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Synthesis characterization and physico chemical analysis of some novel chelates

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Abstract

A novel complex was synthesized by using 3rd row transition elements that is of Fe^{3+}, Co^{3+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} N-piperidine-N'-Benzoylthiourea. Quantification of these complexes done by elemental analysis, infrared spectroscopy (FTIR) and proton NMR studies. The thermal behaviour of those complexes judged by thermos-gravimetric analysis (TGA). It confirms that those complexes are thermally stable up to 300□. TGA study also confirms that Fe^{3+} complexes were outlier by showing three-step decomposition. Whereas other complexes exert two step decomposition. In complexes were a conglomerate of ligands and metal ions, which binds, in a bidentate chelating mode. This type of chelate formation facilitated by deprotonation of the acidic amide (–C (O) N'HC (S)) moiety. An unique pathway was developed for the formation of bis/tris-6-membered chelates of type [M (L-kS,O) x] where x = 2 or 3 denotes divalent or trivalent metal ions, respectively.

Keywords: Metal complexes, Benzoylthiourea ligands

Introduction

In recent days thiourea and thiobiurets/dithiobiurets group of compounds catches the eyes of the scientists due to their likely biological properties and extensive applications the field of thin film, fabrication of metal sulphide and designing of nano particles. This group of compound shows anatomical versatilities. Modification of starting material leads to the formation of numerous numbers of derivatives like N, N -dialkyl- N' -aroyl/acyl-thioureas. This type of compounds reported in literature. Such type of compound synthesized under mild reaction conditions by mixing an acid chloride to KSCN followed by an amine. The biological behaviour of the thiourea executed by the N-C-s moiety present in it. This biological activity of thiourea and thiourea derivatives increased by the genesis of metal conglomerates. Besides biological applications thiourea it is also known for it's extensive industrial applications like corrosion inhibitor, additives in lubricants etc. During the formation of chelates between thiourea derivative and transition metals, thiourea derivatives act as π-donor ligand. It donates its π-electrons from HOMO of C=S bond to the LUMO of the metal centres as result chelates were formed. Metal sulphides nano-materials can be were prepared from single source precursor by using this kind metal chelates.

As a ligand, thiourea exerts versatility by coordinating with various types' metal centres like neutral, mono-anionic, di-anionic etc. It is evident that among all the ligands derived from thiourea, bidentate chelating groups (L-k O, S) were superior. During the synthesis of nano-materials by using thiourea metal chelates, the stoichiometry and the

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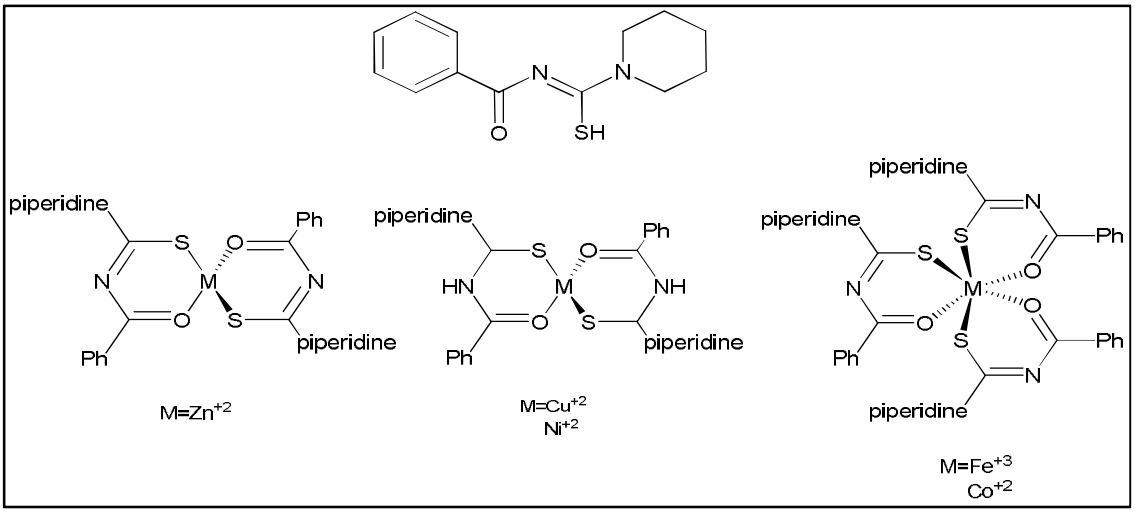
phase of the material were control by the direct sulphur and metal bonds present in the system. Preparation of metal chelates using third row transition elements (Co, Cu, Ni) with thiobiurets and di-thiobiurets were first proposed by Ramasamy et. al. These metal complexes was extensive use as the precursor for metal sulphide thin film by AACVD. Deposition of CuS thin films by AACVD in presence of N, N-diethyl-N'-(1-naphthoyl) thiourea was first proposed by Akhtar et. al. Akhtar group also developed a series of acyl thiourea complex using different transition elements (Ni, Cu, Co and Zn) and check their efficiency in the deposition of thin film by AACVD. The effect of surfactant on the phases of CuS via colloidal synthesis was investigated by Revaprasadu et. al. They have also investigated the deposition of thin film by AACVD using acyl thiourea Cu-complexes. Pbs and Pbs 1-x Se x solid solutions over a wide range of compositions was also prepared by Revaprasadu and his co-workers by using chalcogenourea complex. Nanomaterials and thin films of other elements of chalcogen series also reported like selenide base nanomaterials and thin films made from seleno urea. Photo induced isomers of thiourea were formed due to the presence of versatility and flexible coordination ability in thiourea. The phenomenon photo-isomerisation deals with reversible protonation of Pt^{2+} and Pd^{2+} thiourea complexes, which results in the genesis of series of cis-trans isomers. Plethoras of applications observed for thiourea based metal complexes. Thus, investigation of structural features, different oxidation states, coordination number and coordination geometries of thiourea complexes with different transition metal were much needed. Piperidine which is an amino ether has many applications like it used as optical brighteners, catalyst etc. [28]. Chemical stability under mild condition of dithiocarbamate metal-organic compounds achieved by using piperidine. Thus, piperidine was the most obvious choice for our study. In our study it is reflected that the ligand N - piperidine - N' -benzoylthiourea is successfully coordinated to Cu(II), Co(III), Fe(III), Ni(II) and Zn(II). However, the metal chelates was not studied by using single crystal XRD previously except $Co3^{+}$ and Ni^{2+} complexes (Fig. 1). New polymorphs presented in our study. Our interest in these compounds stems from their potential use as precursors for the synthesis of metal sulfide nanomaterials.



