CHELATING BEHAVIOUR OF 1,1,3,3-PROPANETETRASALISOYL TETRACARBOHYDRAZONE

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ABSTRACT

The reaction of 1,1,3,3-propanetetrasalisoyltetracarboxyhydrazone (H₄PTSTCH) with some metal ions in ethanol-aqueous medium has been studied. The isolated complexes were formulated as [Cu₄(PTSTCH)₈H₂O]·4H₂O, [Co₄(PTSTCH)₁₂H₂O]·6H₂O, [Sn₄(PTSTCH)₈H₂O] and [(UO₂)₄(PTSTCH)₈H₂O] on the basis of elemental and thermal analyses. Their structural assessment was supported by molar conductance, magnetic moment and spectral studies. The NMR (¹H and ¹³C) spectroscopy was used to elucidate the structure of the chelating molecule. Since H₄PTSTCH has four hydrazone moieties -CONHN=CHC₆H₄(ω-OH) each one contains four donor groups, it coordinates with the studied metal ions as ONO system with each of the four metal ions forming tetracnuclear complexes. Each coordinating site binds through the phenolic oxygen, the azomethine nitrogen and the enolic carbonyl oxygen atoms.
INTRODUCTION

Due to the diverse properties of hydrazones and their applications in many fields (synthesis of organic compounds, polymers, pharmacological, analytical and technological etc.) the literature indicates an increased interest in the synthesis of new hydrazones and their complexing affinities toward different metal ions[6-10]. The isolated complexes are quite stable in air and/or the acetate salts of cobalt (II), copper (II), tin (II) and uranyl (II) gives only one type of complexes in which the metal ion coordinates with the enolic form of the ligand. The analytical data with some physical properties are listed in Table I. The isolated complexes are quite stable in air and their molar conductivity values (Table I) in dimethylsulphoxide solution lie in the range reported for non-electrolyte complexes.[13] The Co(II) and Cu(II) complexes had lower magnetic moment values (Table I) due to the existence of four metal atoms in the same unit.

The (\(^{1}H, \^{13}C\)) NMR and IR spectral studies are used to confirm the ligand structure (I). The position of the amide (I) band depends on the degree of hydrogen bonds as well as the physical state of the compound. Two strong bands at 1682 and 1662 cm\(^{-1}\) are attributed to the free and bonded carbonyl groups; these are confirmed from the \(^{13}\)C NMR spectrum in which two signals at 168.7 and 168.2 ppm are observed. The NH stretching vibrations are observed at 3212 cm\(^{-1}\) as a broad band due to the intramolecular hydrogen bond which is supported by the appearance of two weak bands at 2348 and 2369 cm\(^{-1}\) due to the N-H...O vibrations.[14]. The amide (II and III) bands are observed at 1560 and 1215 cm\(^{-1}\). The v(C-H) aromatic band is observed at 3058 cm\(^{-1}\); its protons are identified in the \(^{1}\)H NMR spectrum as quartet and doublet signals at 6.9, 7.2 and 7.9 ppm. The integration provides for the total number of aromatic protons in the ligand. The distinct strong bands at 2940 and 2874 cm\(^{-1}\) are attributed to \(v_{as}\) and \(v_{s}\) (C-H) aliphatic vibrations[15]. The increased value indicates that the methylene group is part of a strained ring. The position of CH and CH2 protons in the \(^{1}\)H NMR is at 3.65 and 4.0 ppm, respectively with integration corresponding to the presence of four protons. The \(^{13}\)C NMR spectrum shows a signal at 140.3 ppm due to the C=O group; its existence reveals the tautomeric structure which is due to acidic protons, the amide and the carbonyl groups. The \(v(\text{OH})\) and \(v(\text{C}=\text{O})\) of the phenolic group appear at 3445 and 1368 cm\(^{-1}\) in the IR spectrum of the ligand; the C-O group is also confirmed from the \(^{13}\)C NMR spectrum which has its signal at 157.1 ppm. A doublet observed in the \(^{1}\)H NMR spectrum at \(\delta = 8.3\) and 8.4 ppm which is characteristic for the four protons of (\(\text{CH} = \text{N}\)) groups; their appearance as doublet is due to the effect of the vicinal CH aromatic ring. The IR spectrum provides band at 1614 cm\(^{-1}\) due to the \(\nu\) (\(\text{C}=\text{N}\)) vibration. The \(^{1}\)H NMR spectrum also shows signals at \(\delta = 10.0\), 11.1, 11.5 and 11.9 ppm assigned to the imino and hydroxyl protons, respectively with integration indicating two protons for each signal. All these evidences support structure I for \(\text{HgPTSTCH}\).

EXPERIMENTAL

All the chemicals used were of BDH quality.

