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Structure and Magnetism of Bis(2-chloropyridine)tetrakis(μ-trichloroacetato(*O,O'*))-dicopper(II). Influence of the Bridging Ligand on Magnetic Properties of Dimeric Copper(II) Carboxylate Adducts

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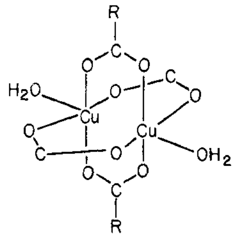
The 2-chloropyridine adduct of copper(II) trichloroacetate has been subjected to a crystal structure analysis and to magnetic susceptibility measurements for T = 82.5–310 K. Crystals of $[Cu(O_2CCCl_3)_2(2\text{-}ClC_5H_4N)]_2$ are triclinic, space group $P\bar{1}$, with one dimeric molecule in a cell of dimensions a = 9.316 (9) Å, b = 10.707 (10) Å, c = 10.493 (11) Å, α = 57.22 (2)°, β = 107.02 (3)°, and γ = 100.01 (3)°. The structure determination was based upon 2165 independent nonzero reflection data; least-squares refinement converged to a final conventional R factor of 0.054. The dimeric molecules have the familiar bridged copper(II) acetate structure, with a long Cu–Cu distance of 2.766 (3) Å. Interpretation of magnetic susceptibility measurements yields $2J = -217$ cm^{-1}, which represents the smallest magnetic interaction yet observed in a discrete dimeric copper(II) carboxylate adduct. No structural basis for the small magnitude of this interaction is evident, though it appears to be a consequence of the trichloromethyl substituent on the bridging carboxylate group. The structural and magnetic results are compared with those for a series of related dimers.

Introduction

Although a large number of copper(II) carboxylate monoadducts, $[Cu(O_2CR)_2L]_n$, have been prepared and subjected to magnetic study, no clear picture has yet emerged of the factors which determine the magnetic properties of these complexes.[1,2] The monoadducts invariably exhibit substantial magnetic coupling between copper(II) ions and, with the exception of one series of one-dimensional chain structures,[3-5] all have the familiar bridged dimeric copper(II) acetate monohydrate structure I. For dimers of this structure, an obvious question which may be asked relates to the effects of variations of the carboxylate substituent R and of the axial donor ligand L upon the exchange coupling constant $2J$, a measure of the magnitude of the Cu–Cu interaction. Of these two variable factors, the greater amount of attention has centered on the substituent R because its properties could be varied over a wider range and because it appeared to influence $2J$ more strongly than did L.



I

An early proposed correlation suggested that the magnitude of $2J$ in the dimeric carboxylates was inversely related to the basicity of the bridging group, as measured by the pK_a of its parent carboxylic acid.[6] This relationship found some experimental support and has been shown to be consistent with the results of a molecular orbital analysis of the bridged dimeric structure.[7] Nonetheless, it is now clear that the existing experimental data cannot be rationalized in so simple a fashion. The originally proposed relationship was based upon room-temperature magnetic measurements on anhydrous carboxylates, some of which have now been shown not to be dimeric.[8-10] One example of such a material is anhydrous copper(II) trifluoroacetate, in which the observed small magnetic interaction (effective room-temperature magnetic moment $\sim 1.8\ \mu_B$) was originally attributed to the electron-withdrawing ability of the CF_3 group.[6] Subsequent experiments strongly suggested that this compound was not dimeric.[8-10] When an authentic example of a dimeric copper(II) trifluoroacetate adduct (with L = quinoline) was prepared and characterized, it proved to have $2J = -310$ cm^{-1}, a value comparable to that typically found for copper(II) acetate adducts.[11] A crystal structure analysis confirmed structure I for the trifluoroacetate dimer and revealed an unusually long Cu–Cu distance of 2.886 (2) Å (cf. 2.616 (1) Å in copper(II) acetate monohydrate).[12]

From the similarities of the observed $2J$ values of the dimeric acetate and trifluoroacetate adducts, one was tempted to hypothesize that, at least in the dimeric halocarboxylates, the properties of the substituent R do not exert a substantial effect upon the magnitude of $2J$. However, published magnetic and EPR data for a dimeric copper(II) trichloroacetate adduct with L = 2-chloropyridine appeared to be at variance with this generalization.[13-15] The estimated $2J$ value for this material was -179 cm^{-1}, representing a significantly smaller interaction than is observed in any other well-characterized copper(II) carboxylate adduct of structure I. In view of these results, we initiated structural and magnetic studies of the 2-chloropyridine monoadduct of copper(II) trichloroacetate with the objectives of verifying and extending the published magnetic data, of determining whether this adduct possessed structure I, and, if so, of searching for a possible structural basis for its small Cu–Cu interaction. The results of these studies are reported in this paper.

Experimental Section

Preparation of the Complex. Anhydrous copper(II) trichloroacetate was prepared by the method of Bateman and Conrad.[16] Equimolar amounts of anhydrous cupric trichloroacetate and 2-chloropyridine were dissolved in anhydrous degassed methanol, according to the method of Ablov et al.[15] Any excess of 2-chloropyridine led to a violet product, presumed to be the bis adduct $Cu(O_2CCl_3)_2(2\text{-}Cl\text{-}py)_2$ (2-Cl-py = 2-chloropyridine). The solution was warmed and stirred for several hours. The filtered solution produced a green powder upon evaporation. Recrystallization from chloroform yielded light green crystals. Analyses were performed by Chemalytics, Inc., of Tempe, Ariz. Anal. Calcd for $CuC_9H_4NO_4Cl_7$: C, 21.54; H, 0.80; N, 2.79; Cl, 49.45. Found: C, 21.6; H, 1.0; N, 3.1; Cl, 49.6.

