1194. *The Chemistry of Polynuclear Compounds. Part III.*[1] *Magnetic Properties of Some Carboxylic Acid Derivatives of Copper*(II)

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The magnetic moments over the temperature range 80—300°K are reported for 24 complexes of copper(II) with arylcarboxylic acids. A number of these has been shown to possess the magnetic behaviour expected for a binuclear system and the values of the exchange integrals have been calculated. The corresponding entropy and heat change for the singlet–triplet equilibrium has also been calculated.

The formation of binuclear derivatives has been correlated with the $\mathrm{p}K_a$'s of the acids and with steric factors. In certain instances it is possible to prepare more than one magnetic form of a given derivative. The reflection and solution spectra of a number of these compounds are reported. For compounds believed to be binuclear in structure the presence of a spectral band in the region of 400 mμ is established.

ABNORMAL magnetic behaviour in carboxylic acid complexes of copper(II) has been the subject of extensive studies over the past few years.[2] Martin *et al.*[3-5] investigated a series of copper(II) alkylcarboxylates and found that, with the exception of copper(II) formate, they all exhibit magnetic moments of approximately 1·4 B.M., very much reduced from the value of 1·9—2·0 B.M. normally observed for copper(II) compounds. These compounds apparently all have a binuclear configuration similar to that found in copper acetate hydrate [6] in which four acetate groups bridge two copper ions in the *syn-syn* arrangement (Figure 1a).

It has been suggested that the spin–spin interaction of the adjacent copper(II) ions, occurs by direct overlap of the metal orbitals with formation of either a δ-bond, $d_{x^2-y^2}$ orbital overlap,[3] or a σ-bond, d_{z^2} orbital overlap.[7] However we cannot exclude the possibility that the whole or part of the interaction occurs *via* the bridging acetate groups.

Copper(II) formate tetrahydrate, and blue and turquoise forms of anhydrous copper(II) formate have sub-normal room-temperature magnetic moments of 1·64, 1·61, and 1·75 B.M., respectively,[4] which are low compared to normally observed moments for copper(II), but higher than the moments observed for the other copper(II) alkanoates. This difference in magnetic behaviour has been attributed to a difference in structure of the compounds. The " formates " have polymeric structures [8,9] in which layers of copper ions are held together by bridging formate groups in an *anti-anti* (Figure 1b) or *anti-syn* arrangement (Figure 1c), whereas in the case of copper(II) acetate and the higher homologues the *syn-syn* arrangement of carboxylate groups hold the copper ions close enough together to allow the possibility of direct copper–copper interaction. The copper ions in the formates are

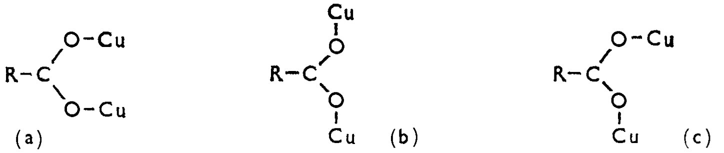

FIGURE 1. Carboxylate bonding configurations: (a) *syn-syn*; (b) *anti-anti*; (c) *anti-syn*

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[1] Part II is considered to be J. Lewis and F. E. Mabbs, *J.*, 1965, 3894.
[2] M. Kato, H. B. Jonassen, and J. C. Fanning, *Chem. Rev.*, 1964, **64**, 99.
[3] B. N. Figgis and R. L. Martin, *J.*, 1956, 3837.
[4] R. L. Martin and H. Waterman, *J.*, 1957, 2545; 1959, 1359, 2960.
[5] R. L. Martin and A. Whitley, *J.*, 1958, 1394.
[6] J. N. van Niekerk and R. F. L. Schoening, *Acta Cryst.*, 1953, **6**, 227.
[7] L. S. Forster and C. J. Ballhausen, *Acta Chem. Scand.*, 1962, **16**, 1385.
[8] R. Kiriyama, H. Ibamoto, and K. Matsuo, *Acta Cryst.*, 1954, **7**, 482.
[9] G. A. Barclay and C. H. L. Kennard, *J.*, 1961, 3289.

much further apart and any spin–spin interaction between them must occur in this instance *via* the bridging carboxylate groups. This interaction is presumed to be much weaker than the " direct " copper–copper interaction which occurs in the " acetates " and hence results in a smaller reduction in the moment. In fact copper(II) formate dihydrate and a royal-blue form of anhydrous copper(II) formate have room-temperature moments of 1·9 B.M. which show practically no temperature dependence, thus indicating no measurable anti-ferromagnetic interaction.

In summing up the evidence from the various copper(II) n-alkanoates and some of their adducts, Martin and Waterman [4] conclude that because of the proximity of copper ions in the binuclear structure, this structure will be unstable and the *anti-anti* or *anti-syn* configurations favoured if a large residual charge remains on the copper ions after bonding with the carboxylate groups. The acid dissociation constants of the parent organic acids are taken as an indication of the available σ-electron density on the carboxylate oxygen atoms. Stronger acids than acetic give carboxylate ligands which are less polarisable than the acetate group and thus have less available σ-electron density on the carboxylate oxygens. This leaves greater residual charge on the copper ions and favours the *anti-anti* or *anti-syn* arrangements found in the formates. In addition to the electrostatic repulsion term, the higher effective charge on the copper atom will contract the *d*-orbitals, which may modify considerably the overlap in the metal–metal bond, and significantly affect the stability of the dimeric unit.

In order to investigate further the effect of changing the polarisability of the ligand on the magnetic behaviour of copper(II) carboxylates we have studied a number of aryl-carboxylates of copper(II). This group of complexes was chosen as it is possible to vary the acidity of the parent acid, and hence the polarisability of the ligand, over a much wider range than for alkyl carboxylic acids. Also, it is possible to look for any steric effects which may occur by substitution in the benzene nucleus. A preliminary account of this work has been published elsewhere.[10]

EXPERIMENTAL

Where variations in preparative procedures yielded products of identical chemical composition, but different magnetic properties, it is possible that these products are different structural forms of the same compound. In this Paper such products are distinguished by placing the letters (A), (B), or (C) after the name or formula of the compound.

Preparations.—The general method described below was employed for the preparation of the complexes (Table 1). Where deviations from this method occurred, cases are treated individually.

A solution of the sodium salt of the relevant acid was prepared, and the pH adjusted to 5 or below. This was achieved by manipulation of the quantities of acid and sodium hydroxide used to prepare the sodium salt solution, or alternatively commencing with a sodium salt solution of pH $\sim$ 8, and adding small quantities of mineral acid until the pH was in the desired region. Addition of a slight excess of cupric sulphate in the form of a concentrated aqueous solution usually resulted in the immediate precipitation of the complex (often as a hydrated species). The precipitated complexes were collected, washed with either a dilute solution of the parent acid or water acidified to a pH of $\sim$4 with mineral acid. The product was dried in a vacuum desiccator over silica gel or calcium chloride. Anhydrous complexes were prepared from the hydrates by dehydration in a vacuum drying pistol at $\sim$120° for $\sim$24 hr.

Deviations from the General Method.—*Copper*(II) *benzoate* (*anhydrous*). The benzoate trihydrate was refluxed in acetone for several hours. After filtration and concentration of the resulting solution, blue-green crystals of copper benzoate were obtained, probably as an acetone complex. Drying in the vacuum pistol yielded the anhydrous compound. The product was recrystallised from acetone and re-dried.

Copper(II) m-*methylbenzoate* (B). Recrystallisation of the (A) form of the compound (prepared by the general method) from acetone, followed by drying the product in the vacuum pistol yielded the (B) form of the anhydrous compound.

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[10] J. Lewis and R. C. Thompson, *Nature*, 1963, **200**, 468.

