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Stability constants of thiocyanato complexes of cobalt(II), nickel(II) and copper(II) in methanol

Mustayeen Khan^{a,*}, Gilles Bouet^a, Roomina Tanveer^b, Riaz Ahmed^b

^a *Laboratoire de Chimie de Coordination, Université d'Angers, Faculté de Pharmacie, 16 Boulevard Daviers, F-49100 Angers, France*

^b *Nuclear Chemistry Division, PINSTECH, PO Nilore, Islamabad, Pakistan*

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Abstract

A spectrophotometric study of cobalt(II), nickel(II) and copper(II) thiocyanato complexes was carried out in methanol at 25°C and at a constant ionic strength of 1 M. Under the experimental conditions, two mononuclear complexes are identified with each of the three metal ions. Their stability constants are determined with a recent PC program SIRKO and the calculated values are: for cobalt, $\log \beta_1 = 1.6$, $\log \beta_2 = 2.7$; for nickel, $\log \beta_1 = 1.8$, $\log \beta_2 = 3.0$; and for copper, $\log \beta_1 = 3.0$, $\log \beta_2 = 3.6$. © 1999 Elsevier Science Inc. All rights reserved.

Keywords: Metallic complexes; Stability; Thiocyanates; Methanol

1. Introduction

Thiocyanates ions show several toxic effects towards vertebrates and in the last few years many papers have reported the results of such studies. For example, potassium thiocyanate accelerates the production of large DNA fragments, as well as the induction of trace amounts of internucleosomal DNA cleavage in human peripheral blood polymorphonuclear leukocytes [1]. The exposure of rat conjunctiva to tobacco smoke leads to higher levels of plasma thiocyanate and conjunctivas were thinned, atrophied and microvillous projections and desmosomal connections were absent in comparison with the control conjunctivas [2]. Thiocyanate ions are released to the aquatic environment as a result of the treatment of cyanide-bearing wastes from precious-metal mining activity and it has been demonstrated that juvenile rainbow trouts were less tolerant than alevine [3].

We have, therefore, undertaken the study of the stability of some thiocyanato metallic complexes in several solvents, mainly alcohols. Though the thiocyanato complexes of cobalt(II), nickel(II) and copper(II) have already been studied, divergent results have been reported in the literature. With copper as the central metal ion, Tanaka and Takamura [4] reported the formation of four complexes while Kullberg [5] identified three in aqueous solutions and Nancollas and

Torrance [6] reported the presence of only one complex. The value of the stability constant of the first complex is about 55, except in the work of Nancollas and Torrance who calculated it as 213. In the case of thiocyanato complexes of cobalt, Silber and Murguia [7] have reported four complexes in water and in methanol and so have Ishiguro and Ozutsumi [8] in dimethylformamide (DMF). However, Bjerrum [9] and Waki and Miyazaki [10] have been able to detect only one complex in aqueous solutions and that too of feeble intensity. In organic media, the stability constants have, as usual, high values.

Mieziš [11] performed a comprehensive study of thiocyanato complexes of nickel(II) in different non-aqueous solutions such as trimethylphosphate (TMP), dimethylsulfoxide (DMSO), dimethylacetamide (DMA) and acetonitrile (AN). He postulated the formation of four complexes in all the solvents, the value of β_1 ranging from 5×10^2 to 5×10^3 . For Kullberg in aqueous nickel solutions three complexes are formed whereas Nancollas as well as Malyavinskaya and Turyan [12] and Das et al. [13] reported only one. Again Ishiguro mentioned four complexes with high values of stability constants in DMF.

We have already reported the results of the halide complexes of copper in water [14,15], methanol [16] and different organic solvents [17–22]. The results of the methanolic solutions with cobalt(II) and nickel(II) have already been given [23,24] with global results describing

* Corresponding author. Fax: +33-241-486-733; e-mail: mustayeen.khan@univ-angers.fr

central ion effects [25] as well as the solvent effects [26] on the stabilities of the species present in solution.

