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# Synthetic and Physicochemical Studies of Polymeric Homotrimetallic Complexes Involving [(8-Hydroxy-5-quinolyl)imino]mercaptoacetic Acid

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Coordination polymers of [(8-hydroxy-5-quinolyl)imino]mercaptoacetic acid have been prepared with the metal ions, $Cu^{2+}$, $Ni^{2+}$, $Co^{2+}$, $Cd^{2+}$, and $Hg^{2+}$. The polymeric complexes have been characterized by elemental analyses, TGA, molar conductance as well as electronic and IR spectral measurements. It was found that the ligand behaves as a triprotic tetradentate one. The coordination takes place through the oxygen and nitrogen atoms of the quinolinol moiety as well as through the mercapto and carboxyl groups of the mercaptoacetic acid. The analytical data depict the formation of complex compounds with the stoichiometry 3 : 2 (metal : ligand). Tetrahedral stereochemical configuration is suggested for these polymeric complexes.

Our interest in the coordination chemistry of biologically active compounds is continued to study the ligating properties of some 5(substituted amino)-8-quinolinol derivatives whose coordination chemistry is less developed in the literature.[1,2] The 8-quinolinol derivatives act as antibacterial, antifungal, and antiprotozoal agents as well as germinators for wheat seeds.[3—6] This paper describes the synthesis and characterization of $Cu^{2+}$, $Ni^{2+}$, $Co^{2+}$, $Cd^{2+}$, and $Hg^{2+}$ complexes of [(8-hydroxy-5-quinolyl)imino]mercaptoacetic acid.

## Experimental

Solvents and chemicals used in this study were of analytical grade (BDH or Merck). [(8-Hydroxy-5-quinolyl)imino]mercaptoacetic acid was prepared by reacting ethanolic solution of 5-nitroso-8-quinolinol with mercaptoacetic acid, under reflux, on water bath for 2 h. The resulting precipitate was filtered off, washed with ethanol, recrystallized from absolute EtOH and stored in vacuum over $P_4O_{10}$.

**Preparation of the Complexes.** A hot solution of the ligand (2 mmol) in ethanol (30 ml) was added dropwise under stirring to a solution of the given metal salt (3 mmol) ($CuCl_2\cdot 2H_2O$, $NiCl_2\cdot 6H_2O$, $CoCl_2\cdot 6H_2O$, $CdCl_2\cdot 2H_2O$, and $HgCl_2\cdot 2H_2O$) in 2 : 3 aqueous ethanol (30 ml). The mixture was stirred for one hour and the precipitated complex was filtered, washed with ethanol, and recrystallized from ethanol then dried in vacuo over $P_4O_{10}$.

**Physicochemical Methods for Characterization of the Complexes.** C,H,N analyses were carried out using a Perkin–Elmer 240C instrument. The IR spectra of the solids were scanned on a Perkin–Elmer 599 B (4000—600 $cm^{-1}$) as KBr discs. The electronic spectra were recorded by a CECIL 599 spectrophotometer (250—800 nm) using 1-cm matched silica cells. The conductivity measurements were carried out using a Bye-bridge at $10^{-3}$ M solution (1 M=1 mol dm$^{-3}$) of the complexes in DMF. Thermogravimetric analyses were carried out in air with Dupont models 951, 910, and 1090 Thermal Analyzers at a heating rate of 10 °C min$^{-1}$.

## Results and Discussion

The ligand used in this study can be regarded as diprotic (I) or triprotic (II) one of flexidentate nature (Chart 1). However, elemental analysis, conductivity, and spectral data are in favor of its coordination in the fully ionized triprotic form (II). The analytical data (Table 1) reveal the formation of homotribuclear complexes having the general formula $[M_3L_2\cdot 2H_2O]$; where M=Cu(II), Ni(II), Co(II), Cd(II), or Hg(II); L = [(8-hydroxy-5-quinolyl)imino]mercaptoacetic acid. This seems to take place according to the equation

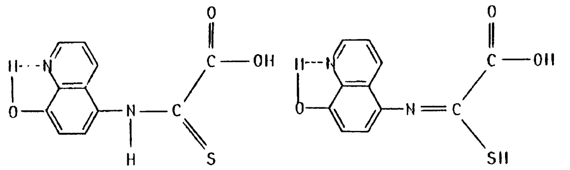

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Chart 1.

$$3MCl_2\cdot nH_2O + 2H_3L = [M_3L_2\cdot 2H_2O] + 6HCl + (n-2)H_2O. \quad (1)$$

Molar conductance value of 7.8—11.2 Ohm$^{-1}$ cm$^2$ mol$^{-1}$ (Table 1) for DMF solution of the complexes is indicative of their nonionic nature.[7]

**IR Spectra.** The IR group frequencies of diagnostic importance are collected in Table 2. The absence of S–H stretching frequency band at ca. 2500 $cm^{-1}$ in the spectrum of the free ligand, excludes the possibility of the existence of its "thiol" form in the solid state. However, the aforementioned reaction Eq. 1 indicates that this ligand exists as the thiol tautomer in solution. Confirmation for this is obtained from the IR spectra of the complexes where no bands due to NH stretching vibration could be recognized in the 3200—3000 $cm^{-1}$ region. This reveals coordination of the thiol form (II) to metal ion. The absence of $\nu_{SH}$ band around 2500 $cm^{-1}$ is, of course, due to liberation of the SH group proton upon coordination.

