

effects, then, it is possible to make an estimate of λ_0' by means of the model of Murao¹⁶ where

$$\lambda_0' = \lambda_0 [1 - (a/z_0) \sum_n (2 - P_n) (\beta_n')^2]^4 \quad (11)$$

and λ_0 is the free ion spin-orbit coupling constant²⁶ (250 cm.⁻¹), a is the d-d screening constant, P_n is the number of electrons in the n th orbital when the ion is in an ionic state, and β_n' is the coefficient of the n th linear combination of the ligand orbitals in the metal-ligand antibonding orbital.

By using eq. 8 and 9, the value of κ is found to be nearly independent of P in the range $0.001 \leq P \leq 0.02$ cm.⁻¹ and is calculated to be 0.63 ± 0.04 . By means of an iterative procedure, in which it was assumed that $S_1 = S_2 = 0.1$ and $(\alpha')^2 = (\delta')^2$, eq. 6-11 were used to calculate the appropriate parameters. Our values of

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κ is considerably lower than those reported by other workers.^{2b,7} Kivelson and Lee^{2b} have shown that κ varies considerably in VO²⁺ complexes. Kuska and Rogers²⁷ have shown that κ is not necessarily constant for copper complexes. Furthermore, relatively low values of the hyperfine coupling constants in two other V(IV) complexes have recently been reported by Otherton, Locke, and McCleverty.²⁸

The resulting values of λ_0' and P were 156 and 0.0108 cm.⁻¹, respectively. We also obtain $\alpha = 0.95$, $\beta = 0.91$, and $\gamma = 0.97$, which suggests that the bonding is moderately covalent. The value of λ_0 is reduced by about 62% owing to screening effects, and these bonding parameters are comparable to those found in various cupric and vanadyl complexes.^{2, 8, 7, 20}

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Magnetic Studies with Copper(II) Salts. VII. The Structure of Copper(II) α,ω -Dicarboxylates and Their Amine Derivatives^{1,2}

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Received July 26, 1965

The magnetic susceptibility at temperatures between 80 and 350°K. is reported for copper(II) α,ω -dicarboxylates and their monoaniline and monopyridine derivatives of formula $\text{Cu}(\text{O}_2\text{C}(\text{CH}_2)_n\text{CO}_2)_n\text{L}$. Copper(II) malonate ($n = 1$) is magnetically uncomplicated; copper(II) oxalate ($n = 0$) exhibits the behavior of a linear antiferromagnet; copper(II) succinate ($n = 2$), glutarate ($n = 3$), and adipate ($n = 4$) display $\chi_M(T)$ behavior characteristic of singlet and triplet states in thermal equilibrium. With $L = 0$, water, and pyridine, the singlet-triplet separation is about 310-330 cm.⁻¹; with $L = \text{aniline}$ the interval is reduced to about 80-100 cm.⁻¹. The reflectance spectra of all polymeric dicarboxylates show broad absorption at about 7000 Å. (band I), but only the succinate, glutarate, and adipate contain an additional near-ultraviolet band at 3750 Å. (band II). Band I is sensitive and band II insensitive to changes of the axially situated amine. These electronic properties are consistent with copper acetate type dimers linked in infinite nets *via* the bifunctional dicarboxylate anions only when $n = 2, 3$, and 4. Quite different structures are proposed for copper(II) malonate and copper(II) oxalate.

Introduction

The copper(II) acetate dimer is the prototype⁴ of a rapidly expanding class of polynuclear molecules with metal-metal bonds.⁵⁻¹⁰ Valence bond¹¹⁻¹⁵ and

molecular orbital^{16,17} methods have both been used to substantiate claims that either δ bonding¹¹⁻¹⁶ or σ bonding¹⁷ is involved between the pairs of metal atoms. Some workers have assumed that the Cu-Cu interaction is weak,¹¹⁻¹⁵ others^{16,17} that it is strong. The emergent theories have had their strengths and limitations; all have failed to provide a convincing interpretation of the observed electronic spectrum.

The possible conformations of the acetate anions are such that it can bridge copper atoms either in discrete contiguous pairs (the *syn-syn* conformation) or in infinite arrangements which involve either the *anti-anti* or *anti-syn* conformations.¹⁸ Few examples have yet been confirmed of the acetate anion chelating simply to give a four-membered ring, although this geometry

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has now been established by X-ray methods for the complex uranyl(VI) acetate anion.¹⁹

The present work was originally undertaken as one part of an extensive series of physicochemical studies¹ designed to characterize and to elucidate the structures of various classes of substituted copper(II) carboxylates as well as the nature of the metal-metal bond. Ploquin had previously reported²⁰ that the paramagnetic susceptibilities at room temperature of a number of α,ω -dicarboxylates were anomalously low, a fact confirmed subsequently by our own work¹ and by that of Asai, *et al.*²¹ While it was clear at the time that the observed exchange demagnetization at room temperature was probably the result of structural features resembling those of the copper acetate dimer, confirmatory evidence in the form of studies of the temperature dependence of magnetism, of electronic spectra, and of crystal structure has remained unpublished.²

The single-crystal analysis of copper(II) succinate dihydrate is now nearing completion and the main structural features are reported in the following paper.²² Since these recent and independent studies complement our earlier physicochemical work,² the two papers are now presented together. In this paper we describe the temperature dependence of the paramagnetic susceptibility for the copper(II) derivatives of oxalic, malonic, succinic, glutaric, and adipic acids, and of a new series of their derivatives which involve axial substitution of either pyridine or aniline bases. The electronic spectra of all compounds have been recorded in reflectance.

