Supporting Information

Influence of Nitrogen Donor Ligands on the Supramolecular Architecture of Copper (II) 2-Nitrobenzoate Complexes: Structures, DFT Calculations and Magnetic Properties

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Thermogravimetric Analysis.

Thermogravimetric analysis of complexes 1-3 was examined from 33 to 1000° in air to study the thermal stability (Fig. S1-S3). In the TG curve of 1 the first weight loss step (calc = 23.99%, expt = 22.75%) from 74-158 °C corresponds to loss of one molecule of \( \gamma \)-picoline and one nitro molecule from one nitrobenzoate moiety. In 2, the first weight loss step (calc = 5.82%, expt = 6.00%) from 70-108 °C corresponds to the loss of two coordinated water molecule whereas the second and the third steps correspond to loss of one \( \square \)-pic molecule (calc = 15.06%, expt = 14.99% from 108-175 °C) and two nitrobenzoate moieties (calc = 54.00%, expt = 51.99% from 179-235 °C) respectively. In 3, the first and second weight loss corresponds to the loss of two lattice water (calc = 4.55%, expt = 4.74% from 30-104 °C) and one 2-nitrobenzoate moiety (calc = 20.99%, expt = 20.52% from 104-198 °C) respectively.

IR and electronic spectroscopy

Infrared spectrum of the newly synthesized complex salts have been recorded in the region 4000-400 cm\(^{-1}\) and tentative assignments have been made on the basis of earlier reports in literature [K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, 1997, John Wiley & Sons, New York, 5th Ed.; J. Bellamy, The Infrared Spectra of Complex Molecules, 1980, Chapman & Hall, London/ New York, Ed.]. The strong band in the region 3371 cm\(^{-1}\) in 2 and 3418- 3225 cm\(^{-1}\) in 3 may be attributed to OH(H\( _2\)O) stretching and OH of triethanolamine and H\( _2\)O stretching, respectively. The bands varying from weak to medium intensity in the region 2877–3167 cm\(^{-1}\) and 1607-1601 cm\(^{-1}\) in complexes 1, 2 and 3 may be respectively attributed to CH stretching. In 1-3, the bands between 1593 -1578 cm\(^{-1}\) and 1393- 1385 cm\(^{-1}\) may be ascribed to \( \nu_{as}(\text{COO}) \) and \( \nu_{s}(\text{COO}) \), respectively. The \( \Delta \nu_{\text{COO}} = \nu_{as}(\text{COO}) - \nu_{\text{sym}}(\text{COO}) \) values are 175 cm\(^{-1}\) in 1, 200 cm\(^{-1}\) in 2 and 216 cm\(^{-1}\) in 3 which indicates the presence of bidentate bridging in 1 and monodentate in 2 and 3. The bands between 1340- 1367 cm\(^{-1}\) and 1524-1537 cm\(^{-1}\) in all complexes may be assigned to asymmetric and symmetric stretching mode of nitro group respectively. The bands at 835, 836 and
813 cm\(^{-1}\) may be ascribed to \(\delta(\text{NO}_2)\) in 1, 2 and 3 respectively. The bands at 4597, 554 cm\(^{-1}\) in 1, at 463, 538 cm\(^{-1}\) in 2 and 466 and 568 cm\(^{-1}\) in 3 are ascribed to \(\nu(\text{Cu-N})\) and \(\nu(\text{Cu-O})\) vibrations. The bands at 648, 493 cm\(^{-1}\) in 1 and at 649, 513 cm\(^{-1}\) in 2 were ascribed to coordinated in plane and out plane ring deformation of \(\gamma\)-picoline and \(\beta\)-picoline, respectively. IR spectra are available as Figures S4-S6.

The electronic spectra of complex 1, 2 and 3 were recorded in methanol. Complex 1 showed absorption at 732 (\(\varepsilon_{\text{max}} = 94.07\ \text{mol}^{-1}\ \text{L} \text{cm}^{-1}\)) whereas complex 2 and 3 showed maximum absorption 738 nm with \(\varepsilon_{\text{max}} = 102.5\ \text{mol}^{-1}\ \text{L} \text{cm}^{-1}\) and with \(\varepsilon_{\text{max}} = 63.41\ \text{Lmol}^{-1}\text{cm}^{-1}\) respectively, due to the d-d transitions. These values are agreement with those observed by O\(_4\)N\(_2\) chromophore [F. A Cotton, G. Wilkinson, C. A Muritto, M. Bochmann, \textit{Advanced Inorganic Chemistry}, sixth ed., 1999, John Wiley and Sons, New York, 869; R. P. Sharma, A. Saini, S. Singh, A. Singh, P. Venugopalan, P. Starynowicz, J. Jezierska, \textit{J. Mol. Struct.} 2011, 994, 21–28].
Figure S1. The TGA of complex salt 1

Figure S2. The TGA of complex salt 2
Figure S3. The TGA spectrum of 3

Figure S4. IR spectrum of complex 1
Figure S5. IR spectrum of complex 2

Figure S6. IR spectrum of complex 3
Figure S7. Packing diagram of complex 1 viewed down a axis

Figure S8. Packing diagram of complex 2 viewed down b axis
Figure S9. Packing diagram of complex 3 viewed down a axis