TABLE 1

Analytical data

Compound	Found (%)			Calc. (%)		
	C	H	Cu	C	H	Cu
$Cu(p\text{-}CH_3C_6H_4CO_2)_2$	58·2	4·2	19·1	57·5	4·2	19·0
$Cu(p\text{-}CH_3C_6H_4CO)_2)_2,H_2O$	53·7	4·6	18·1	54·6	4·6	18·1
$Cu(m\text{-}CH_3C_6H_4CO_2)$ (A)	57·7	4·3	18·8	57·5	4·2	19·0
$Cu(m\text{-}CH_3C_6H_4CO_2)_2$ (B)	57·5	4·3	18·8	57·5	4·2	19·0
$Cu(C_6H_5CO_2)_2$	55·1	3·5	20·6	54·9	3·3	20·8
$Cu(C_6H_5CO_2)_2,3H_2O$	46·9	4·4	17·8	46·7	4·4	17·7
$Cu(p\text{-}ClC_6H_4CO_2)_2$ (A)	44·7	2·3	16·9	44·8	2·1	16·9
$Cu(p\text{-}ClC_6H_4CO_2)_2$ (B)	44·8	2·6	16·8	44·8	2·1	16·9
$Cu(p\text{-}ClC_6H_4CO_2)_2$ (C)	44·8	2·2	16·9	44·8	2·1	16·9
$Cu(p\text{-}ClC_6H_4CO_2)_2,H_2O$	42·8	2·9	16·0	42·8	2·6	16·2
$Cu(o\text{-}CH_3C_6H_4CO_2)_2$	57·5	4·5	18·8	57·5	4·2	19·0
$Cu(m\text{-}ClC_6H_4CO_2)_2$ (A)	44·4	2·4	16·9	44·8	2·1	16·9
$Cu(m\text{-}ClC_6H_4CO_2)_2$ (B)	45·2	2·9	17·0	44·8	2·1	16·9
$Cu(m\text{-}ClC_6H_4CO_2)_2,2H_2O$	40·3	3·1	15·3	40·9	3·0	15·5
$Cu(m\text{-}NO_2C_6H_4CO_2)_2$	42·2	2·2	15·6	42·4	2·0	16·0
$Cu(m\text{-}NO_2C_6H_4CO_2)_2,2H_2O$	39·2	2·9	14·6	38·9	3·2	14·7
$Cu(p\text{-}NO_2C_6H_4CO_2)_2$	42·2	2·1	16·0	42·4	2·0	16·0
$Cu(p\text{-}NO_2C_6H_4CO_2)_2,H_2O$	41·7	2·2	15·5	40·7	2·4	15·4
$Cu(o\text{-}NO_2C_6H_4CO_2)_2$	42·0	2·0	15·8	42·4	2·0	16·0
$Cu(o\text{-}NO_2C_6H_4CO_2)_2,H_2O$ (A)	40·9	2·5	15·3	40·7	2·4	15·4
$Cu(o\text{-}NO_2C_6H_4CO_2)_2,H_2O$ (B)	40·7	2·7	15·4	40·7	2·4	15·4
$Cu(o\text{-}ClC_6H_4CO_2)_2$	44·7	2·2	16·8	44·8	2·1	16·9
$Cu(o\text{-}ClC_6H_4CO_2)_2,H_2O$	43·1	2·6	15·9	42·8	2·6	16·2

Copper(II) p-*methylbenzoate* (*anhydrous*). This was prepared by dehydrating the monohydrate in air at 110°, followed by recrystallisation from acetone and drying in a vacuum pistol.

Copper(II) o-*nitrobenzoates*. Employing the general method, precipitation from concentrated solution gave the (A) monohydrate. When using much more dilute solutions, immediate precipitation of the hydrate did not occur. The addition of cupric sulphate solution to the sodium salt–acid solution gave a deep green solution. Standing this on a steam-bath for a few hours yielded deep green crystals of the (B) hydrate. The anhydrous compound was obtained by dehydrating the (A) hydrate.

Copper(II) m-*chlorobenzoate* (B). Drying the dihydrate in air at ~120° followed by recrystallisation from *p*-dioxan yielded a copper(II) *m*-chlorobenzoate–dioxan complex. Removal of solvent in the vacuum pistol yielded the (B) form of the anhydrous compound.

Copper(II) p-*chlorobenzoates*. The (A) form of the anhydrous compound was prepared by the general method. Recrystallisation of the (A) form from *p*-dioxan followed by removal of solvent from the resulting dioxan complex in a vacuum pistol yielded the (B) form. The (C) form was prepared as follows. *p*-Chlorobenzoic acid was suspended in 50% aqueous ethanol and aqueous sodium hydroxide solution was added dropwise until all the acid had dissolved. An excess of cupric chloride in 50% aqueous ethanol was added, a blue precipitate immediately being obtained. This was collected, dried *in vacuo* over silca gel, followed by drying in a vacuum pistol. The anhydrous compound was obtained as a deep blue powder.

Pyridinecopper(II) *o*-chlorobenzoate. Anhydrous copper(II) *o*-chlorobenzoate dissolved readily in pyridine to give a dark blue solution. Standing this solution over sulphuric acid in a vacuum desiccator yielded dark blue crystals of the trispyridine complex. The crystals lost pyridine on standing in air to give the pale green monopyridine complex. Although carbon and hydrogen analyses for this compound were unsatisfactory, the nitrogen and metal analyses agree with this formulation (Found: Cu, 14·0; N, 2·8. Calc. for $Cu(o\text{-}ClC_6H_4CO_2)_2py$: Cu, 14·0; N, 3·1%).

Samples of copper(II) *o*-methylbenzoate and copper(II) *o*-chlorobenzoate were recrystallised from acetone followed by drying in a vacuum pistol. In both cases recrystallised and unrecrystallised specimens had identical room-temperature magnetic moments, indicating that no change of crystal form resulted from such a procedure. The magnetic measurements described in the Paper were performed on unrecrystallised samples.

Magnetic-susceptibility Measurements. Room-temperature magnetic-susceptibility measurements for all samples were done on powdered specimens using the Gouy method with a field strength of *ca.* 5000 gauss. The molar susceptibilities listed in Table 4 have been corrected for the diamagnetic contribution of all atoms, χ. Values of χ were obtained by making use of a combination of published values [11] of the diamagnetic susceptibilities of the organic acids (where available) and Pascal's constants. They include -13×10^{-6} for water and -13×10^{-6} for copper. Magnetic moments, μ, were calculated from the equation $\mu = 2{\cdot}84\ [(\chi'_{\rm M} - N\alpha)T^{\frac{1}{2}}$, where $N\alpha$ corrects for the temperature-independent paramagnetism of copper(II). The value 60×10^{-6} was used for this. An aqueous nickel chloride solution was used as calibrant, according to the method described by Nettleton and Sugden.[12] The apparatus used for measuring magnetic susceptibility temperature dependences was similar in design to the one described by Figgis and Nyholm.[13]

Molecular-weight Measurements. Molecular weights in dioxan at 37° were determined using a "Mechrolab Inc." vapour-pressure osmometer. The AnalaR dioxan, used in these measurements, was previously kept over sodium for at least 48 hr. and then distilled. Because of the low solubility of the compounds in dioxan and the consequent dilute nature of the solutions, the accuracy of the measurements is no better than about ±10%.

TABLE 2

Molecular weights in dioxan

Compound	Concn. (moles/l.)	*M* (Obs.)	*M* (Calc. for dimer)
$Cu(C_6H_5CO_2)_2$	0·0249	570	612
$Cu(o\text{-}CH_3C_6H_4CO_2)_2$	0·0239	660	668
$Cu(m\text{-}CH_3C_6H_4CO_2)_2$ (A)	0·0429	630	668
$Cu(m\text{-}CH_3C_6H_4CO_2)_2$ (B)	0·0415	590	668
$Cu(p\text{-}CH_3C_6H_4CO_2)_2$	0·0273	640	668
$Cu(o\text{-}NO_2C_6H_4CO_2)_2$	0·0252	840	792
$Cu(o\text{-}ClC_6H_4CO_2)_2$	0·0176	780	749

Spectroscopic Measurements.—Visible and u.v. spectra were recorded on a Beckman DK2A spectrophotometer.

DISCUSSION

The magnetic susceptibilities of a number of anhydrous and hydrated copper(II) arylcarboxylates have been measured over the temperature range 80—320°K and the experimental data are given in Table 3. Room-temperature magnetic moments of a few of the compounds investigated in this work have been reported previously and are given in Table 4 along with room-temperature moments obtained for all the compounds studied.

