

Synthesis of a Novel Copper (II) Complex Capable of Trapping Hazardous Cations Present in Water

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Introduction

Coordination complexes containing macrocyclic ligands play a significant chemical role in biological systems. Recently, a novel dicopper macrocyclic complex synthesized has shown a significant affinity towards trapping halide ions (Udugala-Ganehenege *et al.*, 2001). Extension of such a study to synthesize a new, simple metal macrocyclic system capable of trapping hazardous molecules and ions present in the environment was the major objective of the present study. It was found that there were wide varieties of medicinally important transition metal complexes synthesized by using dithiooxamide (rubeanic acid) as a macro ligand. Many of these complexes have been polymeric due to the fact that dithiooxamide is being a tetradentate ligand. It has been reported that a polymeric structure is formed by chelating the N and S ends of the dithiooxamide with metal ions such as Hg(II), Pb(II), and Pd(II). However, N, N chelation is preferred for metal ions such as Ni(II) and Cu(II). Further, macro ligands such as N,N-bis(2-aminoethyl)-1,3-propanediamine are first coordinated to divalent metal ions (M^{2+}) such as Cu(II) and Ni(II), followed by condensation reactions with acetylacetone to form M(II)ATH₂ type macrocyclic complexes during the template synthesis (Martin and Cumming, 1973). In the present study, we attempted to synthesize a similar monomeric complex by using dithiooxamide for preparing corresponding dimeric or polymeric complexes of the type reported previously by the author. Due to the unusual insolubility of the complex formed, the research was focused towards trapping cations into the complex. This research report describes the synthesis and the specific ion trapping capacities of the Cu(II) complex of which the possible structures are shown in Figure 1.

Materials and methods

Synthesis

The chemicals used in the synthesis were of reagent grade. $Cu(CH_3COO)_2 \cdot H_2O$ (0.831 g,

0.0042 mol) was dissolved in distilled water (70 cm³). Recrystallized dithiooxamide (1.000 g, 0.0084 mol) was dissolved in methanol (140 cm³) and this solution was added into the blue colored $Cu(CH_3COO)_2 \cdot H_2O$ solution. A portion (50 cm³) of the resulting greenish black colored mixture was decanted off and the precipitate (Complex-a) was filtered, washed with methanol and distilled water, and dried. Acetylacetone (5 cm³) was added into the remaining mixture and refluxed for two hours. After refluxing, it was kept at room temperature for 30 min. Then the resulting black colored precipitate (Complex-b) was filtered, washed with methanol and distilled water, and dried.

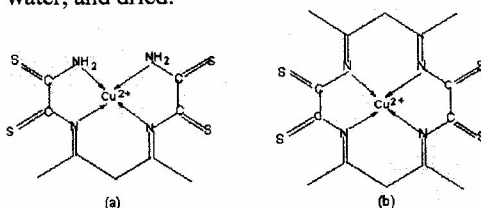


Figure 1. Possible structures for the Cu(II) complex (Complex-b)

Ion exchange study

A column with a 0.5 cm diameter and a 5 cm height was packed by Complex-b. An aqueous Ag(I) ion solution [$0.01 \text{ mol dm}^{-3} (M)$, 3 cm^3 at a time with a flow rate of $0.8 \text{ cm}^3 \text{ min}^{-1}$] was passed through the column. The effluent was tested with aqueous NaCl (1.0 M) and conc. ammonia. Similarly, aqueous solutions of Pb(II), Cd(II), Ni(II) and Zn(II) were passed through separate columns packed by Complex-b and precipitated with suitable reagents. Atomic absorption (AAS) and cyclic voltammetric (CV) data were collected for the effluents after passing dilute solutions of the above cations.

Results

Physical Properties of the complex is shown in Table 1. FTIR and XRD spectra of Complex-b are shown in Figure 2 and Figure 3, respectively.

Table 1. Physical Properties of Complex-b

Colour and Appearance	Shiny, black solids
Hardness	2.5-3.0 (Mohs scale)
Solubility	Insoluble in almost all solvents except conc. HNO ₃ and HCl
M.P.	> 280 °C
Streak colour	Dark gray

