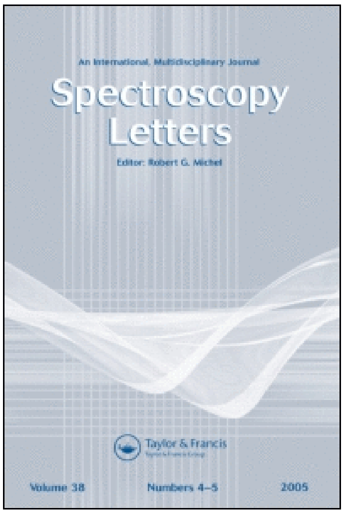

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Complex Compounds of Copper (II) Chromate with 2-(2'-Pyridyl) Lmidazole.: I. Electronic and Infrared Spectra

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COMPLEX COMPOUNDS OF COPPER(II) CHROMATE WITH 2-(2'-PYRIDYL)IMIDAZOLE.

I. ELECTRONIC AND INFRARED SPECTRA

KEY WORDS: Copper(II) chromate complexes, coordination of the chromate ion, UV/Vis/NIR, IR, FIR spectroscopy, conductometric data

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ABSTRACT

Copper(II) chromate and dichromate complexes with 2-(2'-pyridyl)imidazole were synthesized and characterized (IR, FIR, UV-VIS-NIR spectroscopy and conductometric data). The coordination of the chromate and dichromate ions has been found which is in accordance with the recently obtained biological results.

INTRODUCTION

The chromium(VI) ion is a well known carcinogen and mutagen [1-5]. Recently, the possibility of decreasing its genotoxic nature *via* the complexation effect of the chromate ion has been proposed [6,7]. In the detoxyfying system: [metal ion-organic ligand-Cr(VI)] the bioessential copper(II) ion seemed to be a good candidate for a central atom. The lowering of the mutagenic potency of copper chromate complexes with heterocyclic bases in comparison to potassium chromate was explained through the *coordination* of the chromate ion to the copper ion [6]. This coordination can lead to the stopping of the resulting large complex entity by the cellular membrane and/or the blockage of the Cr(VI) reduction process in the cell.

In continuation of our investigation on the possibility for decreasing the genotoxic nature of hexavalent chromium, we report here the synthetic procedure and physicochemical studies of a number of copper chromate coordination compounds with 2-(2'-pyridyl)imidazole (pyim). The copper complexes containing the imidazole ring have a vital biological functions being, for example, a component of various copper proteins and enzymes [8-10]. In this report, we undertook a study of the novel [Cu(II)-pyim-Cr(VI)] system with the following goals in mind:

- further searching for the possibility of the CrO_4^{2-} ion coordination;
- study on the influence of the anion used *i.e.* chloride, sulfate, nitrate, on the chemical composition of the isolated complexes (such dependence was found in our previous studies [11]);
- study on the influence of the chemical composition of the complexes on the symmetry of the copper environment.

EXPERIMENTAL AND CALCULATIONS

2-(2'-pyridyl)imidazole (m.p. 136°C) was synthesized by previously reported method [11];other chemicals were p.a.. from POCh-Gliwice.

Generally, the compounds were formed during the reaction of the methanolic solution of ligand previously mixed with a water solution of K_2CrO_4, and a water solution of the respective copper salt: $CuSO_4$, $CuCl_2$ and $Cu(NO_3)_2$. Dichromate complexes were formed from a mixture of CrO_3 and $CuSO_4$ to which a methanolic solution of ligand was added. The powder precipitates were formed immediately. The precipitates were washed with water and methanol and dried over $CaCl_2$ and in vacuo at room temperature. Attempts to obtain single crystals are being undertaken, up to now, without success.

(I) $[CupyimCrO_4(H_2O)_2]_2$

A methanolic solution of 2(2'-pyridyl)imidazole (10 cm^3, 0.75 M) was added dropwise upon stirring to K_2CrO_4 solution (30 cm^3, 0.25 M). This was mixed with the same amount of 0.25 M $CuSO_4$, $Cu(NO_3)_2$ or $CuCl_2$.

