Research Article

Solution Studies on Co(II), Ni(II), Cu(II), and Zn(II) Complexes of Hexamethylenetetramine in Aqueous and Non-Aqueous Solvents

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Potentiometric studies in aqueous medium and spectrophotometric study in non-aqueous medium were used to understand the behavior of hexamethylenetetramine (HMTA) complexes. The protometric studies of HMTA enabled us to confirm that only one basic site of this ligand is protonated in acidic medium and this ligand is decomposed in acidic medium. In aqueous medium, only hexa-aqua complexes in which HMTA is present in the second coordination sphere forming H-bonds with hydrogen atoms of coordinated and uncoordinated water molecules are obtained. In non-aqueous solvents, HMTA coordinates to metal ions displaying diversity in the structures of the resulting complexes in which HMTA can either be monodentate, bridged bidentate, tridentate, or tetradentate.

1. Introduction

Hexamethylenetetramine (HMTA) is a heterocyclic ligand with four nitrogen donor atoms, having three rings merged in a chair conformation as shown in Figure 1.

HMTA can therefore form various metal complexes possessing interesting structural features and applications [1–5]. Hexamethylenetetramine as a ligand can bind either in a monodentate manner to a metal [6, 7], acting as bridging ligand linking two, three, or four metals [8–11], or bind to metal-containing species through the formation of hydrogen bonding [5, 12–16]. The combination of both covalent and hydrogen bonding in certain complexes of hexamethylenetetramine leads to the formation of three-dimensional structures that easily decompose by thermal treatment to give thin films of metal oxides [15, 16].

The formation of covalently bonded and hydrogen-bonded compounds of hexamethylenetetramine is influenced by several factors such as the nature of the solvent, steric hindrance of the counter ion, and the pH of the solution [17].

When water is used as the solvent during synthesis, metal-aqua complexes are obtained which bind to HMTA through H-bonds, forming ionic species [18]. When non-aqueous solvents are used for synthesis, metal-HMTA covalent species are formed [10, 15]. Recently, we reported the isolation of metal-HMTA covalently bonded species isolated from ethanol [19]. Metal-H₂O-HMTA ionic species involving H-bonds isolated from ethanol/water mixture have also been reported [5, 12–16, 20].

We report here the results of the study on the influence of solvent on the electronic and structural properties of metal-HMTA complexes in aqueous and non-aqueous solvents.

FIGURE 1: Structure of hexamethylenetetramine.

2. Experimental

2.1. Chemicals. All solvents were purified by conventional procedures [21] and distilled prior to use. All the chemicals commercially available (Aldrich) and metallic salts (Fluka) were used as supplied without further purification.

2.2. Physical Measurements

2.2.1. Protometry. Stock solutions of metal nitrates were prepared from commercially available reagents (Fluka) of the highest purity (>99%) and were used without further purification. Their concentrations were determined by EDTA titration at pH = 10, using murexide as an indicator for Ni^{2+} , and PAN [1-(2-pyridyl-azo)-2-naphtol] for Cu^{2+} . Ionic strength was kept constant ($I = 0.1$) by the addition of potassium nitrate (Fluka) of the highest purity (>99 %). The solutions of carbonate-free titrating base KOH $0.1 \text{ mol}\cdot\text{L}^{-1}$ were prepared from standardized $1 \text{ mol}\cdot\text{L}^{-1}$ solutions (Pro-labo).

Protometric titrations were performed with a Metrohm 665 Dosimat and a Metrohm 654 pH meter. The combined glass electrode was standardized with nitric acid $10^{-2} \text{ mol}\cdot\text{L}^{-1}$ (pH = 2.00) and the slope determined from a refinement of titration curves of acetic acid solutions. All measurements were performed at 20°C under a nitrogen stream. Titration curves were fitted with the refining program PROTAF [22, 23]. The solutions of both ligands used for the determination of the protonation and complexation constants were titrated with KOH 0.1 mol/L . Their concentrations ranged from 5×10^{-3} to $10^{-2} \text{ mol}\cdot\text{L}^{-1}$, and the ratios C_L/C_M from 1 to 4.