The purpose of this study is to determine the stability constants of the thiocyanato complexes with cobalt(II), nickel(II) and copper(II) in methanol using a new PC calculating program. The resurgent interest in this system is mainly due to the results of recent studies showing that the transition metal complexes in general [27,28], particularly those with semicarbazones and thiosemicarbazones as ligands, have anti-cancerous or antiviral properties [29–33], and that the cytotoxic activities vary greatly as a function of the binding coordinating atom.

2. Experimental

2.1. Reagents and apparatus

Anhydrous methanol (Merck) was used without further treatment. Stock solutions of cobalt perchlorate, nickel perchlorate, and copper perchlorate, all hexahydrated and all Fluka, were prepared by dissolving calculated quantities in the solvent. Exact concentrations were determined gravimetrically.

The same procedure was applied for the stock solutions of the ligand sodium thiocyanate (Fluka) and sodium perchlorate (Fluka) which was used to stabilize the ionic strength at 1 M.

The final analytical concentrations for cobalt, nickel and copper were 2×10^{-3} , 9×10^{-3} and 10^{-3} M, respectively. The ligand concentration was progressively increased from zero to 1 M. As the ligand concentrations were always kept higher than those of the metal, the possibility of formation of polynuclear complexes has been neglected.

All experiments were carried out on a Hitachi U-2000 spectrophotometer using quartz cells of 1 and 0.5 cm. Methanol was used as the solution of spectrophotometric reference. The temperature was maintained at $25.0 \pm 0.2^\circ\text{C}$ for all measurements.

2.2. Method of calculation and data treatment

The equilibrium: $\text{M}^{2+} + j\text{SCN}^- \rightleftharpoons \text{MSCN}_j^{(j-2)-}$, where M = Co, Ni or Cu, is defined by the overall stability constant:

$$\beta_j = \frac{[\text{MSCN}_j]^{(j-2)-}}{[\text{M}^{2+}][\text{SCN}^-]^j}$$

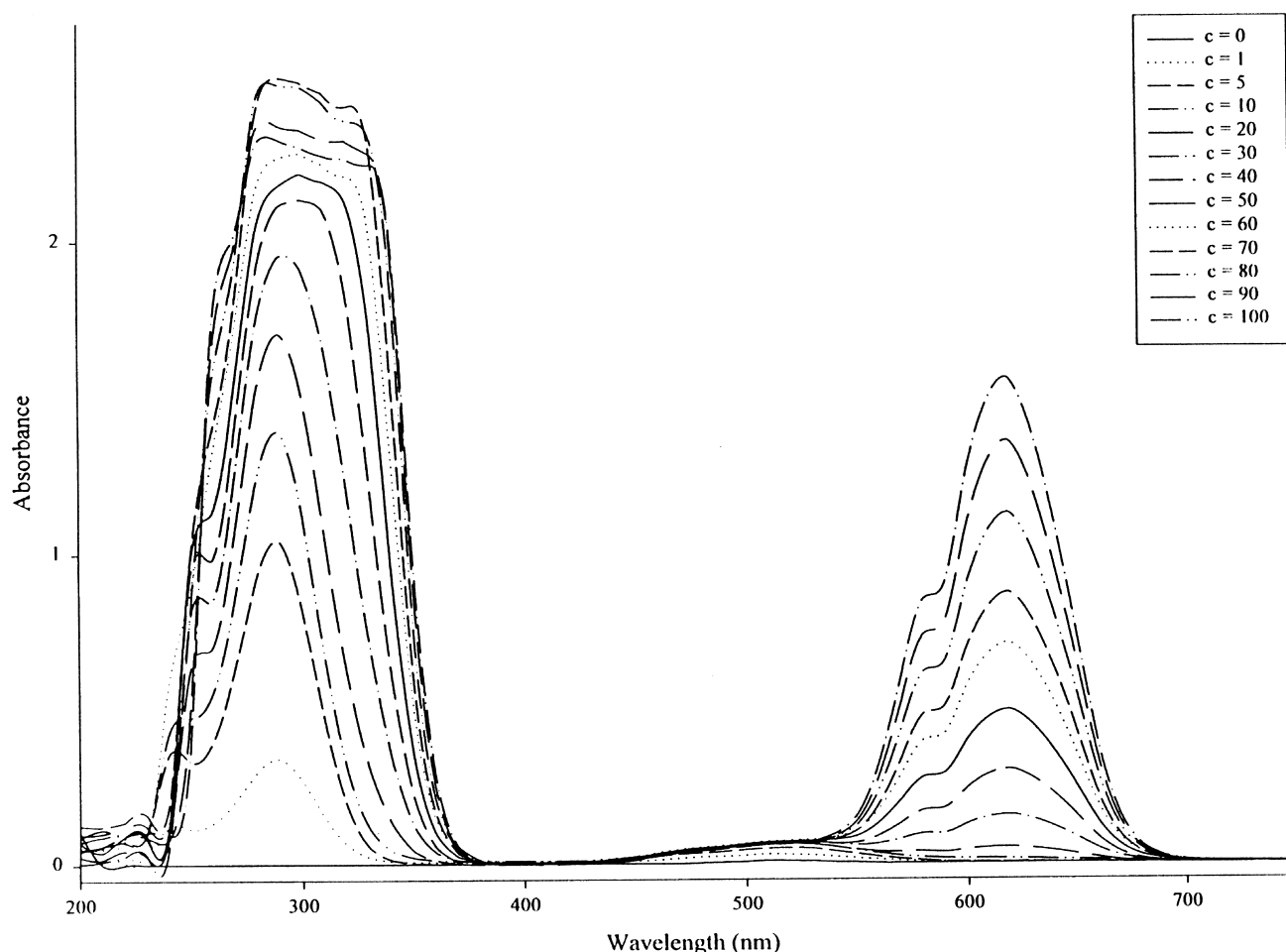


Fig. 1. Absorption spectra of cobalt(II) in sodium thiocyanate methanolic mixtures. $[\text{Co}^{2+}] = 2 \times 10^{-3}$ M, $l = 1$ cm; $c =$ ligand concentration multiplied by 10^3 M.

The calculation of the stability constants is based on the computer program SIRKO which was conceived for the calculation of these and allied parameters from spectrophotometric, calorimetric and potentiometric experimental data [34]. The stability constants of the complexes constitute the parameters of the system and these parameters are calculated by a least-squares method, the best set of values being that which minimises the sum S :

$$S = \sum_i \sum_j W_{ij} (F_{ij}^{\text{exp}} - F_{ij}^{\text{calc}})^2$$

where i is the number of experiments, j the number of experimental points, W_{ij} terms take into consideration the respective weight of each factor and F_{ij} is called the response function.

In order to test the compatibility of the theoretical model with the experimental data, the R factor is defined as

$$R = \left[\frac{S}{\sum W_i (F_i^{\text{exp}})^2} \right]^{1/2}$$

For a good harmony between the experimental and theoretical models, R must be as small as possible, certainly less than 5%.

3. Results and discussion

3.1. Experimental data

The representative experimental spectra of thiocyanate solutions of cobalt(II), nickel(II) and copper(II) are given in Figs. 1–3, respectively.

In the case of cobalt solution, an absorption band appears at about 300 nm as soon as the ligand is added. This maximum increases with ligand concentration and finally fuses with the maximum at 220 nm, thus presenting a broad band. In the visible region, the characteristic maximum of cobalt with a shoulder peak is observed at about 600 nm. The nickel solutions have nearly the same kind of evolution with the appearance at first of a large band centred between 240 and 280 nm, which is certainly a fusion of two maxima. The modification in the spectrum is significant from $[\text{SCN}^-] > 0.4 \text{ M}$ when the second peak becomes more intense than the first one. As regards copper solutions, a maximum appears at 380 nm for ligand concentration as low as $5 \times 10^{-4} \text{ M}$. This band increases in intensity and stabilises at 400 nm at higher concentrations.