Data Collection and Reduction. Precession photographs displayed no evidence of monoclinic or higher symmetry. Triclinic symmetry was confirmed by a Delaunay reduction. Lattice parameters were obtained by least-squares refinement[17] of the setting angles of 13 reflections which had been accurately centered on a Picker four-circle x-ray diffractometer. The density was determined by flotation in a CCl_4/CH_2Br_2 mixture. Crystal data are tabulated in part A of Table I. The tabulated cell parameters are those for a nonreduced cell in

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Table I. Crystal Data and Experimental Parameters

A. Crystal Data

Formula	$Cu_2C_{18}H_8O_8N_2Cl_{14}$	Formula wt	1003.70
a	9.316 (9) Å	*V*	841.3 $Å^3$
b	10.707 (10) Å	*Z*	1
c	10.493 (11) Å	Density (obsd)	1.94 (2) g/cm^3
α	57.22 (2)°	Density (calcd)	1.98 g/cm^3
β	107.02 (3)°	Space group	$P\bar{1}$
γ	100.01 (3)°	μ(Mo Kα)	24.5 cm^{-1}

B. Experimental Parameters

Radiation	Mo Kα $\lambda(K\alpha_1)$ 0.709 30 Å 0.003-in. Nb filter	Scan range	−0.60 to +0.60° in 2θ from $K\alpha_1$ peak
Temp	23 °C	Background counting	20 s fixed counts at each end of scan
Receiving aperture	5 mm square, 30 cm from crystal	2θ (max)	47°
Takeoff angle	1.5°	Data collected	2502
Scan rate	1.0°/min in 2θ	Data with $F_o^2 > 3\sigma(F_o^2)$	2165

terms of which all results are reported. The three shortest noncoplanar lattice translations define a reduced cell with $a' = 9.316$ Å, $b' = 10.153$ Å, $c' = 10.493$ Å, $\alpha' = 62.46°$, $\beta' = 107.02°$, and $\gamma' = 96.85°$. The reduced cell axes are defined by $a' = a$, $b' = b - c$, and $c' = c$.

Intensity data were collected from a green six-sided plate of dimensions 0.33 × 0.30 × 0.41 mm whose bounding planes were of the {100}, {010}, {001}, and {011} forms. The crystal was mounted approximately along the crystallographic *a* axis. Narrow-source open-counter ω scans through several reflections displayed an average full width at half-maximum of 0.12°, indicative of an acceptably low mosaic spread. The data were collected by use of procedures previously described.[19] Experimental parameters are tabulated in part B of Table I. Copper foil attenuators were automatically placed in the diffracted beam when the count rate exceeded ~10 000 counts/s. Only 33 reflections required attenuation. Four standard reflections were monitored after every 100 data. Only random variations no greater than ±4% were noted for the standards. Methods previously described[19] were employed in processing the data. The *p* factor used in estimation of the standard deviations of the observed intensities was 0.05.

Structure Solution and Refinement. The coordinates of the copper atom and three oxygen atoms were obtained from a three-dimensional Patterson map. All remaining nonhydrogen atoms were located on a subsequent difference Fourier map. Isotropic refinement of all nonhydrogen atoms converged to $R_1 = \sum||F_o| - |F_c||/\sum|F_o| = 0.178$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.262$. The relatively high *R* factors were apparently a result of considerable anisotropy in the thermal motion of the CCl_3 groups. Futher refinement employed anisotropic temperature factors for all nonhydrogen atoms. The hydrogens were included as fixed contributions with idealized trigonal geometry (C–H = 0.95 Å, C–C–H = 120°). New hydrogen positions were calculated after each cycle. An absorption correction was applied at this point in the refinement. Based upon a linear absorption coefficient of 24.3 cm^{-1}, the calculated transmission factors ranged from 0.44 to 0.54. The final refinement converged to $R_1 = 0.054$ and $R_2 = 0.081$. A final difference map had a highest peak of 1.1 e/$Å^3$ located near one of the chlorine atoms.

In all structure factor calculations, the atomic scattering factors of Cromer and Waber[20] were used for Cu and Cl, those tabulated in ref 21 were used for C, O, and N, while those of Stewart et al.[22] were used for H. The $\Delta f'$ and $\Delta f''$ values of Cromer[23] were employed in correction of the F_c values for anomalous scattering by the copper and chlorine atoms. The quantity minimized in the least-squares refinements was $\sum w(|F_o| - |F_c|)^2$, where $w = 4F_o^2/\sigma^2(F_o^2)$. The final standard deviation of an observation of unit weight was 2.6. Calculation of mean $w(\Delta F)^2$ values as functions of F_o, uncorrected intensity, and Bragg angle showed no significant trends. The largest parameter shift in the last cycle was 0.5σ. Calculation of structure factors for data with $F_o^2 \leq 3\sigma(F_o^2)$ revealed 26 reflections with $||F_o| - |F_c||/\sigma(F_o) \leq 3$; only 8 of these had $\Delta F/\sigma > 4$.

Final atomic positional and thermal parameters are given in Table II. Bond distances and angles are tabulated in Tables III and IV, respectively. Principal amplitudes of thermal motion for atoms refined anisotropically are presented in Table A.[24] Information on molecular planes and dihedral angles is given in Table V. Table B[24] lists the observed and calculated structure factors.