Preparation of \(\text{HgPTSTCH}\)

Molar ratio of 4:1 salicyaldehyde to 1,1,3,3-propanetetracarbohydrazine were mixed in ethanol solution with continuous stirring. The reaction mixture was refluxed on a water bath for one hour. A white precipitate thus formed was filtered, washed with ethanol and left to dry over MgSO4. The structure of the ligand was elucidated by the elemental analysis, IR and NMR spectroscopic data.

Preparation of the metal complexes

A hot ethanolic solution of \(\text{HgPTSTCH}\) (0.01 mol) was mixed with an aqueous ethanolic solution of the metal salts (0.04 mol Cu(AC)\(_{2}\)\(\cdot\)2H\(_{2}\)O, Co(AC)\(_{2}\)\(\cdot\)2H\(_{2}\)O, UO\(_{2}\)(AC)\(_{2}\)\(\cdot\)2H\(_{2}\)O, CuSO\(_{4}\)\(\cdot\)5H\(_{2}\)O or SnCl\(_{2}\)\(\cdot\)2H\(_{2}\)O). The mixture was refluxed on a water bath for 3-5 h and concentrated to its half volume. The product thus formed was filtered, washed with ethanol and dried in vacuum over anhydrous CaCl\(_{2}\).

Physical measurements

Metal ions were determined by the standard methods[12]. Carbon and hydrogen analyses were carried out in the microanalytical unit of Cairo University. Magnetic measurements were carried out by the Gouy method using Hg[Co(NCS)\(_{4}\)] as a calibrating agent. IR spectra (4000-200 cm\(^{-1}\)) were recorded on a Perkin-Elmer 1430 model with continuous stirring. The reaction mixture was refluxed on a water bath for one hour. A white precipitate thus formed was filtered, washed with ethanol and left to dry over MgSO4. The structure of the ligand was elucidated by the elemental analysis, IR and NMR spectroscopic data.
The IR spectra of polynuclear complexes [M₄(PTSTCH)₆H₂O] (where M = Cu(II), Co(II), Sn(II) and UO₂(II); n = 8-12) show the disappearance of the NH and carbonyl groups with the appearance of new bands in the 1625-1605 cm⁻¹ region which are related to the stretching vibration of the conjugated C=N-N=C system. The absence of ν(OH) and amide III [ν(NH)] bands is taken as an evidence for the dissociation of their protons on complex formation. The lower shifts in ν(C-O) and ν(C=N) vibrations by 15-30 cm⁻¹ in the IR spectra of the complexes indicate the participation of phenolic oxygen and azomethine nitrogen in bonding with the metal atoms. Another evidence for O and N coordinations comes from the appearance of new bands at ca. 360 and 410 cm⁻¹ due to ν(M-N)[16] and ν(M-O)[17] respectively. The characteristic bands of coordinated water molecules appear as a broad band in the regions 3445-3383, 879-871 and 651-648 cm⁻¹ assigned to ν(OH), νₚ(H₂O) and νₚₚ(H₂O) vibrations[18] respectively.

The thermal analysis of [Cu₄(PTSTCH)₈H₂O]₄H₂O and [Co₄(PTSTCH)₁₂H₂O]₆H₂O was studied with the help of DTA, DTG and TG techniques. The thermograms of Cu(II) complex show an exothermic peak starting at 80 °C with a weight loss of 6.13% corresponding to the amount of water outside the sphere (Calc. 6.2%). The figure also shows an endothermic peak at 160-170 °C; the weight loss (12.3%) corresponds to the removal of all coordinated water. The anhydrous complex begins to decompose through some exothermic peaks; the first one at 260 °C (17.7%) corresponding to the decomposition of the organic moiety. The second and third peaks observed at 385 and 470 °C correspond to the decomposition of the organic moiety. At higher temperature, a series of exothermic peaks; the first one at 410 °C, the second and third peaks observed at 835 and 470 °C correspond to the combustion of aliphatic and aromatic carbon atoms. At higher temperature, a series of exothermic peaks with the final one corresponding to CuO; (the remaining mass) is in good agreement with that found in the determination of the metal ion complexometrically. The DTG and TG thermograms of Co(II) complex show peaks at 80-120, 160-200 °C accompanied by a weight loss of 8.6 and 17.2% corresponding to the removal of uncoordinated and coordinated water (Calc. 8.6% and 17.4% respectively). A broad exothermic peak in the 220-400 °C range corresponds to the melting and combustion of the organic moiety. In the range 400-620 °C, a broad exothermic peak is attributed to the combustion of aliphatic and aromatic residue. At higher temperature (600-780 °C), a broad exothermic peak is observed with no peaks while at 840 °C, an exothermic peak corresponds to the formation of Co₃O₄[19] which is readily decomposed to CoO at 870 °C. The remaining mass is in good agreement with the calculated one.

All the evidence gathered from IR spectra and thermal studies reveal structure-II for [Co₄(PTSTCH)(H₂O)₉H₂O] as an example for the polynuclear complexes.

REFERENCES


