Inorg. Chem. **1984**, *23*, 997–999

Articles

Contribution from the Department of Chemistry,
University of California, Irvine, California 92717

Preparation, Structure, and Magnetic Properties of Dimeric Copper(II) Tribromoacetate Adducts. Influence of the Substituent R on the Magnetic Behavior of the Series of Dimers $[Cu(O_2CR)_2L]_2$ (R = H, CH_3, CF_3, CCl_3, CBr_3)

LEIGH C. PORTER and ROBERT J. DOEDENS*

Received July 25, 1983

Dimeric monoadducts of copper(II) tribromoacetate with 2-chloropyridine, 2-methylpyridine, and quinoline have been prepared and characterized. The magnitude of the exchange coupling constant $2J$ has been determined by fitting magnetic susceptibility data to the Bleaney–Bowers equation. The $2J$ values obtained, ranging from -173 to $-180\ cm^{-1}$, are smaller than those found in a series of related adducts. This observation is consistent with a correlation noted earlier between the magnitude of $2J$ and the polarizability of the group R. The dimeric structure of the 2-chloropyridine adduct was confirmed by a crystal structure determination. Crystals of this compound are triclinic, space group $P\bar{1}$, with $a = 10.452\ (4)$ Å, $b = 9.767\ (4)$ Å, $c = 10.697\ (4)$ Å, $\alpha = 69.87\ (3)°$, $\beta = 116.44\ (3)°$, and $\gamma = 98.57\ (3)°$. Full-matrix least-squares refinement, based upon 2285 non-zero intensity data, converged to a conventional R factor of 0.070. The centrosymmetric dimer has the familiar copper acetate structure with a Cu–Cu distance of 2.766 (3) Å.

Introduction

The dimeric copper(II) carboxylates and their adducts, $[Cu(O_2CR)_2L]_2$, have played a major role in the development of the concept of exchange interaction between paramagnetic centers in discrete molecules.[1-5] Despite a vast number of experimental and theoretical studies, our understanding of the factors determining the magnitude of the copper–copper coupling in these systems is still imperfect. Even the empirical question of how properties of the groups R and L influence the magnitude of the magnetic interaction, as measured by the coupling constant $2J$, remains incompletely answered. It is clear that the substituent R has a greater effect upon the value of $2J$ than does the addend L; however, attempts to correlate variations in $2J$ with specific properties of R have not been particularly successful.

The present study is based upon an apparent relationship between $2J$ and the polarizability of the group R.[6] This relationship seems to hold for the series of R groups $H < CF_3 \sim CH_3 < CCl_3$, where the ordering shown is that of less negative $2J$ values and also of increasing group polarizabilities of R. Although this empirical correlation applies only to a limited set of R groups, the range of $2J$ values spanned covers almost the entire spectrum of interactions observed in dimeric copper(II) carboxylate complexes. The synthetic, magnetic, and structural studies of copper(II) tribromoacetates reported herein were carried out in order to extend the range of R-group polarizabilities for which magnetic data are available on well-characterized complexes and thereby to further test the suggested relationship.