(II) $[Cu(pyim)_2CrO_4]_2 \cdot 2H_2O$ and (III) $[Cu(pyim)_2CrO_4](pyim) \cdot 2H_2O$

These compounds were prepared as for (I) but using 20 cm^3 and 30 cm^3 of the solution of ligand, for (II) and (III), respectively.

(IV) $[Cu_2(pyim)_2Cr_2O_7SO_4(H_2O)_4](pyim)$

A solution of $CuSO_4$ (40 cm^3, 0.2 M) was added to the solution of CrO_3 (40 cm^3, 0.2 M). Finally pyim in methanol (100 cm^3, 0.25 M) was added dropwise.

Elemental analyses (C, H, N, S) (Table 1) were run on a model 240 Perkin-Elmer CHN Analyzer.

IR spectra (4000-400 cm^{-1}) in KBr and FIR spectra (400-70 cm^{-1}) with specimens applied as suspensions of the complexes in Nujol into a polyethylene window, were recorded on Perkin-Elmer 180 spectrophotometer.

The molar conductivity was measured in formamide solutions (10^{-3} M) using Radelkis conductometer type OK-102.

The diffuse reflectance spectra for the pyim ligand and obtained complexes were measured in Li_2CO_3 pellet and the absorption spectra in the formamide solution in the spectral range 12000 - 48000 cm^{-1} with Hitachi 365 UV/VIS spectrophotometer interfaced with IBM PC/XT/AT computer. Additionally, the formamide solution spectra were recorded on a Beckmann UV 5240 (10000 - 48000 cm^{-1}) and Cary 5 UV-Vis-NIR (5500-20000 cm^{-1}) instruments. The resolution processing of the weakly resolved bands in the diffuse reflectance spectra has been performed by applying the variable digital filter recently described

TABLE 1
Analytical and conductivity data for the complexes

Complex (colour)	Found (Calcd.) (%)				Λ *)
	C	H	N	S	
I $[Cu(pyim)CrO_4(H_2O)_2]_2$ brown-green	26.88 (26.63)	3.25 (3.08)	11.41 (11.65)		-
II $[Cu(pyim)_2CrO_4]_2 \cdot 2H_2O$ light-green	39.73 (39.39)	3.18 (3.31)	16.62 (17.23)		13
III $[Cu(pyim)_2CrO_4](pyim) \cdot 2H_2O$ yellow-green	44.49 (44.28)	3.92 (3.87)	19.30 (19.36)		12
IV $[Cu_2(pyim)_2Cr_2O_7SO_4(H_2O)_4](pyim)$ pearl green	30.41 (30.45)	3.54 (3.09)	12.26 (13.32)	3.90 (3.39)	18

*) $\Lambda\,[\Omega^{-1}\ \mathrm{cm}^2\ \mathrm{mol}^{-1}]$

by Biermann and Ziegler [13] and used sucessfully by others [14] and us [15, 16] for resolution of the electronic spectra. The filter acts by a single convolution of the spectral data with a filter function.

$$T(k) = \sum_{n=-N}^{N} a(n) \times f(k-n) \quad (1)$$

$$a(n) = \left\{ \frac{2\alpha + 1}{2N + 1} - \frac{2\alpha|n|}{N(N+1)} \right\} \quad (2)$$

where T(k) is the filtered spectrum with k measured points. (All points have to be equally distanced), a(n) is the filter function, f the unfiltered spectrum, N – the filter with integer number greater then |n|, and α is a continuous parameter determining the degree of the resolution enhacement. By varying α and N one can achieve different degrees of noise reduction and also increase of height and decrease of width of the component bands.

Distribution of charge density for a 2-(2'-pyridyl)imidazole was calculated by AM1 method . This method was described earlier in [17].