Experimental Section

Materials. (a) **Copper Derivatives of Dicarboxylic Acids.**—To warm (70–80°) aqueous solutions of the appropriate dicarboxylic acids, copper carbonate was added in small amounts at 0.5-hr. intervals with constant stirring. The reaction mixtures were left to stand for 24 hr. to ensure complete reaction. They were then filtered and the collected materials washed with water and dried over calcium chloride. Copper oxalate–0.5-water. *Anal.* Calcd. for $C_2H_2O_4 \cdot 0.5Cu$: C, 14.96; H, 0.63; Cu, 39.59. Found: C, 14.85; H, 0.42; Cu, 39.33. Copper oxalate was also prepared by the method of Figgis and Martin,²² material of composition $Cu(C_2O_4) \cdot 0.3H_2O$ being obtained. *Anal.* Calcd.: Cu, 40.6. Found: Cu, 40.3. The tabulated magnetic data refer to this preparation. Copper malonate–2.5-water. *Anal.* Calcd. for $C_3H_2O_6 \cdot 2.5Cu$: C, 17.11; H, 3.05; Cu, 30.19. Found: C, 16.92; H, 3.05; Cu, 29.96. Copper succinate–2-water. *Anal.* Calcd. for $C_4H_4O_6Cu$: C, 22.31; H, 3.74; Cu, 29.49. Found: C, 22.10; H, 3.44; Cu, 29.30. Copper glutarate. *Anal.* Calcd. for $C_5H_4O_8Cu$: C, 31.00; H, 3.12; Cu, 32.82. Found: C, 30.36; H, 3.06; Cu, 32.31. Copper adipate. *Anal.* Calcd. for $C_6H_4O_8Cu$: C, 34.69; H, 3.88; Cu, 30.60. Found: C, 34.72; H, 4.13; Cu, 30.36. Anhydrous copper oxalate, malonate, and succinate were obtained after heating the hydrates at 140° for 10 hr. Copper oxalate. *Anal.* Calcd. for C_2O_4Cu : C, 15.85; Cu, 41.94. Found: C, 15.89; Cu, 41.79. Copper malonate. *Anal.* Calcd. for $C_3H_2O_6Cu$: C, 21.76; H, 1.22; Cu, 38.39. Found: C, 21.39; H, 1.71; Cu, 38.11. Copper succinate. *Anal.* Calcd. for $C_4H_2O_8Cu$: C, 26.74; H, 2.24; Cu, 35.39. Found: C, 27.08; H, 2.58; Cu, 35.14.

(b) **Pyridine Derivatives of Copper Derivatives of Dicarboxylic Acids.**—Treatment of the appropriate copper dicarboxylate with pyridine yielded blue diammines which when left in alcohol or heated in air at 80–90° lose one molecule of pyridine to form the emerald-green derivatives. Copper succinate–pyridine. *Anal.* Calcd. for $C_9H_9O_4NCu$: C, 41.78; H, 3.50; N, 5.42; Cu, 24.58. Found: C, 41.50; H, 3.49; N, 5.63; Cu, 24.31. Copper glutarate–pyridine. *Anal.* Calcd. for $C_{10}H_{11}O_8NCu$: C, 44.01; H, 4.06; N, 5.13; Cu, 23.31. Found: C, 43.94; H, 3.79; N, 4.99; Cu, 23.48. Copper adipate–pyridine. *Anal.* Calcd. for $C_{11}H_{13}O_8NCu$: C, 46.06; H, 4.57; N, 4.88; Cu, 22.17. Found: C, 45.83; H, 4.49; N, 5.12; Cu, 21.96.

(c) **Aniline Derivatives of Copper Derivatives of Dicarboxylic Acids.**—The appropriate anhydrous copper dicarboxylates were left to stand in a 1:4 aniline:benzene solution for 10–15 hr. Petroleum ether was then added and the green compounds were filtered off and washed with petroleum ether. Copper succinate–aniline. *Anal.* Calcd. for $C_{10}H_{11}O_4NCu$: C, 44.02; H, 4.06; N, 5.14; Cu, 23.31. Found: C, 44.18; H, 4.05; N, 5.25; Cu, 23.12. Copper glutarate–aniline. *Anal.* Calcd. for $C_{11}H_{13}O_8N$: C, 46.06; H, 4.57; N, 4.88; Cu, 22.17. Found: C, 45.74; H, 4.65; N, 5.03; Cu, 21.89.

Copper was estimated iodometrically using 0.01 *N* thiosulfate solution while carbon, hydrogen, and nitrogen were determined by standard microanalytical procedures.

Magnetic Measurements.—The magnetic susceptibilities at room temperature were determined by the Gouy method as described previously.¹¹ The effective magnetic moment, μ_{eff} , was calculated from the expression $\mu_{eff} = 2.839[(\chi_M - N\alpha)T]^{1/2}$ where $N\alpha = 60 \times 10^{-6}$ represents the temperature-independent contribution to the susceptibility. The experimental data are listed in Table I. The diamagnetic correction, Δ , was determined experimentally on samples of the free acids and amines. Data for copper sulfate are included for comparison purposes.

Absorption Spectra in Visible and Near-Ultraviolet Regions.—Reflectance spectra of copper(II) dicarboxylates and their amine derivatives were recorded between 3250 and 8000 Å., a Beckman DK-2 spectrophotometer being used. The wave length maxima of the absorption bands I and II are listed in Table II and typical spectra are illustrated in Figure 6.

Results and Discussion

The compounds selected for study include the first five members of the aliphatic α,ω -dicarboxylic acid derivatives of divalent copper, as well as their axially substituted hydrates, aniline, and pyridine derivatives of general formula $Cu(O_2C(CH_2)_nCO_2)L$. The magnetic properties at room temperature collected in Table III generally confirm the early data of Ploquin²⁰ and the attenuated curve of Asai, *et al.*,²¹ obtained by plotting magnetic moment against the chain length n . Thus, the moment of copper(II) oxalate ($n = 0$) is highly depressed to 1.15 B.M.; that of copper(II) malonate ($n = 1$) is close to the "spin-only" value 1.73 B.M., while those of the remaining derivatives succinate ($n = 2$), glutarate ($n = 3$), and adipate ($n = 4$) fall in the range 1.3 ± 0.1 B.M. common to the binuclear alkanoates.^{23–25} The introduction of pyridine in axial positions does not modify the magnetism significantly, the monopyridinates of the succinate, glutarate, and adipate being scattered about $\mu_{eff} = 1.4 \pm 0.1$ B.M. In accord with our previous observations,²⁶ aniline in axial positions significantly weakens the

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TABLE I
MAGNETIC DATA, $\chi_M(T)$ AND $\mu_{\text{eff}}(T)$, FOR $\text{Cu}(\text{O}_2\text{C}(\text{CH}_2)_n\text{CO}_2)_L$

