STRUCTURE ELUCIDATION AND ANALYTICAL APPLICATION OF THE ISOTHIOCYANATO-PYRIDINE COMPLEXES OF SOME TRANSITION METAL IONS USING IR AND FIR SPECTROSCOPY

By

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The aim of this work was to extend the application of IR spectrophotometric quantitative analysis to the determination of some inorganic cations without separation, using their complexes formed with organic reagents.

The investigations were directed to transition metal ions most frequently occurring in alloys [Fe(II), Co(II), Ni(II), Mn(II), Cu(II), Cd(II), Zn(II) and Cr(II)], which form insoluble precipitates with pyridine as selective reagent in aqueous medium in the presence of isothiocyanate ions. Precipitate formation reaction and the structures of the resulting precipitates can be seen in Fig. 1.

The IR spectra of the complexes, despite the great similarity, show certain differences depending on the central metal atom and the steric structure, manifesting in the different number of bands and some frequency shifts. The IR spectra of the complexes of bivalent transition metals studied can be seen in Fig. 2, 3 and 4.

Utilizing the differences observed, the reaction selective for a group of metals can be made specific for the individual metal ions, by applying absorption bands in the IR spectrum of the isothiocyanato-pyridine complex of the metal which do not appear in the spectra of the complexes of other metals in the alloy. In such a way, "analytical sites" have been determined for the metal ions, shown for the bivalent metals in Fig. 5. As an example, it can be seen from the figure that Mn(II) ions can be determined in the presence of Ni(II) and Cu(II) quantitatively, without separation, on the basis

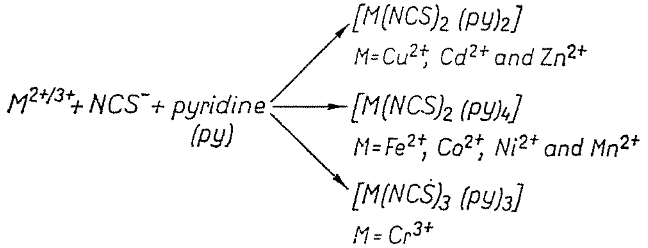

Fig. 1. The structures of the isothiocyanato-pyridine complexes of some transition metal ions

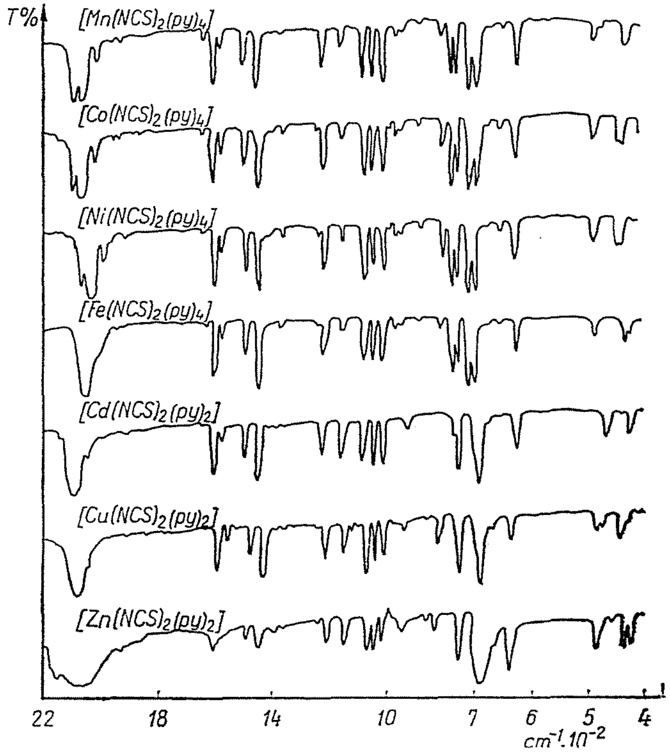
T%
[Mn(NCS)$_2$(py)$_4$]
[Co(NCS)$_2$(py)$_4$]
[Ni(NCS)$_2$(py)$_4$]
[Fe(NCS)$_2$(py)$_4$]
[Cd(NCS)$_2$(py)$_2$]
[Cu(NCS)$_2$(py)$_2$]
[Zn(NCS)$_2$(py)$_2$]
22
18
14
10
7
6
5
4
cm^{-1}.10^{-2}

Fig. 2.

