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Substituted Benzoic Acid Complexes of Copper(II)[1]

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Solutions of p-*cyano,* p-*fluoro,* p- *and* m-*hydroxy-benzoic acids in ehtanol react with aqueous solutions of copper-(II) acetate to yield complexes of empirical formula* $[Cu(X\text{-}C_6H_4CO_2)(OH)]$. *The use of similar reaction conditions for* p-*chloro-,* p-*bromo- and* p-*iodo-benzoic acids affords ethanol adducts of the corresponding copper benzoates,* $Cu(X\text{-}C_6H_4CO_2)_2 . C_2H_5OH$. *The latter compounds display subnormal magnetic moments and antiferromagnetism similar to that noted for copper acetate monohydrate. The presence of analogous binuclear structural species is proposed. On the basis of the normal moments and infrared spectral evidence, it is suggested that the complexes containing hydroxy groups are composed of polymeric hydroxide-bridged structural units. The magnetic behavior of these derivatives has been related to previously experienced difficulties in correlating the magnetic susceptibilities of copper(II) salts of substituted benzoic acids with the substituents on the phenyl ring.*

Introduction

Recently there has been considerable interest in the magnetic and spectral properties of copper(II) salts of substituted benzoic acids.[2] In the course of our investigation into the preparation of solvated adducts, of the general formula $Cu(p\text{-}XC_6H_4CO_2)_2 . L$ where L = molecule of solvent, the use of ethanol-water mixtures was considered and several interesting compounds were isolated. Since these apparently shed some light upon the complications inherent in systems of this sort they are reported here.

Experimental Section

Substituted Benzoic Acids. These were obtained from Eastman Organic Chemicals and were used without further purification.

Preparation of the Complexe. The complexes were prepared by the addition of a warm, solution of the acid in 50 ml. ethanol to a filtered solution of copper(II) acetate monohydrate (0.67 g.) in 150 ml. water. A molar ratio acid: copper acetate of 2:1 was employed. The products generally precipitated immediately and were filtered, washed with water and ethanol, and dried in the air.

With *m*-hydroxybenzoic acid no product was isolated under these conditions. The use of more concentrated solutions of the reactants, i.e. 15 ml. ethanol and 50 ml. water respectively, afforded the product after standing at 0°C for several days.

Analytical Data. Microanalyses for carbon, hydrogen, nitrogen, and halogen were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee. Copper analyses were determined by EDTA titration using Snazox as indicator.[3] The analytical data are presented in Table I.

Table I. Analytical Data

Complex		Analyses			
		% H	% C	% Halogen	% Cu
$[Cu(p\text{-}CNC_6H_4CO_2)(OH)]_n$	Found:	42.53	2.47	6.03 [a]	
	Calcd:	42.39	2.22	6.18 [a]	
$[Cu(p\text{-}FC_6H_4CO_2)(OH)]_n$	Found:	38.49	2.43		
	Calcd:	38.27	2.29		
$[Cu(p\text{-}HOC_6H_4CO_2)(OH)]_n$	Found:	38.46	2.90		
	Calcd:	38.62	2.77		
$[Cu(m\text{-}HOC_6H_4CO_2)(OH)]_n$	Found:	38.62	2.89		
	Calcd:	38.62	2.77		
$Cu(p\text{-}ClC_6H_4CO_2)_2 . C_2H_5OH$	Found:	45.49	3.58	17.05	15.18
	Calcd:	45.64	3.33	16.89	15.11
$Cu(p\text{-}BrC_6H_4CO_2)_2 . C_2H_5OH$	Found:	37.63	2.71	31.07	12.64
	Calcd:	37.63	2.75	31.36	12.48
$Cu(p\text{-}IC_6H_4CO_2)_2 . C_2H_5OH$	Found:	31.91	2.33	42.32	10.41
	Calcd:	31.83	2.38	42.08	10.53

[a] Per cent nitrogen.

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(1) Part VI of the series «Spin-Spin Coupling in Binuclear Complexes».
(2) W. E. Hatfield, C. S. Fountain and R. Whyman, *Inorg. Chem.*, 5, 1855 (1966), and references therein.
(3) G. Guerrin, M. V. Sheldon and C. N. Reilley, *Chemist-Analyst*, 49, 36 (1960).

Magnetic Measurements. Magnetic susceptibilities were determined as a function of temperature by the Faraday method, using equipment and procedures which have been described previously.[2] Mercury tetrathiocyanatocobaltate(II) was used as magnetic susceptibility standard[4] and diamagnetic corrections were estimated from Pascal's constants.[5] The molar magnetic susceptibilities were calculated on the basis of a molecular weight per copper(II) ion in all cases and magnetic moments were obtained using the expression $\mu_{eff} = 2.84\ (\chi_m^{corr}\ T)^{1/2}$.

Infrared Spectra. Infrared absorption spectra were measured as mineral oil mulls with a Perkin Elmer 237B grating spectrophotometer.

Results and Discussion

The addition of a solution of *p*-cyano-, *p*-fluoro, *p*- and *m*-hydroxy-benzoic acids in ethanol to aqueous solutions of copper acetate afforded complexes which analyzed as $[Cu(X\text{-}C_6H_4CO_2)(OH)]$. In contrast, the use of similar conditions with *p*-chloro-, *p*-bromo- and *p*-iodo-benzoic acids yielded the expected compounds $Cu(X\text{-}C_6H_4CO_2)_2 . C_2H_5OH$. The hydroxide-containing complexes are air- stable, whereas the ethanol adducts lose weight slowly, indicating gradual loss of the molecule of solvent.