Cu(O ₂ CCO ₂)·0.3H ₂ O														
Temp., °K.	98.0	116.2	143.5	174.7	206.0	235.6	251.0	258.5	266.0	273.2	276.8	297.3	321.0	355.
10 ⁶ χ _g	3.70	3.85	3.99	4.09	4.16	4.19	4.20	4.21	4.21	4.19	4.17	4.15	4.11	4.00
10 ⁶ χ _M	486	509	531	547	558	563	564	565	563	563	560	557	551	533
μ _{eff} , B.M.	0.66	0.73	0.83	0.93	1.01	1.09	1.12	1.14	1.16	1.17	1.18	1.22	1.26	1.30
Cu(O ₂ C(CH ₂)CO ₂)·2.5H ₂ O														
Temp., °K.	95.5	105.5	115.0	126.5	160.2	206.3	239.8	268.6	318.8					
10 ⁶ χ _g	20.9	19.6	17.4	16.3	11.9	9.29	8.03	6.94	5.79					
10 ⁶ χ _M	4503	4219	3766	3516	2604	2049	1783	1554	1311					
μ _{eff} , B.M.	1.85	1.88	1.85	1.88	1.81	1.82	1.80	1.80	1.79					
Cu(O ₂ C(CH ₂)CO ₂)														
Temp., °K.	94.1	101.0	105.0	113.2	125.0	145.7	176.7	211.7	244.7	300.0				
10 ⁶ χ _g	20.9	19.6	19.0	18.1	16.9	14.7	12.5	10.7	9.50	7.90				
10 ⁶ χ _M	3505	3306	3198	3052	2862	2485	2127	1834	1624	1388				
μ _{eff} , B.M.	1.62	1.63	1.63	1.65	1.68	1.69	1.72	1.74	1.76	1.78				
Cu(O ₂ C(CH ₂) ₂ CO ₂)·2H ₂ O														
Temp., °K.	82.0	100.0	153.0	204.7	256.2	289.3	320.7	352.3						
10 ⁶ χ _g	0.35	0.40	2.10	2.99	3.36	3.44	3.42	3.35						
10 ⁶ χ _M	162	173	540	732	811	828	824	809						
μ _{eff} , B.M.	0.25	0.30	0.77	1.05	1.24	1.34	1.40	1.46						
Cu(O ₂ C(CH ₂) ₂ CO ₂)														
Temp., °K.	82.5	96.2	153.2	222.5	261.0	292.8	328.0	360.1						
10 ⁶ χ _g	0.54	0.76	2.60	3.87	3.96	4.00	3.97	3.83						
10 ⁶ χ _M	157	198	526	755	771	778	773	748						
μ _{eff} , B.M.	0.25	0.33	0.76	1.12	1.22	1.30	1.37	1.41						
Cu(O ₂ C(CH ₂) ₂ CO ₂)·pyridine														
Temp., °K.	86.5	103.7	132.0	201.5	254.0	295.0	333.5	382.0						
10 ⁶ χ _g	1.09	1.31	1.85	3.20	3.64	3.74	3.72	3.66						
10 ⁶ χ _M	390	447	587	935	1048	1075	1070	1053						
μ _{eff} , B.M.	0.48	0.57	0.75	1.19	1.42	1.55	1.65	1.75						
Cu(O ₂ C(CH ₂) ₂ CO ₂)·aniline														
Temp., °K.	92.9	100.6	109.5	120.2	135.0	157.5	210.1	252.0	310.0					
10 ⁶ χ _g	8.80	8.47	8.10	7.62	7.05	6.35	5.05	4.34	3.60					
10 ⁶ χ _M	2522	2433	2332	2201	2043	1853	1498	1305	1103					
μ _{eff} , B.M.	1.35	1.39	1.41	1.44	1.47	1.51	1.56	1.59	1.61					
Cu(O ₂ C(CH ₂) ₃ CO ₂)														
Temp., °K.	84.7	97.1	162.4	221.6	262.6	292.0	325.7	351.0	378.5					
10 ⁶ χ _g	0.36	0.70	2.65	3.54	3.72	3.76	3.70	3.64	3.49					
10 ⁶ χ _M	121	215	600	776	813	821	808	796	766					
μ _{eff} , B.M.	0.20	0.35	0.84	1.13	1.26	1.34	1.40	1.44	1.47					
Cu(O ₂ C(CH ₂) ₃ CO ₂)·pyridine														
Temp., °K.	94.0	104.5	189.7	233.7	274.2	302.6	324.5	350.7	375.2					
10 ⁶ χ _g	0.24	0.48	2.08	2.41	2.52	2.56	2.54	2.50	2.46					
10 ⁶ χ _M	185	223	687	778	808	819	814	803	791					
μ _{eff} , B.M.	0.31	0.37	0.98	1.16	1.29	1.36	1.41	1.45	1.49					
Cu(O ₂ C(CH ₂) ₃ CO ₂)·aniline														
Temp., °K.	80.6	92.8	105.0	121.5	152.4	198.7	251.3	312.3	358.7					
10 ⁶ χ _g	8.24	7.82	7.57	7.19	6.46	5.46	4.66	3.95	3.50					
10 ⁶ χ _M	2497	2379	2305	2197	1986	1699	1471	1267	1137					
μ _{eff} , B.M.	1.26	1.32	1.38	1.44	1.54	1.62	1.69	1.74	1.76					
Cu(O ₂ C(CH ₂) ₄ CO ₂)														
Temp., °K.	83.8	88.1	101.9	142.4	199.0	252.4	281.1	313.9	337.9	349.2	378.7	396.6		
10 ⁶ χ _g	0.14	0.25	0.39	1.17	2.28	2.69	2.83	2.89	2.82	2.81	2.76	2.69		
10 ⁶ χ _M	112	136	164	326	556	641	670	681	668	665	655	640		
μ _{eff} , B.M.	0.19	0.23	0.29	0.55	0.89	1.09	1.18	1.25	1.29	1.30	1.35	1.37		
Cu(O ₂ C(CH ₂) ₄ CO ₂)·pyridine														
Temp., °K.	85.5	110.0	162.5	238.3	273.3	312.5	339.0	375.2						
10 ⁶ χ _g	0.67	1.06	1.85	2.52	2.62	2.67	2.66	2.57						
10 ⁶ χ _M	322	434	661	852	883	895	892	866						
μ _{eff} , B.M.	0.42	0.57	0.89	1.23	1.34	1.45	1.51	1.56						

copper-copper interaction, with moments of 1.60 and 1.73 B.M. being observed for the succinate and glutarate derivatives. These data clearly demonstrate that the higher ($n = 2, 3,$ and 4) α,ω -dicarboxylates are

bifunctional and can effectively bridge magnetically isolated copper(II) acetate type dimers in either two- or three-dimensional networks *via* $(-\text{CH}_2-)_n$ chains of the type proposed by Asai, *et al.*, shown in Figure 1.