Warning: Sixvalent chromium compounds are toxic and genotoxic. They cause also an allergic contact *dermatitis* in man. As similar compounds i.e. copper chromate complexes with bpy and phen are explosive [11], these complexes are likely to be explosive as well.

RESULTS AND DISCUSSION

The molecule of 2-(2'-pyridyl)imidazole is a member of the extensive family of ligands containing the imidazole ring. The calculations showed that it has two donor nitrogen centers available for chelation (Fig.**1**). The chemical composition of obtained four complexes (Table 1) was found to be independent of the anion of the Cu(II) salt used but dependend only on the ratio: metal/ligand/chromate. The values of the conductivity measured for the formamide solutions (Table **1**) suggested that in such conditions the complexes are non-ionic.

Infrared spectra

The IR data found for the complexes and the proposed assignment are given in Table **2**. The complexation effect is mainly pronounced via Cu-N, Cu-O-Cr and Cu-O(H_2O) vibrations. We made the Cu-N assignments at 247-280 cm^{-1} on the basis of known literature data for the Cu(II) complexes with 2-2'-bipyridyl [10, 18] and imidazole [19-22]. The position of the ν_s (ca 550 cm^{-1}) and ν_{as} (ca 770 cm^{-1}) (here the later obscured by strong organic ligand bands) are due to two Cu-O-Cr bridges. Addittionally, the Cr-O-Cr vibrations in (**IV**), can be elucidated from the earlier transitions of the M-O-Cr bridge [23-26]. The ν Cu-O(H_2O) vibrations [27, 28] at ca 440 cm^{-1} were found exclusively in (**I**) and (**IV**) complexes. Lattice water vibrations in aqua complex found previously at 535 cm^{-1} are shifted in our complexes to ca 600 cm^{-1}.

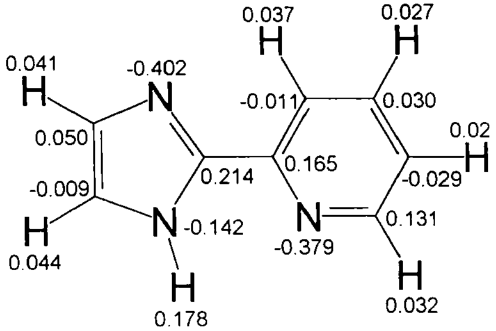

FIGURE 1. 2-(2'-pyridyl)imidazole.

The well defined splittings in the 300-400 cm^{-1} region are due to three ν_4 (F_2) components of Cr-O vibrations ascribed to C_2 site symmetry. Among two active stretching modes in this region i.e. ν_4 and ν_2, only the former one was split into three components, as expected [29, 30]. Unfortunately, the strong bands in the 750-950 cm^{-1} associated with splitting components of the totally symmetric ν_1 and ν_3 vibrations in the chromate ion were completely obscured by the strong organic ligand vibrations. The coordination effect is seen in this region through the broadness of the bands. Thus the complexation of the chromate ion is found in the FIR region exclusively. Weak bands at ca 200 cm^{-1} are associated with the bending and rocking modes of the O_2CrO_2 entity [23].

Electronic Spectra

Tables 3 and 4 present the band positions in the electronic absorption and diffuse reflectance spectra resolved with the digital filter method [13]. Generally, the diffuse reflectance spectra are weakly resolved whereas the formamide solution spectra are better resolved but unfortunately, they exhibit much shorter absorption range due to the lack of solvent transmission in the ultraviolet.

The unfiltered, room temperature, electronic spectra of the formamide solutions of the compounds measured in the region 5500-40000 cm^{-1} consist of the three rougthly separated areas of absorption: (1) -a weak shoulder (compound **III**) at about 11000 cm^{-1}; and a common features for all compounds: (2) - a very broad band with slightly greater than (1) intensity at 15000 - 16000 cm^{-1} as well as (3) - an intense, very broad absorption region 21000 - 40000 cm^{-1} with the single, very intense band centered at 33000 cm^{-1}. The last band has a shoulder on the lower energy side. A weakly resolved vibrational progression is seen superimposed over the shoulder (Fig.2). The digital filtration revealed several components of these absorption regions (Table 3&4).