3.2. Numerical analysis and stability constants

Using the program SIRKO, different models were tested and under the experimental conditions the results indicated

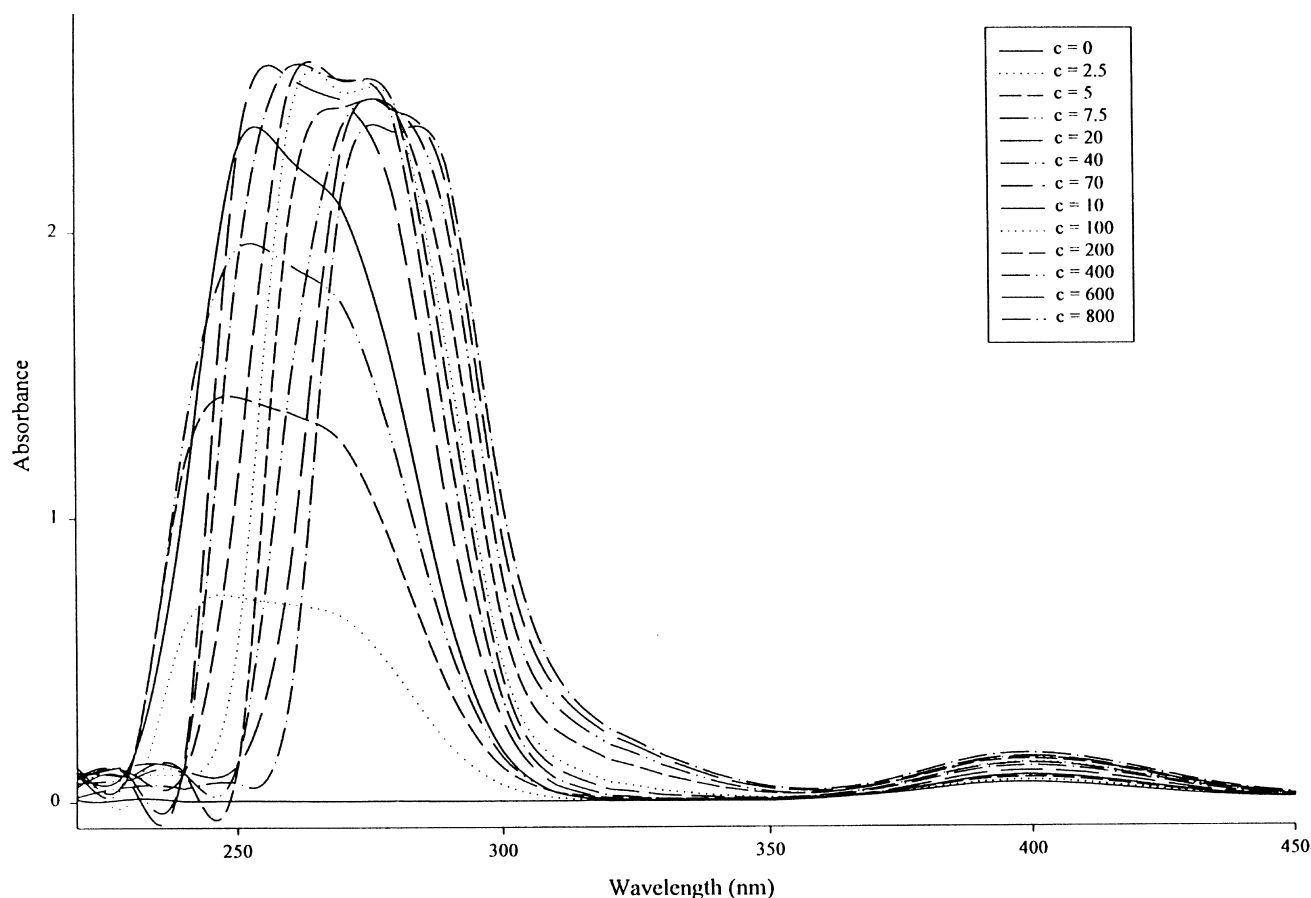


Fig. 2. Nickel(II) thiocyanate absorption spectra in methanol. $[\text{Ni}^{2+}] = 9 \times 