Magnetic Susceptibility Measurements. Magnetic susceptibilities were measured between 82 and 310 K by the Faraday method on a powdered sample under nitrogen at a field strength of ca. 8000 G on an Alpha Model 1402 magnetic susceptibility system. The calibrant employed was $HgCo(NCS)_4$, for which the magnetic susceptibility was taken as 16.44 × 10^{-6} cgs units at 20 °C. The data were corrected for the diamagnetism of the sample holder and for the temperature-independent paramagnetism of the copper atoms (60 × 10^{-6} cgsu per copper). The correction for the diamagnetism of the constituent

Table II. Atomic Positional and Thermal Parameters for $[Cu(O_2CCCl_3)_2C_5H_4ClN]_2$

Atom	*x*	*y*	*z*	B_{11}[b]	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	−0.03947 (7)[a]	−0.01979 (8)	0.12708 (7)	2.64 (4)	3.57 (4)	2.95 (4)	−0.03 (2)	0.77 (2)	−1.79 (3)
O(1)	−0.1411 (5)	−0.1921 (5)	0.1195 (5)	4.22 (21)	4.08 (21)	4.28 (21)	−1.25 (16)	1.59 (17)	−2.44 (18)
O(2)	0.0780 (5)	0.1656 (5)	0.0823 (5)	4.35 (21)	4.34 (21)	5.34 (24)	−1.48 (17)	2.53 (19)	−3.05 (19)
O(3)	0.1494 (5)	−0.1235 (5)	0.2402 (5)	2.98 (18)	5.09 (22)	3.32 (18)	0.87 (16)	0.43 (15)	−1.70 (17)
O(4)	−0.2088 (5)	0.1001 (5)	−0.0394 (5)	3.87 (21)	5.83 (26)	3.55 (21)	1.67 (18)	0.15 (16)	−2.37 (19)
C(1)	−0.1442 (6)	−0.2252 (6)	0.0237 (7)	2.54 (24)	3.14 (26)	4.08 (29)	−0.16 (20)	0.46 (21)	−1.88 (24)
C(2)	−0.2512 (8)	−0.3554 (7)	0.0322 (8)	4.41 (30)	3.73 (30)	4.70 (32)	−0.87 (24)	1.22 (25)	−2.34 (26)
C(3)	0.2291 (6)	−0.1442 (7)	0.1777 (7)	2.44 (23)	3.30 (26)	3.64 (29)	−0.06 (19)	0.52 (20)	−1.79 (23)
C(4)	0.3694 (7)	−0.2403 (7)	0.2848 (8)	3.68 (28)	4.02 (30)	3.87 (29)	0.64 (23)	0.37 (23)	−1.57 (25)
Cl(1)	−0.2927 (3)	−0.4685 (2)	0.2143 (3)	8.12 (13)	4.50 (9)	6.84 (11)	−2.05 (8)	3.94 (10)	−2.71 (8)
Cl(2)	−0.1763 (4)	−0.4629 (3)	−0.0085 (4)	15.58 (25)	5.86 (12)	13.88 (22)	−3.56 (14)	9.70 (20)	−6.66 (14)
Cl(3)	−0.4148 (3)	−0.2728 (3)	−0.1083 (3)	5.30 (12)	10.17 (18)	8.92 (16)	−2.02 (11)	−1.37 (11)	−3.58 (14)
Cl(4)	0.4242 (3)	−0.2480 (4)	0.4633 (3)	6.09 (12)	13.67 (21)	4.84 (10)	4.30 (13)	−1.25 (8)	−4.41 (12)
Cl(5)	0.3210 (4)	−0.4149 (3)	0.3187 (5)	9.71 (19)	4.41 (12)	20.36 (36)	1.80 (12)	−4.45 (21)	−5.24 (17)
Cl(6)	0.5188 (2)	−0.1684 (4)	0.2007 (3)	3.71 (8)	13.71 (21)	6.28 (12)	1.60 (11)	1.10 (8)	−3.55 (13)
N	−0.1281 (5)	−0.0320 (6)	0.3007 (6)	2.63 (20)	4.37 (25)	3.23 (22)	−0.06 (18)	0.67 (10)	−2.28 (20)
C(5)	−0.1261 (7)	−0.1457 (8)	0.4426 (8)	3.20 (27)	5.09 (34)	3.76 (29)	−0.64 (23)	1.01 (22)	−2.41 (27)
C(6)	−0.1746 (8)	−0.1432 (11)	0.5525 (9)	3.93 (32)	9.17 (55)	4.52 (34)	−1.06 (33)	1.43 (27)	−4.53 (38)
C(7)	−0.2316 (9)	−0.0115 (11)	0.5070 (9)	4.57 (36)	9.20 (57)	5.11 (40)	−0.45 (36)	1.43 (30)	−4.78 (42)
C(8)	−0.2390 (8)	0.1094 (9)	0.3604 (9)	4.19 (33)	6.64 (44)	6.19 (42)	−0.03 (29)	0.98 (29)	−4.78 (38)
C(9)	−0.1861 (7)	0.0982 (9)	0.2595 (8)	3.33 (29)	7.55 (45)	4.61 (33)	−0.22 (28)	0.79 (24)	−4.13 (33)
Cl(7)	−0.0519 (3)	−0.3052 (2)	0.4926 (2)	7.55 (12)	4.70 (9)	4.25 (9)	0.48 (8)	1.80 (8)	−1.39 (7)
H(6)[c]	−0.1689	−0.2324	0.6598	[d]					
H(7)	−0.2686	−0.0040	0.5830						
H(8)	−0.2824	0.2044	0.3279						
H(9)	−0.1894	0.1869	0.1524						

[a] Numbers in parentheses in all tables and in the text are estimated standard deviations in the least significant figures. [b] The form of the anisotropic thermal ellipsoid is $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$. [c] The numbering of the hydrogen atoms corresponds to that of the carbon atoms; e.g., H6 is bound to C6, etc. [d] Hydrogen atoms were assigned isotropic thermal parameters of 6.0 A^2.

