PREPARATION, SPECTROSCOPIC AND THERMAL STUDIES ON THE ZINC(II), CADMIUM(II), TIN(II), LEAD(II) AND ANTIMONY(III) CREATININE COMPLEXES

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ABSTRACT. Zinc(II), cadmium(II), tin(II), lead(II) and antimony(III) complexes of creatinine with the composition of [M(creat)2Xn]xH2O, (X = Cl or NO3; n = 2-6) were prepared. The complexes were characterized by analytical and spectral methods. The analysis of FT-IR and Raman spectra helps to understand the coordination properties of the creatinine ligand and to determine the probable structure of the complexes. The shift in the resonances of cyclic NH proton in the 1H NMR when compared to the ligand indicated that cyclic nitrogen coordinates. Conductivity measurements in DMSO suggested that the complexes are non-electrolytes. Thermal decomposition behavior of the complexes was also discussed.

KEY WORDS: Creatinine, TGA/DTA, Metal complexation, Raman spectroscopy

INTRODUCTION

Creatinine (2-amino-1-methyl-imidazolidinone) is a metabolite of creatine and is eliminated from the human body through urinary excretion [1]. The concentration of creatinine in urine and serum can reveal the status of renal, muscular, and thyroid functions [2-6]. The ability of creatinine to complex is widely known, and investigations on metal ion interactions with creatinine may contribute to the elucidation of creatinine metabolic pathways [7-10]. The investigation of this ligand's binary and ternary complexes should be of interest because creatinine metabolism may be linked to its complexation with other metal ions [11]. Five co-ordination modes have been established by X-ray crystallography: bidentate bridging through N(l)(ring) and exocyclic NH site deprotonated [12], N(l) (ring) and exocyclic O(C=O) are used to bind bidentate [13]; monodentate binding through he N(l)(ring)sites; monodentate binding through the exocyclic O(C=O); and monodentate fashion through the deprotonated exocyclic NH group (Figure 1) [13-15].

Figure 1. Coordination modes for transition metal-creatinine complexes.

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Several tautomeric forms of creatinine have been suggested, with the C=N bond to the five-membered ring is found to coexist by comparing its experimental and calculated Raman spectra. A water dimer being used to solvate creatinine would make the thermodynamic energy favorable to convert from the imino tautomer to the amino tautomer [12, 16]. The formation of cationic complexes of creatinine with heavy metal ions such as Cu(II), Co(II), Pt(II), Pd(II) and Hg(II) in water medium suggests a significant influence of creatinine on the metabolisms of these metal ions and their excretion [8]. Metal complexes of a creatinine ligand with Mn(II), Co(II), Cr(III), Cu(II), and Fe(III) were tested against COVID-19 protease (6LU7), Fe(III) complex showed largest ability to inhibit the COVID-19 protease (6LU7) as compared to other metal complexes according to free energy of binding and interacting amino acids [17]. The purpose of this article is to present biomolecules capable of accumulating metal ions in aqueous media that can be used in filtration techniques. Some methods already exist, using alginate or chitosan beads, or biomolecule-grafted magnetic beads for example, to isolate heavy metals from the aqueous medium. The use of functional creatinine as biomolecules in heavy metal processing can also be considered, even if it is an emerging process. In continuation to the same research topic, we have also studied the complexation between creatinine as biomolecules with some heavy metals like zinc(II), cadmium(II), tin(II), lead(II) and antimony(III).

**EXPERIMENTAL**

*Chemicals and equipment’s*

In this work, the purity of the used chemicals was very high and did not require any additional purification. Sigma-Aldrich Chemical Company, USA provided creatinine, SnCl₂, ZnCl₂, Pb(NO₃)₂, CdCl₂, and SbCl₃. The equipment that follows is used to structure and analyze the prepared compounds (Table 1).

| Analytical method                  | Instrumental models                      |
|-----------------------------------|------------------------------------------|
| Analyses of the elements          | Perkin Elmer CHN 2400                    |
| Conductance                       | Jenway 4010 conductivity meter            |
| FTIR spectra                      | Bruker FTIR Spectrophotometer            |
| Raman laser                       | Bruker FT Raman with laser 50 mW         |
| ¹HNMR spectra                     | Varian Mercury VX-300 NMR spectrometer, 300 MHz |
| TGA/DTGA                          | Quanta FEG 250 equipment                  |

