*Inorganica Chimica Acta*, 48 (1981) 77–80
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

# Magnetic and Spectroscopic Characterisation of Copper(II) 2-Halogenobenzoates with some Heterocyclic N-oxides

MILAN MELNIK, MARIA ZIVOROVÁ
*Department of Inorganic Chemistry, Slovak Technical University, 880 37 Bratislava, Czechoslovakia*

and JERZY MROZINSKI
*Institute of Chemistry, Wrocław University, 50-383 Wrocław, Poland*

Received July 16, 1980

---

*The preparation of* $Cu(2X\text{-}C_6H_4COO)_2\cdot pyNO$ *(X = F, Cl, Br or I; pyNO = pyridine N-oxide) and* $Cu(2BrC_6H_4COO)_2\cdot picNO$ *(picNO = 2-, 3-, or 4-picoline N-oxide) is described. The spectroscopic and magnetic behaviours of the compounds are compared with those of binuclear copper(II) alkanoates. The EPR spectra of the powdered solid are consistent with spin S = 1. The exchange interaction parameters are* $-2J \approx 380$ *cm*$^{-1}$*, except for* $Cu(2I\text{-}C_6H_4COO)_2pyNO$*. The structures of the compounds are discussed.*

## Introduction

Copper(II) compounds with heterocyclic N-oxides have been studied extensively because the oxygen atom of such N-oxides often acts as monodentate or a bridge enabling the strong superexchange magnetic interaction between copper(II) ions [1–3]. X-ray examination of $[CupyNOCl_2]_2$ (pyNO = pyridine N-oxide) revealed that the dimeric molecule consisted of two distorted tetrahedra sharing an edge with the oxygen atoms from the pyridine N-oxide ligands acting as the bridging units [4]. The magnetic susceptibility data for the complex suggested that the spin–spin coupling occurred by a superexchange mechanism, with the value of $-2J = 720$ cm$^{-1}$, operating through the orbitals of the bridging oxygen atoms [5, 6]. As a consequence of the dimeric structure, substituents on the pyridine ring have a remarkable effect on the magnetic properties, the trend in the singlet-triplet splitting energies parallels notions concerning the electron-donating properties by resonance of the alkyl group [7]. A few examples of dimeric copper(II) carboxylates with a moderate bond of heterocyclic N-oxides have been done [6, 8, 9] and found the singlet-triplet separation about 300 cm$^{-1}$.

Hibden and Nelson [10] found that the magnitude of magnetic interaction, in the case of copper(II) acetate compounds of 4-substituted pyridine N-oxides increased as the basicity of the N-oxide decreased.

It should by mentioned that no such study of copper(II) halogenobenzoates with heterocyclic N-oxide has been reported. The present investigation deals with syntheses of heterocyclic N-oxide compounds with copper(II) 2-halogenobenzoates. Magnetic and spectroscopic investigations on the compounds are reported herein.

## Experimental

### *Syntheses*

The copper(II) monohalogenobenzoate compounds of composition $Cu(2X\text{-}C_6H_4COO)_2\cdot L$, where X = F, Cl, Br or I; and L = pyridine N-oxide (pyNO), 2-picoline N-oxide (2picNO), 3-picoline N-oxide (3picNO) or 4-picoline N-oxide (4picNO), were prepared by treating L in excess with $Cu(2X\text{-}C_6H_4COO)_2\cdot H_2O$ and a small amount of the corresponding free acid in hot methanol solution. In the case of copper(II) 2-iodobenzoate was used a mixture of ethanol-ether (1:1). The fine green microcrystals which precipitated at about 273 K were filtered off, washed with cold ether and dried at room temperature. The elemental analyses of the isolated compounds are given in Table I.

### *Spectroscopic Studies*

Electronic spectra in the region 1.0–2.8 $\mu$m$^{-1}$ were measured with a Perkin-Elmer 450 spectrophotometer and infra-red spectra in the region 400–3600 cm$^{-1}$ with the UR 10 spectrophotometer. In both cases the nujol suspension technique was used. Electron paramagnetic resonance spectra of the powdered samples were made on a Varian Model E4 spectrometer at room temperature.

