

279. *Magnetic Studies with Copper(II) Salts. Part III.¹ The Constitution of Copper(II) n-Alkanoates in Solution.*

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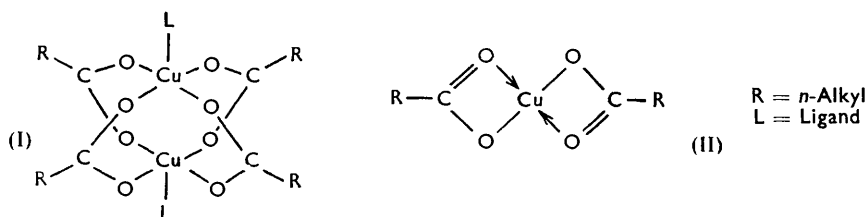
The anomalously low room-temperature magnetic moments observed for powdered copper(II) salts of straight-chain alkanolic acids¹ are shown to persist in dioxan and in benzene solutions. The solutions are non-conductors of electricity, and cryoscopic measurements indicate that the salts, when soluble, are dimeric in dioxan. Spectrophotometric studies in the visible and the near ultraviolet region reveal that, in addition to the familiar "copper band" occurring at *ca.* 7000 Å, the solutions are characterised by a well-defined absorption band at 3750 Å. These observations leave little doubt that the compounds retain their binuclear configuration in the above solvents, and unambiguously establish that exchange demagnetisation in copper *n*-alkanoates is intramolecular rather than intermolecular.

In contrast, magnetic, electrical conductivity, cryoscopic, and spectrophotometric measurements in aqueous solutions demonstrate that the binuclear structure is destroyed by water, and confirm that the compounds are largely dissociated into ions by this solvent.

The heavier alkanoates exhibit the critical solution (Krafft) phenomenon both in dioxan and in benzene, and in the latter produce remarkably small elevations of boiling point. These observations reflect a change in degree of dispersion of the compounds from molecular to micellar at the critical solution temperature, each micelle most probably consisting of aggregates, $[\text{Cu}_2(\text{R}\cdot\text{CO}_2)_4]_n$, of binuclear molecules, bound together by weak polar forces in conjunction with residual attractive forces between peripheral hydrocarbon chains.

Copper formate has been obtained in the binuclear configuration for the first time, in the form of a dioxan complex which has a particularly low magnetic moment, $\mu \sim 1$ B.M.

PREVIOUSLY^{1,2} it was shown that a number of copper(II) salts of *n*-alkanoic acids exhibit a temperature variation of their magnetic susceptibility which is anomalous in the sense that antiferromagnetic rather than Curie-law behaviour is observed. The shapes of all the susceptibility-temperature curves were so closely similar that it was suggested that, in the solid state, copper *n*-alkanoates adopt the acetate-type binuclear configuration (I) rather than the uninuclear structure (II). If this postulate is correct, the anomalous magnetic behaviour is readily understood in terms of intramolecular exchange interaction between contiguous copper atoms within each binuclear molecule.



However, an alternative suggestion, favouring structure (II), was made by Gilmour and Pink,³ to account for the anomalous magnetic behaviour of copper laurate, namely, that supposedly planar laurate molecules stack crystallographically to form layers of copper atoms separated by fatty acid groups extending in both directions. They further suggested

¹ Part II, Martin and Waterman, *J.*, 1957, 2545.

² Figgis and Martin, *J.*, 1956, 3837.

³ Gilmour and Pink, *J.*, 1953, 2198.

that the resulting intermolecular exchange interaction would be antiferromagnetic and thus account for both the diminished susceptibility and its anomalous temperature dependence. Although they too now⁴ favour structure (I) for copper laurate, it remains important to examine their earlier postulate in more detail. Furthermore, it is of interest to elucidate the constitution of these compounds both in non-ionising and in aqueous solvents.

A crucial test for the binuclear structure lies in ascertaining whether the magnetic moment will remain quenched when the possibility of intermolecular exchange is removed by dissolving the compounds in solvents such as dioxan or benzene. If the binuclear structure (I) is present in solution, intramolecular exchange will persist and the magnetic moment will remain diminished. If, on the other hand, the uninuclear structure (II) is favoured, all copper-copper interactions will be eliminated and the moment will rise to the value usually observed for magnetically dilute copper(II) compounds.

An additional stringent test is obviously provided by molecular-weight determinations in the above solvents. Another criterion has been recently provided by Tsuchida and Yamada^{5,6} who suggest that the presence of an absorption band at 3750 Å in chloroform or alcohol solutions of these compounds is diagnostic for the binuclear structure.

