Synthesis, Physicochemical Studies and Molecular Modeling of Some Zwitterionic Buffer Complexes

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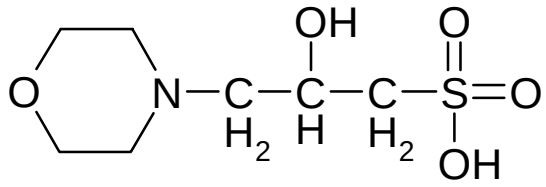
Interaction of the zwitterionic buffer 3-(N-morpholinol)-2-hydroxy-propane sulfonic acid (H_2MOPSO) with the divalent cobalt, nickel and copper ions gave the solid [Co(MOPSO)($H_2O)_4$].12H_2O, [Ni(MOPSO)-($H_2O)_4$].9H_2O and [Cu(MOPSO)($H_2O)_4$].3H_2O complexes. The complexes were characterized by elemental analysis, mass and infrared spectrometry. The solid complexes were also investigated by thermal (DTA and TG) analysis. Molecular modeling of the complexes expected that the molecular geometry of the three complexes could have distorted octahedral arrangements.

Introduction

Interaction between metal ions and amino acids has become of considerable interest as models for biological systems in which the properties of the proteins are modified by the fact that the metal ions are attached to amino acids moieties [1]. In case of iron-storage protein, bacterioferritin, the dinuclear metal binding site (ferroxidase center) is essential for fast iron core formation [2]. The electroneutrality of the ferroxidase center is preserved on binding a pair of divalent ions and may have mechanistic implications for the iron (II) binding process. Good and co-workers [3] recommended a series of zwitterionic buffer compounds compatible with most media of physiological and biological importance. The apparent dissociation constant of the zwitterionic buffer 3-(N-morpholinol)-2-hydroxypropane sulfonic acid (MOPSO) has a significant physiological value [4]. The important role of this buffer and the participation of the metal ions in the biochemical reactions of nucleotides and nucleic acids have drawn great interest in the determination of the structure of the metal-buffer complexes.

In this paper, we describe the synthesis and structural determination of Co(II), Ni(II) and Cu(II)–MOPSO complexes. Molecular modeling of the reported complexes using the technique developed by Goodford was investigated [5]. This technique is a simple molecular mechanics based approach for calculating optimum ligand atom location in a binding site with minimization of energy.



Experimental

Chemicals

3-(N-morpholinol)-2-hydroxypropane sulfonic acid was purchased from sigma chemical Co. Ethanol was of analytical grade. $CoSO_4$, Ni SO_4 and Cu SO_4 were supplied from BDH.

Physical Measurements

IR measurements (KBr discs) were carried out on a Perkin-Elmer 883 spectrophotometer. Conductivity measurements were made on a YSE conductance meter model 32. Samples of concentration *ca.*$1x10^{-3}$-$1x10^{-6}$ M in DMSO were used for the measurements. Thermal analyses (DTA and TG) were carried out under nitrogen with a heating rate of 10 ^{o}C/min. using a Shimadzu DT-50 thermal analyzer. The complexes were also characterized by elemental

analyses (Perkin-Elmer 2400 CHN elemental analyzer) and mass spectroscopy (Electron Impact Finnigan MAT SSQ 7000 spectrometer). The data are given in Table I.

Preparation of complexes

The complexes were prepared by mixing stoichiometric amounts of ligand and metal ion (1:1 molar ratio) in aqueous medium. The reaction mixture was stirred for about one hour at about 70 ^{o}C. On cooling, the solid complex was precipitated. The formed precipitate was filtered and washed several times with hot water. The complex was then recrystaillised from hot ethyl alcohol. The complex was left to dry under vacuum for several hours.

3D-Molecular Modeling

3D molecular modeling of the proposed structure of the complexes were performed using Hyper-Chem 5 molecular modeling software. The correct stereochemistry was assured through the manipulation and modification of the molecular coordinates to obtain reasonable low energy molecular geometries. The potential energy of the molecule was the sum of the following terms:

$$E = E_{str} + E_{ang} + E_{tor} + E_{vdw} + E_{oop} + E_{ele}.$$

Where all E's represent the energy values corresponding to the given types of interaction (kcal/mol). The subscripts str, ang, tor, vdw, oop, and ele denote bond stretching, angle bonding, torsion deformation, Van der Waals interactions, out of plane bending and electronic interaction, respectively.