The equilibrium constants were determined by fitting the titration curves into the least squares refinement PROTAF software [22, 23]. The PROTAF software allows the calculation of the formation constants of the protonated or hydroxyl complex species containing one or several metal cations (maximum of three) and one or several ligands (maximum of three). The overall formation constants, β_{mlh} (1) corresponds to equilibria of the type (charges are omitted):

FIGURE 2: Titration curve of HMTA ligand by KOH ($C_L = 10^{-2} \text{ mol}\cdot\text{L}^{-1}$ and $C_{\text{OH}} = 0.1 \text{ mol}\cdot\text{L}^{-1}$): HMTA solution freshly prepared in acidic medium and HMTA solution one week after its preparation in acidic medium.

2.2.2. Spectrophotometry. In order to show the complexation of HMTA to metal ions in non-aqueous medium, a spectrophotometric study was carried out in a mixture of ethanol/dimethylformamide. Job's continuous variation method [24] was used to study the coordination of the metal ions to HMTA and to determine the stoichiometry of the metal complexes formed.

Equimolar solutions ($0.1 \text{ mol}\cdot\text{L}^{-1}$) of metal chloride (CoCl_2 , NiCl_2 , and CuCl_2) and HMTA ligand were prepared in a mixture of ethanol/dimethylformamide in 65 : 35 (v : v); DMF is used to avoid precipitation of formed complexes. A fixed volume of each metal is placed in a series of beakers; a volume of ligand is added progressively into these beakers in a manner that the ligand/metal (L/M^{2+}) ratio ranges from 0 to 4. Spectrophotometric titrations were carried out in quartz cells of 1 cm pathlength using Shimadzu UV-2401-PC spectrophotometer equipped with a TCC-240A temperature controlled cell holder.

3. Results and Discussion

3.1. Protometric Study. This study involves the titration of an aqueous solution of $10^{-2} \text{ mol}\cdot\text{L}^{-1}$ HMTA to which was added a solution of $4 \times 10^{-2} \text{ mol}\cdot\text{L}^{-1}$ of HNO_3 and $0.1 \text{ mol}\cdot\text{L}^{-1}$ KNO_3 by a $0.1 \text{ mol}\cdot\text{L}^{-1}$ KOH. This titration was repeated after 7 days and the results obtained are represented in Figure 2.

Figure 2 shows that HMTA deteriorates in acidic medium. In the presence of HNO_3 , HMTA dissociates progressively and is transformed into other products, probably ammonia and formaldehyde [25].

In order to avoid the degradation of HMTA prepared in acidic medium, a solution of $9.7610^{-3} \text{ mol}\cdot\text{L}^{-1}$ of HMTA (prepared without adding the nitric acid) was titrated directly using $5 \times 10^{-2} \text{ mol}\cdot\text{L}^{-1}$ nitric acid in $0.1 \text{ mol}\cdot\text{L}^{-1}$ KNO_3 medium. The neutralization curve (Figure 3) of this ligand shows a decrease in pH corresponding to the protonation of one basic site of the ligand.

FIGURE 3: Titration curve of the ligand HMTA ($C_L = 9.76 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$) with HNO_3 $5 \times 10^{-2} \text{ mol}\cdot\text{L}^{-1}$.

FIGURE 4: Titration curves of the HMTA ligand alone and of the HMTA- M^{2+} systems with HNO_3 $5 \times 10^{-2} \text{ mol}\cdot\text{L}^{-1}$ ($\text{M} = \text{Co}, \text{Ni}, \text{Cu}$, or Zn ; $C_M = 5 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$ and $C_L = 5 \times 10^{-2} \text{ mol}\cdot\text{L}^{-1}$, $I = 0.1$, $T = 25^\circ\text{C}$).

The value of the deprotonation constant obtained is 4.89. This value is close to the value of 5.59, reported in the literature [26], indicating that only one of the four nitrogen donor atoms is protonated in water.

