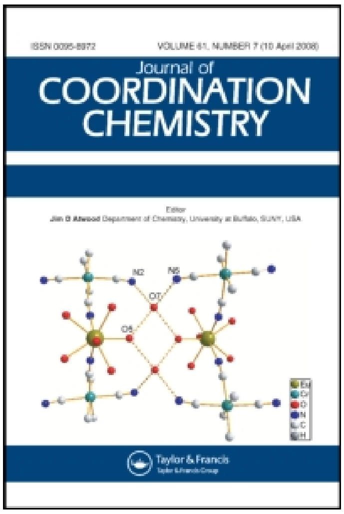

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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

Milan Melnik[a]; Jerzy Mrozinski[b]; Clive E. Holloway[c]
[a] Department of Inorganic Chemistry, Slovak Technical University, Bratislava, Czechoslovakia [b] Institute of Chemistry, Wroclaw University, Wroclaw, Poland [c] Department of Chemistry, York University, Ontario, Canada

To cite this Article Melnik, Milan , Mrozinski, Jerzy and Holloway, Clive E.(1993) 'PREPARATION AND CHARACTERIZATION OF NICOTINAMIDE COMPLEXES OF COPPER(II) HALOGENO-CARBOXYLATES', Journal of Coordination Chemistry, 29: 4, 209 — 213

To link to this Article: DOI: 10.1080/00958979308037426
URL: http://dx.doi.org/10.1080/00958979308037426

J. Coord. Chem. 1993, Vol. 29, pp. 209–213
Reprints available directly from the publisher
Photocopying permitted by license only

NOTE

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

MILAN MELNIK

Department of Inorganic Chemistry, Slovak Technical University, 81237 Bratislava, Czechoslovakia

JERZY MROZINSKI

Institute of Chemistry, Wroclaw University, 50383 Wroclaw, Poland

and CLIVE E. HOLLOWAY*

Department of Chemistry, York University, North York, Ontario M3J 1P3, Canada

(Received 24 June 1992)

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

---

* Author for correspondence.

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)$_2$nia$_2$.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 16.44×10^{-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, ν_{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

		Spectroscopic splitting factors				
		g_1		g_2	g_3	$g_i\langle g\rangle$
Compound	T (K)		$g_\perp$		$g_\parallel$	
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 $d_{x^2-y^2}$. 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 μ_{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]	μ_{eff} (B.M.)[c]	C ($cm^3\,mol^{-1}$)	θ (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]

Acknowledgements

The authors wish to thank the Ministry of Education of the Slovak Republic and York University for financial support.

References

1. B.L. Kindberg, E.H. Griffith and E.L. Amma, *J. Chem. Soc., Chem. Comm.*, 461 (1977).
2. K. Smolander, M. Macko, M. Valko and M. Melnik, *Acta Chem. Scand.*, **46**, 29 (1992).
3. F. Paulik, J. Paulik and L. Erdy, *Z. Anal. Chem.*, **160**, 241 (1971).
4. B.N. Figgis and R.S. Nyholm, *J. Chem. Soc.*, 4190 (1958).
5. E. Konig, "Magnetic Properties of Coordination and Organometallic Transition Metal Compounds", (Springer-Verlag, Berlin, 1966).
6. L.L. Funck and T.R. Ortolano, *Inorg. Chem.*, **7**, 567 (1968).
7. J. Gazo, I.B. Bersuker, J. Garaj, M. Kabešova, J. Kohout, H. Langfelderova, M. Melnik, M. Serator and F. Valach, *Coord. Chem. Rev.*, **19**, 253 (1976).
8. M. Melnik, *Coord. Chem. Rev.*, **47**, 239 (1982).