

NOTE

**Thermodynamic and structural studies of complexes of manganese(II), cobalt(II), nickel(II) and copper(II) with aminofuropyridine carboxamide**

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(Received 11 September 2002, revised 27 January 2003)

*Abstract:* Complexes of Mn(II), Co(II), Ni(II) and Cu(II) with 2-aminofuro[3,2-b]pyridine-3-carboxamide have been prepared. The stability constants of the formed complexes were determined at 20, 30, 40 and 50 °C at a fixed ionic strength,  $I = 0.1 \text{ mol dm}^{-3}$  (KCl). The values of the thermodynamic functions associated with complex formation were calculated and analyzed in terms of electrostatic and non-electrostatic components. The complexes were characterized with the help of chemical and spectral data.

*Keywords:* aminofuropyridine carboxamide, thermodynamic, conductometric, photometric, spectral properties.

INTRODUCTION

The coordination chemistry of nitrogen donor ligands is an activate area of research. Organic compounds containing a pyridine ring play an important role in many biological reactions.<sup>1</sup> The formation of different complexes of aminohydroxypyridine with Co(II), Ni(II) and Cu(II) was tested using IR spectroscopy.<sup>2</sup> The ligand is an N, N, O donor in case of the Co and Ni complexes but N, N in the case of the Cu complex. The ligand interacts also with Zn(II), Cd(II), Hg(II), As(III), Sb(III) and Bi(III) through N, N donor sites.<sup>3</sup> On other hand, ternary complexes of pyridine and quinoline were characterized spectroscopically.<sup>4</sup>

In continuation of our work in the area of the physical properties of organic complexes,<sup>5,6</sup> the present study deals with the potentiometric determination of the stability constants and related thermodynamic parameters of 2-aminofuro[3,2-b]pyridine-3-carboxamide complexes with Mn(II), Co(II), Ni(II) and Cu(II). The probable stoichiometric ratio of the complexes was examined conductometrically and photometrically. The infrared spectra were used to illustrate the bonding sites of the ligand.

<sup>#</sup> In memory of the late Professor S. M. Metwally.

## EXPERIMENTAL

All the employed chemicals were of pure laboratory grade. The prepared ligand (m.p. 217 °C) was provided by Dr. H. Saad.<sup>7</sup> A digital pH-meter, Cole Parmer 5800-05-solution analyzer, was used to determine the stability constants of the complexes at 20, 30, 40 and 50 °C at constant ionic strength (0.1 M KCl). Three aqueous solutions (total volume 50 ml in each case) were titrated with 0.01 M KOH: *i*) 1 ml HCl (0.0095 M), *ii*) 1 ml HCl (0.0095 M) + 2 ml ligand (0.01 M) and *iii*) 1 ml HCl (0.0095 M) + 2 ml ligand (0.01 M) + 0.4 ml metal ion (0.01 M).

To illustrate the possible stoichiometric ratio of the complexes, conductometric titrations were carried out at room temperature by titrating 30 ml metal ion solution (0.001 M) with the ligand solution (0.01 M) as the titrant. A Cole Parmer 5800-05 digital conductivity-meter was employed. Photometric titration was also used to ascertain the possible composition of the complexes. A Milton Roy, Spectronic 1201 spectrophotometer was employed. The concentration of the metal ion was kept constant (0.001 M) while that of ligand was varied between  $0.1 \times 0.001$  M and  $4.0 \times 0.001$  M to give a series of ligand/metal ratios.

Solid complexes of mole ratio M : 2L were prepared by mixing an ethanolic aqueous solution of the calculated amount of ligand with the respective metal chloride. The reaction mixture was refluxed on a water bath for three hours. The precipitated manganese (pale rose), cobalt (pink), nickel (pale green) and copper (greenish blue) complexes were filtered, washed several times with ethanol and finally dried over anhydrous CaCl<sub>2</sub>. All the prepared complexes melted above 330 °C. The formed complexes were identified from their FT-IR spectra recorded using a Perkin Elmer FT-IR 1650 instrument. The KBr disc technique was employed.