3.2. Metal Complex in Solution. The formation of metal-HMTA complexes is expected when metal cations are introduced and would lead to the modification of the acid-base equilibrium compared to that of the ligand alone.

In this respect, aqueous solutions ($5 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$) of Co(II) , Ni(II) , Cu(II) , and Zn(II) salts, respectively, were prepared and placed in a thermo-regulated cell containing a solution of $10^{-2} \text{ mol}\cdot\text{L}^{-1}$ of HMTA ligand ($0.1 \text{ mol}\cdot\text{L}^{-1}$ of KNO_3 medium) and the mixture titrated with a solution of $5 \times 10^{-2} \text{ mol}\cdot\text{L}^{-1}$ HNO_3 . Different curves showing the variation

of the pH as a function of the volume of nitric acid for the different systems studied are illustrated in Figure 4.

In general, the formation of a complex in solution entails increase in the acidity of the reaction medium (ligand + metal) compared to that of the ligand alone. In this study, the neutralization of the HMTA-metal salt mixture shows a decrease in pH at equal volume of nitric acid solution and a displacement of equivalent volumes as those of the ligand. The titrations curves of the HMTA-metallic salt systems ($\text{M} = \text{Co}, \text{Ni}, \text{Cu}$, or Zn) are perfectly superimposed onto that of ligand within the pH range of our study. This superposition of the curves indicates that the complexation did not occur. In order to better visualize this non-complexation, we represented the curves of $\bar{n}_H$ as a function of pH (Figure 5) where $\bar{n}_H$ represents the average number of protons per mole of ligand (free or/and coordinated ligand). The curve should enable the determination of the level of protonation of the various species within the pH range under consideration.

The set of five curves for pH 3.5 to 5.5 correspond to the titration of the free ligand and the four metal-ligand systems. The curves are perfectly superimposed indicating that at the time of the competition between the proton and the metallic cation to bind to the ligand, only protonation of the ligand takes place, thus confirming that there is no complexation in aqueous medium. This observation is in agreement with the observation that in most syntheses of complexes with HMTA in aqueous medium, the ligand does not coordinate directly to the metal, but it is found in the crystalline structure, out of the coordination sphere, stabilizing the crystal lattice by hydrogen bonds [14–18, 27].

3.3. Spectrophotometric Study. Potentiometric studies on HMTA showed that only one basic site is protonated in acidic medium and all attempts to get this ligand coordinated to different metal ions in water failed. There is therefore no direct coordination in aqueous medium between HMTA and metal ions. This spectrophotometric study using the continuous variation method was therefore carried out in order to understand the behavior of HMTA in non-aqueous solvent (ethanol/DMF) and to study the influence of HMTA on the geometry of metal-HMTA species in non-aqueous solvents.

3.3.1. Copper(II)-HMTA System. The electronic spectra obtained for the study of the copper(II)-HMTA system are presented in Figure 6.

The electronic spectra obtained for the study of the copper(II)-HMTA system at various ratios, $R = [\text{HMTA}]/[\text{Cu}^{2+}]$, show a large dissymmetric band whose maximum absorption is situated at 804 nm ($\epsilon = 40 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$) for the species $[\text{Cu}(\text{DMF})_6]^{2+}$ (Figure 6). This maximum absorption displaces progressively with the addition of the HMTA ligand up to 772 nm ($\epsilon = 64 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$) for $R = [\text{HMTA}]/[\text{Cu}^{2+}] = 1.5$.

When R is in the range 1.5 to 2.5, the absorbance is practically constant and decreases for $R = 3$. The variation of λ_{max} on the electronic spectra when HMTA ligand is added is

FIGURE 5: The curves of $\bar{n}_H$ versus pH for the M^{2+} -HMTA systems ($M = \text{Cu, Zn, Co, or Ni}$).

in agreement with the coordination of HMTA to the metallic cation.