Experimental Section

Preparation of the Complexes. Bis(tribromoacetato)copper(II) was prepared by adding solid cupric carbonate to an aqueous solution containing a slight excess of tribromoacetic acid. The light blue solid obtained after removal of solvent was dried over P_2O_5. Because the copper(II) tribromoacetate adducts of quinoline, 2-methylpyridine, and 2-chloropyridine were insoluble in most solvents in which they did not decompose, it was necessary to devise a procedure for obtaining a pure crystalline sample directly from the reaction solution. This was accomplished by dropwise addition of the neat ligand to an excess of the anhydrous tribromoacetate in diethyl ether. When the resulting solution was allowed to stand overnight, green crystals of the monoadducts were obtained. Purple crystals, presumably containing the monomeric bisadducts, were also obtained if the solution was allowed to stand for too long before filtration. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tn. Anal. Calcd for $C_{10}H_7NO_4Br_6Cu$ (2-methylpyridine adduct): C, 16.04; H, 0.94; N, 1.87; O, 8.56; Br, 64.10; Cu, 8.50. Found: C, 16.0; H, 1.0; N, 2.0; O, 8.5; Br, 64.3; Cu, 8.3. Calcd for $C_9H_4NO_4ClBr_6Cu$ (2-chloropyridine adduct): C, 14.05; H, 0.52; N, 1.82; O, 8.33; Br, 62.38; Cu, 8.26. Found: C, 14.0; H, 0.5; N, 1.6; O, 8.0; Br, 62.4; Cu, 8.0. Calcd for $C_{13}H_7NO_4Br_6Cu$ (quinoline adduct): C, 19.90; H, 0.89; N, 1.79; O, 8.16; Br, 61.15; Cu, 8.11. Found: C, 18.9; H, 0.9; N, 1.6; O, 7.6; Br, 61.3, Cu 8.1.

Table I. Crystal Data

formula	$Cu_2C_{18}H_8N_2O_8Cl_2Br_{12}$	fw	1537.11
a, Å	10.452 (4)	vol, Å^3	918.1 (6)
b, Å	9.767 (4)	*Z*	1
c, Å	10.697 (4)	*d*(obsd), g cm^{-3}	2.77
α, deg	69.87 (3)	*d*(calcd), g cm^{-3}	2.78
β, deg	116.44 (3)	space group	$P\bar{1}$
γ, deg	98.57 (3)	μ(Mo Kα), cm^{-1}	151.6

Crystal Structure of the 2-Chloropyridine Adduct. The general experimental methods of the crystal structure analysis have been described.[7] Crystal data are summarized in Table I. Intensity data were collected by the θ–2θ scan technique and corrected for absorption. Additional experimental details are included with the supplementary material. Anisotropic refinement of all non-hydrogen atoms converged to final conventional discrepancy factors of $R1 = 0.070$ and $R2 = 0.084$.[8]

---

(1) Kato, M.; Jonassen, H. B.; Fanning, J. C. *Chem. Rev.* **1964**, *64*, 99–128 and references therein.

(2) Martin, R. L. In "New Pathways in Inorganic Chemistry"; Ebsworth, E. A. V., Maddock, A. G., Sharpe, A. G., Eds.; University Press: Cambridge, England, 1968; pp 175–231 and references therein.

(3) Sinn, E. *Coord. Chem. Rev.* **1970**, *5*, 313–347 and references therein.

(4) Jotham, R. W.; Kettle, S. F. A.; Marks, J. A. *J. Chem. Soc., Dalton Trans.* **1972**, 428–438 and references therein.

(5) Doedens, R. J. *Prog. Inorg. Chem.* **1976**, *21*, 209–231 and references therein.

(6) Moreland, J. A.; Doedens, R. J. *Inorg. Chem.* **1978**, *17*, 674–679.

(7) Sams, D. B.; Doedens, R. J. *Inorg. Chem.* **1979**, *18*, 153–156.

(8) Computer programs used were those of a locally modified version of the UCLA Crystallographic Computing Package (Strouse, C. E., personal communication). All computations were carried out on the local VAX 11/780 system.

(9) Goodgame, D. M. L.; Hill, N. J.; Marsham, D. F.; Skapski, A. C.; Smart, M. L.; Troughton, P. G. H. *J. Chem. Soc., Chem, Commun.* **1969**, 629–630.

(10) Moreland, J. A.; Doedens, R. J. *J. Am. Chem. Soc.* **1975**, *97*, 508–513.

(11) Figgis, B. N.; Martin, R. L. *J. Chem. Soc.* **1956**, 3837–3846.