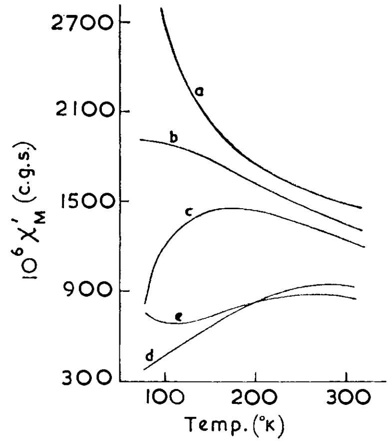

FIGURE 2. Typical susceptibility *vs.* temperature curves for copper(II) carboxylates. (a) Magnetically dilute compounds. (b) Compounds possessing large, positive, Weiss constants, indicating appreciable antiferromagnetic interaction. (c) Binuclear compounds for which $2J$ is of the order of 150 cm.$^{-1}$. (d) Binuclear compounds for which $2J$ lies in the region usually observed for binuclear copper(II) carboxylates, *i.e.*, *ca.* 300 cm.$^{-1}$. (e) Compounds which are mixtures of two crystal forms. The scales are approximate

The impurity most likely to be present in a copper(II) carboxylate is the corresponding

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[11] G. Foex, "Diamagnetisme et Paramagnetisme," Masson and Co., Paris, 1957.

[12] H. Nettleton and S. Sugden, *Proc. Roy. Soc.*, 1939, *A*, **173**, 313.

[13] B. N. Figgis and R. S. Nyholm, *J.*, 1959, 331.

TABLE 3

Cryomagnetic data

Copper(II) *p*-methylbenzoate

T (°K)	308·3	288·9	279·9	264·0	255·8	245·5	229·5	216·2	209·6	183·0	162·9	142·2	118·6	101·2
$10^6\chi'_M$	840	849	850	852	852	848	843	835	829	788	744	696	652	635
μ_{eff}	1·39	1·35	1·33	1·29	1·27	1·24	1·20	1·16	1·14	1·03	0·94	0·85	0·75	0·68

Copper(II) *p*-methylbenzoate monohydrate

T (°K)	298·4	289·1	274·2	258·8	243·7	231·9	216·0	199·1	183·8
$10^6\chi'_M$	1846	1912	2024	2172	2321	2454	2666	2937	3248
μ_{eff}	2·06	2·07	2·08	2·09	2·10	2·11	2·12	2·14	2·17
T (°K)	168·8	153·9	137·9	123·9	111·6	99·8	87·9	81·8	
$10^6\chi'_M$	3615	4088	4770	5543	6352	7390	8846	9878	
μ_{eff}	2·19	2·23	2·28	2·33	2·37	2·42	2·49	2·54	

Copper(II) *m*-methylbenzoate (A)

T (°K)	309·9	296·2	285·1	276·9	271·8	258·9	247·6	245·8	233·4
$10^6\chi'_M$	905	905	917	922	924	919	910	915	902
μ_{eff}	1·45	1·42	1·40	1·38	1·37	1·33	1·30	1·30	1·25
T (°K)	217·5	202·1	183·5	169·0	153·3	135·3	118·2	102·1	
$10^6\chi'_M$	890	864	834	799	736	673	592	528	
μ_{eff}	1·20	1·14	1·07	1·00	0·91	0·81	0·71	0·62	

Copper(II) *m*-methylbenzoate (B)

T (°K)	303·4	295·8	276·7	262·8	250·2	231·8	212·2	196·6
$10^6\chi'_M$	1245	1265	1322	1368	1400	1452	1522	1579
μ_{eff}	1·70	1·69	1·67	1·65	1·64	1·61	1·58	1·55
T (°K)	183·4	167·0	150·6	129·8	116·1	109·7	98·1	
$10^6\chi'_M$	1630	1680	1737	1793	1830	1840	1845	
μ_{eff}	1·52	1·47	1·42	1·34	1·28	1·25	1·18	

Copper(II) benzoate

T (°K)	322·7	306·7	298·6	278·4	277·8	264·2	249·2	234·4	219·8
$10^6\chi'_M$	850	861	866	864	865	856	847	835	809
μ_{eff}	1·43	1·40	1·39	1·34	1·34	1·30	1·25	1·21	1·15
T (°K)	204·2	189·2	186·6	173·4	160·2	144·3	130·3	115·7	89·5
$10^6\chi'_M$	771	754	745	715	660	590	535	475	381
μ_{eff}	1·08	1·02	1·01	0·95	0·88	0·78	0·70	0·62	0·48

Copper(II) benzoate trihydrate

T (°K)	293·4	282·9	264·8	247·2	233·1	220·3	204·3
$10^6\chi'_M$	1705	1742	1843	1930	2012	2089	2226
μ_{eff}	1·97	1·95	1·94	1·92	1·91	1·89	1·88
T° (K)	191·5	174·6	148·0	132·8	117·3	89·0	
$10^6\chi'_M$	2336	2518	2870	3118	3411	4242	
μ_{eff}	1·87	1·85	1·82	1·80	1·77	1·73	

Copper(II) *p*-chlorobenzoate (A)

T (°K)	312	294·4	294·0	286·5	271·5	253·4	237·5	222·7	208·0	192·3
$10^6\chi'_M$	1048	1105	1101	1116	1153	1203	1231	1278	1332	1377
μ_{eff}	1·57	1·57	1·57	1·56	1·54	1·52	1·49	1·47	1·45	1·42
T (°K)	177·0	161·2	147·0	133·0	121·0	110·5	97·7	90·1	77·7	
$10^6\chi'_M$	1410	1504	1573	1674	1786	1898	2070	2231	2667	
μ_{eff}	1·38	1·37	1·33	1·31	1·29	1·28	1·25	1·25	1·27	

Copper(II) *p*-chlorobenzoate (B)

T (°K)	390	376	361	343	328	308	293	281	261	245
$10^6\chi'_M$	779	832	836	869	884	903	914	914	933	944
μ_{eff}	1·51	1·53	1·50	1·50	1·48	1·45	1·42	1·39	1·36	1·32
T (°K)	227	212	197	182	162	146	128	112	97	
$10^6\chi'_M$	959	982	989	1016	1042	1064	1083	1109	1196	
μ_{eff}	1·28	1·26	1·22	1·19	1·11	1·07	1·01	0·97	0·94	

Copper(II) *p*-chlorobenzoate (C)

T (°K)	299·4	291·9	289·9	274·8	260·0	244·3	230·3	219·7	214·4	199·2	190·0	183·4
$10^6\chi'_M$	932	936	943	940	949	943	943	947	949	943	932	925
μ_{eff}	1·45	1·43	1·43	1·39	1·36	1·31	1·28	1·25	1·23	1·19	1·15	1·13
T (°K)	170·3	155·4	140·9	140·0	130·7	120·3	110·6	110·0	100·0	88·0	80·8	
$10^6\chi'_M$	908	880	807	848	794	775	743	762	724	754	822	
μ_{eff}	1·07	1·01	0·92	0·94	0·88	0·83	0·78	0·79	0·73	0·70	0·70	

TABLE 3 (*Continued*)

Copper(II) *p*-chlorobenzoate hydrate

T (°K)	307·8	292·4	276·2	263·2	247·2	232·8	218·6	202·5	186·7
$10^6\chi'_M$	1639	1762	1867	1972	2102	2239	2413	2623	2872
μ_{eff}	1·97	2·00	2·00	2·01	2·01	1·99	2·03	2·04	2·05
T (°K)	172·4	158·9	145·9	131·2	121·2	109·3	101·0	93·7	78·1
$10^6\chi'_M$	3144	3443	3841	4347	4798	5380	5894	6593	8435
μ_{eff}	2·06	2·07	2·10	2·12	2·14	2·16	2·17	2·21	2·29

Copper(II) *o*-methylbenzoate

T (°K)	295·3	279·2	263·6	248·4	235·1	219·1	204·9	190·9	172·0
$10^6\chi'_M$	902	913	918	917	909	901	885	854	813
μ_{eff}	1·41	1·38	1·35	1·31	1·26	1·22	1·16	1·10	1·02
T (°K)	158·3	146·2	145·7	129·7	113·1	110·4	106·6	98·6	87·8
$10^6\chi'_M$	762	724	728	640	579	578	565	529	490
μ_{eff}	0·94	0·88	0·88	0·78	0·69	0·68	0·66	0·61	0·55

Copper(II) *m*-chlorobenzoate (A)

T (°K)	306·0	295·4	295·4	284·0	270·6	250·7	235·0	221·5	204·0	192·2
$10^6\chi'_M$	1276	1320	1327	1406	1356	1525	1601	1684	1792	1901
μ_{eff}	1·73	1·73	1·73	1·75	1·68	1·71	1·70	1·70	1·68	1·68
T (°K)	175·8	160·2	144·8	130·0	120·9	108·0	99·4	89·6	78·4	
$10^6\chi'_M$	2017	2176	2394	2568	2728	2926	3117	3376	3756	
μ_{eff}	1·66	1·65	1·64	1·61	1·61	1·57	1·56	1·54	1·52	