Results and Discussion

Infrared Spectra

Reactions of 3-(N-morpholinol)-2-hydroxypropane sulfonic acid with Co(II), Ni(II) and Cu(II) ions in aqueous media required elevated temperatures (equation 1). The stoichiometries of the complexes were obtained from elemental analyses and mass spectroscopy (Table I). Coordinated water molecules as well as the number of water of crystallization were determined by mass spectrometry and thermal gravimetric plots of the complexes.

$$MSO_4 + H_2MOPSO + 4\,H_2O \xrightarrow{\Delta} [M(MOPSO)(H_2O)_4] + H_2SO_4 \quad (1)$$

(M = Co, Ni and Cu)

The IR spectrum of H_2MOPSO ligand displayed a broad band at 3300 cm^{-1} due to OH stretching frequency. It also showed a composite pattern consisting of

four bands corresponding to asymmetric and symmetric stretching frquencies of S=O bonds in the sulphonate group, Table (II). On the other hand, the IR spectra of the three complexes showed that the ν(S=O) were shifted to lower frequency due to complex formation, Table (II). The IR spectra also showed broad bands due to OH stretching frequencies of the water molecules. Conductivity measurements of dilute solutions of the three complexes in DMSO exhibit conductance of non-elctrolyte species. This indicates that the complexes are neutral. From the spectroscopic and analytical data, it can be concluded that the ligand coordinates the metal ion from the OH and sulphonate groups with the release of two protons. The octahedral structure was then attained by coordination of four water molecules.

Table (1): The elemental analyses and mass spectroscopy data of the complexes.

Formula (Mol. Wt.)	Color	% Yield	M.p	**Elemental analysis**						MS m/z
				% C		% H		% N		
				Theo.	Found	Theo.	Found	Theo.	Found	
$[Co(MOPSO)(H_2O)_4].12H_2O$ $C_7H_{45}CoNSO_{20}$ (554.54)	Rose	60	>300 decomp	15.16	15.21	8.11	8.19	2.52	2.50	339
$[Ni(MOPSO)(H_2O)_4].9H_2O$ $C_7H_{39}NiNSO_{17}$ (500.09)	Pale green	63	>300 decomp	16.81	16.79	7.79	7.83	2.80	2.83	338
$[Cu(MOPSO)(H_2O)_4].3H_2O$ $C_7H_{27}CuNSO_{11}$ (396.83)	Pale blue	70	>300 decomp	21.18	21.22	6.80	6.79	3.53	3.51	343

Table (2): The Important IR Data of H_2MOPSO and its Cobalt, Nickel, and Copper Complexes. ([a] s, strong; m, medium; w, weak; b, broad.)

Compound	IR data (cm^{-1})[a]			
	ν(OH)	ν(S=O)	ν(C-N)	ν(C-S)
H_2MOPSO	3300 m	1230 s, 1180 s, 1150 s, 1030 s	1015 m	620 m
$[Co(MOPSO)(H_2O)_4].12H_2O$	3470 b, 3200 b	1210 s, 1150 s, 1060 s	1020 m	630 m
$[Ni(MOPSO)(H_2O)_4].9H_2O$	3430 b, 3250 b	1130 s, 1060 s, 1045 s	1017 m	625 m
$[Cu(MOPSO)(H_2O)_4].3H_2O$	3380 b, 3220 b	1215 s, 1150 s, 1100 s	1000 m	632 m

3d- Molecular Modeling

Molecular modeling of the studied complexes reveals minimum energy values associated with the octahedral geometry. This is in a good agreement with the experimental results and confirms the expected octahedral structure. As an example, data for selected bond lengths and bond angels of Co-Mopso complex are represented in Table (3), and Figure (1) illustrates the octahedral geometry.