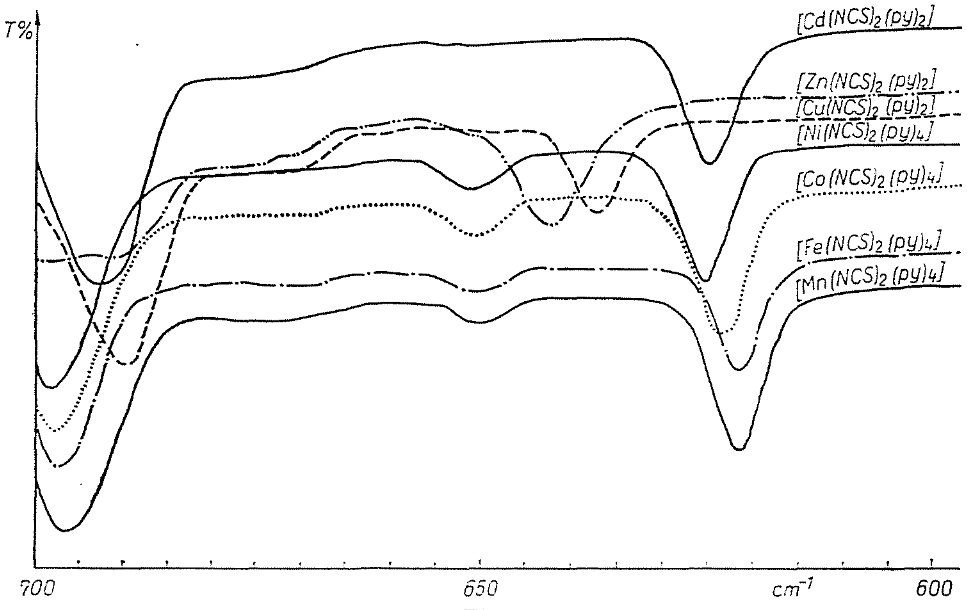
T%
[Cd(NCS)$_2$(py)$_2$]
[Zn(NCS)$_2$(py)$_2$]
[Cu(NCS)$_2$(py)$_2$]
[Ni(NCS)$_2$(py)$_4$]
[Co(NCS)$_2$(py)$_4$]
[Fe(NCS)$_2$(py)$_4$]
[Mn(NCS)$_2$(py)$_4$]
700
650
cm^{-1}
600

Fig. 3.

