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Synthesis, characterization and thermal degradation of 1-D coordination polymers of the type Cu_xZn_{1-x}(dadb)·yH_2O (dadb = 2,5-diamino-3,6-dichloro-1,4-benzoquinone; and x = 1.0, 0.5, 0.0625 and 0)

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ABSTRACT

New complexes of the type [{$M_xM'_{1-x}$(dadb)}$_n$·yH_2O] {where dadbH_2 = 2,5-diamino-3,6-dichloro-1,4-benzoquinone (1); M = Cu(II); M′ = Zn(II); x = 1 (2), 0.5 (4), 0.0625 (5), 0 (3); y = 0–2 and n = degree of polymerization} were synthesized and characterized. Distinct identities of heterobimetallic complexes are revealed from nature and position of their PXRD lines. Complexes under present study are hygroscopic in the temperature range RT–60 °C. The TGA, DTA and DSC thermograms suggest that complexes first lose water molecules followed by loss of HCl molecules under 2nd step of thermal degradation which is catalyzed by Cu(II) ions, whereas elimination of CO under 3rd step is catalyzed by air. Residue from 2 and 3 corresponds to 1/2 mole of metallic copper and zinc, respectively, under nitrogen atmosphere, whereas, one mole of CuO and half mole of ZnO, respectively under air. Thermal degradation pattern of the ligand moiety around Cu(II) have been observed to be different than that around Zn(II) ion.

1. Introduction

The dadb molecule is reported to possess two parallel conjugated strands (Fig. 1a) across the molecule [1–3]. Supramolecular structure (Fig. 1b) of the 2,5-diamino-3,6-dichloro-1,4-benzoquinone (dadb) molecule [4] shows one dimensional stacking through π–π interaction between ring carbon atoms of adjacent molecules and exhibits metallic conductivity. Due to presence of donor atoms at each end of conjugated strands of the dadb molecule, it is expected to form 1-D coordination polymer like that of CA (chloranilic acid) [5] (Fig. 1c). Two metal ions coordinated simultaneously to same conjugated dadb ligand are expected to be in electronic communication with each other like Creutz-Taube ion [6,7] (Fig. 1d). The extent of electronic communication depends upon nature of metal ion and intermittent ligand [7]. During electronic communication between two metal ion, electron (charge densities) will pass through intermittent coordinated ligand, i.e. electron of metal ion will be delocalized on ligand. Consequently, charge density on various atoms of the coordinated ligand may vary upon variation of adjacent metal ion coordinated to ligand in 1-D chain. Thus, coordination polymer of transition metal ions with π-conjugated ligand dadb is expected to exhibit their application as good conducting material as metallic/semiconducting materials [8]. Therefore, study of thermal stability of such useful materials is foremost important and is undertaken. Further, thin film deposition (MOCVD) of metal and metal oxides have been achieved by pyrolytic cleavage of metal complexes for their application in electronic industries [9]. Metal/metal oxides formed under different environment exhibit different characteristics, therefore, thermal studies of the new title metal complexes were under taken to predict the pyrolytic product which may be useful in future as gas sensors [10], optical switch [11], magnetic storage media [12], lithium batteries [13], solar cells [14] owing to its photoconductive and photochemical properties and catalyst [15].

Electronic environment on the ligand atoms changes by varying the adjacent coordinated metal ion in 1-D coordination polymer, therefore, it may be expected that the thermal degradation of the ligand moiety of the complexes should be influenced by changing the coordinated metal ion. This may change morphology, texture and composition of useful pyrolytic product hence its properties [16,17]. In view of above, present investigation was under taken to study the thermal stability, degradation pattern, final pyrolytic product and observe variation of degradation pattern and final residue of heterobimetallic complexes w.r.t. their monometallic complexes. Further, the reports on metal complexes of dadb are lacking except one study on thermovolumetric [18] measurement of cobalt(II), iron(II) and manganese(II) complexes of dadb under

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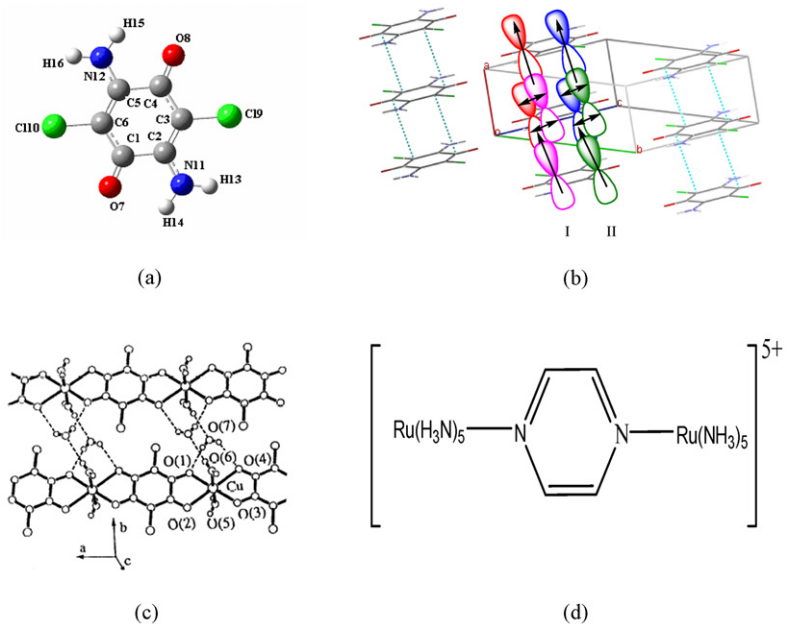

Fig. 1. (a) Optimized molecular structure of 1. (b) 1-D stacking via $\pi-\pi$ interactions. (c) Structure of $[Cu(CA)]_n$. (d) Creutz-Taube ion.

nitrogen atmosphere upto 300 °C. In present communication synthesis, characterization and thermal degradation pattern of 1-D coordination polymers of the type Cu_xZn_{1-x}(dadb) (x = 1.0, 0.5, 0.0625 and 0) is being reported.