Table III. Intramolecular Distances (Å)

(a) Copper Coordination Sphere			
Cu-O(1)	1.952 (5)	Cu-O(3)	1.941 (4)
Cu-O(2)	1.973 (5)	Cu-O(4)	1.962 (4)
Cu-N	2.145 (5)	Cu-Cu'[a]	2.766 (3)
(b) Trichloroacetate Groups			
O(1)-C(1)	1.226 (7)	O(3)-C(3)	1.237 (7)
O(2)-C(1)'	1.234 (7)	O(4)-C(3)'	1.222 (7)
C(1)-C(2)	1.543 (8)	C(3)-C(4)	1.545 (8)
C(2)-Cl(1)	1.741 (7)	C(4)-Cl(4)	1.750 (7)
C(2)-Cl(2)	1.726 (7)	C(4)-Cl(5)	1.704 (8)
C(2)-Cl(3)	1.736 (7)	C(4)-Cl(6)	1.708 (7)
(c) 2-Chloropyridine Ligand			
N-C(5)	1.315 (8)	C(6)-C(7)	1.372 (12)
N-C(9)	1.377 (9)	C(7)-C(8)	1.364 (11)
C(5)-C(6)	1.371 (10)	C(8)-C(9)	1.357 (10)
C(5)-Cl(7)	1.702 (7)		

[a] Primes denote atoms related to those in the asymmetric unit by the crystallographic center of symmetry.

Table IV. Intramolecular Angles (deg)

(a) Copper Coordination Sphere			
O(1)-Cu-O(2)	163.99 (19)	O(3)-Cu-O(4)	163.32 (19)
O(1)-Cu-O(3)	91.47 (20)	O(2)-Cu-O(3)	87.21 (21)
O(1)-Cu-O(4)	87.92 (21)	O(2)-Cu-O(4)	88.80 (22)
O(1)-Cu-N	100.12 (19)	O(3)-Cu-N	105.26 (19)
O(2)-Cu-N	95.62 (19)	O(4)-Cu-N	91.24 (20)
Cu'-Cu-N	171.85 (13)	Cu'-Cu-O(3)	82.89 (14)
Cu'-Cu-O(1)	79.73 (14)	Cu'-Cu-O(4)	80.60 (15)
Cu'-Cu-O(2)	84.27 (14)		
(b) Trichloroacetate Groups			
Cu-O(1)-C(1)	126.8 (4)	Cu-O(3)-C(3)	123.3 (4)
Cu-O(2)-C(1)'	119.9 (4)	Cu-O(4)-C(3)'	125.4 (4)
O(1)-C(1)-O(2)'	129.1 (6)	O(3)-C(3)-O(4)'	127.7 (6)
O(1)-C(1)-C(2)	115.5 (6)	O(3)-C(3)-C(4)	117.5 (5)
O(2)'-C(1)-C(2)	115.3 (6)	O(4)'-C(3)-C(4)	114.8 (5)
C(1)-C(2)-Cl(1)	112.0 (5)	C(3)-C(4)-Cl(4)	111.4 (5)
C(1)-C(2)-Cl(2)	111.2 (5)	C(3)-C(4)-Cl(5)	106.7 (4)
C(1)-C(2)-Cl(3)	105.2 (4)	C(3)-C(4)-Cl(6)	111.1 (4)
Cl(1)-C(2)-Cl(2)	108.9 (4)	Cl(4)-C(4)-Cl(5)	108.9 (4)
Cl(1)-C(2)-Cl(3)	109.2 (4)	Cl(4)-C(4)-Cl(6)	106.8 (4)
Cl(2)-C(2)-Cl(3)	110.3 (4)	Cl(5)-C(4)-Cl(6)	112.0 (4)
(c) 2-Chloropyridine Ligand			
Cu-N-C(5)	127.7 (4)	Cl(7)-C(5)-C(6)	118.5 (6)
Cu-N-C(9)	115.1 (4)	C(5)-C(6)-C(7)	116.2 (7)
C(5)-N-C(9)	117.1 (5)	C(6)-C(7)-C(8)	121.4 (7)
N-C(5)-Cl(7)	116.5 (5)	C(7)-C(8)-C(9)	118.6 (8)
N-C(5)-C(6)	124.9 (7)	C(8)-C(9)-N	121.8 (7)

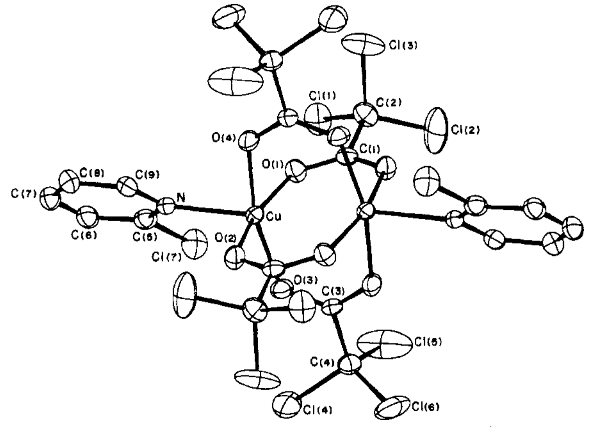

Figure 1. A view of the molecular structure of $[Cu(O_2CCCl_3)_2(2\text{-}ClC_5H_4N)]_2$. Thermal ellipsoids are drawn at the 25% probability level. Hydrogen atoms have been omitted for clarity.

atoms was calculated by use of Pascal's constants and found to be -239.7×10^{-6} cgsu per copper. The magnetic data were fitted to the usual dimer equation[2] by a least-squares procedure. Observed and calculated magnetic susceptibilities are presented in Table VI.