The curves in the visible spectra of the Cu^{2+} -DMF systems and Cu^{2+} -HMTA-DMF are similar; this indicates that the environment of the Cu^{2+} cation is the same for the different complex species. The electronic transition bands and the molar extinction coefficient of the different complexes are in agreement with an octahedral coordination around the Cu^{2+} ion [28].

A plot of the absorbance versus the ligand/ M^{2+} ratio, R , at two wavelengths $\lambda = 760 \text{ nm}$ and 670 nm (Figure 7) reveal curves of the same shapes presenting maxima at the same R values $R = 1.5$ and $R = 3.5$ showing the progressive fixing of the HMTA ligand on Cu^{2+} cation up to a maximum of 1.5 and 3.5 and the reaction can be represented as follows (2):

HMTA is a tetradentate ligand, not being able to form a chelate and we are therefore left with two possibilities for the structure of this complex.

A dinuclear copper(II) complex is obtained in which every Cu^{2+} cation is bound to one HMTA ligand and the third HMTA linked to the two metallic centers to give a structure of formula $[\text{Cu}_2(\text{HMTA})_3(\text{DMF})_8]^{4+}$ (Figure 8). A similar structure has been isolated with the cobalt metal in ethanolic medium by Ndifon et al. [19].

A polymer in which the central Cu^{2+} is bound to three molecules of DMF and three HMTA, with these last ligands being linked to three other metallic centers, could also be obtained (Figure 9). This structure can also be compared to the cobalt coordination polymer synthesized in ethanolic medium [19]. The slight depressions observed at $R = 2$ and 3

FIGURE 6: Variation of the electronic spectra of the Cu^{2+} -HMTA system according to the ratio $R = [\text{HMTA}]/[\text{Cu}^{2+}]$: (a) $R = 0$; (b) $R = 0.5$; (c) $R = 1$; (d) $R = 1.5$; (e) $R = 2$; (f) $R = 2.5$; (g) $R = 3$; (h) $R = 3.5$; (i) $R = 4$.

FIGURE 7: Variation of the absorbance A with HMTA/ Cu^{2+} ratio R .

FIGURE 8: Dinuclear complex $[\text{Cu}_2(\text{HMTA})_3(\text{DMF})_8]^{4+}$ with $D = \text{DMF}$.

probably represent the fixation of 2 or 3 HMTA molecules, respectively, forming unstable intermediate species which are stabilized as more HMTA molecules are fixed.

When $1.50 \leq R < 2.5$, the absorbance varies very slightly with R ; the curve suggests the formation of metal-HMTA species.

When $R = 2$, the absorbance decreases and two HMTA ligands coordinate on the metal ion giving a mononuclear structure (3):

FIGURE 9: Polymer complex $[\text{Cu}(\text{HMTA})_{1.5}(\text{DMF})_3]^{2+}$ with $\text{D} = \text{DMF}$.

FIGURE 10: Mononuclear complex $[\text{Cu}(\text{HMTA})_3(\text{DMF})_3]^{2+}$ with $\text{D} = \text{DMF}$.

FIGURE 11: Variation of the electronic spectra of the Ni^{2+} -HMTA system with $R = [\text{HMTA}]/[\text{Ni}^{2+}]$ (a) $R = 0$, (b) $R = 0.5$, (c) $R = 1.5$, (d) $R = 2$, (e) $R = 2.5$, (f) $R = 3$, and (g) $R = 3.5$, $R = 4$.

When $R = 2.5$, the absorbance increases slightly as the coordination of five HMTA ligands on two metal ions is suggested giving a dimer with an HMTA forming a bridge.

When $R = 3$, the absorbance decreases and the value of the R ratio indicates the coordination of three ligands on the metal ion (4) to probably give a structure similar to the mononuclear structures described by Bai et al. [6] for nickel and by Shang et al. [29] for cobalt:

The steric hindrance of the HMTA ligand prevents the formation of a coordination polymer possessing six HMTA ligands around every metallic cation.