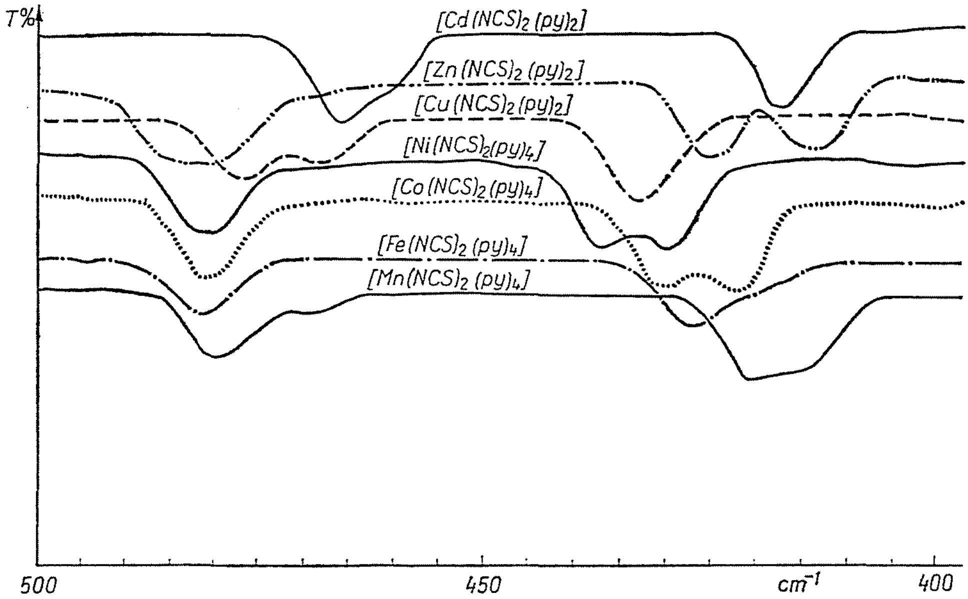

Fig. 2, 3, 4. The IR spectra of the isothiocyanato-pyridine complexes of some transition metal ions

of the concentration — absorbance relationship of the 420 cm^{-1} band of [diisothiocyanato-tetrakis(pyridine) Mn(II)] complex.

Of the many possibilities shown in the figure, several have been used as a basis of analytical methods, developed to solve particular problems occurring in the practical analysis of alloys [1—3].

(See Fig. 5 on page 81)

Experimental methods and results

A method is discussed here applicable for the analysis of chromium-iron alloys, which is an extension of the possibilities given in Fig. 5 for the determination of Cr(III) ions.

The complexes were separated from 100 cm^3 of aqueous solutions with concentrations of 0.1 g of metal ion. 100 cm^{-3} by the addition of 1 g of ammonium rhodanide and 5 cm^3 of pyridine [4—12]. On the basis of the literature data and elementary analysis we have found that from the solution of iron(II) trans-[Fe(NCS)$_2$(Py)$_4$], and from that of chromium(III) [Cr(NCS)$_3$(Py)$_3$] complexes separate. The IR spectra of the complexes formed from the solutions containing Fe(II) and Cr(III) ions separately and simultaneously (in 1 : 1 ratio), and from a solution obtained by dissolving a chromium-iron alloy are shown in Fig. 6. It can be seen that complexes of identical structure are formed from the solution obtained by mixing the solutions of metal ions and from the dissolved alloy, with the difference that in our case the bands assigned to the complex of Fe(II) are stronger for the solution of the alloy than for the solution containing the two metal ions in a 1 : 1 ratio.

Studying the IR spectra of the isothiocyanato-pyridine complexes of Fe(II) and Cr(III) ions in order to find analytical sites for their simultaneous determination, it can be concluded that at 1622 cm^{-1} [triisothiocyanato-tris(pyridine)-Cr(III)], whereas at 1042 cm^{-1} [diisothiocyanato-tetrakis-(pyridine)-Fe(II) has such a band which is not disturbed by the other component, since it has a grey-body-like absorption in the region concerned (Fig. 7).