TABLE II
 REFLECTANCE SPECTRA OF $\text{Cu}(\text{O}_2\text{C}(\text{CH}_2)_n\text{CO}_2)_L$

Compound ^a	Band I, μm	Band II, μm
$\text{Cu}(\text{CH}_3\text{CO}_2)_2$	650	375
$\text{Cu}(\text{O}_2\text{CCO}_2)$	730	...
$\text{Cu}(\text{O}_2\text{C}(\text{CH}_2)\text{CO}_2)$	775	...
$\text{Cu}(\text{O}_2\text{C}(\text{CH}_2)_2\text{CO}_2)$	655	369
$\text{Cu}(\text{O}_2\text{C}(\text{CH}_2)_3\text{CO}_2)$	652	382
$\text{Cu}(\text{O}_2\text{C}(\text{CH}_2)_4\text{CO}_2)$	655	380
$\text{Cu}(\text{CH}_3\text{CO}_2)_2 \cdot \text{py}$	680	370
$\text{Cu}(\text{O}_2\text{C}(\text{CH}_2)_2\text{CO}_2) \cdot \text{py}$	670	378
$\text{Cu}(\text{O}_2\text{C}(\text{CH}_2)_3\text{CO}_2) \cdot \text{py}$	678	377
$\text{Cu}(\text{O}_2\text{C}(\text{CH}_2)_4\text{CO}_2) \cdot \text{py}$	684	381
$\text{Cu}(\text{O}_2\text{C}(\text{CH}_2)_2\text{CO}_2) \cdot \text{an}$	652	375
$\text{Cu}(\text{O}_2\text{C}(\text{CH}_2)_3\text{CO}_2) \cdot \text{an}$	656	380

^a py, pyridine; an, aniline.

 TABLE III
 MAGNETIC PROPERTIES OF COPPER(II) α, ω -DICARBOXYLATES AT ROOM TEMPERATURE

Compound ^a	$-10^6 \Delta$	$10^6 \chi_M$	μ_{eff} , B.M.
Oxalates			
$\text{Cu}(\text{O}_2\text{CCO}_2)$	36	625	1.15
$\text{Cu}(\text{O}_2\text{CCO}_2) \cdot 0.5\text{H}_2\text{O}$	42	625	1.15
Malonates			
$\text{Cu}(\text{O}_2\text{C}(\text{CH}_2)\text{CO}_2)$	56	1370	1.75
$\text{Cu}(\text{O}_2\text{C}(\text{CH}_2)\text{CO}_2) \cdot 2.5\text{H}_2\text{O}$	90	1395	1.77
Succinates			
$\text{Cu}(\text{O}_2\text{C}(\text{CH}_2)_2\text{CO}_2)$	60	780	1.30
$\text{Cu}(\text{O}_2\text{C}(\text{CH}_2)_2\text{CO}_2) \cdot 2\text{H}_2\text{O}$	86	830	1.34
$\text{Cu}(\text{O}_2\text{C}(\text{CH}_2)_2\text{CO}_2) \cdot \text{py}$	107	1075	1.54
$\text{Cu}(\text{O}_2\text{C}(\text{CH}_2)_2\text{CO}_2) \cdot \text{an}$	121	1135	1.60
Glutarates			
$\text{Cu}(\text{O}_2\text{C}(\text{CH}_2)_3\text{CO}_2)$	75	815	1.34
$\text{Cu}(\text{O}_2\text{C}(\text{CH}_2)_3\text{CO}_2) \cdot \text{py}$	120	815	1.34
$\text{Cu}(\text{O}_2\text{C}(\text{CH}_2)_3\text{CO}_2) \cdot \text{an}$	134	1325	1.73
Adipates			
$\text{Cu}(\text{O}_2\text{C}(\text{CH}_2)_4\text{CO}_2)$	83	675	1.20
$\text{Cu}(\text{O}_2\text{C}(\text{CH}_2)_4\text{CO}_2) \cdot \text{py}$	130	890	1.40

^a py, pyridine; an, aniline.

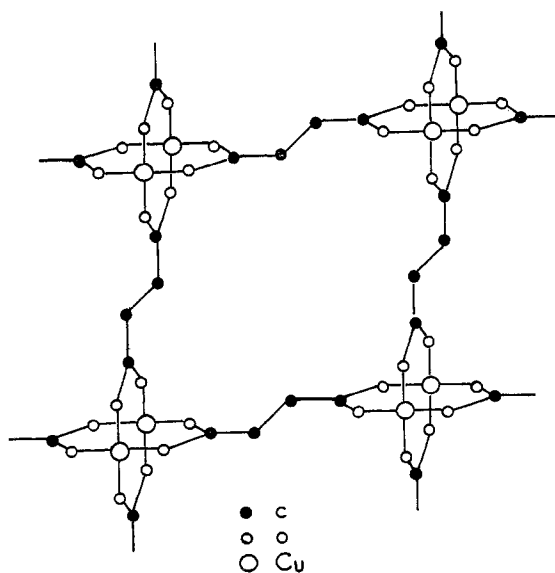


Figure 1.—Structure of copper(II) succinate proposed by Asai, Kishita, and Kubo.²¹

The single-crystal X-ray structure of copper(II) succinate dihydrate reported in the following paper²² reveals that, in fact, adjoining dimers are bridged in

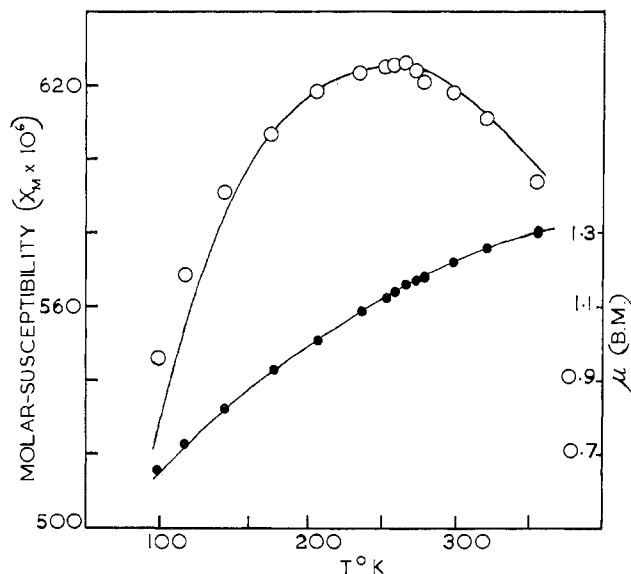


Figure 2.—Variation of molar susceptibility (χ_M) and magnetic moment (μ_{eff}) with temperature for hydrated copper(II) oxalate. Full curves calculated from eq. 1 and 2. Experimental data as shown: circles, χ_M ; solid circles, μ_{eff} .

infinite chains by *two* dicarboxylate residues rather than *one* as originally proposed by Asai, *et al.*²¹

Magnetism and Structure of Copper(II) Oxalate.—

The variation with temperature of the magnetic susceptibility of copper(II) oxalate (Figure 2) is characterized by an unusually broad maximum at 260°K. Although a corresponding maximum is observed for the binuclear copper(II) acetates, the susceptibility of the present compound is much less sensitive to temperature, with values of χ_M falling in the narrow range $546\text{--}626 \times 10^{-6}$ c.g.s.e.m.u. between 98.0 and 356°K.