### *Magnetic Susceptibility Measurements*

The magnetic susceptibilities of powdered samples were determined at different temperatures by a Gouy

TABLE I. Analytical Data.

| Compound | | % Cu | % C | % H | % N |
|---|---|---|---|---|---|
| $Cu(2FC_6H_4COO)_2$ pyNO | calcd | 14.54 | 52.24 | 3.0 | 3.2 |
| | found | 14.4 | 51.9 | 2.95 | 3.3 |
| $Cu(2ClC_6H_4COO)_2$ pyNO | calcd | 13.52 | 48.58 | 2.79 | 2.98 |
| | found | 13.2 | 48.5 | 2.7 | 2.9 |
| $Cu(2BrC_6H_4COO)_2$ pyNO | calcd | 11.19 | 40.85 | 2.35 | 2.5 |
| | found | 10.9 | 40.0 | 2.4 | 2.4 |
| $Cu(2IC_6H_4COO)_2$ pyNO | calcd | 9.72 | 35.06 | 2.0 | 2.14 |
| | found | 9.4 | 34.6 | 2.0 | 2.0 |
| $Cu(2BrC_6H_4COO)_2$ 2picNO | calcd | 11.09 | 41.94 | 2.64 | 2.44 |
| | found | 11.3 | 41.3 | 2.6 | 2.2 |
| $Cu(2BrC_6H_4COO)_2$ 3picNO | calcd | 11.09 | 41.94 | 2.64 | 2.44 |
| | found | 11.0 | 42.0 | 2.6 | 2.3 |
| $Cu(2BrC_6H_4COO)_2$ 4picNO | calcd | 11.09 | 41.94 | 2.64 | 2.44 |
| | found | 11.1 | 41.7 | 2.7 | 2.5 |

TABLE II. Infrared Spectra.

| Compound | $\nu_{as}COO^-$ [a] ($cm^{-1}$) | $\nu_sCOO^-$ [a] ($cm^{-1}$) | $\nu_{NO}$ [a] ($cm^{-1}$) | ($\nu_{NO}$ of free l)[b] |
|---|---|---|---|---|
| $Cu(2FC_6H_4COO)_2$ pyNO | 1635s, 1610m | 1410m | 1230s | (1243) |
| $Cu(2ClC_6H_4COO)_2$ pyNO | 1620s | 1405m | 1235s | |
| $Cu(2BrC_6H_4COO)_2$pyNO | 1630s, 1620m | 1408m | 1225s | |
| $Cu(2IC_6H_4COO)_2$pyNO | 1625s | 1410m | 1225s | |
| $Cu(2BrC_6H_4COO)_2$ 2picNO | 1630s, 1610m | 1400 m | 1225 m | (1242) |
| $Cu(2BrC_6H_4COO)_2$ 3picNO | 1620s | 1405m | 1260s | (1280) |
| $Cu(2BrC_6H_4COO)_2$ 4picNO | 1620s | 1400m | 1205m | (1228) |

[a] s = strong; m = medium. [b] Refs. 14, 15.

method standardised with mercury tetrathiocyanatocobaltate(II) [11]. The molar susceptibilities were corrected for diamagnetism using Pascal constants [12] and for t.i.p equals $60 \cdot 10^{-6}$ $cm^3$ $mol^{-1}$ per Cu atom. The effective magnetic moments were calculated using the expression $\mu_{eff} = 2.83(X_M T)^{1/2}$.

## Results and Discussion

The compounds of $Cu(2Br\text{-}C_6H_4COO)_2 \cdot L$ and $Cu(2I\text{-}C_6H_4COO)_2 \cdot L$ are unstable and they decompose slowly in air, but are stable in a desiccator.

The assignments of the infrared absorption frequencies for the compounds are given in Table II. Each compound exhibits the carboxylate stretching frequencies, $\nu_sCOO^-$ and $\nu_{as}COO^-$, at very similar energies to those reported for copper(II) alkanoates [13]. In each case $\nu_{NO}$, the nitrogen–oxygen stretching frequency, is shifted to lower energy with comparison to that of the free heterocyclic N-oxide (Table II). The lowering of the NO stretching energy is attributed to a decrease in the N–O bond order upon coordination. This indicates that heterocyclic N-oxides coordinate to copper through the oxygen atom of the NO group.