10^{-3} \text{ M}$, $l = 1 \text{ cm}$; $c =$ ligand concentration multiplied by 10^3 M .

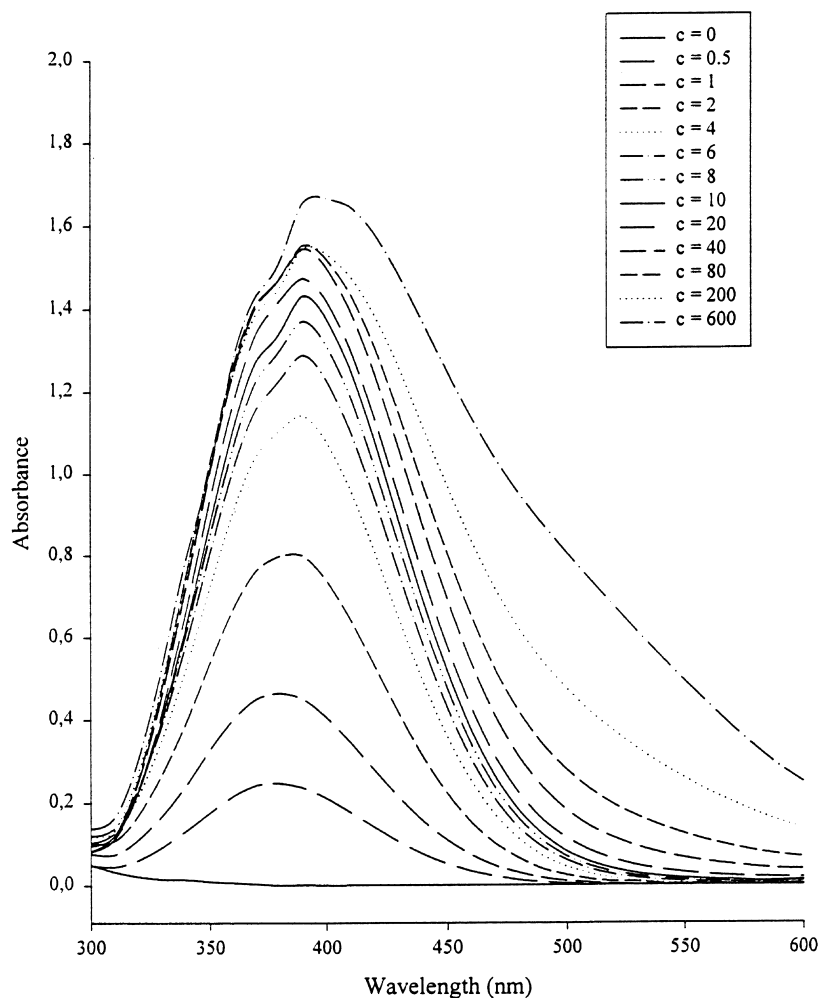


Fig. 3. Absorption spectra of copper(II)-sodium thiocyanate solutions in methanol. $[Cu^{2+}] = 10^{-3}$ M, $l = 1$ cm; c = ligand concentration multiplied by 10^3 M.