With these objects in mind, magnetic, cryoscopic, and spectrophotometric measurements have been made of solutions in dioxan, benzene, and water. In addition, the electrical conductivity of the aqueous solutions has been determined to verify ionic dissociation in this solvent. The compounds selected were the copper(II) salts of formic, acetic, propionic, butyric, valeric, lauric, stearic, and behenic acids, *i.e.*, $H\cdot[CH_2]_n\cdot CO_2H$, where $n = 0, 1, 2, 3, 4, 11, 17,$ and 21 , these being salts of acids available very pure and providing a range adequate to interpolate properties of intermediate members.

EXPERIMENTAL

Materials.—The preparation of copper(II) salts of acetic, propionic, butyric, lauric, stearic, and behenic acids has been described.^{1,2} Copper formate tetrahydrate was prepared by treating Merck's "purissimus" grade copper carbonate with an excess of the diluted acid and allowing the solution to crystallise (Found: C, 10.7; H, 4.50; Cu, 28.1; H₂O, 32.0. Calc. for $CuC_2H_2O_4\cdot 4H_2O$: C, 10.6; H, 4.47; Cu, 28.2; H₂O, 31.9%). The anhydrous salt was prepared by dehydration at 100° over phosphoric oxide in a vacuum pistol (Found: C, 15.6; H, 1.25; Cu, 41.3. Calc. for $CuC_2H_2O_4$: C, 15.6; H, 1.31; Cu, 41.4%).

Copper valerate was prepared by metathesis of aqueous copper acetate with an alcoholic solution of valeric acid. Blue-green needle-shaped crystals of the anhydrous valerate were slowly deposited (Found: C, 44.9; H, 6.6; Cu, 24.1. Calc. for $CuC_{10}H_{18}O_4$: C, 45.2; H, 6.8; Cu, 23.9%).

The degree of hydration, colour, and solubility of copper alkanoates is relevant. The pale blue formate with a magnetic moment, $\mu \sim 1.6$ B.M., considerably higher than those of its blue-green homologues, $\mu \sim 1.38$ B.M., crystallises as a tetrahydrate, in marked contrast to the acetate, propionate, butyrate, and valerate,⁶ which all crystallise as monohydrates. It was found that copper butyrate can also crystallise as a dihydrate if the mother-liquor is dilute with respect to butyric acid. However, the dihydrate readily loses one water molecule under mild dehydrating conditions (*e.g.*, standing over $CaCl_2$), whereas vacuum drying (over P_2O_5) at 100° is required for complete dehydration of the monohydrate. Hence, it is concluded that the dihydrate should be formulated as the hydrated aquo-complex, $[Cu_2(C_3H_7\cdot CO_2)_4(H_2O)_2]\cdot 2H_2O$. The laurate, stearate, and behenate are anhydrous.

The formate, acetate, propionate, and butyrate are soluble in water giving blue solutions which are much more intensely coloured than solutions containing hexaquo cupric ions, *e.g.*, $Cu(ClO_4)_2$. The valerate is barely soluble (*ca.* 0.0005M), and the laurate, stearate, and behenate quite insoluble.

⁴ Herron and Pink, *J.*, 1956, 3948.

⁵ Tsuchida and Yamada, *Nature*, 1955, 176, 1171.

⁶ Tsuchida, Yamada, and Nakamura, *Nature*, 1956, 178, 1192.

The solubility behaviour of these salts in benzene is remarkable. At room temperature, only the butyrate and valerate are slightly soluble. However, the butyrate and higher homologues readily dissolve in warm benzene to give blue-green solutions. The solutions of the butyrate and valerate are stable for some hours when cooled to room temperature, whereas the laurate, stearate, and behenate are immediately reprecipitated from solution in a very finely divided form. Although quantitative determinations of solubility were not made, it was apparent that the heavier alkanooates are practically insoluble below a critical solution temperature (C.S.T.), but when this temperature is reached their solubilities increase tremendously. Similar behaviour has previously been observed with toluene solutions of copper laurate⁷ and copper stearate.⁸

Since the insolubility of copper alkanooates in benzene severely restricted our proposed magnetic and cryoscopic studies, a more effective solvent was sought. Dioxan was particularly suitable, for, in addition to having convenient cryoscopic properties, it dissolves the formate, acetate, propionate, butyrate, and valerate at room temperature, forming blue-green solutions; the laurate, stearate, and behenate, however, exhibit the critical solution phenomenon in this solvent. In boiling dioxan the alkanooates undergo some decomposition, the colour of the solutions changing to green, and in several cases (*e.g.*, copper butyrate) colloidal particles are formed. The C.S.T.'s were roughly determined by gradually warming copper alkanooate-solvent mixtures and estimating visually the onset of solubility; the data are contained in Table 1.