All of the compounds show in their electronic spectra a band at ≈1.36 $\mu m^{-1}$ (band I) which was identified with transitions of the copper ion, and a shoulder at ≈2.60 $\mu m^{-1}$ (band II). The shoulder should be the characteristic of the bridging system with antiferromagnetic interaction [16].

Electron paramagnetic resonance spectra of the powdered samples at 293 K presented the absorption bands of axially symmetric binuclear species, the parameters are summarized in Table III. The g and D values observed for the compounds studied are similar to those usually found for copper(II) halogenocarboxylates [17].

The magnetic data as a function of temperature are given in Figs. 1, 2 and Table IV. The susceptibilities may be described by the equation for exchange coupled binuclear system.

TABLE III. Magnetic and EPR Parameters.

| Compound | $g_\perp$ | $g_\parallel$ | $g_{av}$ | $\lvert D\rvert$ ($cm^{-1}$) | Diamagnetic corrections $\cdot 10^{-6}$ ($cm^{-3}$ $mol^{-1}$) | $-2J$ ($cm^{-1}$) |
|---|---|---|---|---|---|---|
| $Cu(2FC_6H_4COO)_2$ pyNO | 2.08 | 2.38 | 2.18 | 0.350 | −199 | 576 |
| $Cu(2ClC_6H_4COO)_2$ pyNO | 2.07 | 2.36 | 2.17 | 0.365 | −227 | 392 |
| $Cu(2BrC_6H_4COO)_2$ pyNO | 2.07 | 2.38 | 2.18 | 0.367 | −248 | 394 |
| $Cu(2IC_6H_4COO)_2$ pyNO | 2.09 | 2.40 | 2.20 | 0.374 | −276 | 342 |
| $Cu(2BrC_6H_4COO)_2$ 2picNO | 2.10 | 2.42 | 2.21 | 0.375 | −263 | 368 |
| $Cu(2BrC_6H_4COO)_2$ 3picNO | 2.08 | 2.39 | 2.19 | 0.373 | −263 | 384 |
| $Cu(2BrC_6H_4COO)_2$ 4picNO | 2.11 | 2.41 | 2.21 | 0.378 | −263 | 382 |

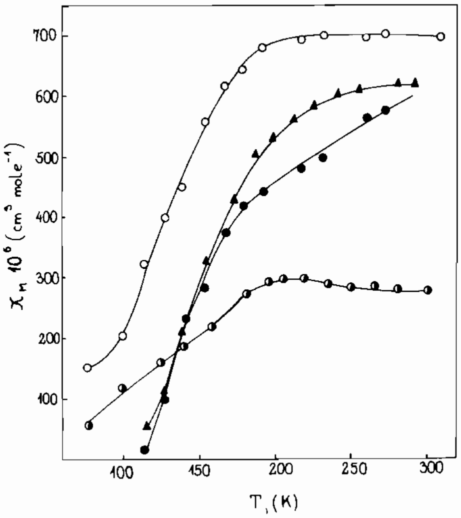

Fig. 1. Temperature dependence of the molar magnetic susceptibility for the binuclear complexes: $Cu(2FC_6H_4COO)_2pyNO$ (◑), $Cu(2ClC_6H_4COO)_2pyNO$ (●), $Cu(2BrC_6H_4COO)_2pyNO$ (▲), $Cu(2IC_6H_4COO)_2pyNO$ (○).

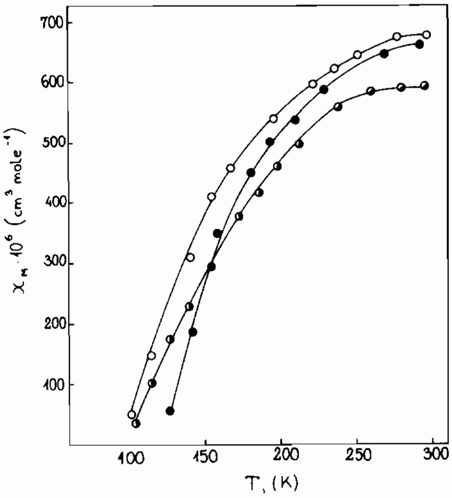

Fig. 2. Temperature dependence of the molar magnetic susceptibility for the binuclear complexes: $Cu(2BrC_6H_4COO)_2 2picNO$ (○), $Cu(2BrC_6H_4COO)_2 3picNO$ (◑) $Cu(2BrC_6H_4COO)_2$ 4picNO (●).