## RESULTS AND DISCUSSION

Information referring to the stability of the aminofuopyridine carboxamide complexes was obtained from the titration data of the three solutions using the Irving-Rossotti formula<sup>5</sup>:

$$n_H = Y + \frac{(V_1 - V_2)(N^o + E^o)}{(V_o + V_1)T_L}$$

$$n = \frac{(V_3 - V_2)(N^o + E^o)}{(V_o + V_1)n_H T_M}$$

$$P_L = \log \left[ \frac{B \left( \frac{1}{\text{anti log } B} \right)^n}{T_L - nT_M} \cdot \frac{(V_o + V_1)}{V_o} \right]$$

where  $V_1$ ,  $V_2$  and  $V_3$  are the volumes of alkali in the three titration curves required to reach the same pH value,  $V_o$  is the total volume of titrating mixture,  $N^o$  and  $E^o$  are the concentration of the alkali and the initial concentration of free acid, respectively.  $Y$  is the number of dissociable protons attached to the ligand,  $T_L$  and  $T_M$  are the total concentration of ligand and metal, respectively. The metal-ligand constant was obtained by plotting  $n$ , the average number of ligands attached to each metal ion, against  $P_L$ , the free ligand exponent and interpolating at  $n = 0.5$  and  $1.5$ . The obtained stepwise stability constants,  $\log K_1$  and  $\log K_2$ ,

are summarized in Table I. It is clear that the Irving-Williams order is obeyed, *i.e.*, the stability of complexes follows the trend:  $Mn < Co < Ni < Cu$ . Also, increasing the temperature leads to a reduction of the stability values. This means that the complexing process is an exothermic reaction demonstrating that the formation of these complexes is favored at lower temperatures.

TABLE I. Stepwise stability constants of the complexes at different temperatures

Compounds	Stability constants	293 K	303 K	313 K	323 K
Ligand	$pK_1$	4.70	4.83	5.00	5.30
	$pK_2$	3.85	3.78	3.55	3.33
Mn complex	$\log K_1$	5.95	5.55	5.10	4.80
	$\log K_2$	5.62	5.35	4.80	4.25
Co complex	$\log K_1$	6.70	6.30	5.95	5.65
	$\log K_2$	6.43	6.10	5.70	5.50
Ni complex	$\log K_1$	7.32	6.80	6.50	6.00
	$\log K_2$	7.00	6.60	6.20	5.80
Cu complex	$\log K_1$	8.55	8.05	7.80	7.20
	$\log K_2$	7.87	7.45	7.10	6.80

From the knowledge of the stability constants at different temperatures, the change in the free energy, enthalpy and entropy accompanying complex formation can be calculated using the relations:

$$\Delta G^{\circ} = -2.303 RT \log K = \Delta H^{\circ} - T\Delta S^{\circ}$$

and

$$\log \frac{K_1}{K_2} = -\frac{\Delta H_o}{2.303R} \left( \frac{T_2 - T_1}{T_1 T_2} \right)$$

The so determined thermodynamic data are given in Table II. The negative values of the three parameters mean that the process of complex formation is spontaneous, exothermic, and the complexed molecules have a more ordered structure than the reactants. In other words, the metal-ligand bonds are fairly strong and the complex formation is strongly driven by enthalpic forces.

In order to clarify the nature of the interaction between the ligand and the metal ions, *i.e.*, ionic or covalent, the thermodynamic data were analyzed and evaluated into electrostatic and non-electrostatic components using the equations<sup>8</sup>:

$$\Delta G^{\circ} = \Delta G_{el}^{\circ} + \Delta G_{non}^{\circ} = nRT \ln M + Rc(a + e^{T/\theta})$$

$$\Delta H^{\circ} = \Delta H_{el}^{\circ} + \Delta H_{non}^{\circ} = Rc(a + (1 - T/\theta)e^{T/\theta})$$

$$\Delta S^{\circ} = \Delta S_{el}^{\circ} + \Delta S_{non}^{\circ} = -nRT \ln M - (Rc / \theta)e^{T/\theta}$$

where  $\theta$  is the temperature characteristic of the solvent and  $M$  is its molality. Comparison of the electrostatic and non-electrostatic components, as evaluated in Table III, illustrates that the  $\Delta G_{\text{non}}^{\circ}$  values are negative compared to those of  $\Delta G_{\text{el}}^{\circ}$ , *i.e.*, the non-electrostatic (covalent) forces are stronger than the electrostatic (ionic) ones for all the examined complexes. Also the  $\Delta H_{\text{non}}^{\circ}$  values are significantly more negative than those of  $\Delta H_{\text{el}}^{\circ}$ , reflecting the covalent nature of the complex molecules.