TABLE 1. *Critical solution temperatures for copper(II) n-alkanoates dissolved in benzene and in dioxan.*

Compound	Cu(C ₁₁ H ₂₃ ·CO ₂) ₂	Cu(C ₁₇ H ₃₅ ·CO ₂) ₂	Cu(C ₂₁ H ₄₃ ·CO ₂) ₂
C.S.T. in { dioxan benzene	37° 62°	43° 64°	60° 72°

Magnetic Measurements.—The magnetic properties of copper alkanooates in solution were examined by the Gouy method, three solvents, water, benzene, and dioxan, being used. Water, doubly distilled in an all-silica still, and "AnalaR" benzene, which was repeatedly recrystallised and carefully fractionated, were used as calibrating liquids. Their specific gram-susceptibilities were taken as $\chi_g(\text{H}_2\text{O}) = -0.720 \times 10^{-6}$ (20°) and $\chi_g(\text{C}_6\text{H}_6) = -0.702 \times 10^{-6}$ (20°). The 1:4-dioxan (B.D.H. "Specially Pure" quality) was dried (Na) and used without further purification. Samples taken from different bottles consistently gave susceptibilities in the range $\chi_g(\text{C}_4\text{H}_8\text{O}_2) = -0.587$ to -0.590×10^{-6} (20°).

The specific gram-susceptibility of each solution was calculated from an expression used by French and Trew,⁹ *viz.*,

$$\chi_{\text{solution}} = \left\{ \chi_{\text{solvent}} - \frac{k_{\text{air}}}{d_{\text{solvent}}} \right\} \left\{ \frac{d_{\text{solvent}} \times F_{\text{solution}}}{d_{\text{solution}} \times F_{\text{solvent}}} \right\} + \frac{k_{\text{air}}}{d_{\text{solution}}}$$

where χ is specific gram-susceptibility, k_{air} the volume susceptibility of air (0.0294×10^{-6}), and d the density measured in a bicapillary dilatometer at the temperature of the magnetic measurements. The resultant thrust, F (mg.), was produced by a magnetic field of *ca.* 5000 gauss acting on an 11 cm. column of liquid contained in a stoppered Pyrex tube. The gram-susceptibility of the dissolved copper salt $\chi_g(\text{salt})$ was then obtained by application of Weidemann's mixture equation:

$$\chi_g(\text{salt}) = \{\chi_{\text{solution}} - (1 - \theta)\chi_{\text{solvent}}\}/\theta$$

where θ represents the weight-fraction of copper salt in solution. The resulting magnetic data (corrected both for the underlying diamagnetism of all atoms, Δ , and for the temperature-independent paramagnetism of copper as previously described^{1,2}) are in Table 2.

Molecular-weight Determinations.—The determination of molecular weights for copper alkanooates dissolved in water, benzene, and dioxan, by conventional ebullioscopic and cryoscopic methods, was beset with a number of experimental difficulties. Of these, partial

⁷ Nelson and Pink, *J.*, 1952, 1744.

⁸ E. P. Martin and Pink, *J.*, 1948, 1750.

⁹ French and Trew, *Trans. Faraday Soc.*, 1945, **41**, 439.

decomposition in boiling dioxan, critical solution behaviour in both benzene and dioxan, and the great affinity of dioxan for atmospheric moisture proved the most troublesome.

(a) *Ebullioscopic measurements.* Neither water nor dioxan could be used for ebullioscopic measurements with the present compounds. In boiling water, the salts are hydrolysed, giving basic salts, whereas in boiling dioxan partial decomposition to give either dark residues or green colloidal solutions vitiated the determinations. On the other hand, benzene was satisfactory for alkanooates other than the insoluble formate, acetate, and propionate.

Remarkably small elevations in the b. p. of benzene were produced by addition of copper alkanooates, e.g., 1.8 g. of anhydrous copper butyrate in 100 ml. of benzene (0.077M) produced no detectable change (i.e., $<0.002^\circ$) in the temperature of the boiling solvent. Copper laurate and copper stearate (0.03M) also gave extremely small b. p. elevations, corresponding to average molecular complexities of 5.7 and 8.0, respectively. The small number of osmotically active

TABLE 2. *Magnetic data for copper(II) n-alkanoates in solution at room temperature.*