On the other hand the strong band occurring at 1600 $cm^{-1}$ in the spectrum of the free ligand due to NH deformation is missing in the spectra of the polychelates and a band of medium intensity is observed at lower frequencies in the range 1590—1580 $cm^{-1}$. This can be better ascribed to the azomethine (C=N) stretching

Table 1. Physical Elemental Analysis and Molar-Conductivity Data of the Polymeric Complexes

| No. | Complexes | Color | Decomp temp/°C | Yield % | Calcd (Found)/% C | H | N | S | M | $\Lambda_m$ $Ohm^{-1}\,cm^2\,mol^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | $[Cu_3(C_{22}H_{10}N_4S_2O_6)(H_2O)_2]$ | Green | 230 | 70 | 36.84 | 1.96 | 7.81 | 8.94 | 26.58 | 10.10 |
| | | | | | (36.60) | (2.20) | (8.10) | (9.10) | (26.30) | |
| 2 | $[Ni_3(C_{22}H_{10}N_4S_2O_6)(H_2O)_2]$ | Yellow | 270 | 55 | 37.60 | 2.00 | 7.97 | 9.12 | 25.06 | 7.80 |
| | | | | | (37.80) | (1.80) | (8.00) | (8.80) | (24.90) | |
| 3 | $[Co_3(C_{22}H_{10}N_4S_2O_6)(H_2O)_2]\cdot 2H_2O$ | Brown | 275 | 60 | 35.74 | 2.45 | 7.57 | 8.67 | 23.91 | 9.30 |
| | | | | | (36.00) | (2.50) | (7.70) | (8.80) | (24.20) | |
| 4 | $[Cd_3(C_{22}H_{10}N_4S_2O_6)(H_2O)_2]$ | Yellow | 260 | 45 | 31.17 | 1.66 | 6.60 | 7.56 | 39.78 | 9.50 |
| | | | | | (30.80) | (1.50) | (6.70) | (7.70) | (40.00) | |
| 5 | $[Hg_3(C_{22}H_{10}N_4S_2O_6)(H_2O)_2]$ | Yellowish | 255 | 40 | 23.42 | 1.25 | 5.96 | 5.68 | 53.33 | 11.20 |
| | | | | | (23.50) | (1.50) | (6.00) | (5.90) | (53.50) | |

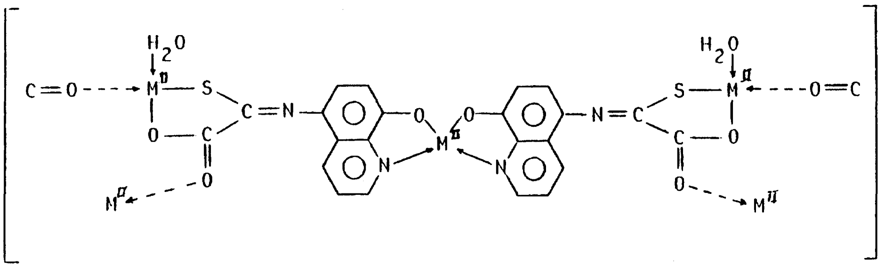

Chart 2.

Table 2. Selected IR Bands of the Free ligand and Its Metal(II) Polymeric Complexes

| Compound | Assignment $\nu_{OH}$ | $\nu_{C=N}$ | $\nu_{as}^{OCO}$ | $\nu_{s}^{OCO}$ | $\nu_{O-Ph}$ |
|---|---|---|---|---|---|
| Free ligand | — | 1600 | — | — | 1250 |
| Cu(II)-L | 3360 | 1590 | 1550 | 1420 | 1230 |
| Ni(II)-L | 3390 | 1590 | 1530 | 1430 | 1235 |
| Co(II)-L | 3470 | 1585 | 1510 | 1430 | 1230 |
| Cd(II)-L | 3465 | 1595 | 1555 | 1485 | 1240 |