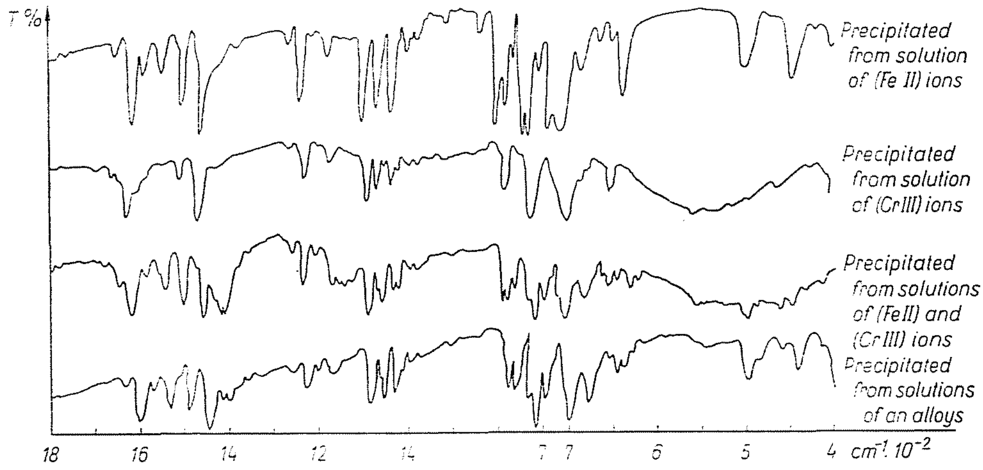

Fig. 6. The IR spectra of isothiocyanato-pyridine complexes precipitated from the solutions of Fe(II) and Cr(III) ions and from the solution of an iron-chromium alloy

For the quantitative analysis stock solutions containing 1 mg.cm^{-3} of the metal ions were mixed as shown in Table 1 to prepare a standard series. The table gives the amount of solutions in cm^3, which is identical to the amount of metal ions (mg), and also to the percentage metal ion contents since the total volume is always 100 cm^3.

Table 1

Standard series for the simultaneous determination of Cr(III) and Fe(II)

	Volumes of stock solutions (cm^3)						
	1	2	3	4	5	6	7
Cr(III)	20	30	40	50	60	70	80
Fe(II)	80	70	60	50	40	30	20

From the standard series precipitates were prepared by adding ammonium rhodanide and pyridine and heating to the boiling point, and by filtering, washing and drying the precipitate for 1 hour in vacuum desiccator. Thereafter potassium bromide discs were prepared by measuring 10.0 mg of precipitate into 1,000 g of KBr, and then the IR spectra were recorded in the vicinity of analytical sites. For all standards three parallel measurements were made. The concentration dependence of the average absorbances determined by baseline correction method at the analytical sites are given in Table 2.

The equations of calibration lines were determined by calculator from the concentration-absorbance data pairs.

The equations: $A_{1622\mathrm{cm}^{-1}} = -0{,}14961 + 0{,}00895 \cdot C_{\mathrm{Cr(III)ion}}$

$A_{1042\mathrm{cm}^{-1}} = -0{,}01832 + 0{,}00824 \cdot C_{\mathrm{Fe(II)ion}}$

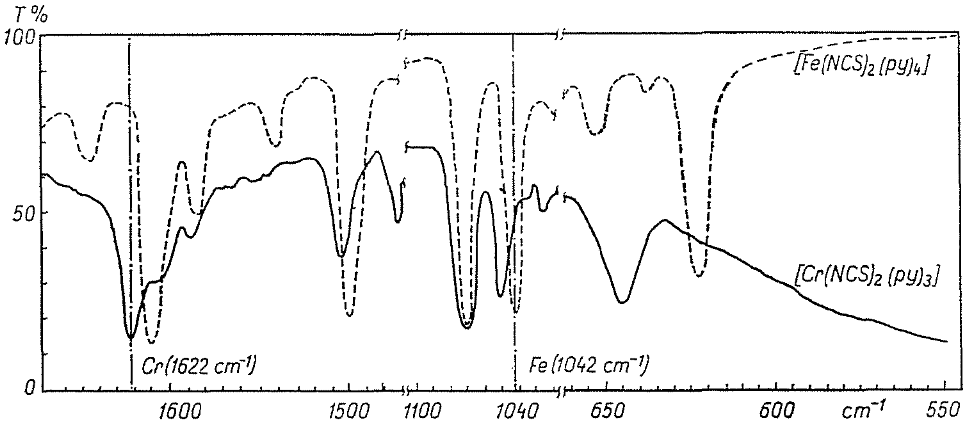

Fig. 7. Analytical sites for the simultaneous determination of Fe(II) and Cr(III) ions