Schematic Molecular diagrams of the ligand and metal complexes.

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Experimental

2.1. Chemicals

Benzoyl chloride, potassium thiocyanate and copper chloride dehydrate of 99% purity was procured from Sigma-Aldrich. Metal salts Fe (III) chloride (97%), Co (III) chloride hexa hydrate (98%), Zn (II) nitrate hexa hydrate (98%), Nickel (II) chloride (98%) were procured from Merck. The solvents hydrochloric acid (37%), ethanol (99.5%), acetone (99.5%), dichloromethane (99%) and piperidine (99%) obtained from SD fine chemical.

The ligand and metal complexes synthesized by slightly recasting reported procedure of our previous work. Physical properties, elemental analysis results and IR data.

2.2. Synthesis of N-morpholine-N'-benzoylthiourea, [morthio] (HL)

At first solution was prepared by dissolving benzoyl chloride (2.0mL, 17mmol) in 50mL of acetone. This solution was added to a suspension of potassium thiocyanate (1.67g, 17mmol) in 30mL of acetone in dropwise manner. The reaction mixture was poured in a 50mL round bottom flask and heated under reflux condition for 30 min. Then the reaction mixture was allowed to cool down to room temperature and mixed with a solution of piperidine, prepared by dissolving piperidine (1.50mL, 17mmol) in 10mL of acetone. The resulting reaction mixture was further stirred for 2h. After the completion of the reaction hydrochloric acid (300mL, 0.1M) was to obtain a solid reaction mass. The reaction mass was procured from the solution by filtration followed by reaction mass was washed with water and purified by recrystallization in ethanol:dichloromethane (1:1)mixture. The obtained purified reaction mass was investigated using ^{1}H-NMR (400 MHz, acetone) and following data were acquired: δ9.68 (s, 1H, NH), 8.02 (m, 2H, C 6 H 5), 7.64 (d, 1H, C 6 H 5), 7.61 (m, 2H, C 6 H 5), 4.21 (s, 4H, CH 2), 3.77 (s, 4H, CH 2).

2.3. Synthesis of the complexes

2.3.1. Synthesis of tris(N- piperidine -N'-benzoylthioureato)iron(III), [Fe(morthio) 3] (1)

A suspension of N-piperidine- N'-benzoylthiourea (ligand) (1.50g, 6mmol) in 50mL of acetone was prepared in a 100mL round bottom flask. A solution of transition metals were prepared by dissolving Fe (III) chloride (0.44g, 2mmol) in 20mL of de-ionised water and this solution was dropwise added to the previously prepared solution in 100mL round bottom flask. The resulting solution was kept under stirring for 1h. After completion of the reaction reaction mass was filtered and recrystallized in a mix of ethanol and dichloromethane for the desirable quality of crystal growth.

2.3.2. Synthesis of tris(N- piperidine -N'-benzoylthioureato)cobalt(III), [Co(morthio) 3] (2)

Same method was followed for the synthesis of complex 2. Only Co (II) chloride hexahydrate (0.48g, 2mmol) metal salt were used instead of Fe^{3+} salt. This reaction is comparatively slow than the previous one as Co (II) was oxidised to Co (III) during the reaction by consuming atmospheric oxygen.