Table V. Least-Squares Planes

(1) $0.5516X - 0.2991Y - 0.7787Z = -1.1043$[a]

O(1)	−0.004[b]	O(4)	0.004
O(2)	−0.004	Cu*	−0.277
O(3)	0.004		

(2) $-0.7098X + 0.3284Y - 0.6232Z = -0.1581$

O(1)	0	C(2)*	0.072
O(2)'	0	Cu*	0.141
C(1)	0		

(3) $0.4236X + 0.8950Y - 0.1399Z = -0.0444$

O(3)	0	C(4)*	−0.045
O(4)'	0	Cu*	−0.094
C(3)	0		

(4) $-0.7771X - 0.5393Y - 0.3245Z = 0.1013$

N	−0.004	C(8)	−0.008
C(5)	0.008	C(9)	−0.004
C(6)	−0.004	Cl(7)*	−0.013
C(7)	−0.004		

Dihedral Angles between These Planes

Planes	Angle, deg	Planes	Angle, deg
1–2	90.3	2–3	85.4
1–3	85.7	2–4	54.8
1–4	90.8	3–4	140.0

[a] The equations of the planes are expressed with respect to coordinates (*X, Y, Z*) referred to an orthogonal system (*A, B, C*) oriented with respect to the crystallographic axes such that *A* is parallel to *a*, *B* is parallel to $c^* \times a$, and *C* is parallel to $A \times B$.
[b] In the calculation of all planes, all atoms listed were given unit weight except those marked with an asterisk, which were given zero weight. Tabulated figures are distances in Å to the plane.

Table VI. Magnetic Susceptibility Data[a]

T, K	χ_M'(obsd)	χ_M'(calcd)	μ_{eff}, μ_B
82.5	575	552	0.58
92.5	709	701	0.69
102	841	830	0.80
112	951	947	0.89
122	1033	1044	0.97
132	1120	1122	1.06
142	1196	1182	1.14
152	1217	1226	1.19
161	1254	1254	1.24
171	1271	1276	1.29
191	1291	1293	1.37
211	1293	1288	1.44
231	1269	1268	1.49
250	1243	1241	1.54
270	1213	1208	1.58
295	1159	1164	1.61
310	1137	1137	1.63

[a] Observed and calculated susceptibility values listed are molar paramagnetic susceptibilities per copper ion in cgs units $\times 10^6$.

Results

Description of the Structure. The crystal structure of bis(2-chloropyridine)tetrakis(μ-trichloroacetato(*O,O'*))-dicopper(II) is comprised of discrete dimeric molecules of the familiar quadruply bridged copper(II) acetate structure. A view of the molecular structure is presented in Figure 1. A noteworthy feature of this structure is the Cu–Cu distance of 2.766 (3) Å, longer by 0.15 Å than the comparable distance in cupric acetate monohydrate.[12] Among copper(II) carboxylate dimers of structure I, only the monoquinoline adduct of copper(II) trifluoroacetate has a longer metal–metal distance (2.886 (2) Å).[11] This elongation of the Cu–Cu distance in the trichloroacetate dimer over that in copper(II) acetate monohydrate is reflected in an increase in the distance of the Cu atom to its basal coordination plane (from 0.19 to 0.28 Å) and in an opening of the mean O–C–O bond angle (from 124.8 to 128.4°). No significant increase in the average Cu–O–C angle is observed (123.8 vs. 123.1°). Qualitatively similar

Table VII. Structural and Magnetic Data for Selected Dimeric Copper(II) Carboxylate Adducts, $[Cu(O_2CR)_2L]_2$

R	L	pK$_a$[a]	2*J*, cm^{-1}	Cu-Cu, A	Bridge length, A[b]	Cu-Cu-L, deg	O-Cu-L range, deg	Ref
CH_3	H_2O	4.8	−284	2.616 (1)[c]	6.458 (5)	174.1	93.3-98.4 (2)	12, 33
H	Urea	3.8	~−500	2.657 (7)	6.45 (2)	174.0 (4)	93.1-99.8 (6)	34, 35
CH_2Cl	α-Picoline	2.8	−321	2.747 (3)	6.443 (14)	175.3 (4)	93.2-101.5	36, 37
CCl_3	2-Cl-py	0.7	−217	2.766 (3)	6.374 (6)	171.85 (13)	91.2-105.3 (2)	This work
CF_3	Quinoline	0.2	−310	2.886 (2)	6.428 (8)	177.74 (18)	97.1-101.8 (3)	11

[a] These are the pK_a values for the parent carboxylic acid of the bridging group O_2CR^-. [b] The bridge length is defined as the mean Cu-O-C-O-Cu distance through the bridging carboxylate groups. Tabulated standard deviations were obtained from published esd's by standard error propagation methods. [c] Structural results quoted for R = CH_3, L = H_2O, are those from a recent x-ray diffraction study. Neutron diffraction results are also available[38] and do not differ significantly from those tabulated.

