

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

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دراسة السلوك المخليبي لمركب ١, ١, ٣, ٣ - بروبان رباعي ساليسيل الكربوهيدرازون

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نتيجة للخواص الهامة لمشتقات الهيدرازون وتطبيقاتها في مجالات الكيمياء التحليلية وتحضير بعض المركبات العضوية والبوليمرات وكذلك في المجالات التكنولوجية وصناعة الدواء، تم الاتجاه لتحضير المركب ١, ١, ٣, ٣ - بروبان رباعي ساليسيل رباعي الكربوهيدرازون (HgPTSTCH) ودراسة سلوكه الارتباطي مع بعض ايونات الفلزات المختلفة كنتيجة لمرونته ومقدرته على الارتباط المتعدد في الفراغ .

وبناءً على نتائج التحليل الكمي الميكروني للعناصر ودراسة التحليل الطيفي في مجال الأشعة تحت الحمراء وتحليل الرنين النووي المغناطيسي (^1H and ^{13}C NMR) وقياس الخواص المغناطيسية والتوصيل الجزيئي ودراسة نتائج التحليل الحراري تم إثبات التركيب الكيميائي للمركب المخليبي وكذلك بعض المتراكبات عديدة الأنوية .

وحيث أن المركب المخليبي يحتوي على أربعة مجموعات هيدرازون فقد تم وضع نموذج للارتباط من خلال ذرات الأكسجين الفينولية ونيروجين الأزوميثين وأكسجين مجموعة الكربونيل في الصورة الاينولية (ONO) مكوناً متراكبات عديدة الأنوية .

Key Words: Complexes, Polynuclear Complexes, Hydrozones

ABSTRACT

The reaction of 1,1,3,3-propanetetrasalisoyltetracarbohydrazone (HgPTSTCH) with some metal ions in ethanol-aqueous medium has been studied. The isolated complexes were formulated as $[\text{Cu}_4(\text{PTSTCH})_8\text{H}_2\text{O}] \cdot 4\text{H}_2\text{O}$, $[\text{Co}_4(\text{PTSTCH})_{12}\text{H}_2\text{O}] \cdot 6\text{H}_2\text{O}$, $[\text{Sn}_4(\text{PTSTCH})_8\text{H}_2\text{O}]$ and $[(\text{UO}_2)_4(\text{PTSTCH})_8\text{H}_2\text{O}]$ 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 ^{13}C) spectroscopy was used to elucidate the structure of the chelating molecule. Since HgPTSTCH has four hydrazone moieties -CONHN=CHC₆H₄(o-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 tetranuclear 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 compounds¹, polymers², pharmacological³, analytical⁴ and technological⁵ etc.) the literature indicates an increased interest in the synthesis of new hydrazones and their complexing affinities toward different metal ions [6-10]. 1,1,3,3-Propanetetrasalisoyltetracarbohydrazone which is prepared from the condensation of 1,1,3,3-propanetetracarbohydrazine [11] with salisaldehyde is considered as an example of a novel hydrazone capable of exhibiting multidentate behaviour and by having flexibility in three dimensional space. It has also the ability to bind more than one metal ion to form polynuclear complexes.

EXPERIMENTAL

All the chemicals used were of BDH quality**Preparation of HgPTSTCH**

Molar ratio of 4:1 salicylaldehyde 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 HgPTSTCH (0.01 mol) was mixed with an aqueous ethanolic solution of the metal salts (0.04 mol Cu(Ac)₂·H₂O, Co(Ac)₂·2H₂O, UO₂(Ac)₂·2H₂O, CuSO₄·5H₂O or SnCl₂·2H₂O). 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 CaCl₂.

Physical measurements

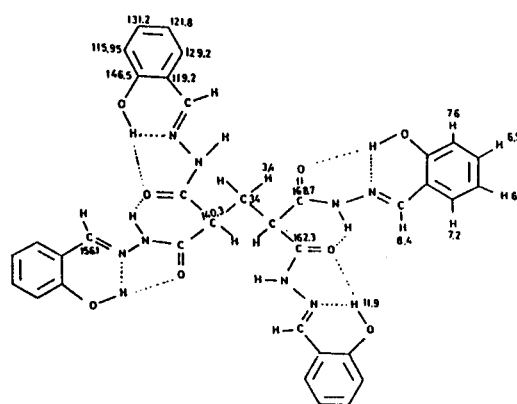
Metal ions were determined by the standard methods [12]. Carbon and hydrogen analyses were carried out in the microanalytical unit of Cairo University. Magnetic measurements were carried out by the Gouy method using Hg[Co(NCS)₄] as a calibrating agent. IR spectra (4000-200 cm⁻¹) were recorded on a Perkin-Elmer 1430 model with samples in KBr pellets. The NMR spectrum of HgPTSTCH was recorded on a EM-390 (90 MHz) NMR spectrometer using deuterated acetone. The molar conductance values were measured with a Leitfohgkeitsme PHYWE bridge. The thermal analyses for some complexes were done using MoM Derivatograph on Egyptian Geological Survey and Mining Authority: 80 mg of the sample was heated by 10 °C/min. up to 950 °C with α-Al₂O₃ as referencne.