0020-1669/84/1323-0997$01.50/0

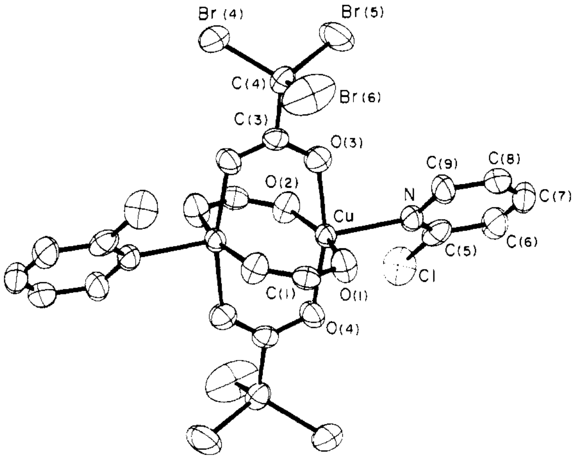

Figure 1. View of the molecular structure of the 2-chloropyridine adduct of copper(II) tribromoacetate. Thermal ellipsoids are drawn at the 50% probability level. For clarity, the CBr_3 groups bound to C(1) and its centrosymmetric equivalent have been omitted.

Table II. Positional Parameters of Non-Hydrogen Atoms

atom	*x*	*y*	*z*
Cu	0.4809 (2)	0.0354 (2)	0.1051 (2)
Br(1)	0.0332 (2)	0.2819 (2)	−0.2470 (2)
Br(2)	0.0535 (2)	0.1875 (3)	−0.4886 (2)
Br(3)	0.2621 (2)	0.4271 (2)	−0.3685 (2)
Br(4)	0.7336 (3)	0.4396 (2)	−0.2553 (2)
Br(5)	0.6843 (3)	0.5124 (2)	−0.0197 (2)
Br(6)	0.9273 (2)	0.2887 (3)	0.0756 (3)
Cl	0.2109 (4)	0.0532 (5)	0.1967 (5)
O(1)	0.6596 (11)	−0.0771 (11)	0.2420 (10)
O(2)	0.3120 (10)	0.1310 (10)	−0.0695 (10)
O(3)	0.5964 (10)	0.2026 (9)	0.0463 (10)
O(4)	0.3797 (10)	−0.1521 (9)	0.1280 (10)
N	0.4741 (13)	0.1209 (11)	0.2649 (11)
C(1)	0.2802 (13)	0.1407 (14)	−0.1991 (15)
C(2)	0.1625 (14)	0.2518 (15)	−0.3174 (14)
C(3)	0.6415 (13)	0.2260 (12)	−0.0476 (13)
C(4)	0.7380 (14)	0.3615 (14)	−0.0640 (13)
C(5)	0.3666 (15)	0.1199 (14)	0.2946 (15)
C(6)	0.3769 (22)	0.1687 (16)	0.4095 (18)
C(7)	0.5073 (23)	0.2170 (17)	0.4902 (17)
C(8)	0.6196 (22)	0.2222 (15)	0.4570 (16)
C(9)	0.6144 (21)	0.1771 (15)	0.3499 (15)

Magnetic Susceptibility Measurements. Magnetic susceptibilities were measured between 10 and 300 K by use of an SHE superconducting SQUID magnetometer at a field strength of 10 kG. The data were corrected for the magnetization of the sample holder. Pascal's constants were used to estimate the correction for diamagnetism of the sample. The corrected magnetic data were fitted to the Bleaney–Bowers equation by a least-squares process. The function minimized was $\Sigma[(\chi_{\rm obsd} - \chi_{\rm calcd})/\chi_{\rm obsd}]^2$. Because the low-temperature susceptibilities suggested the presence of a small amount of paramagnetic impurity in each sample, only data with $T \geq 60$ K were used in the fitting procedure. Effective magnetic moments were calculated from the relationship $\mu_{\rm eff} = [(\chi'_{\rm M} - N\alpha)T]^{1/2}$, where $N\alpha$ was taken as 60×10^{-6} emu/copper atom.