Compound	Concn. (M)	Aqueous solution.				
		<i>t</i>	$10^6 \chi_K$	$-10^6 \Delta$	$10^6 \chi_M$	μ (B.M.)
CuSO ₄	0.185	21.2°	9.64	57	1596	1.91
Cu(H·CO ₂) ₂	0.582	18.6	9.49	48	1505	1.85
Cu(CH ₃ ·CO ₂) ₂	0.226	16.8	8.94	72	1696	1.95
Cu(C ₂ H ₅ ·CO ₂) ₂	0.258	16.6	7.39	96	1646	1.93
Cu(C ₃ H ₇ ·CO ₂) ₂	0.054	18.3	6.03	120	1553	1.87
Benzene solution.						
Cu(C ₃ H ₇ ·CO ₂) ₂	0.022	20.0	3.33	120	912	1.42
Cu(C ₄ H ₉ ·CO ₂) ₂	0.004	20.4	ca. 2.8	144	888	ca. 1.4
Dioxan solution.						
Cu(H·CO ₂) ₂	0.008	18.0	2.89	48	492	1.01
Cu(CH ₃ ·CO ₂) ₂	0.028	23.0	4.21	72	837	1.36
Cu(C ₂ H ₅ ·CO ₂) ₂	0.071	15.8	3.05	96	736	1.26
Cu(C ₃ H ₇ ·CO ₂) ₂	0.123	18.1	2.52	120	719	1.25
Cu(C ₄ H ₉ ·CO ₂) ₂	0.012	21.7	2.19	144	726	1.26
Cu(C ₁₁ H ₂₃ ·CO ₂) ₂	0.008	18.8	1.2	280	860	1.37
Cu(C ₁₇ H ₃₅ ·CO ₂) ₂ ...	0.004	18.0	ca. 0.5	315	770	ca. 1.3

particles in boiling benzene, taken in conjunction with the critical solution behaviour displayed by these alkanooates, indicates the presence of micelles in the boiling solvent. Since it is probable that the degree of dispersion of the copper alkanooates in benzene changes from molecular to micellar at the C.S.T., the ebullioscopic determinations were not further pursued.

The ebulliometer was adapted from the design of Sucharda and Bobranski.¹⁰

(b) *Cryoscopic measurements.* Cryoscopic determinations of the molecular complexity of copper alkanooates in solution were restricted to lower homologues since the higher members display critical solution phenomena well above the f. p.s of dioxan and of benzene. None of the salts was sufficiently soluble in benzene at its f. p. for measurements to be made. However, measurements were made in water for salts in the range formate to butyrate, and in dioxan for salts in the range acetate to valerate.

Dioxan is not usually regarded as a suitable solvent for cryoscopic work on account of its strongly hygroscopic nature. However, efficacy as a solvent for the present compounds, coupled with a convenient f. p. (ca. 12°), made an investigation of its cryoscopic properties most desirable.

The cryoscopic illustrated in Fig. 1 was designed so that measurements could be made in an enclosed moisture-free atmosphere. The stirrer and Beckmann thermometer both pass through a B.45 cone containing mercury which seals the interior of the cryoscope. The solute is contained in two thin-walled bulbs supported on a W-shaped hook. Each bulb can be dropped separately into the solvent by either a clockwise or a counter-clockwise rotation of the supporting B.14 joint; the bulbs are then broken with the stirrer. A drying tube [Mg(ClO₄)₂] attached to a second B.14 cone is necessary to prevent mercury in the seal around the stirrer from being sucked into the solvent when the cryoscope is first cooled below room temperature.

B.D.H. dioxan ("Specially Pure") was dried (Na) and used without further purification. The molar cryoscopic constant, azobenzene being used as calibrating solute, was found to be

¹⁰ Sucharda and Bobranski, *Chem. Ztg.*, 1927, **51**, 568.

$K_f = 5.00^\circ$, a value considerably larger than that recorded for water ($K_f = 1.86^\circ$) but close to that for benzene ($K_f = 4.90^\circ$). Molecular weights in water and dioxan are listed in Table 3, where n = molecular complexity. In dioxan, copper alkanooates exhibit molecular complexities close to 2, whereas in water values considerably less than unity are obtained.

TABLE 3. Cryoscopic molecular weights of copper(II) *n*-alkanoates in solution.

Compound	Concn. (M)	Aqueous solution.			Dioxan solution.			
		M		n	Concn. (M)	M		n
		Obs.	Calc.			Obs.	Calc.	
CuSO ₄	0.0203	97.8	160	0.61	—	—	—	—
Cu(H·CO ₂) ₂ ...	0.040	104	154	0.68	—	—	—	—
Cu(CH ₃ ·CO ₂) ₂	0.100	109	182	0.60	0.0142	348	182	1.92
Cu(C ₂ H ₅ ·CO ₂) ₂	0.101	124	210	0.59	0.0284	403	210	1.92
Cu(C ₃ H ₇ ·CO ₂) ₂	0.016	144	238	0.60	0.0358	480	238	2.02
Cu(C ₄ H ₉ ·CO ₂) ₂	—	—	—	—	0.0084	555	266	2.09

Electrical-conductivity Measurements.—The electrical conductivity of copper alkanooates in each solvent was measured at 25.0° by means of a Philips A.C. Wheatstone bridge (type GM4249). The measurements were made at 1000 c./sec., a Philips immersion cell (type GM4221) with platinised electrodes and a cell constant of 1.395 being used.

