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Spin–Spin Coupling in Binuclear Complexes. III. The Magnetic Properties of Copper Salts of Substituted Benzoic Acids[1,2]

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The magnetic and spectral properties of a series of substituted benzoic acid salts of copper(II) are reported. The compounds, studied as their 1-butanol adducts, all display antiferromagnetic behavior typical of binuclear complexes with copper acetate type structures. For the substituents *p*-H, *p*-CH_3, *p*-CH_3O, *p*-Br, and *p*-NO_2 on the phenyl ring, the Néel temperatures lie within the range 275–284°K.

Introduction

The question of the structure and bonding of copper(II) aryl- and alkylcarboxylates is of current interest; the literature dealing with the subject has been reviewed.[3] Whereas it is readily accepted that the magnetic behavior of the dimeric and polymeric molecules reflects an interaction between unpaired electrons on adjacent copper(II) ions, the mechanism by which the magnetic ordering process occurs is the cause of considerable discussion.

Copper acetate monohydrate has been shown to have a binuclear structure[4] in which copper ions are bridged in pairs by four acetate groups with two water molecules occupying the terminal positions. The metal–metal distance is 2.64 A as measured by X-ray diffraction[4a] or 2.61 A from more recent neutron diffraction measurements,[4b] which is only slightly greater than the interatomic distance of 2.56 A in metallic copper. On this basis a direct bond between the two copper ions has been suggested in order to explain the observed antiferromagnetic behavior. Using the valence bond approach, Figgis and Martin[5] postulated the formation of a δ bond by overlap of the $3d_{x^2-y^2}$ orbitals. Later, Forster and Ballhausen,[6] in a molecular orbital treatment of the bonding, favored the formation of a direct σ bond *via* the $3d_{z^2}$ orbitals. This paper caused a reexamination of the experimental evidence for the bonding in the compound and there have been several refinements and arguments as to the relative merits of the two alternatives.

Both the valence bond and the molecular orbital approaches have been based on the assumption that the magnetic ordering results from a direct copper–copper bond. An alternative explanation is that part or whole of the interaction occurs *via* the carboxylate bridging groups. This was considered less likely by earlier workers in view of the copper–copper distance in cupric acetate monohydrate and that in metallic copper itself. The superexchange mechanism has been postulated to explain the spin–spin coupling in such diverse systems as copper formate monohydrate[7] and the dimeric copper chloride–pyridine N-oxide compounds.[8] Some substituted benzoic acid salts of copper(II) display similar magnetic and spectral characteristics to those of the copper acetate monohydrate system, and the evidence indicates that a similar binuclear structural entity is present in these cases.[9,10] However, the previous work was complicated by structural varieties and preparative difficulties.[10] In an attempt to gain further information on this question the magnetic properties of a number of copper(II) salts of substituted benzoic acids have been measured as a function of temperature and the results are reported here.

Results

For these investigations a series of compounds was selected on the basis of two criteria. The primary requirement was that the substituent must be capable of affecting the electron density in the carboxylate group but yet must not provide any steric hindrance. Secondly, the method of preparation of the compounds must leave no question concerning the integrity of the samples. Previous work in this laboratory has emphasized the experimental difficulties involved in the preparation of acceptable samples.[10] Even gentle heating causes slight decomposition of the compounds, yielding products which mask the magnetic properties of the compounds under study. To circumvent these difficulties it was decided to attempt to crystallize adducts of the dimeric copper benzoates from solution. Although the monopyridine adduct of copper benzoate [$Cu(C_6H_5CO_2)_2(C_5H_5N)$] has been reported,[11] a complete series of substituted benzoic acid–pyridine adducts could not be prepared. Pyridine and other organic amines and bases frequently gave compounds for one or more members of the series in which two or more molecules of the organic base were coordinated to the