Results

The three copper(II) tribromoacetate monoadducts $Cu(O_2CCBr_3)_2L$ (L = 2-chloropyridine, 2-methylpyridine, quinoline) have been prepared. In order to definitively establish the structure of one (and, by implication, all) of these adducts, the crystal structure of the 2-chloropyridine adduct was determined. As expected, it has the well-known bridged dimeric copper(II) acetate structure. The unit cell contains a single centrosymmetric dimer. A view of the structure is shown in Figure 1, and coordinates of non-hydrogen atoms are listed in Table II. The Cu–Cu distance is 2.766 (3) Å. All other details of the structure have been deposited as supplementary material.

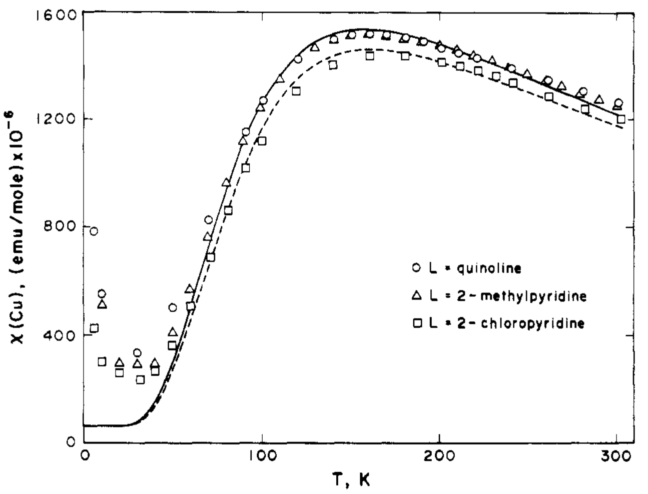

Figure 2. Magnetic susceptibility curves. The solid and dashed lines represent the calculated susceptibilities for the 2-methylpyridine and 2-chloropyridine adducts, respectively. The calculated curve for the quinoline adduct is not shown. Data for $T < 60$ K were not included in the fitting process.

The fitting of the Bleaney–Bowers equation to the observed magnetic susceptibility data yielded the following best-fit parameters: for L = 2-chloropyridine, $g = 2.19$ and $2J = -180$ cm^{-1}; for L = 2-methylpyridine, $g = 2.22$ and $2J = -175$ cm^{-1}; for L = quinoline, $g = 2.21$ and $2J = -173$ cm^{-1}. For each adduct, the mean deviation between observed and calculated susceptibilities is less than 2%. The observed magnetic data and representative calculated curves are shown in Figure 2. Complete tables of magnetic data are available as supplementary material.

Discussion

Three new copper(II) tribromoacetate monoadducts have been prepared and characterized. A crystal structure analysis has shown the 2-chloropyridine adduct to have the well-known dimeric copper(II) acetate monohydrate structure; there is little doubt that this is the structure of all three adducts. The three ligands 2-chloropyridine, 2-methylpyridine, and quinoline have all been shown to promote the formation of dimers for other copper(II) carboxylates;[5] however, this is the first time dimers with all three of these ligands have been characterized for the same carboxylate. The structure of the 2-chloropyridine adduct displays no unusual features, and we will not discuss it further, except to note that its Cu···Cu distance of 2.766 (3) Å is near the midpoint of the range observed for copper(II) carboxylate dimers and is identical with that found in the 2-chloropyridine adduct of copper(II) trichloroacetate.[6]

The observed magnetic susceptibility data for $60 < T < 300$ K are adequately represented by the Bleaney–Bowers equation. Below 60 K, the data deviate substantially from the dimer model, presumably because of the presence of paramagnetic impurities. We made no attempt to fit these low-temperature data to a calculated model, except to note that impurity levels of the order of 1% would be sufficient to account for the observed low-temperature susceptibilities. This level of impurity would be analytically undetectable and would have only a small effect on the magnetic properties at higher temperatures.

