The Magnetic Properties of the Ammonium Chloride Adducts of Copper(II) Fluoroacetate and Copper(II) Bromoacetate

Shuji Emori,* Nobuhide Morishita, and Yoneichiro Muto
Department of Chemistry, Faculty of Science and Egineering, Saga University,
Honjo-machi, Saga 840

(Received November 11, 1986)

Synopsis. Compounds of formula $Cu(XCH_2COO)_2 \cdot nACl$ ($A=NH_4$, CH_3NH_3, $(CH_3)_2NH_2$, $(CH_3)_4N$ and X=F, Br) have been prepared, and characterized by magnetic susceptibility and IR spectroscopy measurements. Factors affecting the magnetic moments of copper(II) salts of monosubstituted alkanoic acids are discussed.

Most copper(II) carboxylates have the familiar bridged copper(II) acetate monohydrate structure,[1,2] and their magnetic properties have been studied extensively to elucidate the factors which determine the magnitude of spin-exchange coupling between copper(II) ions.

According to the Edwards equation with 'hard' base and 'borderline' acid,[3] their stability constants depend primarily to the basicities of the carboxylato ligands. Therefore it seems likely that their magnetic properties relate to the acidities of their parent acids. Actually, in some series of dinuclear copper(II) carboxylates,[4–9] the magnetic moment tends to increase as the pK_a value of the parent acid decreases. This empirical relationship has been explained in terms of the inductive effect of the carboxylato substituents, and is supported by molecular orbital analyses.[10,11]

However, there exist a few exceptions; e.g., the room temperature-magnetic moments of copper(II) haloacetate hydrates[4] vary from 1.32 BM for fluoroacetate to 1.43, 1.54, and 1.49 BM for chloro-, bromo-, and iodoacetates, whereas the pK_a values of the parent acids are 2.66, 2.86, 2.90, and 3.17, respectively. Since the magnitude of the spin-exchange coupling in these hydrates may be affected by other factors, such as the intermolecular hydrogen bonds between the water molecules in the axial positions and the oxygen atoms of the carboxylato groups,[1,2] it is preferable to accumulate the magnetic data and to examine the general tendency for the compounds with the same axial ligands. We have prepared various ammonium chloride adducts of copper(II) fluoroacetate and copper(II) bromoacetate, and compared their magnetic data with those of other dinuclear copper(II) salts of monosubstituted alkanoic acids with chloride ions in the axial positions.

Compounds with a stoichiometry of $Cu(XCH_2COO)_2 \cdot nACl$, where X=F or Br and $A=NH_4$, CH_3NH_3, $(CH_3)_2NH_2$, or $(CH_3)_4N$, were prepared by a previously described method for the corresponding chloroacetates.[8] These compounds were obtained as green crystals.

The effective magnetic moments of these compounds (Table 1) were evaluated from the room-temperature magnetic susceptibilities, corrected for the diamagnetic contribution of the constituent atoms using Pascal constants[12] with a value of $N\alpha=60\times10^{-6}$ emu mol^{-1} (1 emu$=4\pi\times10^{-6}$ m^3).

For the methylammonium chloride adducts of copper(II) fluoroacetate and copper(II) bromoacetate, the temperature dependence of their magnetic susceptibilities was measured in the temperature range of 80—300 K to confirm their dinuclear structures. The results agreed well with the Bleaney-Bowers equation,[13] using the following parameters: $g=2.17$ and $2J=-359$ cm^{-1} for the fluoroacetate and $g=2.19$ and $2J=-300$ cm^{-1} for the bromoacetate, respectively. The IR spectra of the solid compounds show the characteristic bands in the ranges 1450—1460 and 1625—1660 cm^{-1} connected with symmetric and unsymmetric COO stretching vibrations of the carboxyl groups.[14]