TABLE II. Thermodynamic data of the mono- and bis-complexes at 293 K

Compounds	$-\Delta G^{\circ}/\text{kJ mol}^{-1}$	$-\Delta H^{\circ}/\text{kJ mol}^{-1}$	$-\Delta S^{\circ}/\text{J mol}^{-1} \text{K}^{-1}$
Mn complex	33.38	67.83	117.57
	31.53	65.10	114.60
Co complex	37.58	67.01	100.42
	36.07	59.35	79.45
Ni complex	41.06	78.50	127.78
	39.27	67.01	94.68
Cu complex	47.97	80.41	110.75
	44.15	67.01	78.03

The ratio of the electrostatic to non-electrostatic values decreases from manganese to copper complexes indicating that the ionic character of the complexes increases in the order:  $\text{Cu} < \text{Ni} < \text{Co} < \text{Mn}$ , *i.e.*, the ionic character of the complexes increases with increasing number of unpaired electrons of the metals. On the other hand, the thermodynamic data computed for the formation of 1:2 complexes illustrate a marked decrease in the ionic character compared to those of 1:1 complexes. Therefore, it can be concluded that the metal-ligand bonds in the bis-complexes are more covalent in nature than those in the corresponding mono-complexes.

TABLE III. Electrostatic and non-electrostatic components of the thermodynamic functions

Compounds	$\Delta G_{\text{el}}^{\circ}/\text{kJ mol}^{-1}$	$-\Delta G_{\text{non}}^{\circ}/\text{kJ mol}^{-1}$	$-\Delta H_{\text{el}}^{\circ}/\text{kJ mol}^{-1}$	$-\Delta H_{\text{non}}^{\circ}/\text{kJ mol}^{-1}$	$-\Delta S_{\text{el}}^{\circ}/\text{J mol}^{-1} \text{K}^{-1}$
Mn complex	17.82	51.21	6.82	61.00	84.18
	10.13	41.63	3.59	61.21	47.82
Co complex	14.18	51.80	5.44	61.59	67.03
	2.68	38.74	1.05	58.32	12.68
Ni complex	20.00	61.04	7.66	70.84	94.39
	5.90	45.19	2.26	64.77	27.91
Cu complex	16.40	64.35	6.28	74.14	77.36
	2.38	46.53	0.92	66.11	11.25

To obtain meaningful information about the composition of the prepared complexes, conductometric and photometric titrations were performed. The two techniques have in common the fact that the measured quantity is directly proportional to the concentration of one or more of the ions of interest. If the reaction between the metal ions and the complexing titrant (ligand) is essentially complete, a titration curve

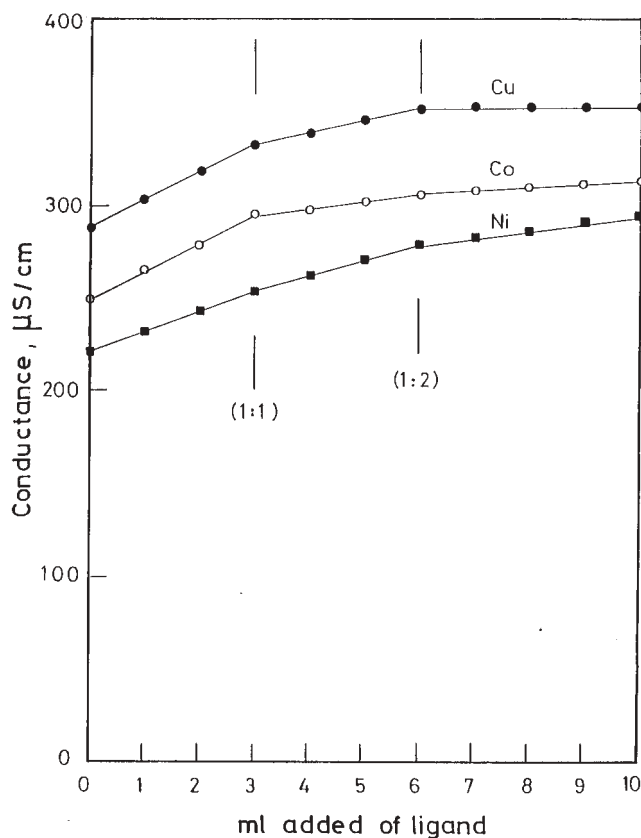


Fig. 1. Conductograms of aminofuopyridine carboxamide with the metal ions.

is obtained that consists of two or more straight, or nearly straight, line segments intersecting at the equivalence point (the stoichiometric ratio) of the complex formed.<sup>9</sup>

The conductograms of aminofuopyridine carboxamide are shown in Fig. 1. It is clear that the conductance value of the metal ion solution increases steadily as the ligand solution is added. The increasing continues until the equivalence point of the titration. The behavior obtained is attributed to the replacement of some ions by complex molecules with different mobility values. With the next drop of added titrant, the ligand remains unreacted and a slight increase is sometimes observed due to the accumulation of excess ligand solution. The conductograms exhibit two obvious slopes, suggesting that the probable stoichiometric ratios of the complexes are  $M : L$  and  $M : 2L$ .