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2.3.3. Synthesis of bis(N- piperidine -N'-benzoylthioureato)nickel(II), [Ni(morthio) 2] (3)

Complex 3 was synthesized by employing the method used during the synthesis of complex 1. Here Ni (II) chloride hexahydrate (0.26g, 2mmol) was used as metal centre and N-piperidine- N-benzoylthiourea (1g, 4mmol) was used as ligand solution by dissolving it in 50mL of ethanol. The complex was analysed by proton NMR (400MHz, $CDCl_3$) and following data were procured: δ= 8.13 (m, 2H; 2-C 6 H 5), 7.51 (d, 1H, 2-C 6 H 5), 7.41 (m, 2H, 2-C 6 H 5), 4.22 (m, 4H, 2-CH 2), 3.78 (m, 4H, 2-CH 2).

2.3.4. Synthesis of bis(N- piperidine -N'-benzoylthioureato)copper(II), [Cu(morthio) 2] (4)

Preparation of complex 4 was carried out by the implementation of the method used for the synthesis of complex 3. Here Cu (II) chloride dehydrate (0.27g, 2mmol) was used as metal salt.

2.3.5. Synthesis of bis(N- piperidine -N'-benzoylthioureato)zinc(II), [Zn(morthio) 2] (5)

Zn (II) nitrate hexahydrate (0.6g, 2mmol) was used for the synthesis of complex 5. Rest of the method was similar with the method followed during the synthesis of complex 3. The metal complex was investigated by using proton NMR (400MHz, $CDCl_3$) and the following data were acquired: δ= 8.17 (m, 2H; 2-C 6 H 5), 7.50 (d, 1H, 2-C 6 H 5), 7.41 (t, 2H, 2-C 6 H 5), 4.27 (m, 4H, 2-CH 2), 3.84 (m, 4H, 2-CH 2).

2.3.6. Synthesis of tris(N- piperidine -N'-benzoylthioureato)indium(III), [In(morthio)2] (6)

Complex 6 was synthesized by following the procedure used during the synthesis of complex 1. Preparation complex 6 carried out under N_2-atmosphere using In (II) chloride (0.44g, 2mmol) as metal salt. Proton NMR (400 MHz, $CDCl_3$) was also taken for this complex and the following data were obtained: δ= 8.12 (m, 2H; 3-C6H5), 7.47 (d, 1H, 3-C 6 H 5), 7.36 (m, 2H, 3-C 6 H 5), 4.16 (m, 4H, 3-CH 2), 3.75 (m, 4H, 3-CH 2).

3.Results and discussion

3.1. Spectroscopic and gravimetric analysis:

Elemental analysis (ESI Table S1) confirms that the complexes prepared using transition metals [Fe(III), Co(II), Ni(II), Cu(II), Zn(II) and In(III)] and organic ligand (N-piperidine-N'-benzoylthiourea) are of high purity and good yield.

FTIR analysis (ESI Table S2) of the synthesized complexes are good agreement with the elemental analysis. Various characteristics peak were observed in FTIR spectra.The absorption peak observed at 3239 cm^{-1} were attributed the stretching frequency of N-H group of the ligand which is adjacent to carbonyl group of HL. C=N functionality gives absorption peak at 1587-1585 cm^{-1}. The disappearance the N-H peak and emergence of the C=N peak in the complex concludes that the deprotonation of the ligand facilitated by the addition of the base, N-piperidine. This deprotonation was further confirmed by ^{1}H-NMR spectroscopy. In pristine HL the chemical shift value of N-H proton was observed at 9.68 ppm whereas this peak was not found after complexation. Shifting of C=O absorption peak towards lower frequency was noticed after complexation. In pristine HL C=O absorption peak was observed at 1663cm^{-1}. This shifting was explained by counting the electron withdrawing nature of the ligands attached in the complex. These data show that

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deprotonation involves delocalisation of the C=O stretching vibration, which is consistent with literature. This interpretation confirms the coordination of the central metal ion with the oxygen atom of the carbonyl group in the complex. In proton NMR spectra multiplets were observed for aromatic aromatic protons in the region between 8.17-7.41ppm for both ligand and complex. Two signals assigned to the methylene protons of morpholine were also observed in the region between 4.27-3.84 ppm.

Conclusion

N -morpholine- N' -benzoylthiourea and its novel complexes of Fe(III), Co(III), Ni(II), Cu(II), Zn(II) and In(III) were synthesized and characterised using various techniques including single crystal X- ray diffraction studies. The trivalent compounds all adopt comparable octahedral structures comprising three monoanionic bidentate ligands coordinated to the metal centre. All the octahedral complexes shows a preference for an S 3 O 3 facial arrangement of coordinating atoms. This ubiquitous geometry was found to be ca. 9 $kJ.mol^{-1}$ lower in energy than the comparable meridional isomer which was quantified by using DFT methods. The divalent metal chelates are square planar in the case of Cu(II) and Ni(II), but tetrahedral for Zn(II). The coordination sphere of the divalent compounds is completed by two of the S,O -donor bidentate ligands. From the TGA and unpublished data, the complexes have shown a potential usefulness as single source molecular precursors for the preparation of metal sulphide nanomaterials.

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