As is evident from Figure 2, the magnetic susceptibility curves for the three adducts are very similar, each displaying a broad maximum at ca. 160 K. This similarity is reflected in the best-fit $2J$ values of −173, −175, and −180 cm^{-1} for the adducts with L = quinoline, 2-methylpyridine, and 2-chloropyridine, respectively. The small range spanned by these three $2J$ values is consistent with the observation[5] that the properties of the bridging carboxylate group have a much greater in-

Table III. Magnetic Properties of Selected Dimers, $[Cu(O_2CR)_2L]_2$[a]

R	L	α[b]	$-2J$, cm^{-1}	ref
H	NCS^-	0.42	485	9
CF_3	quinoline	2.07	310	10
CH_3	H_2O	2.19	284	11
CCl_3	2-Cl-py	7.77	217	6
CBr_3	2-Cl-py	10.95	180	this work

[a] The dimers chosen for this table were those for a given R for which the best combination of crystallographic and magnetic data are available. Inclusion of dimers with other addends L, where available, would not alter the ordering shown. [b] The tabulated values are group polarizabilities, evaluated from the atomic polarizabilities given in: Ketelaar, J. A. A. "Chemical Constitution"; Elsevier: Amsterdam, 1958; p 91.

fluence on the magnetic behavior of copper(II) carboxylate dimers than does the nature of the addend L. This provides further support for the validity of comparing 2*J* values for dimers with different axial ligands.

The principal result of this study is that the three dimers with R = CBr_3 have, by a significant margin, the smallest interaction (i.e., the least negative 2*J* values) of the series of dimers with R = H, methyl, or trihalomethyl. Data for a representative set of such dimers are tabulated in Table III. From these data it is evident that the ordering of 2*J* values is identical with the ordering of group polarizabilities of the substituents R. By providing an extreme point on the polarizability scale, the data for the tribromoacetate adducts significantly strengthen the observed relationship. Although this empirical correlation works remarkably well for one particular series of closely related groups, it does not appear to extend to other, more complicated, substituents. Thus, for example, dimeric adducts of the higher copper(II) alkanoates have 2*J* values of comparable, or slightly greater, magnitude than the acetate adducts.[12] In view of recent theoretical results, which describe the coupling in these dimers as the resultant of several different modes of interaction,[13] it is not surprising that meaningful correlations of 2*J* with ligand properties are found only for sets of dimers in which the bridging carboxylate ligands are closely related.

At this time, the apparent relationship between 2*J* and ligand polarizability for this series of dimers must be regarded as strictly an empirical one, whose fundamental significance (if any) is not clear. However, because of the scarcity of good structure/magnetism correlations for these dimers, it may well be of use as a calibration point for future theoretical efforts. It is certainly more reasonable that 2*J* should be related to a free-ligand property like polarizability than to an aqueous solution property such as the pK_a of the parent acid, which has been the basis for some earlier proposed correlations, including one for the haloacetates.[1]

Acknowledgment. We are grateful to Professor Christopher Reed and Dr. Peter Boyd for their help with the magnetic measurements. The purchase of the SQUID magnetometer at the University of Southern California was made possible by a grant from the National Science Foundation.

Registry No. $[Cu(O_2CCBr_3)_2L]_2$ (L = 2-chloropyridine), 88801-76-7; $[Cu(O_2CCBr_3)_2L]_2$ (L = 2-methylpyridine), 88801-75-6; $[Cu(O_2CCBr_3)_2L]$ (L = quinoline), 88801-77-8.

Supplementary Material Available: Tables of experimental parameters, observed and calculated structure factors, anisotropic thermal parameters, positional parameters of hydrogen atoms, bond distances, bond angles, and magnetic susceptibility data (18 pages). Ordering information is given on any current masthead page.