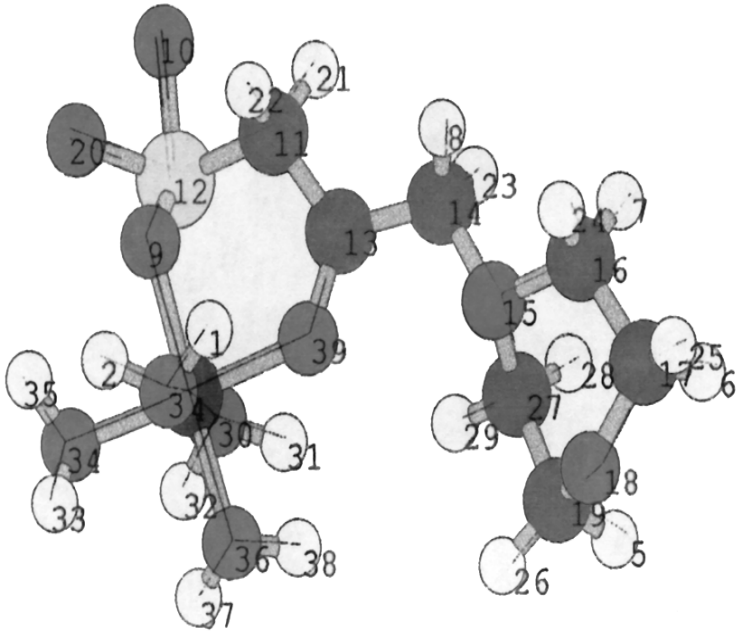


Fig. (1): Molecular modeling display of Co-MOPSO complex with numbered atoms

From Table (3), distortion of the octahedral geometry is pronounced and is attributed to the diversity of the bond angles from those of regular octahedron, in addition to inequality of the bond lengths. Shortening of the Co-O(9) and Co-O(39) bonds is probably due to the electronegativeties of the SO_3 and OH groups, respectively [6]. The bond distances of these groups are shorter than the ionic radii calculated by Shannon [7] and indicating strong interaction between the metal ion and the ligand on coordination. Biological activity of complexes was confirmed to parallel with the strength of the metal – ligand bond [8]. So, it may be expected that the biological activity of the prepared complexes be via the SO_3 and OH groups.

Thermal Analysis

The content of a particular component in a complex changes with its composition and structure. Thus, the content of such components can be

determined based on the mass losses of these components in the thermogravimetric plots of the complex [9, 10]. Therefore, in order to throw more insight into the structure of

Table (3) Data for selected bond lengths and bond angles of Co- Mopso complex.ond length A^0

Bond length A^o		Bond angle ^{o}	
Co (4) - O (3)	1.85538	O(9) – Co (4) - O(3)	85.6604
Co (4) - O (9)	1.84730	O(3) – Co (4) - O(34)	93.2029
Co (4) -O (30)	1.85187	O(34) – Co (4) - O(36)	93.5598
Co (4) -O (34)	1.84994	O(36) – Co (4) - O(30)	91.3554
Co (4) -O (36)	1.85448	O(30) – Co (4) - O(39)	90.2065
Co (4) -O (39)	1.80629	O(39) – Co (4) - O(9)	87.3847
		O(3) – Co (4) - O(30)	171.950
		O(39) – Co (4) - O(34)	175.471
		O(9) – Co (4) - O(36)	165.959

the complexes, thermal studies on the solid complexes using differential thermal analysis (DTA) and thermogravimetric (TG) techniques were performed (Fig.2,3, and 4).

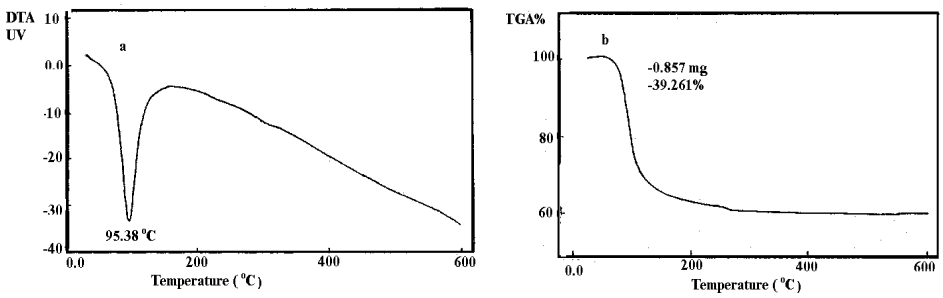


Fig. (2) Thermal analysis curves for the binary Co-MOPSO complex
(a) DTA curve (b) TGA curve.