The experimental data cannot be fitted in terms of an equilibrium between singlet and triplet spin states (compare eq. 3). However, application of a one-dimensional Ising model of antiferromagnetism leads to good agreement between experimental and theoretical results. The Ising model has been successfully applied by Barraclough and Ng²⁷ to describe the linear antiferromagnetism in copper(II) bromide and copper(II) chloride which is interpreted in terms of electron spin interactions along an infinite chain of copper atoms. The salient features of their treatment may be summarized as follows: (i) A simple linear arrangement of Cu atoms is assumed, each with one unpaired electron giving a magnetic moment $\mu = g\beta/2$, where g = spectroscopic splitting factor and β = Bohr magneton. (ii) The model allows for interactions between nearest neighbors and assumes that if a pair of adjacent copper atoms have their electron spins parallel that an interaction energy of $-J$ is involved and if their spins are antiparallel an interaction of $+J$ is involved. Since the system is antiferromagnetic, J takes negative values and the separation between singlet and triplet states is $-2J$. (iii) Above the temperature of maximum susceptibility, T_c , there is no long-range order-

ing of spins so that their alignment is either parallel or antiparallel to the direction of the applied field.

In this region the susceptibility per mole of copper atoms is

$$\chi_M = \frac{N\beta^2}{3kT} \left(\frac{3g^2}{4} \right) (\exp(2J/kT)) + N\alpha \quad (1)$$

(iv) Below T_c , long-range ordering of spins commences and leads to spontaneous antiferromagnetism in a unique direction. The electron spins will be randomly oriented with respect to this direction in a powdered sample which is isotropic. The susceptibility expression in this region is

$$\chi_M = \frac{N\beta^2}{3kT} \left(\frac{g^2}{4} \right) \left(\exp \frac{2J}{kT} \right) + \frac{N\beta^2}{3kT_c} \left(\frac{g^2}{2} \right) (\exp(-1)) + N\alpha \quad (2)$$

The experimental data are compared with a theoretical curve calculated from eq. 1 and 2 in Figure 2. Good agreement between experiment and theory is obtained using the values $g = 2.18$, $T_c = 260^\circ\text{K.}$, and $N\alpha = 60 \times 10^{-6}$ c.g.s.e.m.u. It follows from eq. 1 and 2 that

$$\chi_M = \frac{N\beta^2}{3kT_c} \left(\frac{g^2}{2} \right) (\exp(-1)) + N\alpha$$

$T = 0$ and rises to a maximum value at $T_c = -2J/k$ so that the exchange interaction can be determined directly from the temperature of the maximum, $J = \frac{1}{2}kT_c$. The present values are compared in Table IV with those derived for other divalent copper compounds in which linear antiferromagnetism appears to be involved.

TABLE IV
ESTIMATED VALUES OF g , T_c , AND J FOR
LINEAR ANTIFERROMAGNETIC Cu(II) COMPOUNDS

Compound	g	T_c , °K.	$-2J$		Ref.
			cm. ⁻¹	kcal. mole ⁻¹	
CuCl ₂	2.20	70	49	0.14	27
CuBr ₂	2.18	226	157	0.45	27
Cu(C ₂ O ₄)	2.18	260	181	0.52	This work
Cu(OCH ₃) ₂	2.20	260	181	0.52	a

^a R. W. Adams, E. A. Bishop, R. L. Martin, and G. Winter. *Australian J. Chem.*, in press.

The close similarity between the magnetic properties of the four compounds listed in Table IV points to a common underlying structural feature. The crystal structures of copper(II) chloride and copper(II) bromide have confirmed the presence of chains of copper atoms linked together by bridging halogen atoms.^{28,29} This feature is realized in copper(II) oxalate if structures of the type shown in Figure 3 or 4 are considered. The considerable thermal stability and marked lack of chemical reactivity of copper(II) oxalates are consistent with an infinite chain-like structure, which in the case of the structure shown in Figure 3 might also

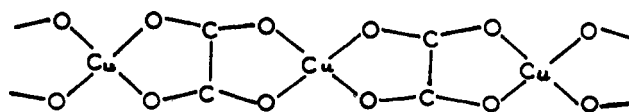


Figure 3.—Possible structure for copper(II) oxalate involving Cu_n chains.

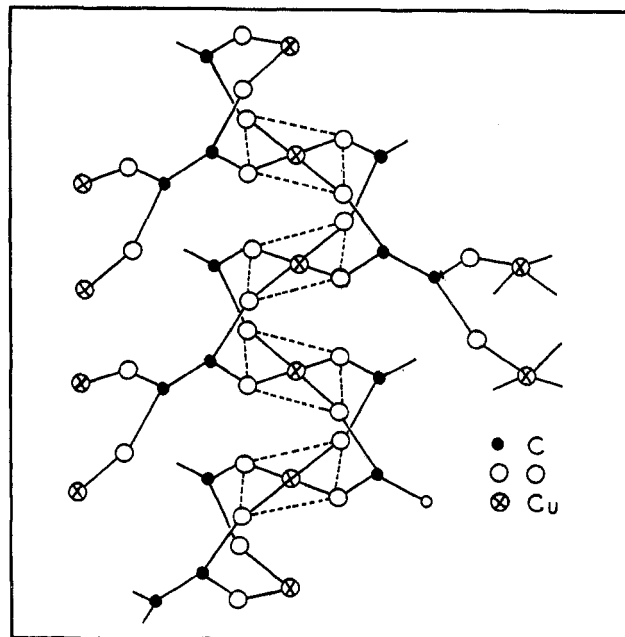


Figure 4.—Alternative structure for copper(II) oxalate involving Cu_n chains.

involve inter-chain interaction to complete a distorted octahedron of oxygen atoms about each central metal atoms. Thus copper(II) oxalate exhibits no thermal decomposition at 290° , is insoluble in all solvents, and does not react with nitrogenous bases such as pyridine and aniline.

Presumably, the exchange mechanism for spin coupling involves the delocalized π cloud of the bridging oxalate ions¹⁸ although direct spin-spin interaction¹¹ is also possible in the structure shown in Figure 4.