2. Experimental

2.1. Physico-chemical measurements

The elemental analysis (Carbon, hydrogen and nitrogen) was performed on a Elemental Analyzer model Carlo Erba 1108. Magnetic susceptibility of the powdered samples was measured at room temperature on a Cahn-Faraday electro balance using $[CoHg(NCS)_4]$ as calibrant. The melting points of the complexes were determined in open capillaries using Gallenkamp apparatus and are uncorrected. Electronic absorption spectra were recorded on a UV-1700 PHARMA SPEC UV–visible spectrophotometer in solid state as Nujol mulls. IR spectra on KBr disc were recorded on a VARIAN 3100 FT-IR spectrophotometer in the region 4000–400 cm^{-1}. The X-ray powder diffraction patterns were recorded on X-ray diffraction SEIFERT RICH. SEIFERT and Co. Gmbh and Co. KG D-2070 Ahrensburg using Cu Kα-radiation and Rigaku D. Max-B Powder X-ray diffractometer with Cu Kα-radiation. The thermogravimetric analysis curves (TGA, DTG and DTA) were recorded on Perkin Elmer, Diamond TG/DTA and NETZSCH STA 409 C/CD. DSC thermograms were recorded on Mettler Toledo TC 15 TA differential scanning calorimeter at rate of 5 °C/min under nitrogen atmosphere using Spec. pure grade indium as standard by taking samples in closed lid aluminium pan. The variable temperature electrical conductivity of the metal complexes was measured using conventional two-probe technique on a Keithley 236 source measure unit.

2.2. Synthesis of metal complexes

All the chemicals used under present investigations were of analytical reagent grade. Solvent were purified and dried prior to the use by standard methods [19]. The ligand 2,5-diamino-3,6-dichloro-1,4-benzoquinone (1) was prepared following literature procedure [18,20].

2.2.1. Metal complexes of the type $[M(dadb)]_n \cdot xH_2O$ [$M = Cu^{2+}$ (2), Zn^{2+} (3)]

To a 0.414 g dadb (2 mmol) and 0.224 g KOH (4 mmol) dissolved in 40 ml 50% ethanolic solution, a solution of metal salt (2 mmol) dissolved in 15 ml distilled water was added slowly drop wise with constant stirring in 30 min and continued stirring for further 5 h. Reaction mixture was heated for 30 min over water bath and allowed to stand at room temperature for 2 h. The precipitated complexes were filtered washed with distilled water thrice. The precipitated complexes were purified by stirring for one hr in a solvent mixture consist of 25% ethanol, 25% acetone, 5% DMF and 45% distilled water and filtered, washed with distilled water thrice followed by ethanol and dried under vacuo over anhydrous $CaCl_2$.

2.2.2. Synthesis of heterobimetallic complexes

2.2.2.1. $Cu_{0.5}Zn_{0.5}(dadb)\cdot xH_2O$ (4). The heterobimetallic complex $Cu_{0.5}Zn_{0.5}$(dadb)·xH_2O was synthesized by adding a 10 ml homogeneous aqueous solution of $ZnSO_4 \cdot 7H_2O$ (0.287 g, 1 mmol) and $CuSO_4 \cdot 5H_2O$ (0.250 g, 1 mmol) into a pink colored 50% ethanolic solution (40 ml) of dadb (0.414 g, 2 mmol) and KOH (0.224 g, 4 mmol) drop wise with constant stirring over a period of 1/2 h. The reaction mixture turned to intense dark color solution. The reaction mixture was further stirred for 5 h followed by digestion over water bath for 30 min and cooled to room temperature. Subsequently same procedures were followed as in Section 2.2.1.

2.2.2.2. $Cu_{0.0625}Zn_{0.9375}(dadb)\cdot xH_2O$ (5). The heterobimetallic complex $Cu_{0.0625}Zn_{0.9375}$dadb was synthesized by adding an aqueous solution of $ZnSO_4 \cdot 7H_2O$ (0.539 g, 1.88 mmol) + $CuSO_4 \cdot 5H_2O$ (0.031 g, 0.12 mmol) into a pink colored 50% ethanolic solution (40 ml) of dadb (0.414 g, 2 mmol) and KOH (0.224 g, 4 mmol) drop wise with constant stirring over a period of 1/2 h. Rest procedure was same as described in Section 2.2.1.

3. Results and discussion

Analytical data agree with composition of the complexes given in Table 1. The solid complexes are stable in presence of air but weakly hygroscopic. Complexes dried over $CaCl_2$ under vacuo gain some weight on exposure to air and extent of weight gain depends