trends are found in other copper(II) carboxylate dimers having long Cu–Cu distances.[25]

Other distances and angles within the dimer are much as expected. The Cu–O distances range from 1.941 (4) to 1.973 (5) Å, with a mean value of 1.957 Å. The axial Cu–N distance of 2.145 (5) Å is a typical value for such a bond to a pyridine or substituted pyridine.[25] The C–Cl distances of the CCl_3 groups show a greater variation than would be expected on the basis of their estimated standard deviations, probably a consequence of the high degree of thermal motion of these groups. The C–C distances within the substituted pyridine ring are equivalent, with a mean value of 1.366 Å. The two N–C distances of the ring differ by an apparently significant amount (1.315 (8) vs. 1.377 (9) Å). As is evident from the data tabulated in Table V, the planes of the two carboxylate groups are nearly perpendicular (dihedral angle = 85.4°) and the 2-chloropyridine ligand adopts a staggered orientation with respect to these planes.

Magnetic Results. Although temperature-dependent magnetic susceptibility data for $[Cu(O_2CCl_3)_2(2\text{-Cl-py})]_2$ had previously been reported,[13] we repeated the magnetic studies in order to extend them to lower temperatures, to obtain numerical susceptibility data (the data previously were available only in graphical form), and to verify that our material was magnetically the same as that previously investigated. The observed and calculated magnetic susceptibilities tabulated in Table VI are shown graphically in Figure 2. The experimental data are well represented by the usual dimer equation,[2] with the best least-squares fit achieved for $g = 2.26$[27] and $2J = -217$ cm^{-1}. These values differ somewhat from those previously reported, though some of this difference may be attributed to different fitting procedures and to the greater temperature range spanned by our data. The important point, however, is that our results are qualitatively similar to those of Ablov et al.[13] in that the $|2J|$ obtained is substantially less than that found for copper(II) acetate monohydrate or for any other copper(II) carboxylate adduct which has been shown to adopt the dimeric structure I.[2]

Discussion

Since the 2-chloropyridine adduct of copper(II) trichloroacetate has, by a significant margin, the smallest $|2J|$ value observed for any dimeric copper(II) carboxylate, it is reasonable to inquire whether this magnetic behavior can be attributed to any specific property of the carboxylate substituent R or the addend L and also whether the complex displays any structural features which may be associated with its small magnetic interaction. Such correlations of ligand properties and/or structural parameters with 2*J* values have been found in several series of dimers with monatomic bridges[28-32] but have to date been lacking in copper(II) dimers of structure I.[2] To serve as a basis for this discussion, a tabulation of structural and magnetic results for a selected group of dimeric copper(II) carboxylate adducts is given in Table VII. Compounds listed in this table were chosen to span the full range of magnetic and structural variation in these dimers, considering only systems for which reliable crystal structures and magnetic susceptibility data are available.

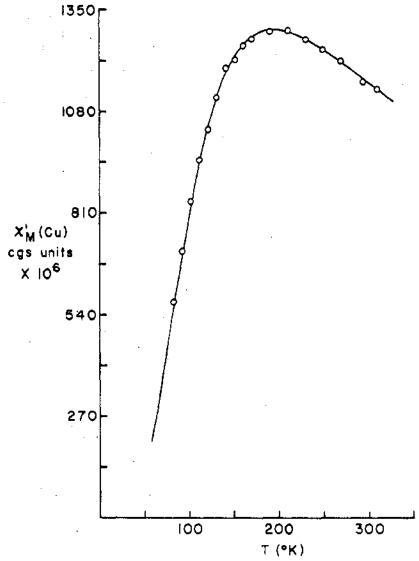

Figure 2. Observed and calculated magnetic susceptibility curves. The solid line represents the susceptibility calculated from the dimer equation with $g = 2.26$ and $2J = -217$ cm^{-1}.

The first point which may be made is that the CCl_3 group clearly plays a significant role in determining the observed 2*J* value in $[Cu(O_2CCl_3)_2(2\text{-Cl-py})]_2$. This conclusion follows from the fact that several other dimers of probable structure I with L = 2-Cl-py (R = $CH_2C_6H_5$, CH_2Cl, CH_2F, $CHCl_2$) show no tendency toward unusually small $|2J|$ values; in fact, this L seems to be associated with interactions which are somewhat larger than those found for many other axial ligands.[1] The reason the CCl_3 group should be associated with a particularly small interaction is not clear. As has been noted above, early proposed relationships between 2*J* in these dimers and the pK_a of the parent carboxylic acid have now been shown to be invalid. This perhaps should not be too surprising, since pK_a is defined for aqueous solutions and need not be a direct measure of the electronic properties of a ligand in an anhydrous crystalline environment. No other property of R which may be correlated with 2*J* is evident, although one intriguing observation may be made. The extreme values of 2*J* are observed for R = H ($2J \sim -500$ cm^{-1}) and for R = CCl_3 ($2J = -217$ cm^{-1}). These two R groups also have the extreme group polarizability values for this series of dimers. On the other hand, the CH_3 and CF_3 groups, which differ in many other respects, have comparable group polarizabilities and the corresponding copper(II) carboxylate dimers have comparable 2*J* values of −284 and −310 cm^{-1}. The significance, if any, of this observation cannot be definitively evaluated on the basis of existing experimental data,[39] but it does suggest possible rational directions for further experiments.