RESULTS AND DISCUSSION

The reaction of HgPTSTCH with the chloride, sulphate 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 1. The isolated complexes are quite stable in air and their molar conductivity values (Table 1) 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 1) due to the existence of four metal atoms in the same unit.

The (¹H, ¹³C) 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 ¹³C 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 ν(C-H) aromatic band is observed at 3058 cm⁻¹; its protons are identified in the ¹H 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 ν_{as} and ν_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 ¹H NMR is at 3.65 and 4.0 ppm, respectively with integration corresponding to the presence of four protons. The ¹³C NMR spectrum shows a signal at 140.3 ppm due to the C=C group; its existence reveals the tautomeric structure which is due to acidic protons, the amide and the carbonyl groups. The ν(OH) and ν(C-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 ¹³C NMR spectrum which has its signal at 157.1 ppm. A doublet observed in the ¹H NMR spectrum at δ = 8.3 and 8.4 ppm which is characteristic for the four protons of (-CH=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 ν (C=N) vibration. The ¹H NMR spectrum also shows signals at δ = 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 HgPTSTCH.

(H₆PTSTCH)

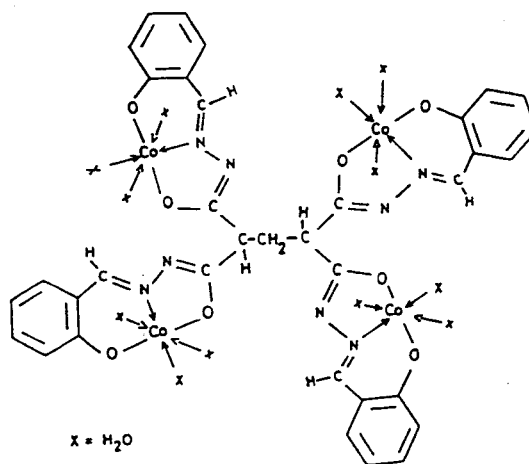
Structure - I

The IR spectra of polynuclear complexes $[M_4(PTSTCH)_nH_2O]$ (where $M = Cu(II), Co(II), Sn(II)$ and $UO_2(II)$; $n = 8-12$) show the disappearance of the NH and carbonyl groups with the appearance of new bands in the $1625-1605\text{ cm}^{-1}$ region which are related to the stretching vibration of the conjugated $C=N-N=C$ system. The absence of $\nu(OH)$ and amide III $[\nu(NH)]$ bands is taken as an evidence for the dissociation of their protons on complex formation. The lower shifts in $\nu(C-O)$ and $\nu(C=N)$ vibrations by $15-30\text{ cm}^{-1}$ 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 $\nu(M-N)$ [16] and $\nu(M-O)$ [17] respectively. The characteristic bands of coordinated water molecules appear as a broad band in the regions $3445-3383$, $879-871$ and $651-648\text{ cm}^{-1}$ assigned to $\nu(OH)$, $\rho_r(H_2O)$ and $\rho_w(H_2O)$ vibrations[18] respectively.

The thermal analysis of $[Cu_4(PTSTCH)_8H_2O]4H_2O$ and $[Co_4(PTSTCH)_{12}H_2O]6H_2O$ was studied with the help of DTA, DTG and TG techniques. The thermograms of Cu(II) complex show an exothermic peak starting at $80\text{ }^\circ\text{C}$ 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 $160-170\text{ }^\circ\text{C}$; 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 $260\text{ }^\circ\text{C}$ (17.7%) corresponding to the decomposition of the organic moiety. The second and third peaks observed at 385 and $470\text{ }^\circ\text{C}$ corresponding 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 $80-120$, $160-200\text{ }^\circ\text{C}$ 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 $220-400\text{ }^\circ\text{C}$ range corresponds to the melting and combustion of the organic moiety. In the range $400-620\text{ }^\circ\text{C}$, a broad exothermic peak is attributed to the combustion of aliphatic and aromatic residue. At higher temperature ($600-780\text{ }^\circ\text{C}$) a stable steady state is observed with no peaks while at $840\text{ }^\circ\text{C}$, an exothermic peak corresponds to the formation of Co_3O_4 [19] which is readily decomposed to CoO at $870\text{ }^\circ\text{C}$. 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 $[Co_4(PTSTCH)(H_2O)_8]4H_2O$ as an example for the polynuclear complexes.

The same complexes were also isolated by a new technique that depends on the electrochemical oxidation of cobalt, copper and/or tin in acetone solution of the ligand. The same complexes were also isolated by a new technique that depends on the electrochemical oxidation of cobalt, copper and/or tin in acetone solution of the ligand. The method is simple, rapid and gives a high yield. This indicates that the complexes having the same empirical formulae can be isolated by different techniques.



Structure - II

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