As a result of the analysis, the spectra were divided in terms of (i) d-d transition in the copper ion; (ii) the charge-transfer spectra within the chromate and dichromate ions; (iii) the intraligand transition in the pyim molecule (Table 3).

(i) the d-d transitions

Table 4 presents the results of the resolved 5500-20000 cm^{-1} absorption region for the studied complexes. No electronic absorption was observed below 10000 cm^{-1}.

The common feature of all spectra is a broad, *ca* 16000 cm^{-1} absorption region with λ_{max} values, 200 - 800 cm^{-1} higher in the solid state in comparison to the solution spectra. (Table 4). The characteristic 16000 cm^{-1} band under digital filtration process resulted in two or three component peaks for all compounds. The EPR studies [36] indicate that **I** and **II** complexes are at room temperature dimers and that for all studied compounds the location of the unpaired electron is on the $d_{x^2-y^2}$ orbital. The preferred stereochemistry of the copper(II) souroundings in **I** -**IV** is a tetragonally distorted octahedron with the following one electron orbital sequence: $d_{x^2-y^2} >> d_{z^2} > d_{xy} > d_{xz}\ d_{yz}$.

However, as the pure tetragonal CuA_4B_2 chromophores (D_{4h}) exists only with monodentate ligands [31], the nonequivalent ligands in the plane change the stereochemistry of the chromophore into six coordinate elongated rhombic

TABLE 2

Important bands in the IR and FIR spectra of complexes (in cm^{-1})

Compound	ν (O-H)	ν C=C + ν C=N	"breathing"	ν(Cu-O)(H_2O)	ρ H_2O	ν (Cu-N)	ν_2,ν_4(Cr-O) CrO_2*	ν_s(Cu-O-Cr) ν(Cr-O-Cr)	other bands
pyim		1590 s 1560 s 1480 s 1455 s	990 s						170 vs 403 vs 468 s 503 s 621 vs
I	3420 m, br	1640 m 1615 m 1565 m 1495 m 1470 s	1020 w	433m	590 m, br	247 m 277 m	310 w ν_2 351 s 373 w ν_4 398 w 212, 225*m	547 m	162 s,189 m 412 m, 488 s 648 s

II	3420 m, br	1610 s 1560 m 1510 m 1470 s	1010 w			262 m 279 m	315 s ν_2 362 s 383 m ν_4 400 m 212, 225*m	514 m	162 m,185 m 411 m,631 s
III	3400 m, br	1610 m 1570 m 1470 s	1000 w			247 m 260 m	309 m ν_2 361 m 381 m ν_4 390 m 213 m, 225*s	547 m	185 m 288 w 415 m 641 vs
IV	3420 m, br	1615 m 1565 m 1495 m 1470 m	1020 w	426 m	605 s, br	249 m 273 m	329 w ν_2 367 m 383 m ν_4 399 m 210*m	532 m	191 s 414 m 485 w

vs - very strong, s - strong, m - middle, w - weak, sh - shoulder, br - broad

TABLE 3

Diffuse reflectance and absorption spectra of the complexes in the 5500-49000 cm region resolved on filtration.The absorption spectra are in the parantheses. The parameters of filtration: step = 100; $\alpha = 250$; N = 20; the energies in cm^{-1}

Complex	d - d	O -> Cr	pyim
	15800	21400; (21900)	29500; (31800)
I	(15300)	25600; (26500)	33000;
		37500; (41800)	(43800)
			47600
		21500; (21700)	28000
II	16000 br	25500; (26400)	(33000)
	(15800)	38200; (38200)	33400
		42000	(44000)
			47400
	(~ 1080 sh)	21400; (21600)	27500 sh
III	15800	25700 vibr.; (26100)	30500
	15000	38500; (36900)	33500 (33100)
		41000	
			44500
			47700
	15800	21300; (21800)	29500
IV	(15300)	25200; (26300)	(32300)
		37900; (38300)	33500
		42200	43300
			47800