*Synthesis of creatinine complexes*

Aqueous solution of corresponding metal salt (SnCl₂, ZnCl₂, Pb(NO₃)₂, CdCl₂, and SbCl₃) (0.2 mol) were mixed with a methanolic solution of the freshly prepared creatinine ligand (0.4 mol). Precipitation occurred instantly, with the color of precipitates varying depending on the metals. The precipitate was filtered and rinsed with distilled water in excess, then methanol and in the end with diethyl ether to remove unreacted ligand and impurities, then the complexes stored under vacuum over anhydrous CaCl₂.

**RESULTS AND DISCUSSION**

*Elemental analysis and physical data*

The new synthesized chelates of Zn(II), Cd(II), Pb(II), Sn(II) and Sb(III) with creatinine are stable in air and insoluble in most of the organic solvents, colored and non-hygroscopic in nature. As
the crystal structures of its complexes have not yet been obtained, elemental analysis, melting point, thermal analysis, measurements of conductivity and magnetic susceptibility as well as spectral techniques characterized the complexes. Elemental analysis and physical data of creatinine and its complexes are listed in (Table 2). The elemental analysis specifically recommended that ML type complexes with 1:2 stoichiometry (M = metal, L = ligand). The chelates were dissolved in DMF and molar conductivity of 10^{-3} M of their solutions was measured at room temperature. All the complexes were soluble in DMF and DMSO. The exquisite physical properties and distinctive data of the creatinine ligand and its chelates were evaluated (Table 2).

Conductance measurements

To decide whether chloride ion and nitrate anions are coordinated or outside the coordination sphere, the conductance of 1.0 × 10^{-3} DMSO solutions of the complexes were measured at room temperature. The observed value for the complexes (Zn(II), Cd(II), Pb(II), Sn(II) and Sb(III)) are 10, 8, 13, 7 and 14 ohm^{-1} cm^2 mol^{-1}, respectively, at ambient temperature indicating non-electrolytic in nature [8]. The presence of chloride and nitrate ions as coordinated ions reported by qualitative reaction is in good agreement with molar conductivity data. The presence of chloride and nitrate as coordinated ions in good agreement with molar conductivity was reported by a qualitative reaction.

Table 2. Elemental analysis and physico-analytical data for creatinine and its metal complexes.

| Complex (MF) Mwt. | Yield% | mp/°C | Color | Conductance (ohm^{-1}cm^2mol^{-1}) | Element | Calc. | Found |
|------------------|--------|-------|-------|-------------------------------------|---------|-------|-------|
| (C_{6}H_{4}N-O) (creatin) (113.12) | - | >350 | White | 11 | %C 42.47 | 6.24 | 37.15 |
| | | | | | %H 18.99 | 7.85 | 16.61 |
| | | | | | %N 19.23 | 6.36 | 18.80 |
| [Sn(C_{6}H_{4}N-O)_{6}(Cl)_{2}]SHO | 75 | >350 | White | 73 | %C 42.47 | 6.24 | 37.15 |
| | | | | | %H 18.99 | 7.85 | 16.61 |
| | | | | | %N 19.23 | 6.36 | 18.80 |
| [Pb(C_{6}H_{4}N-O)_{6}(NO_{3})_{2}]SHO | 77 | >350 | White | 10 | %C 20.42 | 5.57 | 17.86 |
| | | | | | %H 18.88 | 5.70 | 17.80 |
| | | | | | %N 19.21 | 5.70 | 17.80 |
| [Cd(C_{6}H_{4}N-O)_{3}(Cl)_{2}]SHO | 50.01 | >350 | White | 8 | %C 19.23 | 4.85 | 16.25 |
| | | | | | %H 19.23 | 4.53 | 16.82 |
| | | | | | %N 19.23 | 4.53 | 16.82 |
| [Sb(C_{6}H_{4}N-O)_{3}(Cl)_{2}]SHO | 54.01 | >350 | White | 14 | %C 17.65 | 4.44 | 15.44 |
| | | | | | %H 17.94 | 4.40 | 15.32 |

