Magnetic Susceptibility of Copper(II) Propionate β-Picoline

W. E. MARSH, G. O. CARLISLE and M. V. HANSON

The Killgore Research Center, West Texas State University, Canyon, Texas 79016, U.S.A.

Antiferromagnetic exchange in copper(II) carboxylates and associated compounds has recently excited extensive experimental and theoretical work. Related aspects of this problem have been considered and partially evaluated in several recent reviews [1–4]. The explanation for the unusual magnetic properties in copper complexes of n-alkanoates and their monoadducts has been proposed, and widely accepted, in terms of exchange coupling between magnetically isolated pairs of copper(II) ions [5, 6]. Considerable discussion has focused upon the coupling mechanism. Although diversified theories have been proposed, a direct copper–copper interaction [7–9] or super-exchange via the bridging carboxylate ligands [4, 10, 11] has been widely accepted.

The crystal structure of copper(II) propionate β-picoline has been recently resolved [12] and has been found to be similar to that of copper acetate monohydrate having two copper ions bridged by four propionate ligands. The copper–copper distance was determined to be 2.633 Å.

We have determined the magnetic susceptibility over the temperature range of 78–294 °K, and the data obtained provide quantitative parameters which characterize the intensity of spin–spin coupling. We have also related these parameters to those of similar copper carboxylates, and have observed certain general trends between them.

Experimental

Blue–green crystals of the compound were prepared according to the reported procedure [13] and only pure polycrystalline samples were used for the magnetic susceptibility studies. Analysis of the compound yielded the following percentages: Calculated for $Cu(C_3H_5O_2)_2 \cdot C_6H_7N$: 47.60%, C, 5.66% H, 4.63% N. Found: 47.62% C, 5.70% H, 4.65% N. The magnetic susceptibility was determined as a function of temperature using a Faraday system [14]. Mercury tetrathiocyanatocobalt(II) was used as the standard [15] and appropriate diamagnetic corrections were estimated from Pascal's constants [16].

TABLE I. Experimental and Calculated Magnetic Data for Copper(II) Propionate β-picoline.

Temp. (°K)	$10^6 \chi_M$(exp.) (cgs units)	$10^6 \chi_M$(calc.) (cgs units)	μ_{eff}(exp.) (B.M.)	μ_{eff}(calc.) (B.M.)
294	824	807	1.40	1.38
275	815	796	1.34	1.33
252	791	773	1.27	1.25
239	758	755	1.21	1.21
228	733	735	1.16	1.16
217	725	711	1.13	1.12
209	700	691	1.09	1.08
196	650	654	1.01	1.02
185	609	617	0.95	0.96
168	543	551	0.86	0.86
163	526	529	0.83	0.83
159	510	511	0.81	0.81
150	469	470	0.75	0 75
143	427	436	0.70	0.71
130	337	372	0.59	0.62
113	287	292	0.51	0 52
90	213	204	0.39	0.39
78	163	174	0.32	0.32

Results and Discussions

The experimental and calculated magnetic data are given in Table I. Effective magnetic moments were calculated using the equation, $\mu_{eff} = 2.84 (\chi_M \cdot T)^{1/2}$.

The susceptibility was calculated using the Van Vleck equation for exchange coupled dimers [17]. FORTRAN IV programs were written and employed to interpret the data with a DEC System 10 computer. The g-value of 2.15 was obtained from the EPR spectra of the complex dissolved in β-picoline and was used as a constant in the least squares fitting process. The best fit value of 2J was found to be -364 cm^{-1} with a standard deviation of 12.8×10^{-6} cgs units between experimental and calculated magnetic susceptibilities.

The electron spin coupling constants for copper propionate β-picoline and related compounds are given in Table II. An apparent trend is noticeable for the magnitude of |2J| to increase as either the terminal or bridging ligands become stronger electron donors. Thus, the |2J| value tends to increase according to the series of terminal groups: aniline < water ≤ anhydrous < pyridine < picolines ~ SCN⁻ ~ ethanol < dioxane. The $-2J$ value, 364 cm^{-1}, found here for copper(II) propionate β-picoline follows this trend.

