-1})$	$g_{\parallel}$
I $[CuLCrO_4 \cdot (H_2O)_2]_2$			175.9	2.284
II $[CuL_2CrO_4]_2 \cdot 2H_2O$			168.5	2.262
III $CuL_3CrO_4 \cdot 2H_2O$	19.9	2.132	165.3	2.181
IV $Cu_2L_3Cr_2O_7SO_4 \cdot 4H_2O$			173.1	2.285



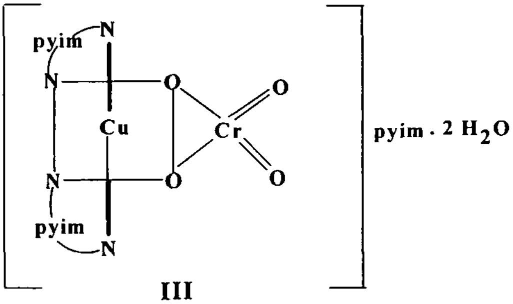
I



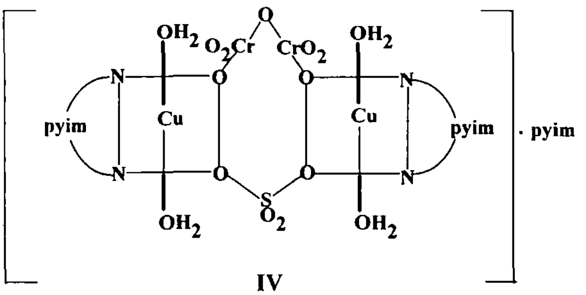
II

FIGURE 4

The proposed structures of the complexes **I-IV**



III



IV

Figure 4. Continued

exchange interaction the zero - field splitting is about 0,055 (for I) and 0,006 (for II) cm^{-1}.

We have not observed the forbbiden bands at low magnetic field for III and IV (both at room and liqiud nitrogen temperature). As III can be a monomer, the situation of IV seems to be more complicated. The conductometric data for the latter show that the complex is also neutral and thus explain its stracture as a dimer with a strong exchange interaction in the ferromagnetic order.

The solid state EPR spectra of III both in room and liquid nitrogen temperature show the octahedral symmetry with some rhombic deformation ($g_3 > 2.04$) and of IV - typical axial spectrum. On lowering the temperature down to liquid nitrogen temperature the intensities of bands decrease and narrow. Frozen solutions of this complexes display nearly axial EPR spectra at 80 K. The observed hyperfine structures at parallel part of EPR spectra are characteristic for the copper electron interactions with I=3/2.

The EPR spectra of the DMF solutions (Fig.3) indicate the copper(II) unpaired electron have to be located on the $d_{x^2-y^2}$ orbital. The $g_{\|}$, $A_{\|}$ and other Hamiltonian parameters are collected in Table 3. The values of $g_{\|}$ are indicative of a tetragonally distorted octahedral geometry around the copper ion in the complexes [10].

CONCLUSIONS

We have presented the synthesis and physicochemical characterization of mono- and dinuclear copper(II) chromate complexes with 2-(2`-pyridyl)imidazole, a biologically relevant ligand. The proposed copper(II) coordinations have been showed on Scheme **1** (Fig.4). The structures have been suggested on the basis of electronic, infrared spectra [1], magnetic moments, EPR and conductometric studies.

Viewed as models, these compounds offer better understanding than those investigated earlier [7] the detoxication process for the carcinogenic Cr(VI) ion. The double bridging effect of the chromate ions seems to be a promising feature regarding the neutralization of the genotoxic activity of the Cr(VI) ion. Very recently, the biological studies showed [11] that complexes **I-IV** are not mutagenic. These facts support both the structures proposed on the basis of the physicochemical studies (this work, Scheme **1**) and the coordination model of the genotoxicity, in general.

Acknowledgments

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