Copper(II) *m*-chlorobenzoate (B)

T (°K)	378	363	346	335	317	298	294	281	260	249
$10^6\chi'_M$	742	745	760	768	772	787	787	787	779	775
μ_{eff}	1·44	1·42	1·40	1·38	1·35	1·32	1·31	1·28	1·23	1·20
T (°K)	239	221	203	185	167	148	128	107	88	
$10^6\chi'_M$	779	775	764	723	656	585	471	391	353	
μ_{eff}	1·18	1·13	1·07	0·99	0·90	0·79	0·65	0·53	0·46	

Copper(II) *m*-chlorobenzoate dihydrate

T (°K)	308·1	294·2	289·4	278·4	265·1	250·2	236·2	221·5	206·6	191·5
$10^6\chi'_M$	1513	1594	1617	1677	1748	1844	1949	2065	2203	2347
μ_{eff}	1·89	1·90	1·90	1·90	1·89	1·89	1·89	1·89	1·88	1·87
T (°K)	177·6	164·6	152·7	141·0	130·4	121·0	110·8	101·2	90·6	78·4
$10^6\chi'_M$	2526	2707	2901	3150	3377	3634	3925	4277	4768	5556
μ_{eff}	1·87	1·87	1·86	1·87	1·86	1·86	1·85	1·85	1·85	1·86

Copper(II) *m*-nitrobenzoate

T (°K)	310·0	295·0	291·2	272·6	263·0	244·4	229·6	218·5	201·5	183·4	171·0	147·2	130·3	109·6
$10^6\chi'_M$	1210	1235	1241	1298	1315	1372	1419	1467	1519	1576	1649	1742	1815	1907
μ_{eff}	1·69	1·67	1·66	1·64	1·63	1·60	1·58	1·57	1·53	1·49	1·47	1·41	1·35	1·27

Copper(II) *m*-nitrobenzoate dihydrate

T (°K)	306·6	290·8	277·8	266·4	250·9	237·1	215·8	205·6	192·9
$10^6\chi'_M$	1439	1503	1570	1626	1718	1833	1984	2079	2209
μ_{eff}	1·84	1·83	1·83	1·83	1·83	1·83	1·82	1·82	1·82
T (°K)	177·9	164·9	154·5	141·9	133·3	123·0	111·0	100·9	92·3
$10^6\chi'_M$	2409	2606	2785	3023	3212	3479	3843	4227	4624
μ_{eff}	1·83	1·83	1·84	1·83	1·83	1·83	1·83	1·83	1·84

Copper(II) *p*-nitrobenzoate

T (°K)	299·3	292·0	286·0	273·6	265·4	252·2	243·0	226·2	215·8
$10^6\chi'_M$	1116	1124	1132	1159	1176	1198	1221	1257	1261
μ_{eff}	1·59	1·58	1·57	1·55	1·54	1·52	1·50	1·47	1·44
T (°K)	201·6	182·7	164·2	149·7	129·6	119·4	115·2	105·6	
$10^6\chi'_M$	1304	1332	1365	1359	1381	1393	1355	1376	
μ_{eff}	1·42	1·36	1·31	1·25	1·17	1·13	1·09	1·05	

Copper(II) *p*-nitrobenzoate monohydrate

T (°K)	298·9	290·0	282·4	273·6	266·5	260·1	255·2	250·2	250·2	247·8
$10^6\chi'_M$	1259	1291	1306	1328	1343	1354	1380	1396	1396	1402
μ_{eff}	1·69	1·69	1·68	1·67	1·66	1·64	1·64	1·64	1·64	1·63
T (°K)	245·6	244·9	240·8	234·8	229·8	224·4	219·7	214·0	199·8	185·2
$10^6\chi'_M$	1396	1391	1412	1427	1449	1464	1480	1496	1538	1602
μ_{eff}	1·62	1·61	1·61	1·60	1·60	1·59	1·58	1·57	1·54	1·51
T (°K)	169·8	155·5	139·7	128·8	117·1	107·8	98·2	87·5	78·3	
$10^6\chi'_F$	1670	1760	1892	1998	2172	2335	2572	2926	3410	
μ_{eff}	1·48	1·46	1·43	1·41	1·41	1·40	1·41	1·42	1·45	

TABLE 3 (*Continued*)

Copper(II) *o*-nitrobenzoate

T (°K)	307·4	297·2	291·3	285·9	285·3	277·7	267·2	253·1	231·5
$10^6\chi'_M$	946	950	953	964	973	964	977	981	959
μ_{eff}	1·48	1·45	1·44	1·44	1·44	1·42	1·40	1·37	1·29
T (°K)	222·3	201·9	186·8	171·8	158·6	144·0	126·5	114·6	92·3
$10^6\chi'_M$	952	904	875	841	783	719	621	558	442
μ_{eff}	1·26	1·17	1·10	1·04	0·96	0·87	0·75	0·68	0·53

Copper(II) *o*-nitrobenzoate monohydrate (A)

T (°K)	299·0	289·7	274·8	261·0	244·4	229·5	212·8	196·8
$10^6\chi'_M$	1521	1549	1586	1613	1657	1689	1724	1765
μ_{eff}	1·87	1·86	1·83	1·80	1·77	1·73	1·68	1·64
T (°K)	180·4	164·8	150·3	135·7	122·8	109·6	99·7	87·9
$10^6\chi'_M$	1809	1845	1897	1956	2033	2144	2272	2455
μ_{eff}	1·59	1·53	1·49	1·43	1·39	1·35	1·33	1·30

Copper(II) *o*-nitrobenzoate monohydrate (B)

T (°K)	303·6	290·0	272·3	258·3	247·1	233·4	217·8	202·0	189·7
$10^6\chi'_M$	819	823	819	807	797	780	752	712	681
μ_{eff}	1·36	1·33	1·29	1·24	1·21	1·16	1·10	1·03	0·97
T (°K)	174·0	160·8	147·6	133·5	119·3	110·9	101·7	91·0	81·9
$10^6\chi'_M$	617	556	490	400	320	270	214	118	36
μ_{eff}	0·88	0·80	0·71	0·60	0·50	0·43	0·35	0·20	0

Copper(II) *o*-chlorobenzoate

T (°K)	308·8	295·4	280·7	265·6	251·8	237·5	222·1	205·5	190·0
$10^6\chi'_M$	1162	1190	1235	1273	1299	1337	1374	1408	1447
μ_{eff}	1·65	1·63	1·62	1·61	1·58	1·56	1·53	1·48	1·45
T (°K)	175·6	161·3	146·0	131·2	120·4	110·7	100·0	89·9	77·0
$10^6\chi'_M$	1469	1490	1496	1471	1437	1396	1319	1209	1030
μ_{eff}	1·41	1·36	1·30	1·22	1·15	1·09	1·00	0·91	0·77

Copper(II) *o*-chlorobenzoate monohydrate

T (°K)	305·4	292·5	275·2	259·6	245·0	229·2	211·2	201·2	187·4
$10^6\chi'_M$	1007	1022	1044	1056	1064	1062	1058	1049	1026
μ_{eff}	1·52	1·50	1·47	1·44	1·40	1·36	1·30	1·26	1·20
T (°K)	172·0	156·7	140·7	130·6	120·9	110·0	100·0	91·7	77·7
$10^6\chi'_M$	996	943	858	798	734	652	568	481	348
μ_{eff}	1·13	1·05	0·95	0·88	0·81	0·72	0·64	0·56	0·42

Pyridinecopper(II) *o*-chlorobenzoate

T (°K)	336·1	323·4	308·4	297·0	296·2	294·3	287·9	278·3	271·5	263·8	258·3	250·9
$10^6\chi'_M$	760	771	767	786	781	759	780	783	771	772	768	756
μ_{eff}	1·37	1·36	1·32	1·31	1·31	12·8	1·29	1·27	1·24	1·23	1·21	1·18
T (°K)	242·3	227·7	211·7	193·7	188·3	176·9	153·0	138·3	123·0	107·5	93·0	
$10^6\chi'_M$	753	743	721	688	660	605	555	481	411	315	263	
μ_{eff}	1·16	1·12	1·06	0·99	0·94	0·88	0·78	0·68	0·59	0·47	0·39	

basic salt $[Cu(RCO_2)(OH)]$.[14] Infrared studies on a number of basic copper carboxylates have shown these compounds to exhibit a sharp band in the region of 3700 cm.$^{-1}$ (O–H stretch)[15] and we have used this band as a diagnostic test for the presence of basic salt impurity in the anhydrous normal carboxylates studied in this work. Both copper(II) *m*-chlorobenzoate (A) and copper(II) *p*-chlorobenzoate (A) have basic salt impurity while the (B) forms are free from basic salt, the recrystallisation from *p*-dioxan having removed this impurity. Studies on the magnetic properties of these basic salts[15] have shown them to have higher magnetic susceptibilities than the normal salts and it is therefore possible that some of the differences in the magnetic properties of the (A) and (B) forms of the *m*- and *p*-chloro-derivatives is due to the basic salt impurity in the (A) compounds. Copper(II) *m*-methylbenzoate (A) also contains basic salt impurity while the (B) form is free from it. In this case, however, since the (A) form has the lower room-temperature magnetic moment it is not possible to explain the difference in the magnetic properties on the basis of basic salt impurity and there seems therefore no doubt that these are two different forms of the

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[14] J. Ploquin and C. Vergneau-Souvray, *Bull. Soc. chim. France*, 1951, **18**, 757.