$$\chi_M^{exptl} - N\alpha = \left\{ \frac{Ng_{av}^2\beta^2}{3kT} \left[1 - 1/3(e^{-2J/kT})\right]^{-1} \right\} \times (1 - x) + \left( \frac{Ng_{imp}^2\beta^2}{4kT} \right) x$$

where $\chi_M^{exptl}$ is the experimental magnetic susceptibility corrected for diamagnetism, x-mole fraction of impurities and N, g, $\beta$, k, T, J have their usual meaning [18].

Algol programs were written and used to interpret the data with an Odra 1305 computer. The g-values were obtained from the EPR spectra and used as constants in the least-squares fitting process. The best fit value of −2J is shown in Table III. The exchange energy (−2J), for $Cu(2F\text{-}C_6H_4COO)_2 \cdot$ pyNO is the highest in the series.

TABLE IV. Magnetic Moments.

| Compound | T (K) | $\mu_{eff}$ (B.M.) |
|---|---|---|
| $Cu(2FC_6H_4COO)_2pyNO$ | 302 | 0.82 |
| $Cu(2ClC_6H_4COO)_2pyNO$ | 297 | 1.21 |
| $Cu(2BrC_6H_4COO)_2pyNO$ | 293 | 1.20 |
| $Cu(2IC_6H_4COO)_2pyNO$ | 293 | 1.29 |
| $Cu(2BrC_6H_4COO)_2$ 2picNO | 297 | 1.26 |
| $Cu(2BrC_6H_4COO)_2$ 3picNO | 295 | 1.18 |
| $Cu(2BrC_6H_4COO)_2$ 4picNO | 294 | 1.25 |

The reason for such ‘anomaly’ is not known and more experimental data will be needed, especially X-ray analysis, for a better understanding of such a case.

TABLE V. The Values of −2J, for Some Copper(II) 2-Halogenobenzoate Compounds.

| Compounds[a] | −2J ($cm^{-1}$) | Ref. |
|---|---|---|
| $Cu(2FC_6H_4COO)_2 \cdot H_2O$ | 260 | 21 |
| $Cu(2FC_6H_4COO)_2 \cdot A$ | 303 | 22 |
| $Cu(2FC_6H_4COO)_2 \cdot C_4H_8O_2$ | 316 | 22 |
| $Cu(2FC_6H_4COO)_2 \cdot DMF$ | 334 | 23 |
| $Cu(2FC_6H_4COO)_2 \cdot pyNO$ | 576 | this work |
| $Cu(2ClC_6H_4COO)_2 \cdot H_2O$ | 245 | 24 |
| $Cu(2ClC_6H_4COO)_2 \cdot A$ | 309 | 22 |
| $Cu(2ClC_6H_4COO)_2 \cdot C_4H_8O_2$ | 317 | 22 |
| $Cu(2ClC_6H_4COO)_2 \cdot DMF$ | 317 | 23 |
| $Cu(2ClC_6H_4COO)_2 \cdot pyNO$ | 392 | this work |
| $Cu(2BrC_6H_4COO)_2 \cdot H_2O$ | 250 | 21 |
| $Cu(2BrC_6H_4COO)_2 \cdot A$ | 306 | 22 |
| $Cu(2BrC_6H_4COO)_2 \cdot 0.5C_4H_8O_2$ | 331 | 22 |
| $Cu(2BrC_6H_4COO)_2 \cdot DMF$ | 300 | 23 |
| $Cu(2BrC_6H_4COO)_2 \cdot pyNO$ | 394 | this work |
| $Cu(2IC_6H_4COO)_2 \cdot H_2O$ | 260 | 21 |
| $Cu(2IC_6H_4COO)_2 \cdot DMF$ | 292 | 23 |
| $Cu(2IC_6H_4COO)_2 \cdot pyNO$ | 342 | this work |

[a] A = antipyrine (1-phenyl-2-3-dimethyl-5-pyrazolone); $C_4H_8O_2$ = 1,4-dioxane; DMF = dimethylformamido; pyNO = pyridine N-oxide.