vibration. This can be considered as further evidence for coordination of this ligand in its thiol form (II). The band occurring at 1620 cm$^{-1}$ in the spectrum of the free ligand, which is assignable to carbonyl stretching frequency of the carboxyl group[8] is missing in the spectra of the polychelates and instead two bands appeared in the range 1570—1510 and 1485—1420 cm$^{-1}$. These two bands are assignable to the asymmetric and symmetric stretching of the carboxylato group respectively.[8] The separation ($\nu_{as}$–$\nu_s$) of the carboxylato stretching vibrations and their relative intensity agrees well with a carboxylato group coordinating in its didentate bridging mode.[9,10] On the other hand a weak broad band is observed at 1930 cm$^{-1}$, in the IR spectra of the free ligand due to the presence of an intramolecular hydrogen bonding of the type O–H···N. This band is absent in the IR spectra of the complexes indicating the coordination of the phenolic oxygen and liberation of a proton. The strong absorption band appeared in the 1250 cm$^{-1}$ in the spectra of free ligand is due to the phenolic C–O stretching. This band is found to locate at a lower values in the IR spectra of the polymeric complexes. This shift illustrates the participation of the quinolinol oxygen atom in complex formation.[11]

A new band at 660—680 cm$^{-1}$ is observed in the IR spectra of the metal polychelates. This band is best ascribed to C–S–M stretching vibration[12] and denotes the coordination of the sulfur atom after deprotonation. This behavior is a further support for the coordination of the mercaptoacetate ligand in its thiol form (II).

The presence of coordinated and lattice water molecules in the prepared polymeric complexes has been confirmed by the new band appeared at 3470—3360 cm$^{-1}$ in the IR spectra of complexes. Also, the rocking mode of coordinated water appeared as a weak vibration band in the neighborhood of 810—960 cm$^{-1}$.[13] The existence of water in polymeric complexes is further substantiated from the results of elemental analyses (Table 1). The water content of the complexes has been verified by TGA where it is found that all the water molecules are lost in a one-step process at relatively high temperatures (170—195 °C). This indicates that the two water molecules are coordinatively bonded to the metal ions. Co(II) complex loses two water molecules at the 125 °C characteristic of non-coordinated water.

Based on the foregoing discussion the following structure is proposed for the present polychelates (Chart 2):

**Electronic Spectra.** Table 3 gives the UV-spectral data of the ligand and visible spectral data for chelates where applicable, in DMF. The UV electronic spectra of free ligand comprised intense bands at 42600, 36100, and 24200 cm$^{-1}$. These could be assigned to Ph–Ph*,

Table 3. Electronic Spectral Bands of the Free Ligand and Its M(II) Complexes

| Compound | $\nu_{\max}/\mathrm{cm}^{-1}(\varepsilon_{\max}/\mathrm{dm}^3\,\mathrm{mol}^{-1}\,\mathrm{cm}^{-1})$ |
|---|---|
| Free L | 42600 (26000); 36100 (21000); 24200 (13600) |
| Cu(II)-L | 17500 (800); 25600 (10400); 38100 (18500) |
| Ni(II)-L | 15900 (1100); 26100 (11000); 36700 (17100) |
| Co(II)-L | 14800 (1400); 25800 (10800); 36700 (14800) |
| Cd(II)-L | 26700 (12300); 37800 (16200); 40500 (20200) |

$\pi$–$\pi^*$ (phenyl), n–$\pi^*$ (quinoline) and n–$\pi^*$ (azomethine) transitions, respectively. The band at 24200 $\mathrm{cm}^{-1}$ blue shifted in the spectra of the polymeric complexes.

The d–d electronic transition of Cu(II), polychelate (Table 2) was observed as an asymmetric band, having $\nu_{\max}$ at 17500 $\mathrm{cm}^{-1}$ which is indicative of tetrahedral configuration for this polymeric complex. Therefore, this band can be assigned to ${}^2\mathrm{E}_{2g}\leftarrow{}^2\mathrm{T}_{2g}$ transition. This suggestion is substantiated by the previous observations described by Lever[14] concerning the electronic spectra of the tetrahedral Cu(II) complexes.

The Co(II) polymeric complex may have a tetrahedral structure also. The existence of one main band at 14800 $\mathrm{cm}^{-1}$, which corresponds to the electronic transition ${}^4\mathrm{A}_2 \rightarrow {}^4\mathrm{T}_1(\mathrm{P})$ is considered to be evidence for the tetrahedral structure around the Co(II) ions.[14]

The square planar Ni(II) complexes usually exhibit a characteristic band at ca. 20000 $\mathrm{cm}^{-1}$. The absence of such a band together with the appearance of a band at 15900 $\mathrm{cm}^{-1}$ in the electronic spectrum of the Ni(II) polymeric chelate may indicate tetrahedral geometry around the Ni(II) ion. This band is characteristic of the ${}^3\mathrm{T}_1 \rightarrow {}^3\mathrm{T}_1(\mathrm{P})$ transition in the pseudo tetrahedral structure of Ni(II) complexes.[14]

The directions of the shifts of all the bands in the IR spectra of all the polymeric complexes here studied are the same and this fact clearly indicates that the bonding patterns in all the polymeric complexes must be similar. It can therefore, be stated that Cd(II) and Hg(II) complexes both possess a tetrahedral stereochemical configuration.

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