[15] Y. C. Lin and R. C. Thompson, unpublished results.

same compound. The presence of the impurity in (A) suggests that the magnetic moment reported here (Table 4) is probably high for this compound.

The remainder of the anhydrous compounds reported here were found to be free from basic salt although the *m*- and *p*-nitro-derivatives did show broad bands around 3500 cm.$^{-1}$ due presumably to the presence of trace amounts of water in these compounds.

Typical χ'_M *vs.* T curves for the anhydrous compounds are shown in Figure 2. On the basis of their magnetic behaviour alone, the compounds may be readily divided into two groups. Group I compounds [copper(II) *o*-nitro-, *o*-methyl-, *m*-methyl- (A), *p*-methyl-, *m*-chloro- (B), *p*-chloro-benzoate (B) and (C), and copper(II) benzoate] all exhibit susceptibilities of $900 \pm 50 \times 10^{-6}$ c.g.s., e.m.u. around room temperature. Moreover for all these compounds * the susceptibility rises as the temperature is lowered below room temperature, reaches a maximum in the range 270 ± 20°K and then decreases as the temperature is reduced further. This magnetic behaviour is very similar to that observed for copper acetate and its higher homologues, and on the basis of this similarity it seems reasonable to suggest that the group I compounds have structures analogous to that of copper(II) acetate monohydrate with a *syn-syn* arrangement of carboxylate groups in dimeric units. The copper ions are thus held in pairs which interact with each other in such a way as to form lower singlet and upper triplet electronic states. For such a situation the molar magnetic susceptibility is given by the expression:[16]

$$\chi'_{\mathrm{M}} = g^2 \frac{\mathbf{N}\beta^2}{3\mathbf{k}T} [1 + \tfrac{1}{3} \exp (2J/\mathbf{k}T)]^{-1} + N\alpha; \qquad (1)$$

where χ'_{M} = molar magnetic susceptibility, g = Landé Spectroscopic splitting factor, $\mathbf{N}$ = Avogadro's number, β = Bohr magneton, $\mathbf{k}$ = Boltzmann constant, T = temperature (°K), J = exchange coupling constant,† $N\alpha$ = temperature-independent paramagnetic contribution [60×10^{-6} c.g.s., e.m.u. for Cu(II)].

TABLE 4

Room-temperature magnetic moments

Compound	T (°K)	$10^6\chi_g$	$-10^6\chi$	$10^6\chi'_{\mathrm{M}}$	μ_{eff} (B.M.)	pK_a	Ref.
Cu(*p*-$CH_3C_6H_4CO_2$)$_2$	292	2·02	173	849	1·36	4·35	14
Cu(*p*-$CH_3C_6H_4CO_2$)$_2$,H_2O	292	4·73	186	1854	2·06	4·35	
Cu(*m*-$CH_3C_6H_4CO_2$)$_2$ (A)	296	2·19	173	905	1·42	4·25	14
Cu(*m*-$C_3C_6H_4CO_2$)$_2$ (B)	295	3·27	173	1265	1·69	4·25	
Cu($C_6H_5CO_2$)$_2$	292	2·35	148	866	1·38	4·18	1, 18
Cu($C_6H_5CO_2$)$_2$,3H_2O	293	4·22	187	1705	1·97	4·18	1, 18
Cu(*p*-$ClC_6H_4CO_2$)$_2$ (A)	294	2·45	183	1101	1·56	4·05	
Cu(*p*-$ClC_6H_4CO_2$)$_2$ (B)	293	1·95	183	914	1·42	4·05	
Cu(*p*-$ClC_6H_4CO_2$)$_2$ (C)	295	2·01	183	936	1·44	4·05	
Cu(*p*-$ClC_6H_4CO_2$)$_2$,H_2O	292	3·99	196	1762	2·00	4·05	
Cu(*o*-$CH_3C_6H_4CO_2$)$_2$	292	2·19	170	902	1·41	3·92	14
Cu(*m*-$ClC_6H_4CO_2$)$_2$ (A)	295	3·03	183	1320	1·73	3·80	
Cu(*m*-$ClC_6H_4CO_2$)$_2$ (B)	294	1·61	183	787	1·31	3·80	
Cu(*m*-$ClC_6H_4CO_2$)$_2$,2H_2O	294	3·37	209	1594	1·91	3·80	
Cu(*m*-$NO_2C_6H_4CO_2$)$_2$	295	2·70	167	1235	1·67	3·47	
Cu(*m*-$NO_2C_6H_4CO_2$)$_2$,2H_2O	291	3·03	193	1503	1·84	3·47	
Cu(*p*-$NO_2C_6H_4CO_2$)$_2$	293	2·42	165	1124	1·58	3·40	
Cu(*p*-$NO_2C_6H_4CO_2$)$_2$,H_2O	294	2·66	178	1281	1·69	3·40	
Cu(*o*-$NO_2C_6H_4CO_2$)$_2$	293	1·99	159	953	1·45	3·21	
Cu(*o*-$NO_2C_6H_4CO_2$)$_2$,H_2O (A)	293	3·29	172	1533	1·86	3·21	
Cu(*o*-$NO_2C_6H_4CO_2$)$_2$,H_2O (B)	296	1·57	172	822	1·34	3·21	
Cu(*o*-$ClC_6H_4CO_2$)$_2$	295	2·69	183	1190	1·62	2·89	
Cu(*o*-$ClC_6H_4CO_2$)$_2$,H_2O	292	2·10	196	1022	1·51	2·89	
Cu(*o*-$ClC_6H_4CO_2$)$_2$py	297	1·22	232	786	1·32	2·89	

Making use of this equation, Figgis and Martin[3,4] were able to satisfactorily account for the magnetic data of copper acetate monohydrate and a series of copper(II) n-alkanoates.

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* Except copper(II) *p*-chlorobenzoate (B).

† Figgis and Martin[3] employ J as the singlet–triplet separation, whereas we use $2J$.

[16] B. Bleaney and K. D. Bowers, *Proc. Roy. Soc.*, 1952, *A*, **214**, 451.