The distances and angles within the trichloroacetate bridges show no features which can be associated with the small $|2J|$

value found in this dimer. Variations in the O–C–O angle of the bridging groups tend to parallel trends in the Cu–Cu separation, a parameter which has been amply demonstrated to have no direct association with $2J$.[11,34,36,40,41] A similar, but much less pronounced, trend is observed for the Cu–O–C angles. It is worthy of note that the "bridging pathway" (the mean Cu–O–C–O–Cu distance through the triatomic bridges) of 6.374 (6) Å is somewhat shorter than most previously observed values.[2,42] This is contrary to the proposal[40] that a shorter bridging pathway is associated with a larger Cu–Cu interaction.

By some measures, the distortion of the central portion of the trichloroacetate dimer from its ideal D_{4h} symmetry is greater than that of any of the other molecules included in Table VII. In particular, the Cu–Cu–N angle of 171.85 (13)° deviates by the largest amount from linearity and the range of 14° observed for the O–Cu–N angles is greater than the corresponding range in other dimers. At this point, it is not clear whether this distortion is steric or electronic in origin or whether it has any connection with the small $|2J|$ value of the trichloroacetate. Again, however, this observation may provide a rational basis for design of additional experiments.

A final structural observation is that the Cu–Cu distance of 2.766 (3) Å is intermediate between the metal–metal distance of 2.747 (3) Å found in the α-picoline adduct of copper(II) chloroacetate[36] and that of 2.886 (2) Å in $[Cu(O_2CCF_3)_2(quinoline)]_2$.[11] Thus, these dimers continue to show a regular increase of Cu–Cu distance with decreasing pK_a of the parent acid of the bridging carboxylate group. In this connection, however, it should be noted that recent structural results include a Cu–Cu distance of 2.624 Å for the dimer with R = CH_2Cl, L = urea, while for R = CH_2Cl, L = quinoline the corresponding distance is 2.724 (2) Å.[26] This indicates that the axial ligand also plays a role in determining the metal–metal distance; in fact, the longer distances have all been found in dimers in which L is an ortho-substitued pyridine.

At this point, one must ask whether the variations in Cu–Cu distances in these dimers stem primarily from the differing steric requirements of their ortho-substituted axial ligands rather than from electronic properties of the carboxylate groups. In $[Cu(O_2CCCl_3)_2(2\text{-}Cl\text{-}py)]_2$, the shortest intramolecular contacts involving Cl(7) are Cl(7)···O(3) = 3.22 (5) Å and Cl(7)···O(1) = 3.286 (6) Å. These may be compared with the sum of the Cl and O van der Waals radii of 3.2 Å and are the only close intramolecular contacts involving Cl(7). Steric interactions undoubtedly play a role in stabilizing the dimeric structure, but it is unlikely that they are the primary factor controlling the distance of each Cu^{2+} ion to its basal coordination plane. This conclusion follows from several observations, of which two major ones are the following. (1) Both dimeric mono adducts, $[Cu(O_2Cr)_2L]_2$, and monomeric bis adducts, $Cu(O_2CR)_2L_2$, are formed with R = CF_3, L = quinoline[11] and R = CCl_3, L = 2-Cl-py.[15] The monomeric adducts are believed to be tetragonal, with apical ligands L, and hence would have the Cu^{2+} ion lying nearly in the equatorial coordination plane. (2) The dimeric quinoline adduct of copper(II) acetate has a Cu–Cu distance of 2.64 Å and a Cu–basal plane distance of 0.2 Å.[43] These distances are 2.886 (2) and 0.32 Å, respectively, in $[Cu(O_2CCF_3)_2(quin)]_2$.[11] Clearly, the quinoline ligand is not the major factor determining the Cu–Cu distances in these systems. in fact, at present the chloroacetate adducts cited above provide the sole example of a large influence of L on Cu–Cu distance.

In summary, this work has shown the 2-chloropyridine adduct of copper(II) trichloroacetate to have the smallest $|2J|$ value of any dimeric copper(II) carboxylate adduct and to have a Cu–Cu distance intermediate between those of dimeric copper(II) acetates and trifluoroacetates. Both of these observations appear to be a consequence of the CCl_3 substituent, although their specific causes are not yet clear. A tentative correlation of $2J$ with the polarizability of the substituent on the bridging O_2CR group provides a rational direction for future experiments.

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Registry No. $[Cu(O_2CCCl_3)_2(2\text{-}ClC_5H_4N)]_2$, 31613-57-7.

Supplementary Material Available: Tables A and B, containing principal amplitudes of thermal motion and structure factor amplitudes, respectively (17 pages). Ordering information is given on any current masthead page.

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Crystal and Molecular Structure of *trans*-Dichloro(dimethyl sulfoxide)(cytidine)platinum(II)

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The crystal and molecular structure of *trans*-dichloro(dimethyl sulfoxide)(cytidine)platinum(II) has been determined by single-crystal x-ray diffraction. The crystals are orthorhombic, space group $P2_12_12_1$ with $a = 6.607$ (3) Å, $b = 24.238$ (12) Å, $c = 10.851$ (11) Å, and $Z = 4$. The structure was refined by full-matrix least-squares analysis to a conventional R factor of 0.043. The coordination around the platinum atom is planar. The bond lengths are Pt–Cl(1) = 2.291 (5) Å, Pt–Cl(2) = 2.310 (4) Å, Pt–S = 2.220 (4) Å, and Pt–N(1) = 2.034 (13) Å. Distances within the ligands are normal. The plane of the pyrimidine ring is at 77.4° to the plane formed by the ligands around the platinum atom.