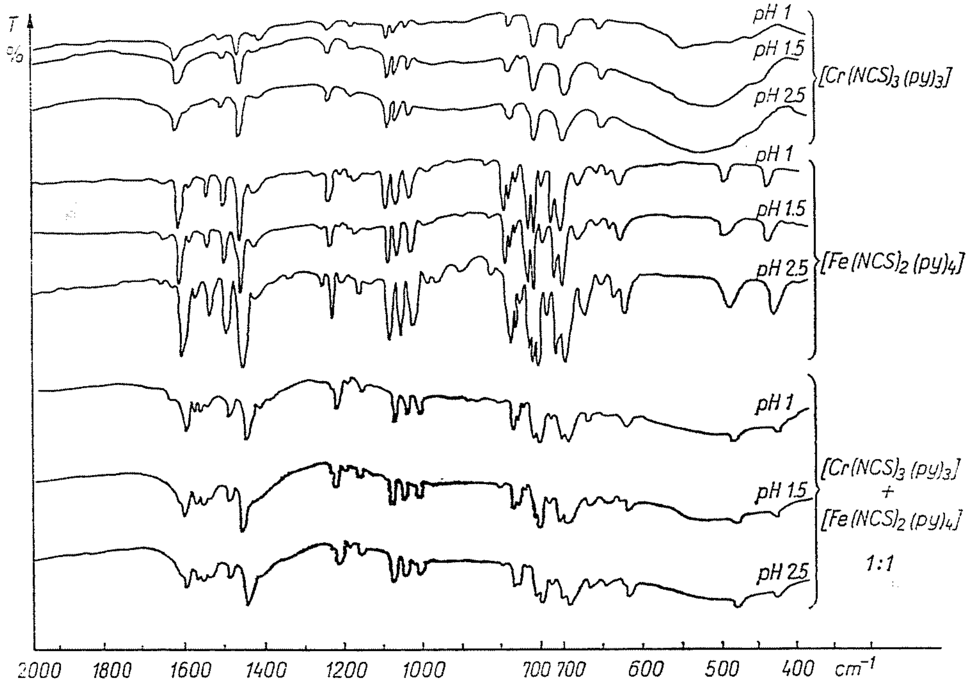

Fig. 8. The IR spectra of the complexes separated at various pH values

Table 2

Concentration dependence of absorbance for the standard series in the simultaneous determination of Cr (III) and Fe(II) ions

Cr(III) %	20	30	40	50	60	70	80
$A_{1622 cm^{-1}}$	0.025	0.120	0.215	0.300	0.385	0.470	0.570
Fe(II) %	20	30	40	50	60	70	80
$A_{1042 cm^{-1}}$	0.140	0.225	0.310	0.405	0.490	0.575	0.615

These equations were tested on a chromium-iron alloy of known composition (Cr: 37.6%, Fe: 61.8%). The alloy was dissolved in 1 : 1 hydrochloric acid solution, by adding 5 cm^3 of acid to 0.1 g of alloy. After dissolution the volume was made up to 100 cm^3. Regarding that the standards were precipitated in neutral solution, and the solution of the alloy contains 2.5 cm^3 of hydrochloric acid in 100 cm^3 solution, the effect of pH had to be studied on the structure of complex and on the quantitativity of precipitation. These investigations led to the following results:

1) The difference between the weights of complexes precipitated from neutral solution and from the solution containing 2.5 cm^3 cc. HCl/100 cm^3 does not exceed the deviation of measurement. This was investigated separately for chromium and iron, and also for their simultaneous presence.

2) Precipitates were prepared from solutions containing Fe(II) and Cr(III) ions separately and also simultaneously in 1 : 1 ratio from neutral solution and from solutions of $pH = 1, 1.5$ and 2.5. The spectra of the resulting complexes are shown in Fig. 8. As can be seen, the pH of the medium, within the range investigated, has no influence on the structures of complexes, insofar as the number, frequencies and intensities of IR bands were the same for all pH values studied.