We have treated our results in an analogous manner and the J and g values obtained are given in Table 5. There is reasonable agreement between theoretical and experimental χ'_M–T curves (Figure 3) although at low temperatures the experimental susceptibilities are often higher than those predicted by theory. Such deviations could be due to the presence of a small amount of an impurity in the samples, for which magnetic interaction is smaller (see ref. 17 for a discussion of the magnetic properties of the chromium basic rhodo-salts). Alternatively, each of these compounds may exist in another crystal form in which the magnetic interaction is weaker. In particular, the deviation between experiment and theory at low temperature is quite large in the case of copper(II) *p*-methylbenzoate. This compound and copper(II) *p*-chlorobenzoate (C) certainly appear to be mixtures of two magnetic forms. Since it appears that an appreciable quantity of a relatively magnetically dilute form is present in the latter compound, it has not been possible to fit the susceptibility–temperature data to a theoretical curve. Although copper(II) *p*-chlorobenzoate (B) has a room-temperature moment almost identical to that of copper(II) *p*-chlorobenzoate (C) no maximum in its χ'_M–T curve is observed. Here presumably the concentration of the magnetically dilute form is even greater than that in the (C) compound. Indeed, in certain instances it has been possible to isolate more than one magnetic form for a given compound, depending very often on the method of preparation used. This has been dealt with specifically in the case of the copper benzoate system previously.[1,18]

The group II compounds [copper(II) *m*-nitro, *p*-nitro-, *m*-chloro- (A), *p*-chloro- (A), *m*-methyl-benzoate (B)] exhibit susceptibilities which are higher than those of the group I compounds, increase as the temperature is lowered, and do not pass through a maximum in the temperature range studied. The χ_M'—T curve for copper(II) *o*-chlorobenzoate, included in Figure 3, exhibits properties of both group I and II curves. This compound will be dealt with later. Plots of the reciprocal of magnetic susceptibility *vs.* temperature are shown in Figure 4 for some group II compounds. In all cases the curves are linear at the highest tempeatures studied, representing Curie–Weiss law behaviour. The extrapolated linear portion of each curve intercepts the temperature axis at a negative value of temperature indicating antiferromagnetic interaction. For the *m*-nitro-, *p*-nitro-, and *m*-methyl-complexes the experimental reciprocal susceptibility values at low temperatures are high with respect to the linear extrapolation which represents Curie–Weiss behaviour. Such deviations are usually observed near the Néel point and indicate that the antiferromagnetism is greater in these compounds than in copper(II) *m*-chlorobenzoate (A) where no such deviation occurs. This difference in the magnitude of magnetic interaction is also reflected in the Weiss constants which are summarised in Table 6, For the *p*-chlorobenzoate, the magnetic properties were dependent upon the preparation. For all three samples prepared, susceptibility–temperature data can be explained in terms of a mixture of two magnetic forms of the complex. The magnetic behaviour of the group II compounds is very similar to that observed for the copper(II) formates and suggests that

TABLE 5

Values for T_c, g, $2J$, $\Delta H°$, and $\Delta S°$

Compound	T_c (°K)	$2J$ (cm.$^{-1}$)	g	$\Delta H°$ (cm.$^{-1}$)	$\Delta S°$ e.u.
$Cu(p\text{-}CH_3C_6H_4CO_2)_2$	260	289	2·10	289 ‡	2·2
$Cu(m\text{-}CH_3C_6H_4CO_2)_2$ (A)	260	289	2·18	284 ‡	2·2
$Cu(C_6H_5CO_2)_2$	280	312	2·18	324 ‡	2·1
$Cu(o\text{-}CH_3C_6H_4CO_2)_2$	250	278	2·13	279 ‡	2·1
$Cu(m\text{-}ClC_6H_4CO_2)_2$ (B)	270	300	2·04	315 ‡	2·2
$Cu(o\text{-}NO_2C_6H_4CO_2)_2$	250	278	2·19	295	2·3
$Cu(o\text{-}NO_2C_6H_4CO_2)_2,H_2O$ (B)	297	330	2·18	339	2·3
$Cu(o\text{-}ClC_6H_4CO_2)_2$	150	167	2·14	180	2·4
$Cu(o\text{-}ClC_6H_4CO_2)_2,H_2O$	220	245	2·17	257	2·3
$Cu(o\text{-}ClC_6H_4CO_2)_2py$	280	312	2·07	312	2·1

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[17] A. Earnshaw and J. Lewis, *J.*, 1961, 396.

[18] M. Inoue, M. Kishita, and M. Kubo, *Inorg. Chem.*, 1964, **3**, 293.

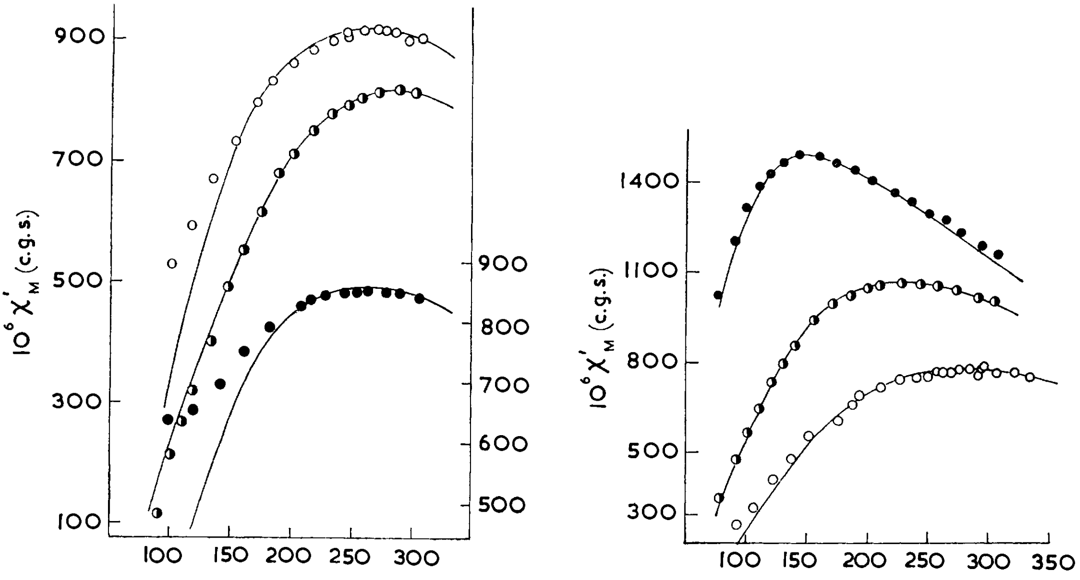

FIGURE 3a.

FIGURE 3b.

Observed and calculated χ'_M *vs.* T curves

(a) Left-hand scale. ○, Copper(II) *m*-methylbenzoate (A). Good fit obtained at high temperatures, but deviation of experimental results from the calculated curve is found at low temperatures. ◑, Copper(II) *o*-nitrobenzoate monohydrate (B). Excellent fit is obtained over the whole temperature range. Right-hand scale. ●, Copper(II) *p*-methylbenzoate. At best a very poor fit is obtained. This indicates that the compound is probably a mixture of two magnetically distinct forms (see text). It is extremely doubtful whether the value of $2J$ deduced from such a fit has any real significance.

(b) ●, Copper(II) *o*-chlorobenzoate; ◑, copper(II) *o*-chlorobenzoate monohydrate; ○, pyridinecopper(II) *o*-chlorobenzoate

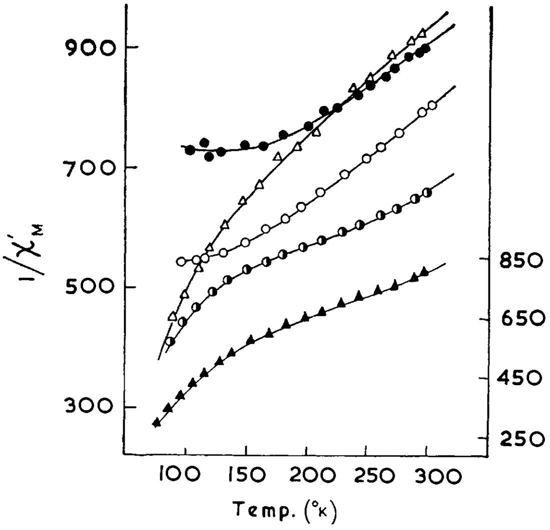

FIGURE 4. Left-hand scale: ●, copper(II) *p*-nitrobenzoate; △, copper(II) *p*-chlorobenzoate (A); ○ copper(II) *m*-methylbenzoate (B); ◑, copper(II) *o*-nitrobenzoate monohydrate

Right-hand scale: ▲, copper(II) *p*-nitrobenzoate monohydrate.

The $1/\chi'_M$ *vs.* T curve for copper(II) *p*-chlorobenzoate (B) is similar to the *o*-nitrobenzoate monohydrate (A) and *p*-nitrobenzoate monohydrate curves.

the compounds of group II have the polymeric " formate " structure in which layers of copper atoms are held together by bridging carboxylate groups in an *anti-anti* or *anti-syn* arrangement.