The spectroscopic and magnetic behaviour of the compounds support the assumption that the studied compounds belong to a binuclear structure of the copper(II) acetate monohydrate type [19]. Copper(II) atoms in the structural units $Cu_2(2X\text{-}C_6H_4\text{-}COO)_4 \cdot 2L$ are bridged in pairs by carboxylic groups while the molecules of L are bonded through oxygen atoms in the terminal positions.

One of the important trends which has been noted for copper(II) carboxylates is for the 2J value to vary according to the pKa of the bridging acid [20–24] and with the different terminal ligands as well as we can see in Table V. The value of −2J for the copper(II) 2-halogenobenzoate compounds with the oxygen donor atoms of ligands tends to increase according to the series of terminal ligands: water < antipyrine < dimethylformamide ⩽ 1,4-dioxane < pyridine N-oxide.

## References

1 R. G. Garvey, J. H. Nelson and R. O. Ragsdale, *Coord. Chem. Rev., 3,* 375 (1968).
2 W. H. Watson, *Inorg. Chem., 8,* 1879 (1969).
3 N. M. Karayannis, L. L. Pytlewski and M. Mikulski, *Coord. Chem. Rev., 11,* 93 (1973).
4 H. L. Schäfer, J. C. Morrow and H. M. Smith, *J. Chem. Phys., 42,* 504 (1965).
5 W. E. Hatfield and J. S. Paschal, *J. Am. Chem. Soc., 86,* 3888 (1964).
6 S. J. Gruber, C. M. Harris, E. Kokot, S. L. Lenzer, T. N. Lockyer and E. Sinn, *Austr. J. Chem., 20,* 2403 (1967).
7 W. E. Hatfield and J. C. Morrison, *Inorg. Chem., 5,* 1390 (1966).
8 J. Kohout and J. Krätsmar-Smogrović, *Chem. zvesti, 22,* 481 (1968).
9 M. Melnik and J. Krätsmar-Smogrović, *ibid., 27,* 594 (1973).
10 D. Hibdon and J. H. Nelson, *Inorg. Chim. Acta, 7,* 629 (1973).
11 B. N. Figgis and R. S.Nyholm, *J. Chem. Soc.,* 4190 (1958).
12 A. Earnshaw, 'Introduction to Magnetochemistry', Academic Press London, pp. 4–8 (1968).
13 M. Kato, H. B. Jonassen and J. C. Fanning, *Chem. Rev., 64,* 99 (1964).
14 S. Kida, I. V. Quagliano, J. A. Walmsley and S. Y. Tyree, *Spectrochim. Acta, 19,* 189 (1963).
15 N. M. Karayannis, C. M.Mikulski, L. L. Pytlewski and M. M. Labes, *Inorg. Chem., 13,* 1146 (1974).
16 L. Dubicki and R. L. Martin, *Inorg. Chem., 5,* 2203 (1966).
17 M. Melnik, *Coord. Chem. Rev.,* in press.
18 T. F. Felthouse and D. N. Hendriekson, *Inorg. Chem., 17,* 2636 (1978).
19 J. N. van Niekerk and F. R. L. Schoening, *Acta Cryst., 6,* 227 (1953).
20 R. W. Jotham, S. F. A. Kettle and J. A. Marks, *J. Chem. Soc. Dalton Trans.,* 428 (1972).
21 J. Lewis, F. E. Mabbs, L. K. Royston and W. R. Smail, *J. Chem. Soc. A,* 291 (1969).
22 M. Melnik and J. Mroziński, *J. Mol. Struct., 57,* 135 (1979).
23 M. Melnik and J. Mroziński, *ibid., 35,* 133 (1976).
24 J. Lewis, Y. C. Lin, L. K. Royston and R. C. Thompson, *J. Chem. Soc.,* 6464 (1965).