In the other technique, by measuring the characteristic absorbance at a suitable wavelength ( $\lambda_L = 310$  nm,  $\lambda_{\text{complex}} = 325 - 340$  nm), the photometric titration curves shown in Fig. 2 are obtained. The absorbance increases nearly linearly with added ligand until the reaction is almost complete. Then, there is a sudden change of slope, and further addition of ligand results in little further reaction and only a gentle dilution. The equivalence point is that point at which the curvature or rate of change of slope is at a maximum.

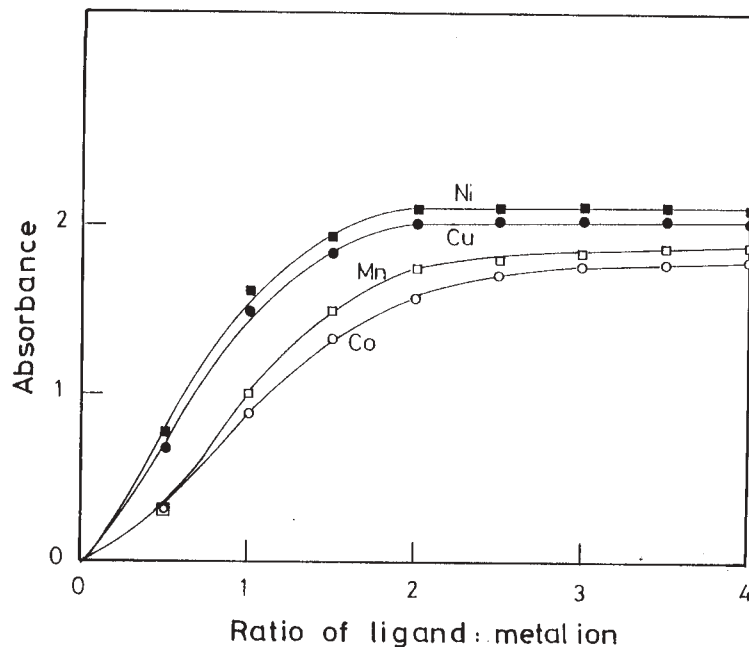


Fig. 2. Photometric titration curves of aminofuopyridine carboxamide with the metal ions.

The data show that the ligand forms stable complexes with stoichiometric ratio  $M : 2L$ , as obtained previously from the potentiometric and conductometric studies.

The conductometric and photometric titrations were not only used to elucidate the composition of the complexes but also to determine their stability constants using the relations:

$$K = \frac{1}{c_L^n} \frac{\Lambda_{\text{exp}} \cdot \Lambda_m^n}{\Lambda_{\text{ML}}^n - \Lambda_{\text{exp}}}$$

$$K_n = \frac{A/A_m}{(1 - A/A_m)^{n+1} c_L^n n^2}$$

where  $\Lambda_{\text{exp}}$ ,  $\Lambda_M$ ,  $\Lambda_{\text{ML}}$  are the conductance values of the solution, uncomplexed and complexed metal ions, respectively,  $n$  is the coordination number,  $A$  is the absorbance at a ligand concentration  $c_L$  and  $A_m$  is the absorbance at full color development. The calculated data are given in Table IV. It is clear that the conductometric data are smaller than those obtained potentiometrically or photometrically. This may be attributed to the fact that the conductometric method gives an accurate result for complexes of low stability constants.

Finally, aminofuopyridine carboxamide has four donor sites for bonding to metal ions. These are the ring nitrogen atom, the nitrogen of the amine group and the nitrogen and oxygen of the amide group. The infrared spectra are of great help in deciding the ligational behavior of the ligand. Fig. 3 presents the spectra of the studied samples. In the spectra of Co and Ni complexes, the bands due to NH-vibrations of the amine