TABLE 6

Weiss constants

Compound	θ (°K)	Compound	θ (°K)
$Cu(p\text{-}CH_3C_6H_4CO_2)_2,H_2O$	−36	$Cu(m\text{-}ClC_6H_4CO_2)_2$ (A)	50
$Cu(m\text{-}CH_3C_6H_4CO_2)_2$ (B)	210	$Cu(m\text{-}ClC_6H_4CO_2)_2,2H_2O$	10
$Cu(C_6H_5CO_2)_2,3H_2O$	40	$Cu(m\text{-}NO_2C_6H_4CO_2)_2$	210
$Cu(p\text{-}ClC_6H_4CO_2)_2$ (A)	210	$Cu(m\text{-}NO_2C_6H_4CO_2)_2,2H_2O$	0
$Cu(p\text{-}ClC_6H_4CO_2)_2,H_2O$	−20	$Cu(p\text{-}NO_2C_6H_4CO_2)_2$	330

Martin and Whitely [5] found that copper acetate and its higher homologues are soluble in dioxan and retain their binuclear configuration in this solvent. We have investigated solutions in dioxan of several of the group I compounds and, in accordance with the earlier results, we find that all these compounds have molecular weights corresponding to dimers (Table 2). Of the group II compounds all, except the (B) form of copper(II) *m*-methylbenzoate, are insufficiently soluble to enable molecular-weight determinations to be made. Such behaviour may be due, in part, to these compounds having a polymeric structure. The dimeric molecular weight observed for the (B) form of copper(II) *m*-methylbenzoate in dioxan may be associated with conversion in solution into the (A) form of the compound which appears to be binuclear in structure. It is important to emphasise that, in solution, the binuclear form of these copper carboxylates is probably associated with the formation of dioxan solvates. In agreement with this the spectra (see below) do imply a variation between the solid and solution.

As discussed above, the magnetic data for the anhydrous compounds can be correlated by consideration of the pK_a's of the acids and substitution in the benzene ring. The pK_a's of the acids employed in this study are given in Table 4. *o*-Nitro-, *m*-nitro-, *p*-nitro-, and *o*-chloro-benzoic acid possess pK_a's below that of formic acid and hence, if the available σ-electron density on the carboxylate oxygens is the only factor determining the structure adopted by the copper salts, these would be expected to have polymeric " formate " structures. In accordance with this, we have been able to prepare only one form of copper(II) *m*-nitrobenzoate and copper(II) *p*-nitrobenzoate and the evidence suggests that these compounds have polymeric structures. However, a low-moment form of the *p*-nitrobenzoate has been prepared recently.[19] Copper(II) *o*-nitrobenzoate and *o*-chlorobenzoate, on the other hand, appear to possess binuclear structures. The latter complex is discussed in detail below. It is believed that substitution *ortho* to the carboxyl group produces a situation wherein *syn-syn* bonding of the carboxylate ion may be preferred on steric grounds. This steric effect may also preclude the preparation of a polymeric form of copper(II) *o*-methylbenzoate.

The pK_a's of benzoic acid, *o*-methyl-, *m*-methyl-, *p*-methyl-, *m*-chloro-, and *p*-chlorobenzoic acids lie between those of acetic acid (4·75) and formic acid (3·75). With the exception of copper(II) *o*-methylbenzoate, which has been obtained only as a binuclear form, the other copper salts can be prepared in two magnetically distinct forms or as mixtures of such forms. The copper benzoate system has been studied by other workers.[1,18] We have prepared both copper(II) *m*-methylbenzoate and copper(II) *m*-chlorobenzoate in two distinct forms. Our specimens of copper(II) *p*-methylbenzoate and copper(II) *p*-chlorobenzoate [(B) and (C)] appear from the magnetic data to be mixtures of two crystal forms.

The behaviour of copper(II) *o*-chlorobenzoate calls for some comment as it exhibits magnetic properties intermediate between groups I and II. The room-temperature moment is similar to that observed for group II but the variation of the susceptibility with temperature is similar to that of group I. A binuclear structure may be expected for steric reasons,

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[19] A. Earnshaw and K. S. Patel, *J. Inorg. Nuclear Chem.*, 1965, **27**, 1805.

but a polymeric structure would be anticipated from the pK_a of the free acid. The susceptibility–temperature data may be fitted in terms of a binuclear model, but the J value obtained is significantly smaller than for the other binuclear complexes reported. It is difficult to calculate the absolute magnitude of J, but this must obviously be related to factors such as molecular dimensions and resultant charge on the metal ion. It is possible, therefore, to account for this decrease in terms of either of these alternatives. In fact it is somewhat surprising that the value of J for a large number of complexes falls into a relatively small range and this possibly implies that the exchange interaction through the bridging carboxylate groups may be of some considerable importance.

We have prepared and studied an adduct of copper(II) *o*-chlorobenzoate with pyridine. This compound exhibits a room-temperature magnetic moment of 1·32 B.M. and a maximum in its χ'_M–T curve at 290° (Table 3) which indicates that magnetic interaction in the pyridine adduct is very much greater than that present in the anhydrous compound. Addition compounds of copper(II) acetate with various Lewis bases, including pyridine, have been prepared[20] and it has been shown[21,22] that the binuclear configuration is maintained in these adducts and moreover, that the magnitude of the magnetic interaction is essentially the same in both the anhydrous compound and its addition products. Martin and Waterman,[4] on the other hand, have been able to "condition" copper(II) formate into the binuclear structure with strong organic bases such as pyridine and dioxan. In these addition compounds, the organic base bonds directly to the copper ions and reduces the residual charge sufficiently to facilitate conversion of the formate into the binuclear configuration. Accompanying this conversion is a marked increase in magnetic interaction. We observe a similar increase in the magnetic interaction in the formation of the monopyridine adduct of copper(II) *o*-chlorobenzoate. In support of the assignment of a binuclear configuration to monopyridinecopper(II) *o*-chlorobenzoate good agreement is obtained between the experimental χ'_M–T curve and the theoretical curve based on equation (1) (Figure 3); the g and J values calculated for this compound are given in Table 5.

Hydrates.—Several compounds prepared in this work precipitated from aqueous solution as hydrates. Most of these compounds have room-temperature magnetic moments (Table 4) in the range normally observed for copper(II) compounds. The trihydrate of copper(II) benzoate has a room-temperature magnetic moment of 1·97 B.M. and over the temperature range studied exhibits magnetic behaviour very close to the Curie–Weiss law with $\theta = 40$. Hence magnetic interaction in this compound is very small. The structure of $Cu(PhCO_2)_2,3H_2O$ has been determined recently[23] and shows that the compound is polynuclear with each copper ion joined to two neighbouring copper ions *via* two bridging carboxylate groups and four bridging water molecules. Assuming that magnetic exchange takes place *via* carboxylate groups it is perhaps not too surprising that copper–copper interaction is much smaller in this compound than it is in the case of the "formates" where each copper ion is joined to four neighbouring copper ions by four bridging carboxylate groups.

The dihydrates of copper(II) *m*-nitrobenzoate and *m*-chlorobenzoate and the monohydrates of copper(II) *p*-chlorobenzoate and *p*-methylbenzoate, judging from their magnetic moments (Table 4) and Weiss constants (Table 6), are essentially magnetically dilute compounds.

Copper(II) *o*-chlorobenzoate monohydrate exhibits a maximum in its χ'_M–T curve at 220°. This compound very probably has a binuclear configuration. Good agreement is obtained between the experimental magnetic-susceptibility values and the theoretical curve of χ'_M *vs.* T, calculated using equation (1) (Figure 3). The g and J values for this compound are listed in Table 5 and, as with the pyridine adduct, have a value similar to the

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[20] E. Kokot and R. L. Martin, *Inorg. Chem.*, 1964, **3**, 1306.

[21] F. Hanic, D. Stempelova, and K. Hanicova, *Acta Cryst.*, 1964, **17**, 633.

[22] G. A. Barclay and C. H. L. Kennard, *J.*, 1961, 5244.

[23] H. Koizumi, K. Osaki, and T. Watanabe, *J. Phys. Soc. Japan*, 1963, **18**, 117.

other binuclear complexes reported here. Similarly with the (B) form of the copper(II) *o*-nitrobenzoate monohydrate, a binuclear structure is indicated from the magnetic measurements. However, the very low susceptibility at liquid-nitrogen temperature is of the order of the temperature-independent term in the equation.

Figure 4 shows the $1/\chi'_M$ *vs.* T curves for copper(II) *o*-nitrobenzoate monohydrate (A) and copper(II) *p*-nitrobenzoate monohydrate. This type of behaviour can be explained by assuming the compounds to consist of comparable proportions of binuclear and polymeric forms. It is difficult to see, however, why the *o*-nitro-compound should possess such a high room-temperature moment (1·86 B.M.).