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TABLE I

MAGNETIC DATA

$Cu(C_6H_5CO_2)_2 \cdot C_4H_9OH$				$Cu(p\text{-}CH_3C_6H_4CO_2)_2 \cdot C_4H_9OH$				$Cu(p\text{-}NO_2C_6H_4CO_2)_2 \cdot C_4H_9OH$				$Cu(p\text{-}CH_3OC_6H_4CO_2)_2 \cdot C_4H_9OH$				$Cu(p\text{-}BrC_6H_4CO_2)_2 \cdot C_4H_9OH$			
T, °K	$\chi_m \times 10^6$ cgs units observed	calculated	μ_{eff} BM	T, °K	$\chi_m \times 10^6$ cgs units observed	calculated	μ_{eff} BM	T, °K	$\chi_m \times 10^6$ cgs units observed	calculated	μ_{eff} BM	T, °K	$\chi_m \times 10^6$ cgs units observed	calculated	μ_{eff} BM	T, °K	$\chi_m \times 10^6$ cgs units observed	calculated	μ_{eff} BM
299	889	898	1.46	298	840	857	1.40	321	875	900	1.51	298	897	907	1.47	298	876	878	1.45
287	900	901	1.44	289	869	859	1.42	298	880	911	1.45	288	912	910	1.45	289	878	880	1.43
279	902	902	1.42	283	873	860	1.41	288	913	913	1.46	280	906	911	1.43	284	887	880	1.42
271	902	902	1.40	276	871	860	1.39	280	927	915	1.45	274	914	911	1.42	278	878	880	1.40
262	900	901	1.38	268	862	859	1.37	273	925	913	1.43	267	912	910	1.40	271	878	879	1.39
255	891	899	1.35	257	850	855	1.33	263	907	913	1.39	256	897	906	1.36	264	869	877	1.36
244	878	893	1.31	247	837	850	1.29	252	899	909	1.35	242	892	897	1.32	255	850	872	1.32
233	871	883	1.28	230	818	833	1.23	241	889	902	1.31	235	879	891	1.29	242	857	862	1.29
217	843	861	1.22	206	780	793	1.14	222	872	880	1.25	219	850	869	1.23	220	824	833	1.21
203	818	833	1.16	190	730	751	1.06	211	838	861	1.19	206	824	843	1.17	207	805	807	1.16
189	778	795	1.09	178	681	710	0.99	203	842	843	1.17	189	785	796	1.09	194	771	772	1.10
173	723	737	1.00	161	615	637	0.89	187	791	797	1.11	171	700	728	0.98	166	667	665	0.90
157	663	662	0.92	148	554	569	0.81	166	702	713	0.97	154	629	643	0.88	138	523	509	0.76
141	562	569	0.80	123	434	412	0.66	151	601	635	0.86	123	471	441	0.68	77	133	125	0.29
123	431	446	0.65	102	237	268	0.44	125	457	463	0.68	97	243	252	0.45				
99	320	271	0.51	77	91	128	0.24	106	329	322	0.53	77	165	135	0.36				
82	190	163	0.35					77	94	138	0.24								

copper ion. These compounds usually have normal magnetic moments; *e.g.*, $[Cu(C_6H_5CO_2)_2(C_5H_5N)_2]$ has a moment of 1.90 BM at room temperature. For reasons demonstrated earlier it was considered unwise to attempt to prepare samples by gentle heating of the 2:1 (or n:1) adducts. By a systematic investigation it was found that 1:1 1-butanol adducts of the entire series of compounds could be crystallized from 1-butanol. The complexes were sufficiently stable to permit packing in a cellulose capsule for low-temperature magnetic susceptibility determinations.

All of the compounds studied exhibited magnetic behavior similar to that reported by Figgis and Martin[5] for copper acetate; *i.e.*, the susceptibility increased with decreasing temperature to a well-defined Néel temperature and then decreased rapidly to a very low value at 77°K. Table I compares the experimental molar susceptibilities, calculated on the basis of a monomeric formula weight, with the values predicted by the best fit of the theoretical expression (1) to the parameters g and $|2J|$.

$$\chi_m = \frac{g^2N\beta^2}{3kT}\left(1 + \frac{1}{3}e^{-2J/kT}\right)^{-1} + N\alpha \qquad (1)$$

This equation describes the temperature dependence of the magnetic susceptibilities of an electronic system composed of singlet and triplet states separated by an energy difference $|2J|$; *i.e.*, with the energy of the singlet term zero, the triplet term lies at $-2J$. In the equation χ_m is the molar magnetic susceptibility; g, the Landé spectroscopic splitting factor; N, Avogadro's number; β, the Bohr magneton; k, Boltzmann's constant; T, the temperature (°K); and $N\alpha$ the temperature-independent paramagnetism. The best values of g and the singlet–triplet splitting energy selected by a GAT program written for the Univac 1105 computer are given in Table II.

Spectral data for butanol solutions of the compounds and reflectance measurements for the solids are recorded in Table III. For the solution spectra molar extinction coefficients based on dimer concentrations are noted in parentheses.