FIG. 1. Cryoscope.

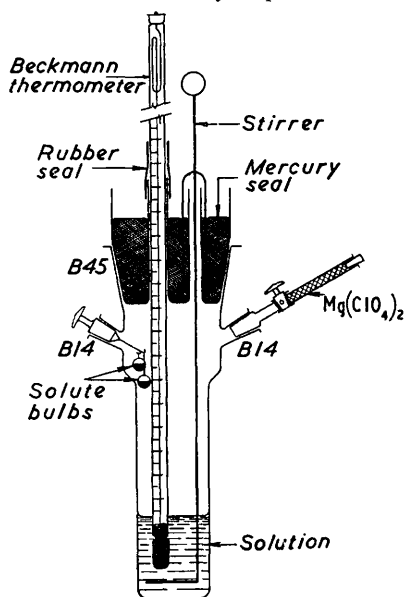
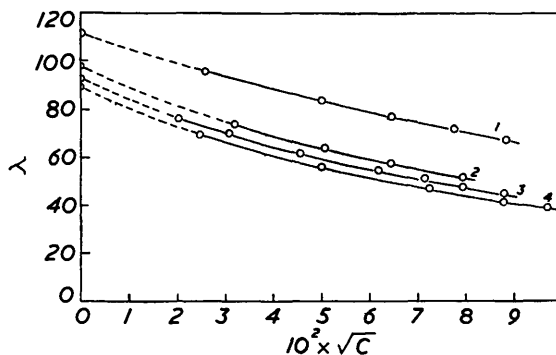


FIG. 2. Equivalent conductivity at 25.0° (λ) of 1, formate; 2, acetate; 3, propionate; and 4, butyrate



The dioxan and benzene solutions were non-conductors of electricity within the limits of the equipment, *i.e.*, the specific resistance of the solutions was greater than 10^6 ohms. In contrast, aqueous solutions were good conductors of electricity. The equivalent conductivities for the formate, acetate, propionate, and butyrate, measured in the concentration range 0.01—0.001M, are listed in Table 4 together with the sum of the limiting equivalent conductivities ($\lambda^\circ_{\frac{1}{2}\text{Cu}^{++}} + \lambda^\circ_{\text{R.CO}_2^-}$) taken from the literature.¹¹ The variation of equivalent conductivity with square-root of concentration, plotted in Fig. 2, is slightly curved, convex with respect to the concentration axis. This curvature precludes extrapolation of the experimental data to zero concentration. However, for each compound, a smooth extension of the experimental curve can be made which includes the calculated sum of the limiting ionic conductances. The

¹¹ Robinson and Stokes, "Electrolyte Solutions," Butterworths Scientific Publications, London, 1955, p. 452.

curves for acetate, propionate, and butyrate lie closely parallel to one another, whereas the curve for copper formate decreases slightly less rapidly with increasing values of \sqrt{C} .

*Absorption Spectra in Visible and Near Ultraviolet Regions.**—The absorption spectra of copper alkanooates dissolved in water, dioxan and benzene were recorded between 3250 and 8000 Å, a Cary recording spectrophotometer (Model 11 MS-50) being used. The spectra of the laurate, stearate, and behenate both in benzene and in dioxan were recorded above the C.S.T.s' of the compounds. The positions of the absorption bands are listed in Table 5; in addition to

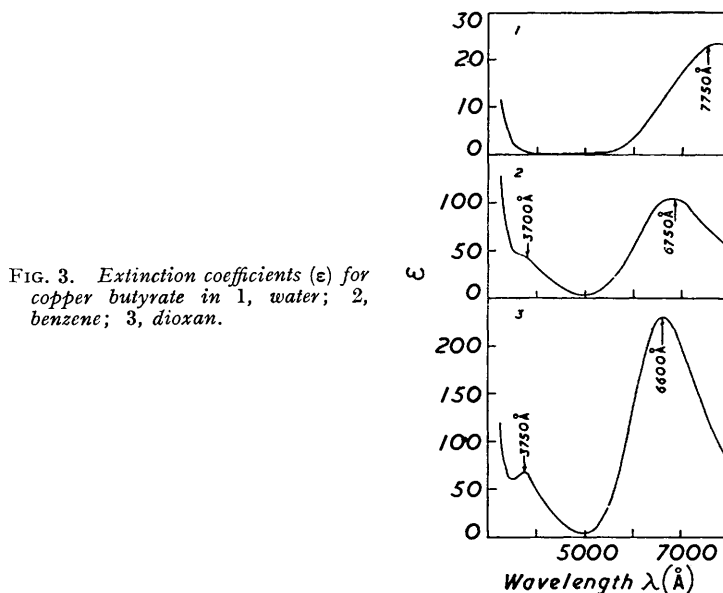


FIG. 3. Extinction coefficients (ϵ) for copper butyrate in 1, water; 2, benzene; 3, dioxan.

these, all the solutions absorbed strongly in the ultraviolet region below 3250 Å. Typical spectra are illustrated in Fig. 3.