Singlet–Triplet Equilibrium.—By treating the magnetic data for the "binuclear" compounds in the manner described by Hatfield, Piper, and Klabunde[24] we have calculated equilibrium constants for the reaction singlet $\rightleftharpoons$ triplet at various temperatures. The slopes of the plots of $-\ln K_{eq}$ *vs.* T^{-1} and $\boldsymbol{R}T \ln K_{eq}$ *vs.* T provided values for ΔH° and ΔS° (Table 5). For the compounds whose susceptibility variation with temperature could be fitted closely to the theoretical expression the plots obtained were linear over the whole temperature range studied. For other compounds, deviations from linearity were observed at low temperatures. (This latter class of compound is indicated by ≠ in Table 5.) The values of ΔH° obtained in this way agree well with the values of $2J$ deduced from curve-fitting. The values found for ΔS° are close to those expected for a singlet–triplet equilibrium (*i.e.*, $\boldsymbol{R} \ln 3 = 2{\cdot}2$).

Spectra.—Reflectance spectra of the solids, and of solutions in dioxan and in methyl cyanide were observed in the range 350—900 mμ (Tables 7 and 8). In the reflectance spectra, all the complexes exhibited a broad absorption band in the region of 690 ± 40 mμ and in addition the complexes believed to be binuclear all show an absorption in the region of 400 mμ. As opposed to the situation in the corresponding alkylcarboxylate series this high-energy band cannot be located accurately since it always occurs as a shoulder on a charge transfer band. The wavelengths quoted for this band therefore must be taken as an indication of the region in which the shoulder is observed.

TABLE 7

Reflectance spectra

Compound	"700" band (mμ)	"400" band (mμ)	Compound	"700" band (mμ)	"400" band (mμ)
$Cu(C_6H_5CO_2)_2$	669	427sh	$Cu(m\text{-}NO_2C_6H_4CO_2)_2$	668	Absent
$Cu(C_6H_5CO_2)_2,3H_2O$	700	Absent	$Cu(m\text{-}NO_2C_6H_4CO_2)_2,2H_2O$	656	Absent
$Cu(o\text{-}CH_3C_6H_4CO_2)$	677	445sh	$Cu(p\text{-}NO_2C_6H_4CO_2)_2$	703	Absent
$Cu(m\text{-}CH_3C_6H_4CO_2)_2$ (A)	679	435sh	$Cu(p\text{-}NO_2C_6H_4CO_2)_2,H_2O$	702	Absent
$Cu(m\text{-}CH_3C_6H_4CO_2)_2$ (B)	696	Absent	$Cu(o\text{-}ClC_6H_4CO_2)_2$	721	422sh
$Cu(p\text{-}CH_3C_6H_4CO_2)_2$	662	434sh	$Cu(o\text{-}ClC_6H_4CO_2)_2,H_2O$	713	422sh
$Cu(p\text{-}CH_3C_6H_4CO_2)_2,H_2O$	706	Absent	$Cu(m\text{-}ClC_6H_4CO_2)_2$ (A)	691	Absent
$Cu(o\text{-}NO_2C_6H_4CO_2)_2$	663	440sh	$Cu(m\text{-}ClC_6H_4CO_2)_2,2H_2O$	691	378sh
$Cu(o\text{-}NO_2C_6H_4CO_2)_2,H_2O$ (A)	712	?	$Cu(p\text{-}ClC_6H_4CO_2)_2$ (C)	648	426sh
$Cu(o\text{-}NO_2C_6H_4CO_2)_2,H_2O$ (B)	702	447sh	$Cu(p\text{-}ClC_6H_4CO_2)_2,H_2O$	728	389sh

sh = shoulder.

Complexes which appear from magnetic measurements to be polymeric do not show this band, with the possible exception of copper(II) *m*-chlorobenzoate dihydrate and copper(II) *p*-chlorobenzoate monohydrate, when a weak band occurs in this region. As discussed above, in both these compounds the magnetic interaction is weak. The assignment of this high-energy band in binuclear complexes has been the subject of considerable discussion.[25] The effect of changing from the alkyl- to the aryl-carboxylic acids does appear to influence the position of this band, as in the alkyl series it occurs in a relatively narrow region about

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[24] W. E. Hatfield, T. S. Piper, and U. Klabunde, *Inorg. Chem.*, 1963, **2**, 629.

[25] I. G. Ross, *Trans. Faraday Soc.*, 1959, **55**, 1058; I. G. Ross and J. Yates, *ibid.*, p. 1064; I. G. Ross, M. L. Tonnet, and S. Yamada, *ibid.*, 1964, **60**, 840.

375 mμ, whereas for the compounds reported here the band falls in the range 378—447 mμ. The variation in the position of this band is consistent with the assignment of this transition to a level in which the ligand orbitals may make a major contribution.

TABLE 8

Solution spectra (in mμ)

	Dioxan			Acetonitrile		
Compound	" 700 " band	" 400 " band	ε " 700 "	" 700 " band	" 400 " band	ε " 700 "
$Cu(C_6H_5CO_2)_2$	669	384sh	270	688	386sh	262
$Cu(C_6H_5CO_2)_2,3H_2O$	666	405sh	—			
$Cu(o\text{-}CH_3C_6H_4CO_2)_2$	669	416sh	280	684	417sh	277
$Cu(m\text{-}CH_3C_6H_4CO_2)_2$ (A)	663	397sh	265	689	400sh	252
$Cu(m\text{-}CH_3C_6H_4CO_2)_2$ (B)	669	402sh	268	682	400sh	267
$Cu(p\text{-}CH_3C_6H_4CO_2)_2$	668	415sh	300			
$Cu(p\text{-}CH_3C_6H_4CO_2)_2,H_2O$	666	420sh	—			
$Cu(o\text{-}NO_2C_6H_4CO_2)_2$	687	Absent	249			
$Cu(o\text{-}NO_2C_6H_4CO_2)_2,H_2O$ (A)	684	Absent	249			
$Cu(o\text{-}NO_2C_6H_4CO_2)_2,H_2O$ (B)	683	Absent	258			
$Cu(m\text{-}NO_2C_6H_4CO_2)_2$	684	Absent	—	704	Absent	224
$Cu(m\text{-}NO_2C_6H_4CO_2)_2,2H_2O$	682	Absent	—			
$Cu(p\text{-}NO_2C_6H_4CO_2)_2$	680	Absent	—			
$Cu(p\text{-}NO_2C_6H_4CO_2)_2,H_2O$	680	Absent	262			
$Cu(o\text{-}ClC_6H_4CO_2)_2$	681	414sh	262			
$Cu(o\text{-}ClC_6H_4CO_2)_2,H_2O$	681	412sh	272			
$Cu(m\text{-}ClC_6H_4CO_2)_2$ (A)	673	421sh	—			
$Cu(m\text{-}ClC_6H_4CO_2)_2,2H_2O$	676	422sh	287			
$Cu(p\text{-}ClC_6H_4CO_2)_2$ (C)	675	410	275			
$Cu(p\text{-}ClC_6H_4CO_2)_2,H_2O$	Insoluble		—			

sh = shoulder.

Solution spectra of the complexes often differ markedly from those of the solids, as would be expected for some solvent interaction with the complexes, and support the suggestion that it may be dangerous to use physical data obtained on solutions to deduce the nature of the species in the solid state. Both the long- and short-wavelength bands appear to change on solvation. In dioxan solution, the long-wavelength band occurs in the region 675 ± 15 mμ with an extinction coefficient of 270 ± 30 l. mole^{-1} cm.$^{-1}$. This peak in methyl cyanide appears to move significantly to longer wavelengths, with a very similar value for the extinction coefficient to that observed in dioxan. The extinction coefficients are similar to those reported by Kokot and Martin [20] for binuclear copper(II) alkylcarboxylic acid derivatives. In contrast to the behaviour of the low-energy band the position of the high-energy band appears to be the same in both solvents.

Several of the hydrates were found to dissolve in dioxan to a limited extent giving solutions whose spectra were similar to those of solutions of the corresponding anhydrous compounds. It would appear, therefore, that the anhydrous and hydrated complexes produce the same species in solution, indicating that dioxan has replaced water in the co-ordination sphere. The polymeric complexes are believed to rearrange to binuclear dioxan solvates on solution. In support of this claim, all spectra of compounds soluble in dioxan, with the exception of those of the nitrobenzoates, show a high-energy absorption in the 400-mμ region. None of the spectra of the copper nitrobenzoates appears to show absorption in this region.

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