TABLE II

NÉEL TEMPERATURES (T_n), SINGLET–TRIPLET SPLITTING ENERGIES ($|2J|$), AND LANDE FACTORS (g)

Compound	T_n, °K	$\|2J\|$, cm^{-1}	g
$Cu(C_6H_5CO_2)_2 \cdot C_4H_9OH$	275	306	2.22
$Cu(p\text{-}CH_3C_6H_4CO_2)_2 \cdot C_4H_9OH$	280	312	2.18
$Cu(p\text{-}CH_3OC_6H_4CO_2)_2 \cdot C_4H_9OH$	278	309	2.24
$Cu(p\text{-}BrC_6H_4CO_2)_2 \cdot C_4H_9OH$	284	315	2.22
$Cu(p\text{-}NO_2C_6H_4CO_2)_2 \cdot C_4H_9OH$	276	306	2.24

TABLE III

SPECTRAL DATA

Compound	Band max, mμ (extinction coefficient)	
$Cu(C_6H_5CO_2)_2 \cdot C_4H_9OH$	705 (313)[a]	...
	710[b]	360
$Cu(p\text{-}CH_3C_6H_4CO_2)_2 \cdot C_4H_9OH$	705 (280)[a]	...
	720[b]	360
$Cu(p\text{-}CH_3OC_6H_4CO_2)_2 \cdot C_4H_9OH$	705 (267)[a]	...
	720[b]	370
$Cu(p\text{-}BrC_6H_4CO_2)_2 \cdot C_4H_9OH$	710 (271)[a]	...
	720[b]	350
$Cu(p\text{-}NO_2C_6H_4CO_2)_2 \cdot C_4H_9OH$	Insol	
	700[b]	360

[a] Approximately 5×10^{-4} M solution in 1-butanol. [b] Reflectance.

Discussion

Structure of the Compounds.—The similarity of the spectral and magnetic properties of this series of 1-butanol adducts of copper *para*-substituted benzoates with those of copper acetate monohydrate and other copper alkanoates suggests that the copper benzoates have dimeric structures. The reflectance spectra of all of the compounds exhibit a well-defined band at *ca.* 700 mμ and a shoulder at *ca.* 350–400 mμ, the latter being characteristic of binuclear copper carboxylates. When the spectra were run as butanol solutions, the 350-mμ band was not resolved but appeared as a slight shoulder on the side of a more intense band. The temperature dependence of the magnetic susceptibilities agrees with those predicted by the theoretical expression for an electronic system composed of singlet and triplet states. If the compounds were of a polymeric nature, then eq 1 would not apply, and it is unlikely that any agreement between the theoretical and experimental susceptibilities could be obtained.

The Magnetic Data.—The most striking feature of the magnetic data is the relative insensitivity of the Néel temperature toward the nature of the substituent on the phenyl ring. Although the range of $|2J|$ for the series of compounds is very small, there is, nevertheless, a discernible trend in singlet–triplet splitting energies which does not run parallel to the trend in the acid pK_a's nor does it correlate with any of the substituent constants which are commonly used. Attempts to rationalize the data in the absence of detailed structural information require extensive speculation and, therefore, will not be presented here.

The absolute values of $2J$ are of a similar order to those observed for other cupric carboxylates where the dimeric structure has been established by X-ray structural examination. In anhydrous copper acetate, copper acetate monohydrate, and the copper acetate–monopyridine adduct, the observed J values are 302,[5] 286,[5] and 325 cm^{-1},[11] respectively. The figures reported here are also very similar in magnitude to those obtained in systems where the dimeric structure has been inferred.[9]

Experimental Section

Preparation of the Compounds.—In a typical preparation a filtered solution of *p*-methoxybenzoic acid (1.01 g) in 1-butanol (50 ml) was added to a filtered solution of cupric acetate monohydrate (0.66 g) in 1-butanol (150 ml). These quantities gave a mole ratio of acid to cupric acetate of 2:1. The bluish green solution was stoppered and allowed to stand in the refrigerator; after several days, crystals of the butanol *adduct* separated. Immediately prior to use, the solutions were filtered and the complexes washed with 1-butanol followed by cautious drying in a stream of warm air.