TABLE 4

Diffuse reflectance and absorption spectra of the complexes resolved in the 5500-20000 cm^{-1} absorption region. ε values are in the parantheses. The parameters of filtration: step=100; α=250; N=8; the energies in cm^{-1}

Complex	Diffuse	Filtration	Absorption	Filtration
I	15800	15300	15300	15200
		16400	(70)	16300
		17700		17500
II	16000	15400		
		16400		15000
		17700	15800	16000 sh
			(85)	
III	15800	15400	1080 sh	
		16400	(~52)	15400
		17700	15300	15700
			(80)	16100
IV	15800	15400	15300	14600
		16400	(170)	16300
		17600		17600

octahedron (D_{2h}) [31]. Usually, in the copper chelates both bond-length and bond angle distortions take place [31,32]. Imidazole itself can act as a bridging molecule [20] but the conductivity data (Table 1) exclude this case. The results point out that in the formamide solutions all the complexes are neutral. Thus, the chromate and sulfate ions are the bridging moities in the dinuclear complexes [36]. The compound **IV** can be also an example of the species with non-equivalent bridging ligands . The magnetic data [36] imply that in the complexes two copper

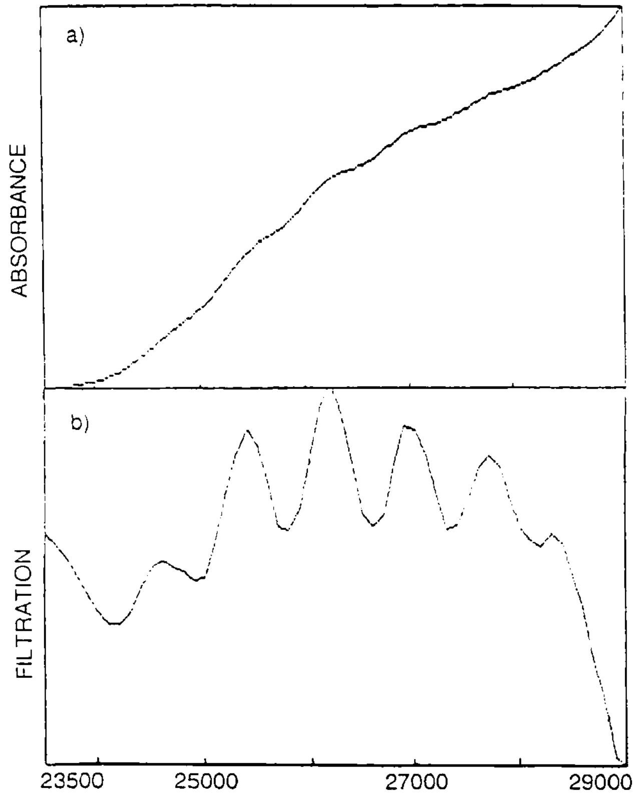

FIGURE 2.

a) The absorption spectra of $[Cu(pyim)_2CrO_4]_2 \cdot 2H_2O$ (**II**) in formamide ($2 \cdot 10^{-4}$ M). Region 23500 - 29000 cm^{-1}.

b) The filtration (step100; $\alpha = 250$; N = 5).

ions are in the quite a distance resulting in the formation of two independent CuA_2B_4 elongated rhombic chromophores.

Additionally, the spectra of the monomer $[Cu(pyim)_2\ CrO_4]pyim\ 2H_2O$ exhibit a weak low energy shoulder at 11000 cm^{-1} [Tables 3-4].