The spectra of copper butyrate in carbon tetrachloride, chloroform, acetone, and alcohol were also recorded to determine whether the solvent influences either the contour or the position of the 3750 Å band. In carbon tetrachloride this band is as well defined as in dioxan solution

TABLE 4. *Equivalent conductivities of copper(II) n-alkanoates in water at 25.0°*

		Copper formate						
$10^4 C$ (moles l^{-1})	0	6.707	25.03	41.77	60.00	78.56		
λ ($cm.^2$ ohm $^{-1}$ equiv. $^{-1}$)	111.2 *	94.7	83.3	76.3	71.1	67.1		
		Copper acetate						
$10^4 C$ (moles l^{-1})	0	10.21	25.68	41.29	63.00			
λ ($cm.^2$ ohm $^{-1}$ equiv. $^{-1}$)	97.5 *	73.4	63.6	57.1	51.4			
		Copper propionate						
$10^4 C$ (moles l^{-1})	0	4.025	9.354	20.99	38.39	51.26	62.81	77.50
λ ($cm.^2$ ohm $^{-1}$ equiv. $^{-1}$)	92.4 *	75.9	69.9	61.4	54.1	50.4	47.0	44.3
		Copper butyrate						
$10^4 C$ (moles l^{-1})	0	6.146	25.03	52.36	77.32	93.96		
λ ($cm.^2$ ohm $^{-1}$ equiv. $^{-1}$)	89.2 *	69.4	55.7	46.3	41.1	38.5		

* Calculated sum of limiting equivalent conductivities.

(cf. Fig. 3). On the other hand, in chloroform, acetone, and alcohol, the contour closely resembles that in benzene (cf. Fig. 3), the band being less well defined and apparently displaced slightly (*ca.* 50–80 Å) to shorter wavelengths. A similar effect may be induced in the dioxan

* Extinction coefficients and molarities in this section are based on formula weights.

spectrum by a rise in temperature; *e.g.*, the definition of the 3750 Å band in dioxan at 70° resembles that in benzene at room temperature.

TABLE 5. Absorption bands (λ_{\max} in Å) in copper(II) *n*-alkanoate solutions.

Compound	Solvent		
	Water	Dioxan	Benzene
Cu(ClO ₄) ₂ ·6H ₂ O	<i>ca.</i> 8000	insol.	insol.
Cu(H·CO ₂) ₂	7750	3750; 6650	insol.
Cu(CH ₃ ·CO ₂) ₂	7650	3700; 6650	insol.
Cu(C ₂ H ₅ ·CO ₂) ₂	7650	3750; 6600	insol.
Cu(C ₃ H ₇ ·CO ₂) ₂	7750	3750; 6600	3700; 6750
Cu(C ₄ H ₉ ·CO ₂) ₂	insol.	3750; 6600	3700; 6750
Cu(C ₁₁ H ₂₃ ·CO ₂) ₂	insol.	3600; 6600	3700; 6750
Cu(C ₁₇ H ₃₅ ·CO ₂) ₂	insol.	3700; 6600	3750 *; 6750
Cu(C ₂₁ H ₄₃ ·CO ₂) ₂	insol.	<i>ca.</i> 3700; 6550	3750 *; 6750

* Poorly defined.

DISCUSSION

The magnetic, cryoscopic, and spectroscopic behaviour of copper alkanoates in dioxan or benzene convincingly demonstrates that these compounds retain their binuclear configuration in solution.

The magnetic moments in dioxan, 1.31 ± 0.06 B.M. (excluding that of copper formate), and in benzene 1.4 B.M., when compared with the moments in the solid state,¹ 1.38 B.M., and in aqueous solution, 1.90 ± 0.05 B.M., show that the partial quenching in the moment of the solid persists in dioxan and benzene solutions. Intermolecular exchange, of the type suggested by Gilmour and Pink,³ must be negligible in the concentration range (0.004—0.123M) at which the present measurements were made, and this, in conjunction with the uniformity of the quenching, confirms the presence of intramolecular exchange demagnetisation between copper atoms within the postulated binuclear $\text{Cu}_2(\text{R}\cdot\text{CO}_2)_4$ molecules. The jump in moment to 1.90 B.M. in aqueous solution, which is paralleled by a marked colour change from blue-green to blue, demonstrates that the dimeric bridged structure is destroyed by water and that all exchange interactions are effectively removed.