---

(12) Martin, R. L.; Waterman, H. *J. Chem. Soc.* **1957**, 2545-2551.

(13) de Loth, P.; Cassoux, P.; Daudey, T. P.; Malrieu, J. P. *J. Am. Chem. Soc.* **1981**, *103*, 4007-4016.

Contribution from the Departments of Chemistry, Columbia College, Columbia, South Carolina 29203,
Florida A&M University, Tallahassee, Florida 32307, and University of South Carolina, Columbia, South Carolina 29208

Solution and Solid-State ^{113}Cd NMR of Cd(α,α'-bpy)$_2X_2$ (X = Cl^-, Br^-, NCS^-, NO_3^-, H_2O) and Crystal Structures of the Nitrate (Monohydrate) and the Isothiocyanate Derivatives

P. F. RODESILER,[†] R. W. TURNER,[‡] N. G. CHARLES,[§] E. A. H. GRIFFITH,[§] and E. L. AMMA*[§]

Received March 17, 1983

The crystal structures of bis(α,α'-bipyridyl)cadmium(II) nitrate hemihydrate (A) and bis(isothiocyanato)bis(bipyridyl)-cadmium(II) (B) have been determined. The structure of A consists of two crystallographically and chemically different Cd^{2+} species separated from each other by ordinary van der Waals distances. Each Cd is approximately octahedrally coordinated, with four N and two O donor ligands. However, the coordinated oxygens for Cd(1) are from a nitrate oxygen and a water of hydration oxygen while for Cd(2) both oxygen atoms are from nitrate oxygen atoms. The CP/MAS solid-state ^{113}Cd NMR of A consists of two resonances at +51 and +123 ppm deshielded from the usual $Cd(ClO_4)_2$ standard. The D_2O solution of this compound is a single resonance at +172, uniquely identifying all three signals as corresponding to water of hydration of 0, 1, and 2, respectively, bound to Cd. The crystal structure of B consists of approximately octahedral Cd^{2+}, with six N donors separated by ordinary van der Waals distances. The CP/MAS ^{113}Cd NMR signal of B is at +216 ppm. The analogous chloride and bromide salts have CP/MAS ^{113}Cd NMR signals +250 and +185 ppm. A: $a = 14.372$ (1) Å, $b = 35.134$ (2) Å, $c = 17.174$ (4) Å, $D_x = 1.74$ g/cm^3, $D_M = 1.93$ g/cm^3, $Z = 16$, *Pcab*, $\mu = 10.63$ cm^{-1}, maximum–minimum transmittance factor = 0.887–0.430, NO = 3636, NV = 604, $R_F = 0.066$. B: $a = 16.274$ (6) Å, $b = 16.75$ (1) Å, $c = 16.136$ (7) Å, $D_x = 1.63$ g/cm^3, $D_M = 1.62$ (2) g/cm^3, $Z = 8$, *Pcab*, $\mu = 11.93$ cm^{-1}, maximum–minimum transmittance factor = 0.899–0.876, NO = 2331, NV = 280, $R_F = 0.032$.

Introduction

^{113}Cd NMR has recently shown itself to be a useful tool as a probe of the geometric and electronic environment of the Cd nucleus in a wide variety of compounds ranging from inorganic species through organometallics to biological macromolecules.[1-42] The potential of ^{113}Cd NMR has been further

---

[†] Columbia College.
[‡] Florida A&M University.
[§] University of South Carolina.

(1) Maciel, G. E.; Borzo, M. *J. Chem. Soc., Chem. Commun.* **1973**, 394.

(2) Kostelnik, R. J.; Bothner-By, A. A. *J. Magn. Reson.* **1974**, *14*, 141-151.

(3) Cardin, A. D.; Ellis, P. D.; Odom, J. D.; Howard, J. W., Jr. *J. Am. Chem. Soc.* **1975**, *97*, 1672-1679.

0020-1669/84/1323-0999$01.50/0