Generally, on the basis of the electronic spectra and EPR data [35], the monomeric copper(II) complexes with 2-(2-pyridyl)imidazole of the type $Cu(L)_2$

X_2 (X-halogen, NCS^-, NO_3^-) depending on the anion may be divided into two types: (a) chloro and thiocyanato complexes with cis-O_h stereochemistry (d_{z^2} ground state) and (b) bromo, iodo and nitrato complexes with the intermediate structure between a regular trigonal- bipyramidal and a regular square-pyramidal ($d_{x^2-y^2}$ ground state). The electronic spectra of **III** are consisted with the (b) type spectra in respect to the presence of the 11000 cm^{-1} shoulder. However, the main 16000cm^{-1} band is significantly (*ca* 1600cm^{-1}) shifted in comparison to the nitrato complex. Thus, possesing the same ground state the chromate monomer exhibits a more tetragonally distorted molecular structure [18]. That means that the exchange the ligand nitrate into chromate influences the stereochemistry of the copper(II) environment without changing the ground state. The literature survey shows that copper(II) imidazole complexes both mono and polynuclear exhibit exlusively elongated tetragonal (ETO) and rhombic tetragonal geometry (RTO) [31].

(ii) the charge transfer spectra of the coordinated chromate ion

Generally, the charge transfer bands observed in the lower symmetry molecules would have characteristics similar to those observed in the "parent" higher symmetry species. The closely grouped orbitals in the lower symmetry exhibit the same gross features, as expected [29, 30]. In the 21000-29000 cm^{-1} absorption region oxygen $p\pi$-chromium $d\pi$ charge transfer transitions predominates. In studying the electronic spectra of the coordinated CrO_4^{2-} and $Cr_2O_7^{2-}$ ions we are dealing with closed shell d^0 molecules with the reduced ($T_d \rightarrow C_{2v}$) symmetries (bridging or chelating ions). Under resolution all complexes exhibit two most characteristic transitions at ca 21000 and 26000 cm^{-1} ,respectively (Table 3). They have been attributed to ligand-to-metal (O →Cr) charge transfer transitions within the coordinated chromate and dichromate ions. The isolated CrO_4^{2-} (T_d) ion exhibits three main absorption regions at ca 26000-30000 ($^1t_1 \rightarrow 2e$), 34-38000 ($6t_2 \rightarrow 2e$) and 42000 cm^{-1} ($6t_1 \rightarrow 2e$) [33]. The most prominent feature of the symmetry lowering effect is the presence of the 21000 cm^{-1} band which appears upon symmetry decreasing $T_d \rightarrow C_s$ [30]. It has been assigned to the lowering symmetry product of the dipole forbidden $^1A_1 \rightarrow {}^1T_1$ transition ($t_1 \rightarrow 2e$; T_d parentage). Generally, the characteristic feature of the band centered at 26000cm^{-1} is the distinct vibrational progression in the totally symmetric $\nu_1(A_1)$ Cr-O mode [11, 30]. The average frequency of ca 800 cm^{-1} is usually reduced of a *ca* 10% in comparison to the ground state value and reflects the weakening of the Cr-O bond in the exciting state [34].

In the unresolved solid state spectra no vibrational structure was detected .However, the digital filter method allowed to exhibit these fine structures (Fig. 1), slightly better regular in the solution spectra than in the diffuse reflectance spectra. It contains six to seven members with an average excited state frequency of 800 cm^{-1}.

In the higher energy absorption area (bands at 38000 cm^{-1} and 42000 cm^{-1}) there is lack of regular vibrational structure (the digital resolution exhibit irregular feature). It is apparent that the charge transfer process within the coordinated anion in this region is more complex due to the overlaping strong intraligand absorption of the pyridylimidazole molecule. The latter exhibits the strong (ε ca. 10000) transitions within organic ligand thus the overlap of various states and transitions can be expected.

The crystallographic studies on various chromate complexes showed that the coordination effect roughly retains chromate internal geometry [30]. However, the tendency to coordination in the case of the dichromate is much weaker [30]. The crystalographic data shows also that the geometry of the chromate ion significantly preferes the bridging structure [30], in accordance to our findings in dimers **I** and **II**.

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