At $R \geq 3$, the absorbance, A , increases very slowly, justifying the complete formation of the complex $[\text{Cu}(\text{HMTA})_3(\text{DMF})_3]^{2+}$ (Figure 10).

3.3.2. Nickel(II)-HMTA System. The electronic spectra of the $[\text{Ni}(\text{DMF})_6]^{2+}$ species and Ni^{2+} -HMTA-DMF are similar. These spectra (Figure 11) show the presence of two bands with λ_{max} at 670 nm presenting a shoulder around 730 nm and λ_{max} at 1175 nm in the near infrared. These bands with weak molar extinction coefficients $[\text{Ni}(\text{DMF})_6]^{2+}$, $8 < \epsilon < 11 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ and $[\text{Ni}(\text{HMTA})_m(\text{DMF})_n]^{2+}$, $10 < \epsilon < 15 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ are characteristic of an octahedral environment around the Ni^{2+} ion [30]. The third transition is probably masked by the metal-ligand charge transfer band. The presence of a shoulder at 730 nm in the second band characterizes the distortion of the octahedral structure.

The progressive addition of the HMTA ligand is characterized by a slight displacement of the first maximum of about 5 nm toward the strong energy and the displacement of this band is less noticed as absorbance increases. These observations are in agreement with the coordination of the N-donor atoms of HMTA ligand to the Ni^{2+} cation.

A plot of absorbance versus R at $\lambda = 670 \text{ nm}$ and $\lambda = 720 \text{ nm}$ (Figure 12) reveals two curves of similar shape that increase with R with a slight drop at 0.5 and 3.5 representing the fixing of 0.5 and 3.5 HMTA ligand on Ni^{2+} ion, respectively.

When $R = 0.5$, the complex can be considered as being dinuclear $[\text{Ni}_2(\text{HMTA})(\text{DMF})_{10}]^{4+}$ (5) with the ligand HMTA linking two Ni^{2+} centers as illustrated in Figure 13:

FIGURE 12: Variation of the absorbance A as a function of the ratio $R = [\text{HMTA}]/[\text{Ni}^{2+}]$.

FIGURE 13: Dinuclear complex $[\text{Ni}_2(\text{HMTA})(\text{DMF})_{10}]^{4+}$ with $\text{D} = \text{DMF}$.

FIGURE 14: Dinuclear complex $[\text{Ni}_2(\text{HMTA})_7(\text{DMF})_4]^{4+}$ with $\text{D} = \text{DMF}$.

Similar structures with cobalt which include $[\text{Co}(\text{HMTA})_2(\text{H}_2\text{O})\text{Co}(\text{H}_2\text{O})_6]$ and $[\text{Co}_2(\text{N}_3)_4(\text{HMTA})(\text{H}_2\text{O})]$ have been reported [9, 31].

When $R = 3.5$, the complex can be considered as dinuclear or polymeric compound. The dinuclear complex $[\text{Ni}_2(\text{HMTA})_7(\text{DMF})_4]^{4+}$ (6) has one HMTA molecule bridging two nickel centres (Figure 14). Each nickel centre is hexacoordinated involving three monodentate HMTA and two molecules of DMF. Carlucci et al. [32] did isolate a similar structure with the silver(I)

The polymeric compound $[(\text{DMF})(\text{HMTA})_2\text{Ni}(\text{HMTA})_{1.5}]_n^{2+}$ (7) in which two ligands are bound to the central nickel(II) and the three others carrying the Ni^{2+} ion and the three other

neighbouring Ni^{2+} ion in which a molecule of DMF completes the octahedral environment around every nickel(II) is obtained (Figure 15):

3.3.3. Cobalt(II)-HMTA System. As in the nickel(II) compounds, the spectra of the $[\text{Co}(\text{DMF})_6]^{2+}$ and Co^{2+} -HMTA-DMF species are similar. These spectra (Figure 16) show the presence of a band at 520 nm with a slight shoulder at 490 nm and a second peak in the near infrared around 1050 nm. The shapes of this band as well as the values of molar extinction coefficient confirm an octahedral environment around the Co^{2+} ion in these compounds.