Magnetism and Structure of Copper(II) Malonate.—The magnetic moment of hydrated copper(II) malonate is 1.77 B.M. at room temperature and the magnetic susceptibility deviates but slightly from a Curie law. Accordingly, it can be safely inferred that the malonate neither adopts a structure which involves pairs of copper atoms bridged by malonate ions in the *syn-syn* conformation¹⁸ nor one based on linear chains of copper atoms. If it is assumed that some water is incorporated by hydrogen bonding in the crystal lattice, the hydrated malonate can be formulated as a simple monomeric entity which may possibly interact with other oxygen atoms in the lattice to achieve a coordination number higher than four for copper.

Dehydration of copper(II) malonate does not appreciably modify its magnetic properties and it is possible that a polymeric network is adopted in which water molecules are replaced by carbonyl oxygen atoms of adjoining malonate groups.

(28) A. F. Wells, *J. Chem. Soc.*, 1670 (1947).

(29) L. Helmholtz, *J. Am. Chem. Soc.*, **69**, 886 (1947).

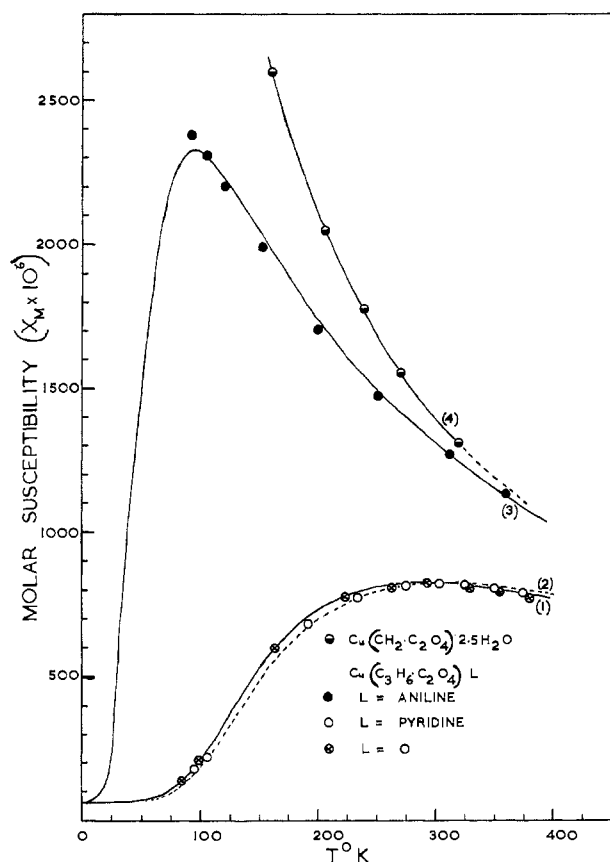


Figure 5.—Variation of molar susceptibility (χ_M) with temperature. Curve 1 calculated from eq. 6; curve 2 calculated from eq. 9; curve 3 calculated from eq. 11; curve 4 calculated from Curie-Weiss law with $\theta = 10^\circ$.

Unlike the homologs of the copper(II) dicarboxylates, the malonate dissolves freely in pyridine to give a magnetically normal blue bis(pyridine) derivative which cannot be converted to a monopyridinate by heating.³⁰

Magnetism and Structure of Copper Succinate, Glutarate, and Adipate.—The variation of magnetic susceptibility with temperature of anhydrous and hydrated copper(II) succinate, anhydrous copper(II) glutarate, and anhydrous copper(II) adipate exhibits the characteristic features so well-established for the copper(II) acetate prototype (*cf.* Figure 5). The experimental data conform reasonably well with the standard singlet-triplet formula

$$\chi_M = \frac{N\beta^2}{3kT} (3g^2) \left(3 + \exp \frac{-2J}{kT} \right)^{-1} + N\alpha \quad (3)$$

and the required values of g , T_c , and J ³¹ estimated by previous procedures are collected in Table V; the full curves in figure 5 have been calculated from the equations

(30) It has been suggested by a referee that the atypical behavior of the oxalate and malonate might arise from the greater stability of the five- and six-membered chelate rings which are possible only for the first two members of the homologous series.

(31) In order to conform with the more usual definition of exchange interaction, $-2J$ is used wherever J appeared in ref. 11.

TABLE V
ESTIMATED VALUES OF g , T_c , AND J FOR $\text{Cu}(\text{O}_2\text{C}(\text{CH}_2)_n\text{CO}_2)\text{L}$

Compound ^a	g	T_c , °K.	$-2J$	
			cm. ⁻¹	kcal. mole ⁻¹
$\text{Cu}(\text{O}_2\text{C}(\text{CH}_2)_2\text{CO}_2)$	2.12	293	324	0.93
$\text{Cu}(\text{O}_2\text{C}(\text{CH}_2)_2\text{CO}_2) \cdot 2\text{H}_2\text{O}$	2.22	300	331	0.95
$\text{Cu}(\text{O}_2\text{C}(\text{CH}_2)_2\text{CO}_2) \cdot \text{py}$	2.60	310	342	0.98
$\text{Cu}(\text{O}_2\text{C}(\text{CH}_2)_2\text{CO}_2) \cdot \text{an}$	~2.2	~90	~100	~0.3
$\text{Cu}(\text{O}_2\text{C}(\text{CH}_2)_3\text{CO}_2)$	2.17	290	320	0.91
$\text{Cu}(\text{O}_2\text{C}(\text{CH}_2)_3\text{CO}_2) \cdot \text{py}$	2.23	305	337	0.96
$\text{Cu}(\text{O}_2\text{C}(\text{CH}_2)_3\text{CO}_2) \cdot \text{an}$	2.16	96	107	0.31
$\text{Cu}(\text{O}_2\text{C}(\text{CH}_2)_4\text{CO}_2)$	2.04	315	348	0.99
$\text{Cu}(\text{O}_2\text{C}(\text{CH}_2)_4\text{CO}_2) \cdot \text{py}$	2.35	310	342	0.98

^a py, pyridine; an, aniline.