The small additional depression of the moment in dioxan solutions may be significant, in spite of the relatively large experimental scatter of ± 0.06 B.M. For example, the moment in dioxan of copper butyrate (the alkanoate most soluble in dioxan and benzene), 1.25 B.M., is *ca.* 0.1 B.M. lower than the moment either in benzene, 1.42 B.M., or in the solid state, 1.37 B.M. That this small lowering may well be real is supported by the consideration that any residual intermolecular exchange forces in the solid would surely be eliminated in solution, and thereby raise the moment in dioxan with respect to that in the solid, as in the case of benzene. It is suggested that this additional depression of 0.1 B.M. in moment, as well as the marked solvating power of dioxan for copper alkanoates, reflects the formation of binuclear $[\text{Cu}_2(\text{R}\cdot\text{CO}_2)_4(\text{C}_4\text{H}_8\text{O}_2)_2]$ molecules in this solvent. The presence of dioxan molecules in the two terminal positions [marked "L" in structure (I)] would then appear slightly to enhance $3d_\delta-3d_\delta$ overlap with a concomitant small decrease of 0.1 B.M. in the magnetic moment.

The cryoscopic data in Table 3 further substantiate any conclusions based on the persistence of a binuclear configuration in non-ionising solvents and its disruption in water. In dioxan, the molecular complexities of acetate, propionate, butyrate, and valerate lie in the range 1.9—2.1, amply confirming their dimeric nature in this solvent. The salts are unfortunately too insoluble at the freezing point of benzene for cryoscopic measurements to be made. In aqueous solution molecular complexities in the range 0.6—0.7 indicate rupture of the alkanoate bridges and the presence of a large number of osmotically active particles in solution.

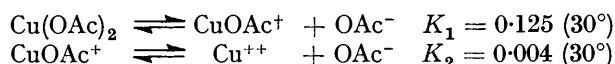
The dioxan and benzene solutions are non-conductors of electricity, a fact equally

consistent with structure (I), structure (II), or the presence of undissociated ion-pairs. Freshly prepared aqueous solutions, on the other hand, are strongly conducting, and equivalent conductivities at a concentration 0.001M are only $20\% \pm 5\%$ lower than the sum of the ionic conductivities ($\lambda_{\frac{1}{2}\text{Cu}^{++}}^{\circ} + \lambda_{\text{R}\cdot\text{CO}_2}^{\circ}$) at zero concentration.

The curvature of the $\lambda-\sqrt{c}$ plot for aqueous copper acetate arises from two competing equilibria involved in the ionic dissociation of this compound. Thus Sircar, Aditya, and Prasad,¹² on the basis of e.m.f. measurements, showed that at concentrations greater than about 0.1M, copper acetate behaves essentially as a fairly strong 1 : 1 electrolyte, whereas at lower concentrations it undergoes feeble dissociation as a 2 : 1 electrolyte. Using a concentration cell of the type



and by assuming that barium acetate is totally dissociated, they determined the following equilibrium constants (l. mole⁻¹):



Their conclusions have been fully supported both by conductivity data,¹³ which give $K_1 = 0.103$ and $K_2 = 0.003$ at 0° , and by spectrophotometric measurements,¹⁴ which give $K_1 = 0.114$ and $K_2 = 0.0033$ at 20° .

The present cryoscopic and conductivity data are in harmony with this interpretation. Furthermore, the curvature of the $\lambda-\sqrt{c}$ plots for formate, propionate, and butyrate so closely match that of the acetate, that it seems probable that the ionic dissociation of these salts should be represented by similar equilibria. The conductivity of these solutions gradually decreases on ageing, and a parallel drop in pH is indicative of slow hydrolysis at room temperature.

The spectroscopic properties of copper alkanooate solutions in the visible and the near ultraviolet region are of particular interest in view of recent single-crystal studies by Tsuchida and Yamada.⁵ Most copper(II) complexes usually exhibit not more than one electronic absorption band of moderate intensity in the red or near infrared region, which French and Lowry¹⁵ have termed a "copper band." However, with copper acetate and propionate, in addition to a broad "copper band" at 7000 Å, Tsuchida and Yamada find a new absorption band of a special kind at 3750 Å which they ascribe to the presence of a direct copper-copper linkage. The absorption of this new band is greatly polarised along the copper-copper axis, which is the reverse of the polarisation property of the "copper band" at 7000 Å. Both bands persist in alcohol or chloroform solutions of all alkanooates between acetate and octanoate, as well as in acetic anhydride solutions of palmitate and stearate.