Contrary to the observation in Cu^{2+} and Ni^{2+} , the progressive addition of the HMTA ligand leads to a slight variation of the absorbance of the $\text{Co}(\text{II})$ complex formed up to $R = 2$, after which the addition of HMTA has little effect on the electronic spectra.

A plot of the absorbance versus R at $\lambda = 520$ nm and 485 nm, respectively, (Figure 17) shows two curves of identical shapes with maxima at $R = 1$ and 2.

When $R = 1$, only one HMTA ligand is coordinated to the Co^{2+} cation and the structures in Figures 18 and 19 are expected and the complex can be a mononuclear with a single HMTA coordinated and the hexacoordination is completed by five molecules of DMF. Bai et al. [6] and Shang et al. [29] isolated compounds with similar structures with nickel ($[\text{Ni}(\text{NCS})_2(\text{C}_6\text{H}_{12}\text{N}_4)(\text{CH}_4\text{O})_2(\text{H}_2\text{O})]$) and cobalt ($[\text{Co}(\text{NCS})_2(\text{C}_6\text{H}_{12}\text{N}_4)(\text{CH}_4\text{O})_2(\text{H}_2\text{O})]$) where an HMTA ligand is coordinated to the central metal.

FIGURE 15: Polymer complex $[(\text{DMF})(\text{HMTA})_2\text{Ni}(\text{HMTA})_{1.5}]^{2+}_n$ with $\text{D} = \text{DMF}$.

FIGURE 16: Variation of the electronic spectra of the Co^{2+} -HMTA system with $R = [\text{HMTA}]/[\text{Co}^{2+}]$: (a) $R = 0$, (b) $R = 0.5$, (c) $R = 1.5$, and (d) $R = 2-4$.

A polynuclear complex $[\text{Co}(\text{HMTA})(\text{DMF})_4]^{2+}$ in which the Co^{2+} ion is coordinated to two HMTA ligands having two other neighbouring cobalt(II) ions and four molecules of DMF which complete the hexacoordination (Figure 19) can also be obtained. This structure is similar to the cobalt coordination polymer isolated from an ethanol solution where the octahedral coordination is completed by two molecules of water [19].

When the ratio $R = 2$, two HMTA ligands are linked to cobalt(II) as shown by the structures in Figures 20, 21, and 22.

4. Conclusion

Our goal was to study the effect of aqueous and non-aqueous media on the coordination of hexamethylenetetramine to metal ions. We used both protometric and spectrophotometric methods. The protometric studies of the HMTA ligand has enabled us to confirm that only one basic site is protonated in acidic medium and this ligand is decomposed in acidic

FIGURE 17: Variation of the absorbance A as a function of the ratio $R = [\text{HMTA}]/[\text{Co}^{2+}]$.

FIGURE 18: Monomer complex $[\text{Co}(\text{HMTA})(\text{DMF})_4]^{2+}$ with $\text{D} = \text{DMF}$.

FIGURE 19: Polymeric complex $[\text{Co}(\text{HMTA})(\text{DMF})_4]^{2+}$ with $\text{D} = \text{DMF}$.

FIGURE 20: Monomer complex $[\text{Co}(\text{HMTA})_2(\text{DMF})_4]^{2+}$ with $\text{D} = \text{DMF}$.

FIGURE 21: Polymer complex $[\text{Co}(\text{HMTA})_2(\text{DMF})_2]^{2+}$ with $\text{D} = \text{DMF}$.

FIGURE 22: Polymer complex $[\text{Co}(\text{HMTA})_2(\text{DMF})_4]^{2+}$ with D = DMF.

medium. In aqueous medium, HMTA ligand does not coordinate directly to the metal ions but rather through the H-bonded species. In non aqueous solvents, HMTA coordinates to metal ions displaying diversity in the resulting structures in which HMTA can either be monodentate, bridged, tridentate, or tetradentate.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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