Magnetic Susceptibility Determinations.—Magnetic susceptibilities were determined as a function of temperature by the Faraday method. The equipment consists of a Varian Associates electromagnet, Model V4004, equipped with constant-gradient pole pieces, a Cahn Gram electrobalance, Model G, a cryostat based on the design described by Richardson and Beauxis,[12] a Welch Model 1426 pump plate, and a 10.25-in. bell jar. The essential features of the equipment are illustrated in Figure 1.

Samples contained in cellulose capsules were suspended from the microbalance beam by Pyrex glass fibers. The bell jar was evacuated and refilled with helium. Since the 1-butanol adducts of the copper benzoates were unstable with respect to the loss of butanol, all determinations were made at atmospheric pressure. For the low-temperature determinations a period of 20–30 min was allowed for the sample to reach thermal equilibrium at the desired temperature.

The cryostat allowed the temperature of the sample to be maintained at ±1° for an indefinite period of time at any temperature in the range 77–350°K. It is illustrated in Figure 2.[13] The inner section of the evacuated and silvered Pyrex dewar flask contains a copper block around which asbestos-covered heater wire is noninductively wound. An aluminum tube is fastened to the copper block and extends into the tail of the flask around the sample compartment. The outer chamber holds the liquid nitrogen. The temperature of the copper block is maintained at a constant value by a control unit which supplies

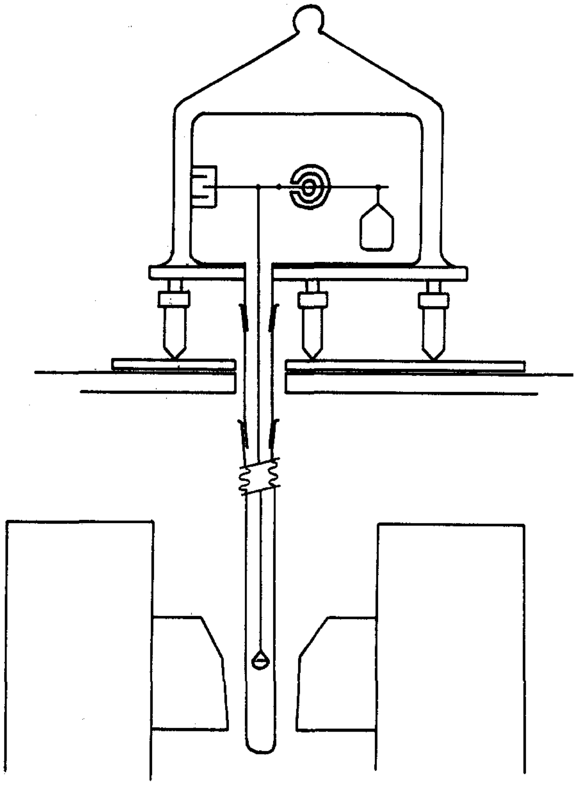

Figure 1.—Schematic diagram of the Faraday magnetic susceptibility equipment.

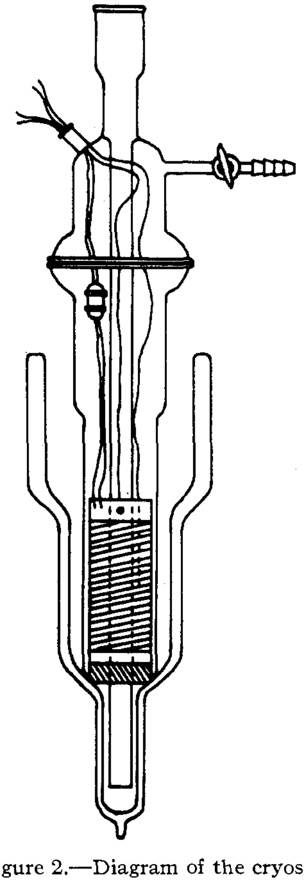

Figure 2.—Diagram of the cryostat.

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[13] The cryostat is commercially available from University Research Glassware, P. O. Box 51, Town Hall, Carrboro, N. C.

electrical energy when required to the resistance wire around the copper block. At equilibrium the temperature of the copper block and the temperature in the thermocouple well near the sample do not differ by more than the limits of error of the potentiometer used to measure the emf of the copper–constantan thermocouples placed at these two points.

Mercury tetrathiocyanatocobaltate(II) was used as magnetic susceptibility standard[14] and diamagnetic corrections were estimated from Pascal's constants.[15] A value of 60×10^{-6} cgs unit was assumed for the temperature-independent paramagnetism per copper ion.

