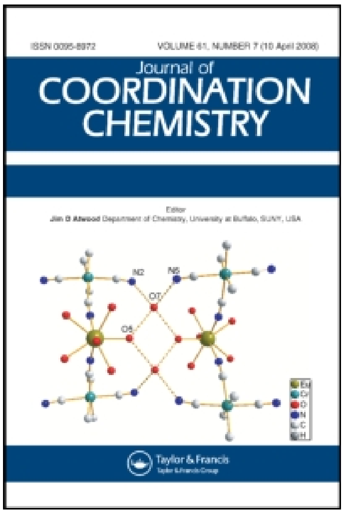

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# PREPARATION AND CHARACTERIZATION OF NICOTINAMIDE COMPLEXES OF COPPER(II) HALOGENO-CARBOXYLATES

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# NOTE

# PREPARATION AND CHARACTERIZATION OF NICOTINAMIDE COMPLEXES OF COPPER(II) HALOGENO-CARBOXYLATES

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The synthesis and characterization of the complexes $CuX_2(nia)_2$ (where X = $ClCH_2COO^-$, $Cl_2CHCOO^-$, $Cl_3CCOO^-$, $CH_3CHClCOO^-$ or $CH_3CCl_2COO^-$, and nia = nicotinamide) is reported. Characterization of the compounds was based on elemental analysis, electronic and EPR spectra, and magnetic susceptibility measurements over a temperature range. Available evidence supports a *pseudo*-octahedral environment around copper(II). The magnetic properties for the compounds indicate the presence of weak antiferromagnetic interactions. EPR spectra of finely ground polycrystalline samples are consistent with an essentially $d_{x^2-y^2}$ ground state.

KEY WORDS: Copper, halogeno-cabroxylates, nicotinamides, EPR, magnetic properties.

## INTRODUCTION

Nicotinic acid and its derivatives possess very interesting pharmaceutical properties and are important from a biological point of view. One important derivative, nicotinamide, the amide of the vitamin, is one of the two heterocyclic components of the essential co-enzymes NAD and NADP. The first structure reported of a metal complex of nicotinamide was carried out by Kindberg et al.[1] The structure was found to consist of isolated neutral molecules of $[Cu(nia)_2(H_2O)_2(BF_4)_2]$ with a *trans*-distorted octahedral environment about copper(II). Nicotinamide was coordinated to copper(II) *via* the ring nitrogens. X-ray analysis of copper bispropionato

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nicotinamide shows[2] that the copper(II) atoms are bridged in pairs by four propionate groups to form centrosymmetric binucleaar molecules, [Cu(prop)$_2$nia]$_2$, with the ring nitrogen of the nicotinamide situated at the vertices of a weakly deformed tetragonal pyramid about each copper(II) ion.

To our knowledge, no copper(II) halogeno-alkyl-carboxylates containing the nicotinamide ligand has been described in the literature. In this study we report on the donor properties of the nicotinamide ligand in the compounds $CuX_2(nia)_2$ (where $X = ClCH_2COO^-$, $Cl_2CHCOO^-$, $Cl_3CCOO^-$, $CH_3CHClCOO^-$, or $CH_3CCl_2COO^-$, and nia = nicotinamide). The compounds were characterized by elemental and thermal analysis, and their spectroscopic and magnetic properties.

## EXPERIMENTAL

### *Synthesis*

The copper(II) carboxylate compounds were prepared by treating nicotinamide (0.02 mol) with a copper(II) carboxylate (0.01 mol) in hot methanol. These were left to stand at room temperature, and the blue-violet crude products which deposited were recrystallized from methanol. When the mother liquid was concentrated after separation of the violet crystals of $Cu(Cl_3CCOO)_2(nia)_2$, one obtained a blue solid which was filtered, washed with cold methanol, and dried in air. Elemental analyses are given in Table 1.

### *Spectroscopic Studies*

Reflectance spectra of diluted compounds in $Li_2CO_3$ were recorded in the range 200–700 nm using the Hitachi 356 spectrophotometer, and undiluted samples were recorded on a Beckman UV 5240 spectrophotometer (350–1500 nm).

Electron paramagnetic resonance spectra were measured with an X-band Radiojan SE/X 2543 spectrometer as powders at room and liquid nitrogen temperatures. A solid sample of Mn(II) in MgO was used as the reference and the magnetic field was calibrated with an MJ 110R nuclear magnetometer.