Therefore, after dissolving the alloy, the solution was not neutralized, and the isothiocyanato-pyridine complexes were precipitated from the mildly acidic solutions in a way described above. The precipitate was filtered, washed and dried, KBr discs were prepared by measuring 10.0 mg of precipitate into 1.000 g of KBr, and the IR spectra were recorded. The averages calculated from the absorbances of three parallel samples measured at the analytical sites were as follows:

$$A_{1622\ \mathrm{cm}^{-1},\ \mathrm{Cr(III)}} = 0.175$$

$$A_{1042\ \mathrm{cm}^{-1},\ \mathrm{Fe(II)}} = 0.490$$

On the basis of the concentration-absorbance relationship 37.0% Cr and 62.5% Fe concentration was obtained. The relative deviation of chromium determination is, therefore, −1.3%, and that of iron determination is 1.3%.

With the purpose of obtaining structural information we measured the far-infrared spectra of the complexes in the 40—400 cm^{-1} region. Far-infrared data and the assignments for the metal ligand and metal-isothiocyanate stretching vibrations are presented in Table.

On the basis of X-ray investigations it has been suggested that the compounds $[M(NCS)_2(py)_4]$ ($M = Co$, Ni; $py =$ pyridine) are transoctahedral monomers with the thiocyanate group bonded to the metal via the nitrogen atom [13]. Then, according to selection rules, in the far-infrared spectra a single M — Py and M — NCS vibration should be observed. Indeed, a single M — NCS band is observed in the spectra of all the trans-octahedral $[M(NCS)_2(py)_4]$ compounds, as required by symmetry considerations (Table 3). The M — Py vibration for most complexes is splitting. The small band splittings (10—15 cm^{-1}) can be attributed to: (a) deviations from perfect octahedral symmetry to remove degeneracy or (b) slight rotation of the coordinated pyridine around the M — N bond [14].

Table 3

Infra-red absorption bands (cm^{-1}) of metal — isothiocyanate complexes of pyridine in the far-infrared region (40—400 cm^{-1})

Compound	νM—Py	νM—NCS	Crystal Lattice Vibrations
Monomeric Octahedral Compounds			
[Mn (NCS)$_2$(py)$_4$]	176, 190	253	60, 75, 119
[Fe (NCS)$_2$(py)$_4$]-trans	192, 202	268	130
[Fe (NCS)$_2$(py)$_4$]-cis	202	250, 268, 300	68
[Co (NCS)$_2$(py)$_4$]	202, 217	270	70, 80, 146, 170
[Ni (NCS)$_2$(py)$_4$]	228	284	70, 80, 162, 173
Tetrahedral Compounds			
[Zn (NCS)$_2$(py)$_2$]	228	268, 314	149, 165
[Cd (NCS)$_2$(py)$_2$]	165	212	137
[Cu (NCS)$_2$(py)$_2$]	— *Polymeric octahedral Structure*		
	182, 254	330	106, 142, 150
[Cu (NCS)$_2$(py)$_2$]	— *Distorted Polymeric Octahedral Structure*		
	208, 291	330, 350, 372	128

In the spectrum of freshly prepared [Fe(NCS)$_2$(py)$_4$] we observed the splitting of the Fe—NCS stretching vibration, which is evidence or a cis-configuration [15]. In a certain time the cis-complex is converted to give the stable trans-configuration with a single Fe—NCS band.