The creatinine was then used for the complexation with Zn(II), Cd(II), Sn(II), Pb(II) and Sb(III) ions. These were prepared by the stoichiometric reaction of the corresponding metal salts (as chlorides or nitrates) and the creatinine in molar ratios M:L of 1:2. The complexes are white colored, amorphous solids, which decompose above 350 °C. A molecular weight and molecular formula of the isolated solid creatinine complexes, yield 71-78%, and elemental microanalysis CHN were listed in Table (2). The thermal nature of the complexes has been obtained by TGA, D/TGA/DTA analysis. The formation of creatinine complexes frameworks and bidentate ON donor nature of the creatinine with metal ions for the formation of complexes were obtained from characteristic band positions in FTIR, electronic spectra, magnetic properties, thermal and elemental analysis. These data of the metal complexes suggest that metal to ligand ratio of the

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metal complexes 1:2 stoichiometry of the types of \( \text{Sn(C}_4\text{H}_7\text{N}_3\text{O)}_2\text{Cl}_2\text{][H}_2\text{O} \) and \( [\text{Pb(C}_4\text{H}_7\text{N}_3\text{O)(NO}_3\text{)}_2\text{][2H}_2\text{O} \), \( [\text{Zn(C}_4\text{H}_7\text{N}_3\text{O)}_2\text{Cl}_2\text{][6H}_2\text{O} \), \( [\text{Cd(C}_4\text{H}_7\text{N}_3\text{O)}_2\text{Cl}_2\text{][5H}_2\text{O} \) and \( [\text{Cd(C}_4\text{H}_7\text{N}_3\text{O)}_2\text{Cl}_2\text{][5H}_2\text{O} \) where \( \text{C}_4\text{H}_7\text{N}_3\text{O} \) is creatinine ligand as shown in Figure 2.

![Figure 2. The coordination mode of Zn(II), Cd(II), Pb(II), Sn(II) and Sb(III) with creatinine.](image-url)

**IR spectral studies**

The IR data of the spectra of creatinine and its complexes are listed in Table 3. To determine the coordination sites that may be involved in chelation, the IR spectra of the complexes are compared to those of the free ligand. Chelation is likely to modify the positions and/or intensities of these peaks. The ring nitrogen, as well as the C=O and/or –NH\(_2\) groups, can help creatinine ligand coordinate. Creatinine typically coordinates to the metal via the ring nitrogen in metal complexes [7-13]. Within the FTIR range of 4000-400 cm\(^{-1}\), the infrared frequencies of the free creatinine ligand and solid manufactured complexes of Zn(II), Cd(II), Pb(II), Sn(II), and Sb(III) metal ions were scanned and compared to the free ligand (Figure 3). According to data in the literature, the assignments of characteristic bands (cm\(^{-1}\)) for creatinine are: \( \nu(\text{NH}_{\text{cyclic}}) = 3326 \text{ cm}\(^{-1}\); \( \nu(\text{NH}_{\text{imino}}) = 3376 \text{ cm}\(^{-1}\); \( \nu(\text{C}=\text{O}) + (\text{C}=\text{N}) = 1799 \text{ and } 1696 \text{ cm}\(^{-1}\); \( (\text{C}=\text{N}) = 1628 \text{ cm}\(^{-1}\) [8-13]. Figure 3 depicts the infrared spectra of creatinine complexes as an illustration (selected samples). The bands corresponding to stretching vibrations \( \nu(\text{NH}) \) in the spectra of the five creatinine complexes show changes in frequency and intensity. At 3376–3326 cm\(^{-1}\), a few bands
are seen, indicating the presence of the creatinine ligand in its amino tautomeric form (Figure 3) [4-7]. The strong band at 1799 cm$^{-1}$ assigned to $\nu$(C=O) in the free creatinine ligand spectrum shifts to lower frequencies at about 1794-1714 cm$^{-1}$ region upon complexation (85-5 cm$^{-1}$). After complexation, the strong band at 1799 cm$^{-1}$ associated to $\nu$(C=O) in the free creatinine ligand spectrum shifts to lower frequencies about 1794-1714 cm$^{-1}$ (85-5 cm$^{-1}$). The impact of coordination through the oxygen atom of the exocyclic O(C=O) group to the metal is responsible for the shifts to lower wavenumbers of the $\nu$(C=O) in the complexes [11]. The wave numbers of creatinine in complexes are compared to those of free creatinine to determine the coordination site of creatinine complexes. Table 3 lists a few selected fundamental modes of complexes. Few bands corresponding to stretching vibrations $\nu$(NH$_2$) have been identified, and their wavenumbers are determined to be larger than those of free creatinine. A greater wavenumber indicates that the ligand is not NH$_2$ bound. These results support the view that the NH$_2$ group of creatinine is not engaged in metal ion coordination and are consistent with those described in the literature [11]. In complexes, the bands with ring contribution at 1500–1498 cm$^{-1}$, 1428–1404 cm$^{-1}$, 1339–1333 cm$^{-1}$, and 687–670 cm$^{-1}$ show intensity changes and shift to higher wavenumbers (27-10 cm$^{-1}$). All these data suggest binding between the metal (II/III) ions towards the exocyclic O(C=O) group and ring N atom of the creatinine. Two weak bands, 599-500 cm$^{-1}$ and 416-411 cm$^{-1}$, are resolved in the 600-400 cm$^{-1}$ region of the spectra and are attributed to $\nu$(M-O) and $\nu$(M-N), respectively [18].