Spectral Measurements.—The spectra of butanol solutions were obtained using a Cary Model 14 recording spectrophotometer. Reflectance spectra of solid samples were measured with a Beckman DU spectrophotometer equipped with the standard reflectance attachment and employing a block of magnesium carbonate as standard. In order to suppress the dissociation

$$[Cu(R\text{-}C_6H_4CO_2)_2\cdot C_4H_9OH]_2 \rightleftharpoons [Cu(R\text{-}C_6H_4CO_2)_2\cdot {}^1/_2C_4H_9OH]_2 + C_4H_9OH$$

the samples were filtered from the mother liquor and placed in a sample cell with traces of butanol adhering to the surface of the sample. The cell was then sealed and the reflectance spectrum measured.

Analyses.—Microanalyses for carbon and hydrogen were performed by Triangle Chemical Laboratories, Inc., Chapel Hill, N. C. Copper analyses were determined by EDTA titration following the method developed by Guerrin, *et al.*[16] The complexes were decomposed in nitric acid and the mixture neutralized with sodium hydroxide and, after the addition of sodium acetate buffer, titrated with standardized EDTA solution using Snazox as an indicator. The analytical data are presented in Table IV.

TABLE IV

ANALYTICAL DATA

Compound		Analyses % C	% H	% Cu
$Cu(C_6H_5CO_2)_2\cdot C_4H_9OH$	Found:	56.63	5.33	16.77
	Calcd:	56.89	5.27	16.73
$Cu(p\text{-}CH_3C_6H_4CO_2)_2\cdot C_4H_9OH$	Found:	58.09	6.09	15.33
	Calcd:	58.84	5.88	15.58
$Cu(p\text{-}CH_3OC_6H_4CO_2)_2\cdot C_4H_9OH$	Found:	54.31	5.82	14.48
	Calcd:	54.56	5.46	14.45
$Cu(p\text{-}BrC_6H_4CO_2)_2\cdot C_4H_9OH$	Found:	40.82	3.66	11.82
	Calcd:	40.18	3.35	11.82
$Cu(p\text{-}NO_2C_6H_4CO_2)_2\cdot C_4H_9OH$	Found:	46.22	4.35	13.39
	Calcd:	46.01	3.83	13.53

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The Oxidation Reactions of Peroxydiphosphate. I. The Kinetics and Mechanism of the Reaction with Tris(1,10-phenanthroline)iron(II)

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The rate of the reaction of lithium peroxydiphosphate with tris(1,10-phenanthroline)iron(II) perchlorate has been studied in neutral, aqueous solutions at 35° and ionic strength 1.00. The observed rate law can be represented by the equation

$$-\frac{d[Fe(phen)_3{}^{2+}]}{dt} = \frac{k_1k_2[Fe(phen)_3{}^{2+}][P_2O_8{}^{4-}]}{k_{-1}[phen] + k_2[P_2O_8{}^{4-}]}$$

which leads to the conclusion that the rate-determining step, when $P_2O_8{}^{4-}$ is in large excess, is the dissociation of the iron(II) complex ion. The reactions of $Fe(phen)_3{}^{2+}$ with Cu^{2+}, Ni^{2+}, EDTA, and $P_2O_7{}^{4-}$ were studied under similar conditions and were found to have similar rate-determining steps. The observed rate constant, k_{obsd}, for all these reactions approached 4×10^{-4} sec^{-1} at concentrations for which first-order behavior was found.

Introduction

A study of the reaction of peroxydiphosphate with tris(1,10-phenanthroline)iron(II) complex ion (hereafter $Fe(phen)_3{}^{2+}$) in aqueous, neutral solutions was undertaken to begin the investigation of the oxidation reactions of this peroxide. While reactions involving $Fe(phen)_3{}^{2+}$ as a reducing agent have been studied,[2-6] very little work has been done on the peroxydiphosphate ions as oxidizing agents.[7-9] The reaction with $Fe(phen)_3{}^{2+}$ should be of interest as a basis for the comparison of the peroxydiphosphate reaction with the peroxydisulfate reaction which was studied by Irvine.[10]

Experimental Section

Materials.—Potassium peroxydiphosphate was synthesized by anodic oxidation of alkaline phosphate solution and converted to the lithium salt for purification according to the method of Chulski.[7,8] Other peroxydiphosphate salts were obtained by

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