Table 1

Calculated stability constants of the thiocyanato complexes of cobalt(II), nickel(II) and copper(II) in methanolic solutions

Constant	Metal		
	Cobalt	Nickel	Copper
Log β_1	1.63	1.77	3.04
Log β_2	2.66	2.98	3.61

the presence of two complexes in each system. Taking into account the fact that the ligand concentrations are much higher than those of the central metal ions, the possibility of the formation of polynuclear complexes is negligible and only successive mononuclear complexes are envisaged. The logarithm of these constants along with their dispersion values and the R factor are: for cobalt, $\log \beta_1 = 1.63 \pm 0.09$, $\log \beta_2 = 2.66 \pm 0.18$, R factor = 2.3%; for nickel, $\log \beta_1 = 1.77 \pm 0.11$, $\log \beta_2 = 2.98 \pm 0.14$, R factor = 1.62%; for copper, $\log \beta_1 = 3.04 \pm 0.05$, $\log \beta_2 = 3.61 \pm 0.19$, R factor = 3.8%. These results are summarized in Table 1.

The absence of the third and fourth complexes which has been widely reported in the scientific literature is quite probably due to the limitation of maximum ligand concentration at 0.1 M. It can readily be observed that the stability increases slightly from cobalt to nickel and then steeply from nickel to copper. This is the famous Irving–Williams series which has been recently verified in similar systems with the halide ions and we may also point out that the pseudo halide ion seems to form more stable complexes than the halide ion in similar conditions: compare in methanol for cobalt $\log \beta_1 = 1.2$, for nickel $\log \beta_1 = 1.3$, and for copper $\log \beta_1 = 2.5$ [22].

Our calculated values for β_1 for cobalt and copper are different from all those reported earlier in the literature, whereas in the case of nickel, the value of 58 is identical to that determined by Nancollas and Torrance in aqueous solutions [6].

3.3. The metal–ligand bond

Nitrogen-bonded ligands, especially with copper as central metal ion, have strong cytotoxic activity as has been recently

reported with furan oximes complexes [29,30]. Very recent results have also confirmed the antiviral activity of thiosemicarbazone complexes of transition metals [31–33]. It is therefore of interest to have a precise idea if the thiocyanato metal complexes are sulfur or nitrogen bonded. Here once again the divergence of the results is such that all possibilities can be taken into account. Mieziš [11] postulates that, in aqueous solutions, the metal–thiocyanate bond is probably electrostatic and the thiocyanate ion is N-bonded upon coordination with the nickel(II) ion. For Kulberg [5] the thiocyanate exhibits linkage isomerism, bonding to the metal ion through either its S or N atom. Finally, Dickinson et al. [35] report that in these systems the complexes are mostly S-bonded in solution and N-bonded in the solid state. Folkesson and Karsson [36] later confirmed that in solid state cobalt is bonded to the N end of the molecule in $K_2[Co(NCS)_4]$; however, the analogous platinum compound is bonded to sulfur.

This study does not allow us to give any sort of precision as to the attachment of the metal to either the sulfur or the nitrogen atom of the thiocyanate ligand. From a theoretical point of view, however, we would be in agreement with authors who favour the sulfur linkage. With the simultaneous possibility of the two atoms donating their pair for the coordinate bonds, chances are that the sulfur atom would donate its pair of electrons more easily than the nitrogen atom which is more electronegative and, hence, has a higher tendency of retaining its electronic pair. Moreover, the thiocyanate ion is considered a soft base and Co^{2+} , Ni^{2+} and Cu^{2+} may be classified as soft acids [37]. The compounds with nitrogen atoms and forming bonds through them are hard bases. According to the theory of Pearson, hard acids are bonded easily to hard bases; the complexes thus formed are more stable than those formed with species of different nature, for example, a hard acid and a soft base. This enhances the hypothesis of sulfur-bonded thiocyanate complexes in solution since the system under investigation consists of a soft base (SCN^-) and soft acids (Co^{2+} , Ni^{2+} , Cu^{2+}).

Similar investigations in higher alcohols (e.g. ethanol) are now in progress in connection with biological properties.

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