Table 1. Analytical Data and Effective Magnetic Moments at 20 °C

Compound	Found (Calcd)/%					μ_{eff}/BM
	Cu	Cl	C	H	N	
$Cu(BrCH_2COO)_2 \cdot 3/2NH_4Cl$	15.07 (15.14)	12.33 (12.67)	11.45 (11.45)	2.46 (2.40)	5.01 (5.01)	1.40
$Cu(BrCH_2COO)_2 \cdot CH_3NH_3Cl$	15.80 (15.62)	8.85 (8.71)	14.84 (14.76)	2.53 (2.48)	3.26 (3.44)	1.41
$Cu(BrCH_2COO)_2 \cdot (CH_3)_2NH_2Cl$	15.02 (15.10)	8.33 (8.42)	17.09 (17.12)	2.81 (2.87)	3.09 (3.33)	1.43
$Cu(FCH_2COO)_2 \cdot 2NH_4Cl$	19.59 (19.58)	21.77 (21.84)	14.77 (14.80)	3.67 (3.73)	8.44 (8.63)	1.29
$Cu(FCH_2COO)_2 \cdot CH_3NH_3Cl$	21.59 (22.29)	12.34 (12.42)	20.77 (21.06)	3.65 (3.53)	4.95 (4.91)	1.27
$Cu(FCH_2COO)_2 \cdot (CH_3)_2NH_2Cl$	20.90 (21.24)	12.42 (11.85)	23.88 (24.09)	3.96 (4.04)	4.59 (4.68)	1.26
$Cu(FCH_2COO)_2 \cdot (CH_3)_4NCl$	19.88 (19.42)	10.81 (10.83)	29.09 (29.37)	4.92 (4.93)	4.18 (4.28)	1.28

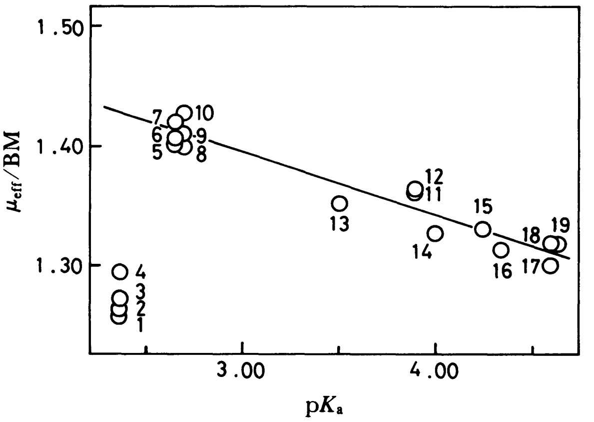

Fig. 1. The magnetic monent at 20 °C plotted against the pK_a value of the parent carboxylic acid for the copper(II) salts of monosubstituted alkanoic acids with chloride ions in the axial positions; the fluoroacetates (**1**—**4**), the chloroacetates (**5**—**7**),[8] the bromoacetates (**8**—**10**), the 3-chloropropionates (**11**, **12**),[15] the ω-ammonioalkanoates (**13**—**16**),[9] the butyrates (**17**, **18**),[15] and the propionate (**19**).[15]

The magnetic and IR spectral data indicate that the present compounds have the bridged dinuclear structure similar to copper(II) acetate monohydrate.[1,2]

In order to examine the correlation between the room-temperature magnetic moment of dinuclear copper(II) carboxyate and the pK_a value of its parent acid, the data for the present compounds, together with those of other dinuclear copper(II) salts of monosubstituted alkanoic acids with chloride ions in the axial positions, are plotted in Fig. 1. The magnetic moments of the chloroacetates[8] were corrected for the difference of room temperature by use of the Bleaney-Bowers equation[13] with $g=2.15$. As can be seen from Fig. 1, the magnetic moments of the fluoroacetates are much smaller than those expected from the pK_a value of fluoroacetic acid. However, except for fluoroacetates, there is a linear relation between these magnetic moments and the pK_a values of the parent acids in the range of those measurements. The best line has a slope of −0.052 BM and the intercept of 1.31$_8$ BM at pK_a=4.56 (the pK_a value of acetic acid). The variation of single-triplet separation values (e.g.,$-2J=278$, 300, and 320 cm^{-1} for the dimethylammonium chloride adduct of copper(II) chloroacetate,[8] the methylammonium chloride adduct of copper(II) bromoacetate, and the copper(II) chloride compound with 4-aminobutyric acid,[9] respectively) is consistent with this general trend, and agrees well with the molecular orbital analyses.[10,11]