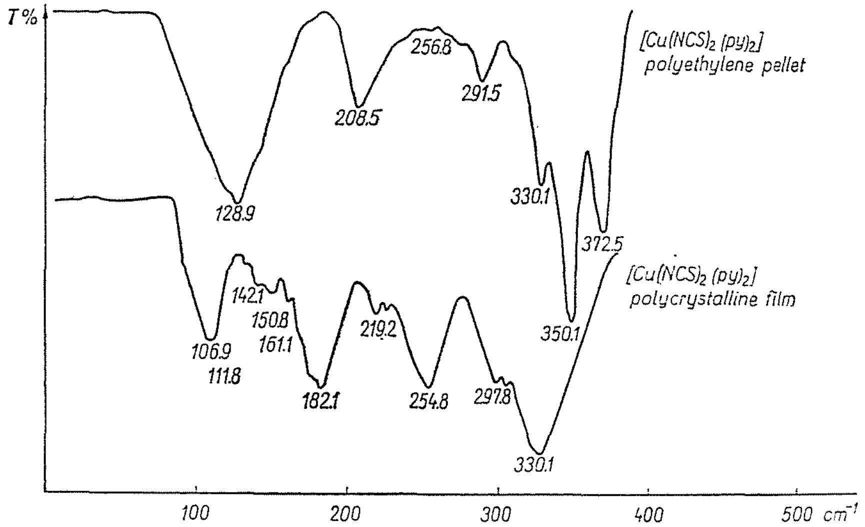

Fig. 9. Far infrared spectra of [Cu(NCS)$_2$(py)$_2$]

Ion to be determined	Characteristic band (cm^{-1})	Analytical places							Components present
		Accompanying ions							
		Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	Cd^{2+}	
Manganese	420				+	+			3
	480							+	2
	621					+	+		3
	649					+	+	+	4
	799					+	+	+	4
Iron	427	+						+	3
	481							+	2
	621					+	+		3
	808					+	+	+	4
Cobalt	422				+	+		+	4
	430	+						+	3
	480							+	2
	623					+	+		3
	802					+	+	+	4
Nickel	429	+					+	+	4
	437	+	+	+			+	+	6
	481							+	2
	624					+	+		3
	801					+	+	+	4
Copper	432	+					+	+	4
	468	+	+	+	+		+		6
	476							+	2
	636	+	+	+	+			+	6
	826	+	+	+	+		+	+	7
Zinc	413		+	+	+	+			5
	424							+	2
	482							+	2
	641	+	+	+	+	+		+	7
	849	+	+	+	+	+		+	7
Cadmium	416		+	+	+	+			5
	465	+	+	+	+		+		6
	624					+	+		3
	932	+	+	+	+		+		6

Fig. 5. Analytical sites for the simultaneous determination of some transition metal ions

The $[Zn(NCS)_2(py)_2]$ and $[Cd(NCS)_2(py)_2]$ complexes, as was concluded on the basis of far-infrared measurements, exist as tetrahedral compounds with trans-configuration.

The most interesting phenomenon was observed for the $[Cu(NCS)_2(py)_2]$ complex. The far-infrared spectrum of the complex measured as polycrystalline film, is consistent with literature data [13, 16] and corresponding to polymeric octahedral structure (Fig. 9). However, the far-infrared spectrum of the complex in polyethylene pellett is different. The Cu — py stretching vibrations for the latter are shifted to higher frequencies. The Cu — NCS vibration appears as three bands at 330, 350 and 372 cm^{-1} (Table 3 and Fig. 9). This phenomenon can be attributed to the pressure induced Jahn-Teller effect, which is usually observed in the case of bis-pryidine copper(II) complexes [17].

Summary

This paper is concerned with the simultaneous determination of Cr(III) and Fe(II) ions in the form of isothiocyanatopyridine complexes, by means of IR spectrophotometric method. The amount of Cr(III) ions can be determined from the concentration-absorbance relationship of the 1622 cm^{-1} band of $[Cr(NCS)_3(py)_3]$ complex, whereas Fe(II) can be determined from that of the 1042 cm^{-1} band of $[Fe(NCS)_2(py)_4]$ complex, within a relative deviation of $\pm 2\%$.

Far infrared data and the assignments for the metal-ligand and metal-isothiocyanate stretching vibrations are presented.

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