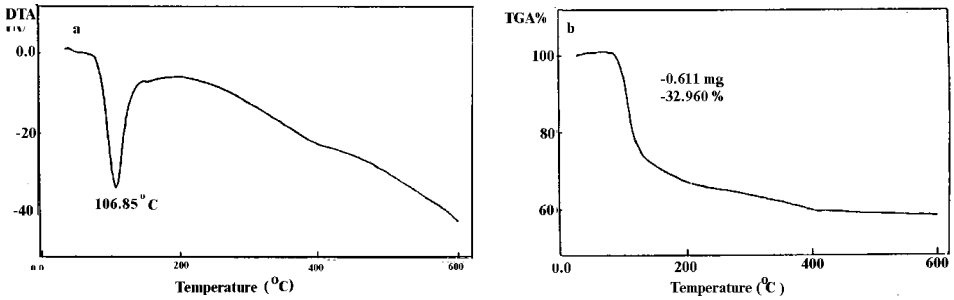


Fig.(3) Thermal analysis curves for the binary Ni-MOPSO
(a) DTA curve (b) TG curve

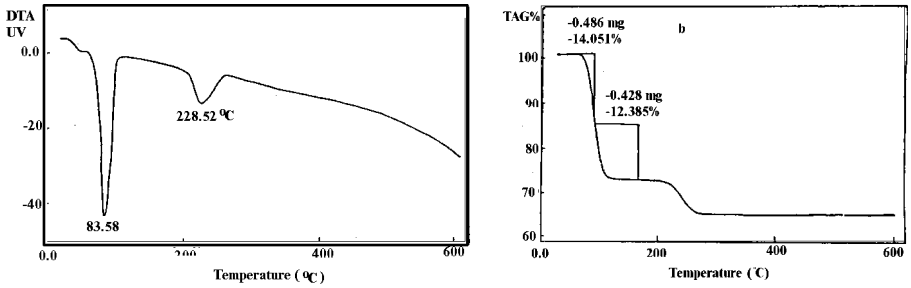


Fig.(4) Thermal analysis curves for the binary Cu-MOPSO
(a) DTA curve (b) TG curve

The DTA curve of the $[Co(MOPSO)(H_2O)_4].12H_2O$ complex revealed only one resolved endothermic peak at the range 63 –130 ^{0}C with decomposition energy of 16.87 kJ/mol due to the elimination of the water of crystallization. This step of decomposition is clearly observed in the TG curve with a percentage loss of 39.26 %, Table IV. The curve did not show other endothermic peaks. This indicates that no elimination of the coordinated water. The DTA curve of $[Ni(MOPSO)(H_2O)_4].9H_2O$ complex, follow the same pattern where endothermic peak at 48 –135 ^{0}C with decomposition energy of 14.24 kJ/mol due to the elimination of the water of crystallization. The TG curve of the complex showed a percentage loss of 32.96 % due to the loss of nine water molecules, Table IV. On the other hand, the DTA curve of the $[Cu(MOPSO)(H_2O)_4].3H_2O$ complex showed two endothermic peaks (a strong peak in the range 63 – 116 ^{o}C, E = 18.36 kJ/mol, and a weak broad peak occurred at 215-268 ^{0}C. The % losses obtained from the TG curve were due to the loss of three molecules of water of crystallization and three coordinated water, respectively (Table IV).

Table (5): Thermal Data of the Cobalt, Nickel and Copper Complexes

Complex	Decomposition Steps, ^{0}C	%Wt. Loss (theor.)	Eliminated Species	Decomposition process
$[Co(MOPSO)(H_2O)_4].12H_2O$	63 –130	39.26 (38.98)	12 H_2O	Endo
$[Ni(MOPSO)(H_2O)_4].9H_2O$	48 –135	32.96 (32.40)	9 H_2O	Endo
$[Cu(MOPSO)(H_2O)_4].3H_2O$	63 – 116 215-268	14.05 (13.61) 12.38 (13.61)	3 H_2O 3 H_2O	Endo Endo

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