### *Thermal Studies*

Thermal decomposition was studied using a derivatograph (MOM, Budapest). The

**Table 1** Elemental analyses for the complexes

| Compound[a] | Cu% Calc. | Found | C% Calc. | Found | H% Calc. | Found | N% Calc. | Found |
|---|---|---|---|---|---|---|---|---|
| **1** | 12.84 | 12.67 | 38.84 | 38.96 | 3.26 | 3.40 | 11.32 | 11.38 |
| **2** | 10.59 | 10.64 | 32.05 | 32.5 | 3.03 | 2.96 | 9.34 | 9.60 |
| **3** | 10.05 | 9.84 | 30.38 | 30.02 | 1.91 | 1.99 | 8.86 | 8.89 |
| **4** | 10.05 | 9.92 | 30.38 | 30.42 | 1.91 | 1.96 | 8.86 | 8.77 |
| **5** | 12.15 | 11.98 | 41.35 | 40.96 | 3.80 | 3.95 | 10.72 | 10.80 |
| **6** | 10.74 | 11.0 | 36.54 | 36.65 | 3.07 | 3.12 | 9.47 | 9.55 |

[a] The compounds are 1: $Cu(ClCH_2COO)_2(nia)_2$; 2: $Cu(Cl_2CHCOO)_2nia_2.2H_2O$; 3: $Cu(Cl_3CCOO)_2(nia)_2$-blue isomer; 4: violet isomer; 5: $Cu(CH_3CHClOO)_2(nia)_2$; 6: $Cu(CH_3CCl_2COO)_2(nia)_2$.

apparatus and its operation have been described by Paulik et al.[3] The rate of temperature increase was 6° per minute. Measurements were made in air.

### *Magnetic Susceptibility*

Measurements were made on polycrystalline samples by the Faraday method over the temperature range 77–290 K using a Cahn RG 2 electrobalance. The applied magnetic field was 5.25 kOe. The calibrant was $HgCO(NCS)_4$, for which the magnetic susceptibility was taken to be $16.44 \times 10^{-6}$ ($cm^3 \, g^{-1}$).[4] Correction for diamagnetism of the constituent atoms was calculated by Pascal's constants.[5] A value of $60 \times 10^{-6} \, cm^3 \, mol^{-1}$ was used for the temperature independent paramagnetism of the copper(II) ion. The effective magnetic moments were calculated by the following equation.

$$\mu_{eff} = 2.83(\chi_M^{corr} T)^{0.5}$$

## RESULTS AND DISCUSSION

The thermal decomposition of the two isomeric forms of $Cu(Cl_3CCOO)_2(nia)_2$ was carried out in air. Differences were observed for the onset of decomposition, being 130°C for the violet and 140°C for the blue species. Decomposition of the blue isomer also appeared to occur at a faster rate. At 180°C the TG curves show a loss of nicotinamide in both isomers. The theoretical mass loss is 38.8%, compared to the observed value of 39.5%. Decomposition of remaining $Cu(Cl_3CCOO)_2$ starts before all of the nicotinamide is eliminated, and it is therefore not isolable.

The electronic spectra (Table 2) of $Cu(ClCH_2COO)_2(nia)_2$ and $Cu(Cl_2CHCOO)_2(nia)_2.2H_2O$ show intraligand transition bands, a charge transfer band (II) at 400 and 396 nm, respectively, and a broad band at 730 and 668 nm, respectively, which can be assigned to d-d transitions. Blue and violet $Cu(Cl_3CCOO)_2(nia)_2$ solid state electronic spectra show differences. The violet isomer exhibits a broad ligand field band with a maximum at 548 nm and a shoulder at 658 nm. The blue isomer has only one band with a maximum at about 660 nm. Similar spectra were also observed for another two compounds, $Cu(CH_3CHClCOO)_2(nia)_2$ and $Cu(CH_3CCl_2COO)_2(nia)_2$, with maxima at 666 nm and 620 nm, respectively. This type of d-d spectrum is typical for tetragonal arrangements around copper(II), corresponding to electron transfer from the one-electron orbital ground state, $d_{x^2-y^2}$. The "blue shift" of the d-d band of the violet isomer indicates a somewhat greater tetragonal distortion around the Cu(II) atom[6] than in the blue isomer.