$$\text{Cu}(\text{O}_2\text{C}(\text{CH}_2)_2\text{CO}_2): \chi_M = [0.557/T] \times [1 + 1/3 \exp(469/T)]^{-1} + 60 \times 10^{-6} \quad (4)$$

$$\text{Cu}(\text{O}_2\text{C}(\text{CH}_2)_2\text{CO}_2) \cdot 2\text{H}_2\text{O}: \chi_M = [0.612/T] \times [1 + 1/3 \exp(480/T)]^{-1} + 60 \times 10^{-6} \quad (5)$$

$$\text{Cu}(\text{O}_2\text{C}(\text{CH}_2)_3\text{CO}_2): \chi_M = [0.585/T] \times [1 + 1/3 \exp(464/T)]^{-1} + 60 \times 10^{-6} \quad (6)$$

$$\text{Cu}(\text{O}_2\text{C}(\text{CH}_2)_4\text{CO}_2): \chi_M = [0.519/T] \times [1 + 1/3 \exp(504/T)]^{-1} + 60 \times 10^{-6} \quad (7)$$

$$\text{Cu}(\text{O}_2\text{C}(\text{CH}_2)_2\text{CO}_2) \cdot \text{py}: \chi_M = [0.837/T] \times [1 + 1/3 \exp(496/T)]^{-1} + 60 \times 10^{-6} \quad (8)$$

$$\text{Cu}(\text{O}_2\text{C}(\text{CH}_2)_3\text{CO}_2) \cdot \text{py}: \chi_M = [0.615/T] \times [1 + 1/3 \exp(488/T)]^{-1} + 60 \times 10^{-6} \quad (9)$$

$$\text{Cu}(\text{O}_2\text{C}(\text{CH}_2)_4\text{CO}_2) \cdot \text{py}: \chi_M = [0.687/T] \times [1 + 1/3 \exp(496/T)]^{-1} + 60 \times 10^{-6} \quad (10)$$

$$\text{Cu}(\text{O}_2\text{C}(\text{CH}_2)_3\text{CO}_2) \cdot \text{an}: \chi_M = [0.579/T] \times [1 + 1/3 \exp(154/T)]^{-1} + 60 \times 10^{-6} \quad (11)$$

The good agreement between the experimental data and the calculated curves confirms that the magnetic interaction is intramolecular, being confined to pairs of carboxylate-bridged copper atoms isolated magnetically from neighboring Cu_2 clusters by the intervening $(-\text{CH}_2)_2$, $(-\text{CH}_2)_3$, and $(-\text{CH}_2)_4$ groups. The mean values of g , T_c , and J fall in the ranges $g = 2.10 \pm 0.06$, $T_c = 302 \pm 12^\circ\text{K.}$, and $-2J = 332 \pm 12 \text{ cm.}^{-1}$, which may be compared with those of copper(II) acetate monohydrate, *viz.*, $g = 2.13$, $T_c = 255^\circ\text{K.}$, and $-2J = 286 \text{ cm.}^{-1}$.

In contrast to the copper monocarboxylates, the higher homologs ($n \geq 2$) of the copper α,ω -dicarboxylates absorb but do not dissolve in pyridine and aniline. Blue adducts of unknown composition are initially formed which readily lose amine to yield emerald-green monopyridinates and brown-green monoanilines either by gentle heating or extraction with ethanol. Unfortunately, purification of these derivatives was not possible, by the usual procedures, and although analyses were satisfactory, the temperature dependence of the susceptibility shows appreciable deviations from eq. 3. Thus the form of the $\chi_M(T)$ curves for the monopyridinates of succinate and adipate indicate the presence of a paramagnetic impurity from

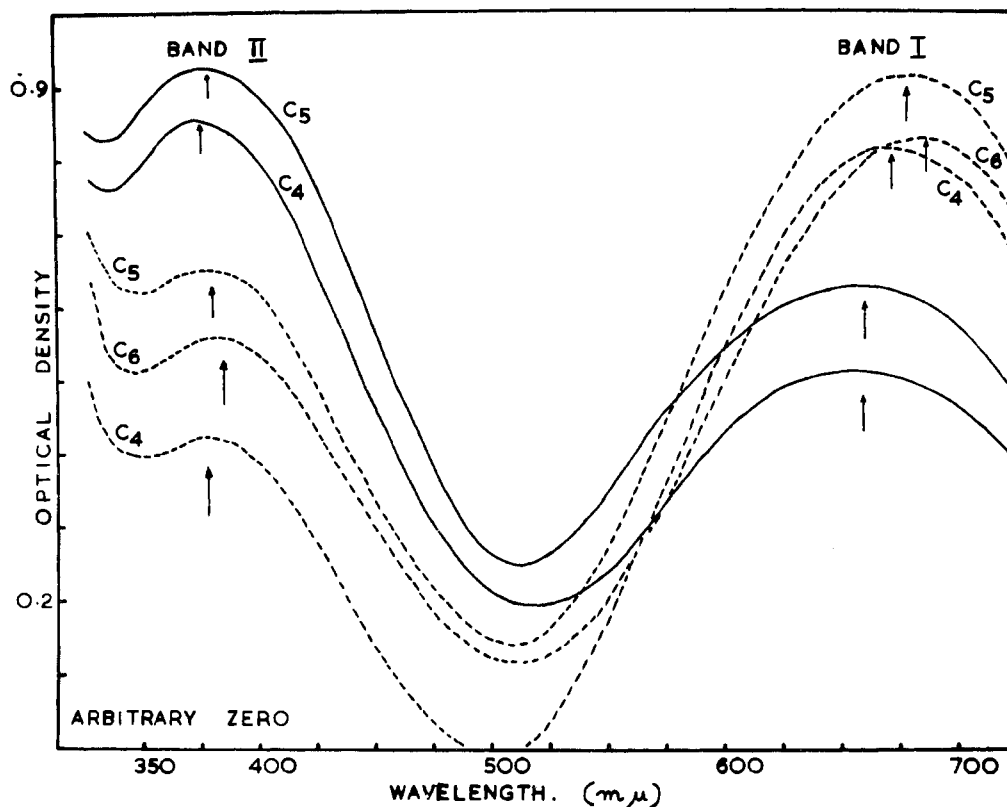


Figure 6.—Reflectance spectra of pyridine and aniline adducts of copper(II) dicarboxylates. Full curves: C₄, Cu(O₂C(CH₂)₂CO₂)·aniline; C₅, Cu(O₂C(CH₂)₃CO₂)·aniline. Dashed curves: C₄, Cu(O₂C(CH₂)₂CO₂)·pyridine; C₅, Cu(O₂C(CH₂)₃CO₂)·pyridine; C₆, Cu(O₂C(CH₂)₄CO₂)·pyridine.

which derive unusually high g values of 2.60 and 2.35, respectively. Likewise, the $\chi_M(T)$ behavior of the monoaniline derivative of copper(II) succinate is poorly described by eq. 3. Even so, the present data are adequate to confirm the pattern of behavior previously established²⁶ for the monopyridine and monoaniline adducts of copper(II) monocarboxylates (*cf.* Figure 5). The singlet-triplet separation, which for the pyridine series lies in the range $-2J = 307 \pm 3 \text{ cm.}^{-1}$, is markedly reduced by substitution of aniline to values of the order of 80–90 cm.^{-1} (*cf.* Figure 5). It is apparent that the polymeric network adopted by the higher copper(II) dicarboxylates in no way impedes a substitution of nitrogenous ligands along the copper-copper axis.