The present spectra of dioxan and benzene solutions also exhibit this ultraviolet band at 3750 Å in addition to a broad "copper band" at 6600 Å in dioxan and 6750 Å in benzene. In contrast, aqueous solutions of copper alkanooates show only one broad absorption band at 7750 Å, which may be compared with the corresponding broad band at ca. 8000 Å in aqueous cupric perchlorate. Since the magnetic and cryoscopic properties unambiguously establish the presence of dimeric molecules in dioxan and benzene solutions, Tsuchida and Yamada's suggestion that the 3750 Å band is diagnostic of binuclear copper alkanooate molecules is now completely substantiated.

One of the most interesting results emerging from the present investigations is that copper formate adopts the binuclear configuration when dissolved in dioxan. This is

¹² Sircar, Aditya, and Prasad, *J. Indian Chem. Soc.*, 1953, **30**, 633.

¹³ Doucet and Cogniac, *Compt. rend.*, 1953, **240**, 968.

¹⁴ Doucet and Marion, *ibid.*, p. 1616.

¹⁵ French and Lowry, *Proc. Roy. Soc.*, 1924, *A*, **106**, 489.

proved both by the low moment, $\mu = 1.01$ B.M., and the presence of an absorption band at 3750 Å in dioxan solution. Clearly, the donor and non-ionising properties of dioxan induce a complete change from the structure of the solid (a layer structure involving elongated CuO_6 octahedra¹⁶), and energetically favour formation of discrete binuclear $[\text{Cu}_2(\text{H}\cdot\text{CO}_2)_4(\text{C}_4\text{H}_8\text{O}_2)_2]$ molecules. This has been confirmed¹⁷ by isolating from the dioxan solution dichroic blue-green crystals with a magnetic moment $\mu \sim 1$ B.M. These crystals contain dioxan and are readily decomposed in the presence of moisture. In aqueous solution, the magnetic moment jumps from the value 1.64 B.M. of the tetrahydrate to 1.85 B.M., showing that strong intermolecular-exchange interactions are present in the crystalline tetrahydrate. A detailed discussion of the magnetic behaviour of copper formate¹⁷ is deferred.

The critical solution (or Krafft) phenomenon exhibited by the laurate, stearate, and behenate, both in dioxan and in benzene, arises from molecular aggregation in solution, which commences at the C.S.T. The careful measurements by Pink and his co-workers,^{7, 8, 18} particularly with zinc alkanooates, provide a sound basis for discussion of the present observations. The slow rise in solubility followed by a sudden and large increase over a very small range in temperature characterises the phenomenon, and, in the present case, is ascribed to a change in the degree of dispersion of the compounds from bimolecular to micellar at this temperature. When cooled below the C.S.T., the alkanooates tend to be precipitated in a very finely divided form. The fact that the heavier alkanooates behave thus even in the presence of a donor solvent like dioxan, together with the observation that the reprecipitated alkanooates contain no dioxan of solvation, indicates that the peripheral hydrocarbon chains are sufficiently long sterically to hinder the terminal positions marked L in structure (I).

The ebullioscopic measurements in benzene show that the average number of molecules per micelle for copper laurate and copper stearate is of the order of 6—8 in 0.03M-solution, whereas for copper butyrate the number must be considerably larger. These values are close to those observed by Pink *et al.* for toluene solutions of the laurate⁷ and stearate⁸ at a similar concentration. The extremely small number of osmotically active entities in boiling benzene solutions of the butyrate is consistent with their conclusion based on the behaviour of zinc soaps, that the number of molecules per micelle increases with decreasing length of the hydrocarbon chain.

Any detailed discussion concerning the micellar structure would necessarily be speculative at this stage. However, it is clear from the present results that the binuclear molecular structure of copper alkanooates in no way inhibits the formation of micelles, which presumably consist of aggregates of dimeric copper alkanooate molecules. This conclusion is favoured by the persistence of the ultraviolet absorption band at 3750 Å in solutions above the critical temperature. The driving force behind micelle formation is likely to be residual forces of attraction between the peripheral hydrocarbon chains [cf. structure (I)] coupled with weak polar attractions, which presumably are present when the terminal positions, L, are unoccupied. These are shown for example, by the small dipole moment, 1.20 D, observed¹⁹ for copper oleate, which we have recently found to have the binuclear structure.

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¹⁶ Kiriyaama, Ibamoto, and Matsuo, *Acta Cryst.*, 1954, **7**, 482.

¹⁷ Martin and Waterman, unpublished results.

¹⁸ Tughan and Pink, *J.*, 1951, 1804.

¹⁹ Banerjee and Palit, *J. Indian Chem. Soc.*, 1950, **27**, 385.