Table 3. Vibrational assignment of important IR(Raman bands) of the creatinine ligand and its metal complexes.

| Compound | Assignment | $\nu$(NH$_2$) | $\nu$(NH$_2$) | $\delta$(C=O) | $\delta$(NH$_2$) + $\nu$(C=O) | $\nu$(M-O) | $\nu$(M-N) |
|----------|------------|---------------|---------------|--------------|------------------|-------------|-------------|
| C$_2$H$_7$N$_2$(O)(creat) | IR cm$^{-1}$ | Raman cm$^{-1}$ | IR cm$^{-1}$ | Raman cm$^{-1}$ | IR cm$^{-1}$ | Raman cm$^{-1}$ | IR cm$^{-1}$ | Raman cm$^{-1}$ | IR cm$^{-1}$ | Raman cm$^{-1}$ |
| Sn(C$_2$H$_7$N$_2$O)(Cl)$_2$5H$_2$O | 3256 | 3286 | 3021 | 3023 | 1799 | 1706 | 1696 | 628 | 1644 | 617 | -- | -- | -- | -- |
| Pb(C$_2$H$_7$N$_2$O)(NO$_3$)$_2$2H$_2$O | 3376 | 3395 | 3260 | 3284 | 1794 | 1766 | 1702 | 519 | 1699 | 531 | 557 | 598 | 416 | 406 |
| Zn(C$_2$H$_7$N$_2$O)(Cl)$_2$6H$_2$O | 3344 | 3349 | 3194 | 3178 | 1750 | 1625 | 1625 | 633 | 1561 | 599 | 557 | 411 | 404 |
| Cd(C$_2$H$_7$N$_2$O)(Cl)$_2$5H$_2$O | 3376 | 3386 | 3263 | 3199 | 1714 | 1709 | 1643 | 593 | 1642 | 599 | 552 | 579 | 415 | 401 |
| Sb(C$_2$H$_7$N$_2$O)(Cl)$_2$5H$_2$O | 3383 | 3348 | 3195 | 3118 | 1766 | 1754 | 1754 | 615 | 1642 | 674 | 500 | 600 | 456 | 400 |

Raman spectrum of creatinine and its complexes

The Raman spectra (Figure 4; selected samples) also agree with FTIR spectra of the Sn(II), Pb(II), Zn(II), Cd(II) and Sb(III)-creatinine complexes. The N–H stretching modes shows large wavenumber shifts (~100 cm$^{-1}$) on complexation. In pure creatinine the $\nu$(NH$_2$) and $\nu$(NH) modes appears at ~3253 and ~3036 cm$^{-1}$ respectively and these shift to ~3340-3353 and ~3120-3284 cm$^{-1}$ respectively in the creatinine complexes. These bands indicate the presence of amino group in creatinine molecule and also in the creatinine complex i.e. creatinine exists in its amino tautomeric form in the complex. The higher wavenumber shift is because the charge cloud has shifted from ring to the amino group region thereby strengthening the bonds in this region. The presence of new frequencies bands within the 600–500 cm$^{-1}$ and 500–400 cm$^{-1}$ range in these complexes are attributed to $\nu$(M-O) and $\nu$(M-N) vibration bands respectively.