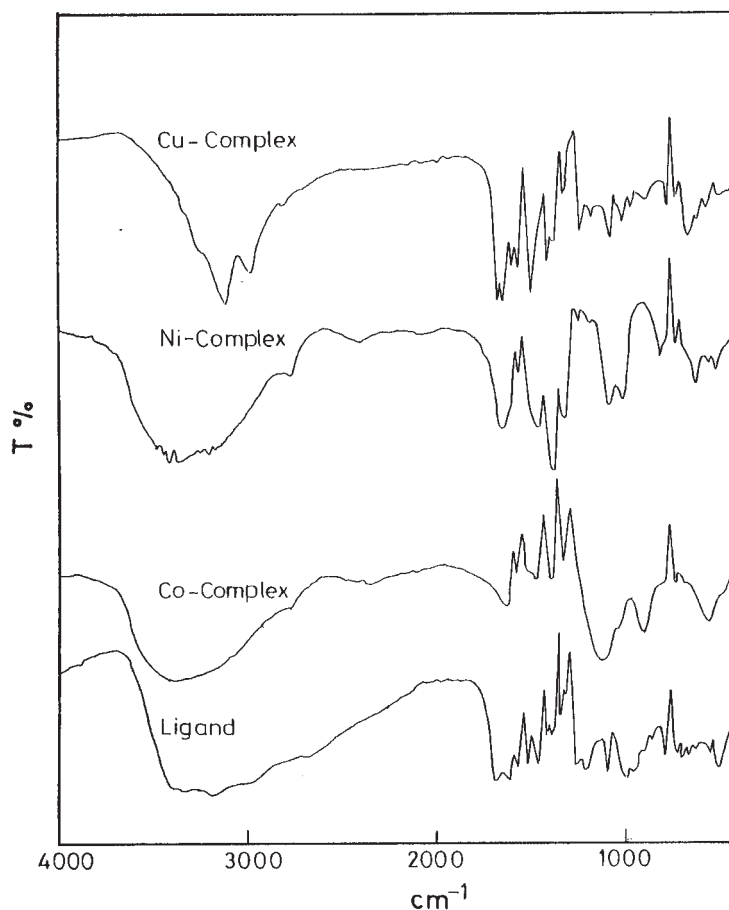


Fig. 3. The infrared spectra of aminofuopyridine carboxamide and its complexes.

group are shifted to higher frequencies, probably due to coordination of the nitrogen atom of  $\text{NH}_2$  group with the metal ion. Also, the bending band of the  $\text{NH}_2$  group at  $1581\text{ cm}^{-1}$  is shifted by  $10\text{ cm}^{-1}$  to lower frequencies. The bands due to  $\nu(\text{NH})$  ( $3196\text{ cm}^{-1}$ ) and  $\nu(\text{C}=\text{O})$  ( $1660\text{ cm}^{-1}$ ) of the amide group are shifted to higher and lower wavenumbers, respectively, after complexation, suggesting that the oxygen atom of carbonyl group is coordinated to the metal ion.<sup>10</sup> In the spectrum of the Cu complex, the vibrational band due to  $\text{C}=\text{O}$  ( $1656\text{ cm}^{-1}$ ) remains unchanged indicating that the oxygen atom of carbonyl group does not participate in the coordination process. The bands due to  $\nu(\text{NH})$  are found at lower wavenumbers than in the free ligand, suggesting that the nitrogen atoms of amino groups have formed bonds with the copper atoms.

In all spectra of the complexes, the characteristic band of the pyridine ring nitrogen at  $1614\text{ cm}^{-1}$  is not appreciably affected showing its non-participation in the coordination process. The appearance of bands around  $1480$  and  $800\text{ cm}^{-1}$  confirms the presence of coordinated water molecules.

TABLE IV. Stepwise stability constants at 300 K using the conductometric and photometric titration techniques.

	Mn complex	Co complex	Ni complex	Cu complex
$\log K_1$	–	6.76	6.81	7.44
$\log K_2$	–	5.42	5.57	5.68
$\log K_1$	6.60	6.86	7.03	7.79
$\log K_1K_2$	11.19	12.04	13.23	14.09

Based on the above observations, it can be concluded that aminofuroopyridine carboxamide acts as a bidentate ligand forming stable complexes with a molar ratio M : 2L. The ligand is an N,O donor in case of Co and Ni complexes, but in case of Cu complex it is an N,N donor. The formation of the complexes is an exothermic process.

## ИЗВОД

ТЕРМОДИНАМИЧКА И СТРУКТУРНА ПРОУЧАВАЊА КОМПЛЕКСА  
 МАНГАНА(II), КОБАЛТА(II), НИКЛА(II) И БАКРА(II) СА  
 АМИНОФУРОПИРИДИНКАРБОКСАМИДОМ

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Припремљени су комплекси Mn(II), Co(II), Ni(II), и Cu(II) са 2-аминофуоро[3,2-b]пиридин-3-карбоксамидом. Одређене су константе стабилности ових комплекса на 20, 30, 40 и 50 °C при константној јонској начини  $I = 0,1 \text{ mol dm}^{-3}$  (KCl). Израчунате су термодинамичке функције за одговарајуће процесе комплексирања и анализирани чланови за електростатичку и неелектростатичку компоненту. Комплекси су карактерисани на основу хемијских и спектроскопских података.

(Примљено 11. септембра 2002, ревидирано 27. јануара 2003)

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