Electronic Spectra of Copper(II) Dicarboxylates.—The marked insolubility in organic solvents precludes the measurement of absorption spectra of the dicarboxylates in solution. However, reflectance spectra of Cu₂(O₂C(CH₂) _{n} CO₂)L₂, with $n = 2, 3,$ and 4 and $L = 0, \text{H}_2\text{O},$ pyridine, and aniline (see Figure 6) closely resemble those of the corresponding monocarboxylates.^{24, 26} The expected two well-defined and well-separated regions of absorption are clearly discerned in the regions 6500–7000 Å. (band I) and 3700–3800 Å. (band II). Band I is displaced by some 200 Å. to shorter wave lengths by substitution of pyridine by aniline, as was observed previously for pyridine and aniline derivatives of copper(II) butyrate. Band II displays the same invariance to axial substituents as noted earlier²⁶ for the monocarboxylate series.

The absence of absorption bands other than I and II provides support for the present formulation of the monoaniline derivative as a true adduct of the binuclear copper species. Thus we find that the reflectance spectrum of mononuclear Cu(O₂C(CH₂)₄CO₂)(*p*-toluidine)₂ has three well-defined regions of absorption at 3930, 5500, and 6750 Å. A physical mixture of this compound with the parent carboxylate would not reproduce the two-band system illustrated in Figure 6. This conclusion is reinforced by the inversion of the relative intensities of bands I and II when aniline is replaced by pyridine in axial positions.

The sensitivity of band I to the nature of the terminal substituent is useful evidence favoring its assignment as an internal transition involving only d orbitals. Arylamines, as discussed elsewhere,³² are comparatively weak bases and coordinate weakly to most metals. Although water, ethanol, and dioxane bind more strongly to central ions, as two-lone-electron-pair donors, they tend to produce smaller ligand field splittings than one-electron-pair donors such as ammonia and the substituted amines.^{33, 34} Thus the "blue-shift" of band I which occurs when pyridine is substituted by water, ethanol, dioxane, or aniline is symptomatic of the increasing tetragonal distortion about the central copper ion. On the other hand, the more weakly bound arylamine should leave a higher net positive

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(34) D. P. Graddon and E. C. Watton, *Australian J. Chem.*, **18**, 507 (1965).

charge on the central copper ion and so reduce the radial extension of copper 3d orbitals and thereby lower the concomitant singlet-triplet separation.³² That is, for the dimer the order of spectrochemical effects is dioxane \sim water \sim ethanol $<$ aniline $<$ pyridine, whereas the order of singlet-triplet reducing power is pyridine $<$ dioxane \sim water \sim ethanol $<$ aniline.

The insensitivity of band II to these ligands is at variance with the original proposal of Yamada, *et al.*,³⁵ that this band is "an indication of the linkage between the two copper atoms." Nor can it be assigned to an internal transition in the partly filled d shell, and we have commented elsewhere²⁸ on other evidence which precludes such an assignment. We have recently completed molecular orbital calculations in the Hückel approximation of the π system of the copper(II) acetate dimer and have concluded that band II may either arise from electron transfer from the highest filled π -nonbonding orbital of the ligand to the empty σ -antibonding $d_{x^2-y^2}$ orbital on copper or possibly from

(35) R. Tsuchida and S. Yamada, *Nature*, **176**, 1171 (1955).

the filled d_{xy} orbital of copper to the empty π -antibonding orbital of the acetate ligands.³⁶ The appearance of a similar near-ultraviolet band in the electronic spectra of monomeric copper(II) acetylacetonate³⁷ and of planar-bridged dimers³⁸ such as 8-hydroxyquinolinatocopper(II) is not unexpected, for closely related copper-ligand π systems are present for each compound.

The reflectance spectra of copper(II) malonate and copper(II) oxalate are atypical of the dicarboxylates in having a single broad region of absorption occurring at 775 and 730 m μ , respectively (see Table II). The absence of band II from the spectra is expected from the magnetic properties of these two derivatives and reinforces our view that this band originates in the π system of the copper acetate dimer.

Acknowledgment.—The authors thank Dr. Ernest Challen of the University of New South Wales for carbon, hydrogen, and nitrogen microanalyses.

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The Magnetic Properties and Structure of the Cupric α,ω -Dicarboxylates

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Received July 26, 1965

The magnetic susceptibilities of five of the cupric α,ω -dicarboxylates have been measured between about 80 and 300°K. The results confirm that, with the exception of the malonate, the structures of the compounds are based upon the dimeric unit found in the cupric monocarboxylates. The succinate, and probably the glutarate and suberate, are formed of chains of magnetically isolated dimeric units joined by $-(CH_2)_n-$ bridges. The oxalate shows most anomalous magnetic behavior, and this is believed to follow from a three-dimensional cross-linked arrangement of the dimers.

The magnetic moments of a considerable number of complexes of bivalent copper are below the more normal value of about 1.9 B.M.¹ and indeed are below the spin-only value for one unpaired electron, 1.73 B.M. In most of the compounds the reduction in the magnetic moment is attributed to magnetic exchange of an anti-ferromagnetic nature consequent upon either the formation of a weak bond between two or more copper atoms² or a superexchange process *via* intervening oxygen or other atoms.³ The most notable instance concerns the acetate and higher monocarboxylic acid derivatives, $Cu_2(RCOO)_4 \cdot 2H_2O$. That series of compounds is based upon the dimeric structure which is established for the acetate by X-ray single-crystal analysis.⁴ The four acetate groups bridge the two copper atoms. One

oxygen atom from each forms part of the square plane about each copper. The octahedral stereochemistry of each copper atom is completed by a water molecule and the other copper atom.

The variation of magnetic susceptibility of the cupric monocarboxylates with temperature is accurately of the form required for magnetic interaction between two sites of spin $1/2$ with exchange integral J .⁵ The susceptibility should obey the relationship

$$\chi_{Cu} = 3g^2 \frac{N\beta^2}{3kT} [3 + \exp(-2J/kT)]^{-1} + N\alpha \quad (1)$$

where g is the Lande splitting factor (near 2.2 for most cupric complexes) and $N\alpha$ is the temperature-independent paramagnetism (about 60×10^{-6} c.g.s./mole for most cupric complexes).⁶ $Cu_2(CH_3COO)_4 \cdot 2H_2O$ is accounted for with $J = -204^\circ$, $g = 2.13$, and $N\alpha =$

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(3) R. L. Martin and H. Waterman, *ibid.*, 1359 (1959).

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