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Figure 3a. FTIR spectrum of creatinine ligand.

Figure 3b. FTIR spectrum of tin(II) complex.
**Thermal studies**

To support the postulated formulae and structures, thermogravimetric studies for produced compounds were carried out under N₂ flow (Table 4). The thermograms of synthetic creatinine complexes, which exhibit a 49-56 percent weight loss up to 1000 °C, which is commensurate with the above-mentioned three processes. According to the literature, the constituents of solid complexes decompose in the following order: water, anion, ligand, and final residue, which corresponds to either metal oxide or free metal. In the thermal decomposition of the Sn(C₆H₇NO₃)₂Cl₃H₂O complex, show three to four decomposition steps within the temperature range 266–1000 °C. The first stage of decomposition takes place at maximum temperatures of 266 °C is accompanied by a weight loss 4.71% (calc. 4.89%) corresponding to the loss of one coordinated water molecule. The second two steps of decomposition within the temperature range 536–613 °C correspond to the loss of 4H₂O + 2N₂O with a mass loss of 25.99% (calc. 25.83%). The third stage of decomposition takes place at maximum temperatures of 749-800 °C is accompanied by a weight loss 49.70% (calc 49.67%) corresponding to the loss of chloride ion + 3C₂H₂ + 1.5NH₃ + CH₄ + HCN then the final thermal decomposition product obtained is antimony oxide polluted with few carbon atoms. The thermal degradation of [Cd(C₆H₇NO₃)₂Cl₃]H₂O complex occurs in four degradation stages, the first stage of decomposition occurs at maximum 352 °C and is accompanied by a weight loss of 17.04 (calc 17.61%) corresponding to loss of 2H₂O + 2C₂H₃. The second step of decomposition occurs at different temperatures and is accompanied by a weight loss of 10.64%; corresponding to the value of 3H₂O molecule theoretically, the weight loss in this step 10.80%. The third stage of decomposition takes place at maximum temperatures of 761-800 °C is accompanied by a weight loss 49.4 % (calc 48.8 %) corresponding to the loss of chloride ion + 2C₂H₂ + 2N₂O + 2NH₃ then the final thermal decomposition product obtained is CdO + 4C. The [Zn(C₆H₇NO₃)₂Cl₃H₂O]·6H₂O complex’s TG curve shows that it decomposes in two phases. The first weight loss stage has decomposition temperature of 391 °C, with weight losses of 30.26 % (calc. 30.55%), which corresponds to the losses 6H₂O + HCN + 0.5CH₄. The second weight loss stage has decomposition temperature of 770 °C, corresponding to the losses of the chloride ion + 2C₂H₂ + 2N₂O + 1.5CH₄ + HCN with weight losses of 56.74% (calc. 56.83%) with its calculated weight percentage of 12.39%, ZnO + C is the final product. The TG curve of [Sn(C₆H₇NO₃)₂Cl₃H₂O]·4H₂O complex, show three steps decomposition. The first step at temperature of 119 °C, with a mass loss 5.29% (calc. 5.14%), may be attributed to the loss of one non-coordinated water molecule + NH₃. The second step at temperature of 421°C with mass loss 16.8% (calc. 16.8%), may be attributed to the loss of 4H₂O + 0.5C₂H₃. The final stage of decomposition takes place is accompanied by a weight loss 54.43% (calc 54.35%) corresponding to the loss of chloride ion + 1.5C₂H₂ + 2N₂O + 2HCN + 1.5CH₄ then the final thermal decomposition product obtained is SnO + 5.5C. When two coordinated water molecules are heated to temperature maximum temperatures of 220 °C to 492 °C in the first stage, the [Pb(C₆H₇NO₃)₂(NO₃)₂]H₂O complex is lost, along with weight loss 11.44% (calc.11.44%). The second stage of decomposition takes place at maximum temperatures of 538 °C and 800 °C is accompanied by a weight loss 53.52% (calc. 53.53%) corresponding to the loss of 4C₂H₂ + 2NH₃ + 2NO₂ + 2N₂O then the final thermal decomposition product obtained are PbO + 9C.
Figure 4a. Raman spectrum of creatinine ligand.

Figure 4b. Raman spectrum of zinc(II) complex.