Introduction

Recently, we have studied the reactions between some nucleosides and *cis*-[Pt(Me_2SO)$_2$$Cl_2$].[1] The latter was chosen partly because dimethyl sulfoxide (Me_2SO) has been used as solvent for testing the antitumor activity of some platinum complexes and partly because it has some common features with *cis*-[Pt(NH_3)$_2$$Cl_2$], a potent antitumor compound, both having two neutral ligands and two chlorine atoms in cis positions. Since *cis*-[Pt(Me_2SO)$_2$$Cl_2$] is not an antitumor compound,[2] it was worth comparing the reaction mechanism of the two platinum complexes with nucleosides, in order to understand variations in the antitumor activities of the platinum compounds. The binding sites of the nucleosides in the reaction products were also investigated.

The reactions were studied by nuclear magnetic resonance.[1] In order to confirm the NMR configuration assignments of the platinum complexes formed in these reactions, some typical products were examined by x-ray diffraction. Here we report the molecular and crystal structure of the first of a series of platinum nucleoside complexes, *trans*-[Pt(Me_2SO)(Cyd)Cl_2].

Experimental Section

The crystals were obtained directly from the reaction of K[Pt(Me_2SO)Cl_3] and cytidine in water. A set of precession photographs indicated the $P2_12_12_1$ space group in the orthorhombic system. The cell parameters were calculated by refinement of the setting angles of 15 independent peaks centered on a Syntex $P\bar{1}$ diffractometer using graphite monochromatized Mo Kα radiation.

Crystal Data. $PtCl_2C_{11}H_{19}N_3SO_6$: formula weight, 587.35; orthorhombic; $P2_12_12_1$; $a = 6.607$ (3), $b = 24.238$ (12), $c = 10.851$ (11) Å; $V = 1737$ (2) Å^3; $d_x = 2.241$, $d_m = 2.23$ (1) g cm^{-3} (flotation); $Z = 4$; μ(Mo Kα) = 89.27 cm^{-1}; λ(Mo Kα) = 0.71069 Å; $T = 22$ °C.

Collection and Reduction of Intensity Data. The intensity data were collected from a crystal measuring 0.624 × 0.104 × 0.052 mm, elongated along the a axis. A total of 2901 independant reflections were measured in the region of $2\theta < 60°$ by the $2\theta/\theta$ scan technique using Mo Kα radiation. During the data collection, three standard reflections were measured after every 47 reflections. Their variations were less than 2% from their respective means. The reflections for which the intensity was less than $2.5\sigma(I)$ were considered as unobserved. The standard deviation $\sigma(I)$ was calculated as already described.[3] A total of 1908 observed reflections remained. An absorption correction based on the equations of the crystal faces was then applied. The transmission factors varied from 0.3784 to 0.5255. The data were finally corrected for the Lorentz and polarization effects. The scattering factors of Cromer and Waber[4] were used for platinum, chlorine, sulfur, oxygen, nitrogen, and carbon; those of Stewart et al.[5] were used for hydrogen. The anomalous dispersion terms[6] of platinum, chlorine, and sulfur were included in the calculations.

Structure Determination. The structure was solved by the conventional heavy-atom method and refined by full-matrix least squares. The position of the platinum atom was easily located from the three-dimensional Patterson map. The positions of all the other atoms, except the hydrogen atoms, were obtained by structure factor and Fourier map calculations. In the early stages of refinement unit weight was assigned to all reflections. Later, individual weights, w, according to the equation $1/w = a + bF_o + cF_o^2$ were calculated. The constants of the equation were adjusted to make the distribution of $w|\Delta F|^2$ almost constant with respect to $|F_o|$ and $(\sin\theta)/\lambda$ ($a = 52.4$, $b = -0.392$, and $c = 0.00092$). An isotropic secondary extinction correction was also made.[7] The hydrogen atoms on the carbon atoms in the cytidine moiety were fixed at the calculated positions (C–H distance = 0.95 Å) and assigned isotropic temperature factors of 7. The refinement of the scale factor, the coordinates, and anisotropic temperature factors of all the nonhydrogen atoms converged to $R = \sum(|F_o| - |F_c|)/\sum|F_o| = 0.043$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.041$. The final difference Fourier map did not show peaks higher than 0.8 e/Å^3. The surroundings of the two methyl carbon atoms in the Me_2SO molecule and of the oxygen and nitrogen atoms in the cytidine were carefully searched but no hydrogen atoms were found. The torsion angles within the ribose segment confirmed the d configuration of the molecule.

The calculations were carried out with a CDC 6400 computer, and the programs used have already been described.[3] A table of observed and calculated structure factors is available.[8]

Results and Discussion

The refined atomic parameters and the anisotropic temperature factors are listed in Table I. A labeled stereoscopic view of the molecule is show in Figure 1. The bond lengths and angles are given in Table II. As expected, the compound is the trans isomer. The dimethyl sulfoxide molecule is bonded to the platinum atom through the sulfur atom and the cytidine molecule is attached to the platinum atom through the other ring nitrogen atom. The coordination around the platinum atom is square planar. The weighted best plane was calculated through the five atoms. The deviations from this plane are the following: Pt, 0.0014; Cl(1), −0.0315; Cl(2), −0.0215; S, −0.0052; N, −0.0375 Å. The angles around the platinum are close to the expected 90 and 180°. The pyrimidine ring is planar and makes an angle of 77.4° with the platinum coordination plane as shown in Figures 1 and 2.

The Pt–Cl bond lengths (2.291 and 2.310 Å) are normal and agree well with the published results which are in the range 2.28–2.32 Å.[3,9-12] The Pt–S bond length (2.222 Å) is in the

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