It is still unclear why the magnetic data for the fluoroacetates deviate from the general trend. Porter and Doedens have pointed out that there is an apparent relationship between the singlet-triplet separation values and the group polarizabilities of the carboxlato substituents.[16] However the ordering for the above-mentioned $-2J$ values is contrary to the proposal that lower $-2J$ values are associated with increasing group polarizabilities. From the study of ^{19}F NMR in the series of fluorochloromethanes,[17] it is known that the fluorine nuclei are shielded in the opposite manner from that predicted by electronegativity considerations. In order to explain these anomalous chemical shifts, Gutowsky and Hoffman have suggested the use of higher energy orbitals in the hybridized orbitals of atoms attached to fluorine atoms.[18] This idea may explain the small magnetic moment observed for the present fluoroacetates, because the higher energy orbitals interact more strongly with the electronic system of neighboring carboxylato group, through which spin-exchange coupling between copper(II) ions operates. However, the elucidation of cause and mechanism depends upon future multilateral studies.

References

1) J. N. van Niekerk and F. R. L. Schoening, *Acta Crystallogr.*, **6**, 227 (1953).

2) G. M. Brown and R. Chidambaram, *Acta Crystallogr.*, **B29**, 2393 (1973).

3) J. O. Edwards and R. G. Pearson, *J. Am. Chem. Soc.*, **84**, 16 (1961).

4) M. Melnik, *Coord. Chem. Rev.*, **36**, 1 (1981).

5) R. W. Jotham, S. F. A. Kettle, and J. A. Marks, *J. Chem. Soc., Dalton Trans.*, **1972**, 428.

6) D. Hibdon and J. H. Nelson, *Inorg. Chim. Acta*, **7**, 629 (1973).

7) Y. Muto, T. Tokii, K. Chijiwa, and M. Kato, *Bull. Chem. Soc. Jpn.*, **57**, 1008 (1984).

8) S. Emori, N. Haramaki, and Y. Muto, *Bull. Chem. Soc. Jpn.*, **58**, 761 (1985).

9) S. Emori, T. Noguchi, and Y. Muto, *Bull. Chem. Soc. Jpn.*, **58**, 2733 (1985).

10) P. J. Hay, J. C. Thibeaul, and R. Hoffmann, *J. Am. Chem. Soc.*, **97** 4884 (1975).

11) P. de Loth, P. Cassoux, J. P. Daudey, and J. P. Malriew, *J. Am. Chem. Soc.*, **103**, 4007 (1981).

12) G. Foex, "Constants Sélectionées, Diamagnétisme et Paramagnétisme," Masson, Paris (1957).

13) J. Lewis, Y. C. Lin, L. K. Royston, and R. C. Thomson, *J. Chem. Soc.*, **1965**, 428.

14) S. Yamada, H. R. Nakamura, and R. Tsuchida, *Bull. Chem. Soc. Jpn.*, **31**, 303 (1958).

15) S. Emori and Y. Muto, unpublished data. The magnetic moments of $Cu(ClCH_2CH_2COO)_2 \cdot CH_3NH_3Cl$, $Cu(ClCH_2CH_2COO)_2 \cdot C_4H_9NH_3Cl$, $Cu(CH_3CH_2CH_2COO)_2 \cdot 2(CH_3)_2NH_2Cl$, $Cu(CH_3CH_2CH_2COO)_2 \cdot CH_3NH_3Cl \cdot H_2O$, and $Cu(CH_3CH_2COO)_2 \cdot (CH_3)_2NH_2Cl \cdot H_2O$ are 1.38, 1.37, 1.30, 1.32, 1.32 BM, respectively, at 20 °C.

16) L. C. Porter and R. J. Doedens, *Inorg. Chem.*, **23**, 997 (1984).

17) L. H. Meyer and H. S. Gutowsky, *J. Phys. Chem.*, **57**, 481 (1953).

18) H. S. Gutowsky and C. J. Hoffman, *J. Chem. Phys.*, **19**, 1259 (1951).