Another important trend has been shown to exist between the pK_a of the bridging acid and the value of $-2J$ [1, 4]. Since the pK_a of an acid can be con-

TABLE II. Electron Spin Coupling Constants for Copper Propionate and Copper Acetate Complexes.

Compound	$-2J\,(\text{cm}^{-1})$	Reference
$Cu(CH_3CH_2COO)_2 \cdot H_2O$	300	18
$Cu(CH_3CH_2COO)_2$	315	4
$Cu(CH_3CH_2COO)_2 \cdot \beta$-picoline	364	this work
$Cu(CH_3CH_2COO)_2 \cdot 1/2$dioxane	386	21
$Cu(CH_3COO)_2 \cdot H_2O$	286	7
$Cu(CH_3COO)_2 \cdot$	302	7
$Cu(CH_3COO)_2 \cdot \beta$-picoline	318	4
$Cu(CH_3COO)_2 \cdot$dioxane	358	20

sidered as a measure of its electron donating power, then the $-2J$ values may also be expected to vary with different bridging acids. The pK_a of acetic acid is 4.75 and for propionic acid, the pK_a is 4.87. Thus, it may be concluded that the $-2J$ values for the copper propionate complexes would be higher than those for the corresponding copper acetate complexes, and this is shown to be true in Table II.

As an example of the trend for terminal ligands, the $|2J|$ value for copper(II) propionate β-picoline is greater than the $|2J|$ value of 350 cm^{-1} for the pyridine complex [19]. Since the methyl group is electron donating, β-picoline will provide greater electronic charge to copper than pyridine. Thus, the methyl group apparently increases the magnitude of spin—spin coupling. However, other factors, such as structural parameters, may also affect the degree of the magnetic interaction. It is clear that additional magnetic studies on a greater variety of dimeric copper carboxylates of known molecular structure be performed in order to accurately determine the effect of terminal ligands on the 2J coupling constant.

References

1 M. Kato, H. B. Jonassen and J. C. Fanning, *Chem. Rev.*, *64*, 99 (1964).

2 C. Oldham, *Progr. Inorg. Chem.*, *10*, 223 (1968).

3 W. E. Hatfield and R. Wyman, *Transition Metal Chem.*, *5*, 47 (1969).

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

5 B. Bleaney and K. D. Bowers, *Proc. Roy. Soc.*, *214A*, 451 (1952).

6 B. Bleaney and K. D Bowers, *Phil. Mag.*, *43*, 372 (1952).

7 B. N. Figgis and R. L. Martin, *J. Chem. Soc.*, 3837 (1956).

8 R. L. Martin, "New Pathways in Inorganic Chemistry", pp. 175 - 231, University Press, Cambridge (1968).

9 R. W. Jotham and S. F. A. Kettle, *Chem. Comm.*, 258 (1969).

10 G. F. Kokoszka, M. Linzer and G. Gordon, *Inorg. Chem.*, *7*, 1730 (1968).

11 K. E. Hyde, G. Gordon and G. F. Kokoszka, *J. Inorg. Nucl. Chem.*, *30*, 2155 (1969).

12 M. M. Borel and A. Leclair, *J. Inorg. Nucl. Chem.*, *38*, 235 (1976).

13 M. M. Borel, A. Busnot and A. Leclair, *Bull. Soc. Chim. Fr.*, *11*, 2455 (1975).

14 P. E. Rush, J. D. Oliver, G. D. Simpson and G. O. Carlisle, *J. Inorg. Nucl. Chem.*, *37*, 1393 (1975).

15 B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 4190 (1958).

16 J. Lewis and R. C. Wilkins, "Modern Coordination Chemistry', p. 403, Interscience, New York (1960).

17 J. H. Van Vleck, "Theory of Electric and Magnetic Susceptibilities", Chapter 9, Oxford University Press, London and New York (1932).

18 R. L. Martin and H. Waterman, *J. Chem. Soc.*, 2545 (1957).

19 M. V. Hanson, G. O. Carlisle and W. E. Marsh, *J. Mol. Struct.*, in press.

20 R. L. Martin and H. Waterman, *J. Chem. Soc.*, 2960 (1959).

21 M. V. Hanson and G. O. Carlisle, *J. Inorg. Nucl. Chem.*, in press.