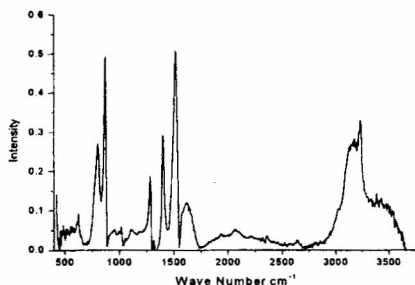


Figure 2. FTIR spectrum of Complex-b

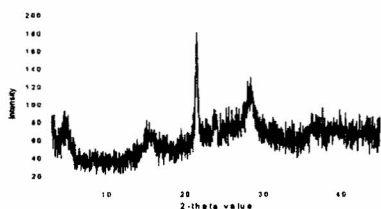


Figure 3. XRD spectrum of Complex-b

Discussion

The hardness of the complexes is between finger nail and calcite according to the Mohs hardness scale. IR data show significant differences in spectra of free dithiooxamide and metallo-derivatives in the region of N-H absorptions. The band at 3137 cm⁻¹ attributed to N-H stretching frequency is sharper and higher in frequency in metallo-derivatives compared to that of free dithiooxamide. The presence of additional strong bands at 872 cm⁻¹ and 1518 cm⁻¹, and the absence of a strong band at 1577 cm⁻¹ corresponding to the C=O stretching frequency of Cu(acac)₂ fragment confirm the formation of a macrocyclic complex. The decrease in the intensity of the major band of the XRD spectrum for Complex-

b may be due to the loss of intensity as a result of scattering of radiation between the pores present in the particles. The particle sizes calculated using XRD data and the Debye-Scherrer formula is 13.24 nm, which is 3 nm smaller compared to that of the corresponding dithiooxamido complex. Interestingly, the reduction in the size of the new complex together with the reduction in intensity of the XRD peaks compared to the copper(II) dithiooxamido complex may also be indicative of the packing of the molecule to form a macrocyclic configuration. Analysis of the data obtained in Tables 2 and 3 implies an interesting affinity of the complex towards Ag(I) ions. However, the test results reveal that the ions such as Pb(II), Cd(II), Zn(II) and Ni(II) neither trap nor release Cu(II) ions by the complex. According to the AAS data shown in Table 3, the copper complex used has trapped Ag(I) up to 20 ppm solutions without releasing Cu(II) ions. When the concentration of the Ag(I) ions exceeds 20 ppm, it starts to release Cu(II) ions from the complex while trapping Ag(I) ions into the complex. This observation is consistent with the XRD data which indicates the presence of some pores with the sizes compatible to the size of Ag(I) ions.

Table 2. Testing for Ag(I) ions using AAS

Concentration of the Ag(I) solution (3 cm ³) passed	Absorption for Ag(I)	Absorption for Cu(II)
5 ppm	-	-
10 ppm	-	-
20 ppm	-	0.002
20 ppm	-	0.004
20 ppm	-	0.005
100 ppm	-	0.029
100 ppm	-	0.046
100 ppm	-	0.065
0.001 M	-	0.092
0.001 M	-	0.122
0.001 M	-	0.141
0.002 M	-	0.172
0.002 M	-	0.233
0.002 M	-	0.254
0.010 M	-	0.614

Table 3. Ion exchange ability (Complex-b)

Aqueous solution passed	Precipitating agent	Precipitate with effluent	Effluent with ammonia
0.01 M Ag (I)	NaCl	-	Blue solution
0.01 M Pb (II)	NaCl	White	No change
0.01 M Cd (II)	NaOH	White	No change
0.01 M Ni (II)	DMG	Red	No change
0.01 M Zn (II)	K ₂ CO ₃	White	No change

Conclusions

In summary, a blackish shiny Cu(II) complex with the particle size of 13.2 nm and hardness of 2.5-3.0 has been synthesized by treatment of Cu(II), dithiooxamide and acetylacetonone. It is difficult to study the solution chemistry of the compound because it is extremely insoluble in almost all the solvents. IR and XRD data reveal that the structure of the new compound is different from both copper(II) dithiooxamido and copper(II) acetylacetonato complexes, and the N-end of dithiooxamide is primarily bonded to the metal center showing a possibility of having pores in the complex. AAS of the effluent collected by passing a

solution of Ag(I) ions through a column packed by the copper(II) complex shows a substitution of Cu(II) ions of the complex only with Ag(I) ions specifically and not with other ions such as Pb(II), Cd(II), Ni(II), Zn(II) at concentrations above 20 ppm. The unusual behavior of the new complex may be used for the application of this type of systems for specific trapping of some other noble ions such as Au(I).

Acknowledgements

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References

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- Udugala-Ganchenege, M.Y., Jane, M., Hryhorczuk, M., Wenger, I.O.E. and Endicott, J.F. (2001) Electron/atom transfer in halo-bridged homo-bimetallic complexes, *Inorganic Chemistry*, 40, 1614-1625.