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Preparation of Zn(II), Cd(II), Sn(II), Pb(II) and Sb(III) creatinine complexes

Table 4. The maximum temperature $T_{\text{max}}$ (°C) and weight loss values of the decomposition stages for creatinine metal complexes.

| Compounds | TGA range (°C) | Number of peaks | Weight loss (%) | Lost species |
|-----------|---------------|----------------|----------------|-------------|
|           |               |                |                | Calcul.     | Found       |
| [Sn(C₄H₇N₃O₂)₂Cl₂H₂O]4H₂O | 119-421, 421-800 Residue | 1, 1 | 5.14, 16.8 | 5.29, 16.8 | H₂O + 0.5 CH₄ |
| [Pb(C₄H₇N₃O₂)(NO₃)₂]2H₂O | 220-492, 538-800 Residue | 3, 2 | 11.44, 53.53 | 11.44, 53.52 | 2H₂O + O₂ |
| [Zn(C₄H₇N₃O₂)₂Cl₂]6H₂O | 391-770, 770-800 Residue | 1, 1 | 30.55, 56.83 | 30.26, 56.74 | 6H₂O + HCN + 0.5CH₄ |
| [Cd(C₄H₇N₃O₂)₂Cl₂]5H₂O | 352-462, 761-800 Residue | 2, 1 | 17.60, 48.80 | 17.04, 49.4 | 3H₂O + 2C₂H₂ |
| [Sb(C₄H₇N₃O₂)₂Cl₂]5H₂O | 266-563-613, 749-800 Residue | 1, 1 | 04.89, 25.83 | 04.71, 25.99 | H₂O + 0.5NH₃ |

$^1$H NMR spectra

The $^1$HNMR spectrum of creatinine and its metals complexes in DMSO-$d_6$ (Table 5 and Figure 5; selected samples) showed the chemical shifts (δ in ppm) of various protons in metal complexes. The $^1$H NMR spectra of creatinine in this solvent exhibit’s resonances at 7.4, 3.67, 3.20 and 2.91 ppm (relative to (TMS), which are due to the cyclic NH, imine NH, -CH₂- and –NCH₃ protons, respectively. Comparison of the spectra of Sn(II), Pb(II), Zn(II), Cd(II) and Sb(III) complexes with that of creatinine revealed that there is a large shift of cyclic N(3)H proton (resonance at 8.4 ppm), while the position of the other protons are unaltered.

Table 5. $^1$H NMR chemical shifts (ppm) for creatinine, Sn(II), Pb(II), Zn(II), Cd(II) and Sb(III) complexes.

| Creatinine | Sn(II) | Pb(II) | Zn(II) | Cd(II) | Sb(III) | Atom position/Assignments |
|------------|--------|-------|--------|--------|---------|--------------------------|
| 7.40       | 8.08   | ----  | 7.62   | 7.87   | 8.91    | Cyclic NH                |
| 3.67       | 3.66   | 3.76  | 3.76   | 3.75   | 3.95    | Imine NH                 |
| 3.20       | 3.28   | 3.28  | 3.29   | 3.50   | 3.19    | CH₂                      |
| 2.91       | 2.97   | 2.91  | 2.91   | 2.95   | 2.91    | NCH₃                     |

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Figure 5a. $^1$H NMR spectrum of creatinine ligand.

Figure 5b. $^1$H NMR spectrum of Sn(II) complex.
CONCLUSIONS

The reaction of SnCl₂, ZnCl₂, Pb(NO₃)₂, CdCl₂, and SbCl₅ transition metal chloride and nitrate salts with a creatinine biomolecule yielded mononuclear metal chelates [Sb(C₆H₅N₂O)₅Cl]SH₂O, [Cd(C₂H₂N₂O)₂Cl]SH₂O, [Zn(C₂H₂N₂O)₂Cl]SH₂O, [Sn(C₂H₂N₂O)₂Cl]SH₂O, [Sb(C₂H₂N₂O)₂Cl]SH₂O, and [Pb(C₂H₂N₂O)₅(NO₃)₂]SH₂O. All metal chelates were non-electrolyte in dimethyl sulfide. The IR and Raman spectra of the obtained compounds agree with the mode of binding derived from the structural analysis. Thermogravimetric data agree with the stoichiometry and formulas proposed.

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