**Table 2** Electronic spectra, $\nu_{max}$ (nm), data

| Compound | Band I | Band II | Intraligand bands |
|---|---|---|---|
| **1** | 730 | 400 (shoulder) | 294, 292 |
| **2** | 668 | 396 (shoulder) | 286 |
| **3** | 600 | | 288 |
| **4** | 658sh 548 | | 294 |
| **5** | 666 | | |
| **6** | 620 | | 294 |

**Table 3** EPR data for the complexes

| Compound | T (K) | Spectroscopic splitting factors | | | | |
|---|---|---|---|---|---|---|
| | | $g_1$ | | $g_2$ | $g_3$ | $g_i\langle g\rangle$ |
| | | | $g_\perp$ | | $g_\parallel$ | |
| **1** | 293 | $2.04_5$ | | $2.11_8$ | $2.21_1$ | $2.12_6$ |
| | 77 | $2.06_5$ | | $2.12_6$ | $2.23_3$ | $2.14_2$ |
| **2** | 293 | | $2.06_2$ | | $2.21_8$ | $2.11_5$ |
| | 77 | | $2.06_7$ | | $2.27_4$ | $2.13_8$ |
| **3** | 293 | $2.06_7$ | | $2.13_4$ | $2.24_8$ | $2.15_1$ |
| | 77 | $2.05_7$ | | $2.12_3$ | $2.23_6$ | $2.14_0$ |
| **4** | 293 | | | | | $2.06_7$ |
| | 77 | | | | | $2.06_0$ |
| **5** | 293 | $2.06_7$ | | | $2.27_3$ | |
| | 77 | | | | | $2.09_8$ |
| **6** | 293 | | | | | $2.07_2$ |
| | 77 | | | | | $2.06_6$ |

The EPR spectra of the compounds were determined at both room and liquid nitrogen temperatures. Those of $Cu(ClCH_2COO)_2(nia)_2$ (**1**) and blue $Cu(Cl_3CCOO)_2(nia)_2$ (**3**) at both temperatures displayed three g values (Table 3) with $g_3$ $(g_\parallel) > (g_2)$, $(g_1)$. This points to the presence of a structure with $S = 1/2$ and basic state $d_x2_{-y}2$. The EPR spectrum of $Cu(Cl_2CHCOO)_2(nia)_2.2H_2O$ (**2**) at both temperatures indicated an axial type with $g_\parallel > g_\perp$ (Table 3). The EPR spectrum of $Cu(CH_3CHClCOO)_2(nia)_2$ (**5**) is anisotropic at room temperature with two values of the g factor, but at liquid nitrogen temperatures it is isotropic (Table 3). Finally, the EPR spectra of violet $Cu(Cl_3CCOO)_2(nia)_2$ (**4**) and $Cu(CH_3CCl_2COO)_2(nia)_2$ (**6**) are isotropic at both temperatures (Table 3). The slightly higher g values of compounds (**1**) and (**2**) at room temperature seem to be associated with a more symmetrical coordination geometry than at liquid nitrogen temperatures. On the other hand, just the opposite is found for the compounds (**3**) to (**6**).

Magnetic susceptibility measurements of polycrystalline samples of $CuX_2(nia)_2$ between 77 and 293 K obey the Curie-Weiss law,

$$\chi_M^{corr} = C/(T-\theta)$$

where the Curie Constant $C = Ng^2p^2S(S+1)/3k$ for $S = 1/2$. The values of $\mu_{eff}$ are slightly dependent on temperature. Since all di-nicotinamide adducts possess negative Weiss constants (Table 4), a weak antiferromagnetic interaction may occur. All compounds seem to possess octahedral stereochemistry with different tetragonal distortions around Cu(II).

The magnetic moment of the violet isomer of $Cu(Cl_3CCOO)_2(nia)_2$ is on average about 0.02 B.M. lower over the whole temperature region explored than the blue isomer, indicating a somewhat greater degree of distortion about Cu(II). Because of this increasing distortion, the energy differences between co-acting term increases, and this leads to a decrease in the values for the magnetic moment. This is in close agreement with the ligand field band position and degree of splitting (Table 2). The

**Table 4** Magnetic data[a] for the complexes

| Compound | $\Delta \times 10^6$ ($cm^3\,mol^{-1}$)[b] | $\chi_M^{corr} \times 10^6$ ($cm^3\,mol^{-1}$)[c] | $\mu_{eff}$ (B.M.)[c] | C ($cm^3\,mol^{-1}$) | $\theta$ (K) |
|---|---|---|---|---|---|
| **1** | −231 | 1530 | 1.91 | 0.474 | −18.9 |
| **2** | −292 | 1530 | 1.91 | 0.469 | −11.5 |
| **3** | −300 | 1490 | 1.87 | 0.507 | −9.5 |
| **4** | −300 | 1400 | 1.85 | 0.434 | −10.3 |
| **5** | −255 | 1440 | 1.87 | 0.453 | −5.4 |
| **6** | −290 | 1510 | 1.90 | 0.453 | −5.4 |

[a] There are over 20 data points between the two experimental temperature limits. [b] Diamagnetic corrections. [c] Data at room temperature

splitting is also indicative of a greater degree of tetragonal distortion. Therefore, these species may in fact be "distortion isomers" of the type described for other Cu(II) compounds.[7,8]

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