Table II. Magnetic Susceptibility Data

Complex	T, °K	$10^6\chi_m^{corr}$, c.g.s. units	μ_{eff}, B.M.
$[Cu(p\text{-}CNC_6H_4CO_2)(OH)]_n$	299	1655	2.00
	196	2768	2.09
	77	9958	2.49
$[Cu(p\text{-}FC_6H_4CO_2)(OH)]_n$	299	1599	1.96
	196	2642	2.04
	77	9099	2.38
$[Cu(p\text{-}HOC_6H_4CO_2)(OH)]_n$	299	1492	1.90
	196	2392	1.94
	77	7071	2.09
$[Cu(m\text{-}HOC_6H_4CO_2)(OH)]_n$	299	1530	1.92
	196	2401	1.95
	77	6879	2.07
$Cu(p\text{-}ClC_6H_4CO_2)_2 . C_2H_5OH$	299	930	1.50
	196	817	1.14
	77	209	0.36
$Cu(p\text{-}BrC_6H_4CO_2)_2 . C_2H_5OH$	299	947	1.51
	196	800	1.12
	77	276	0.41
$Cu(p\text{-}IC_6H_4CO_2)_2 . C_2H_5OH$	299	911	1.48
	196	800	1.12
	77	422	0.51

Magnetic susceptibilities of the complexes described here were measured at 300, 196 and 77°K, and the observed data is summarized in Table II. In view of the limited data it is not possible to say if the susceptibility *vs.* temperature plot exactly parallels the antiferromagnetic curve observed with the l-butanol adducts. However, the similarities of the magnetic moments at the temperatures considered indicate that this is probably the case. Thus the values of 1.45, 1.10 and 0.29 B.M. at 298, 194 and 77°K respectively, observed for the l-butanol adduct of copper *p*-bromobenzoate,[2] are very similar to the moments of 1.51, 1.12 and 0.41 B.M. reported here for the corresponding ethanol adduct.

By analogy with the l-butanol series of derivatives, it appears that the *p*-chloro-, *p*-bromo- and *p*-iodo-benzoic acid salts are composed of binuclear structural units similar to that established for copper acetate monohydrate.[6]

The magnetic behavior of the compounds containing hydroxide groups is more difficult to interpret in terms of structural considerations. The four complexes display normal magnetic moments which increase slightly with decreasing temperature. The reciprocal of the corrected molar susceptibilities ($1/\chi_m^{corr}$) *vs.* temperature curves are all linear with Weiss constants ranging from 15 to 35°, thus implying that there is very little magnetic interaction between neighboring copper ions.

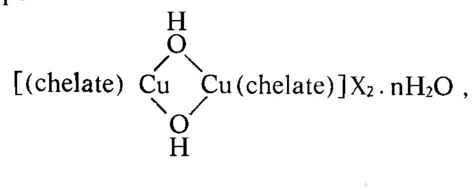
The empirical formula of $[Cu(XC_6H_4CO_2)(OH)]$ suggests the possibility of dimeric or polymeric species containing hydroxide bridging groups. Some support for this suggestion derives from the infrared spectra of the compounds in the 3700-3200 cm^{-1} region. The observed bands are recorded in Table III. For the four complexes formulated as containing hydroxide groups, maxima are observed in the 3600-3550 cm^{-1} range. These are absent in the spectra of the free ligands and in the ethanol adducts. For the latter, peaks occurring at 3400-3390 cm^{-1} are due to absorptions of the hydroxyl group of the ethanol molecule. The infrared spectrum of ethanol itself shows a strong band at *ca.* 3330 cm^{-1}.

Table III. Infrared Spectra in the 3700-3200 cm^{-1} Region

Complex	Maxima, cm^{-1}	
$[Cu(p\text{-}CNC_6H_4CO_2)(OH)]_n$	3560	
$[Cu(p\text{-}FC_6H_4CO_2)(OH)]_n$	3600, 3560	
$[Cu(p\text{-}HOC_6H_4CO_2)(OH)]_n$	3590	3400 (3350)
$[Cu(m\text{-}HOC_6H_4CO_2)(OH)]_n$	3595	3275 (3265)
$Cu(p\text{-}ClC_6H_4CO_2)_2 . C_2H_5OH$		3390
$Cu(p\text{-}BrC_6H_4CO_2)_2 . C_2H_5OH$		3400
$Cu(p\text{-}IC_6H_4CO_2)_2 . C_2H_5OH$		3390

Maxima shown in parentheses occur in the spectra of the free ligands.

Previous workers have assigned maxima in the 3500 cm^{-1} region as arising from the presence of hydroxide bridges between two copper atoms.[7,8] For example, Ferraro and Walker studied a series of compounds of the type



$$[(chelate)\ Cu(OH)_2Cu(chelate)]X_2 . nH_2O\ ,$$

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(4) B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 4190 (1958).

(5) J. Lewis and R. G. Wilkins, «Modern Coordination Chemistry», Interscience Publishers, Inc., New York, N.Y., p. 403 (1960).

(6) J. N. van Nierkerk and F. R. L. Schoening, *Acta Cryst.*, *6*, 227 (1953).

(7) W. R. McWhinnie, *J. Chem. Soc.*, 2959 (1964); *J. Inorg. Nucl. Chem.*, *27*, 1063 (1965).

(8) J. R. Ferraro and W. R. Walker, *Inorg. Chem.*, *4*, 1382 (1965).

where chelate = 2,2′-bipyridine or 1,10-phenanthroline and X = various anions.[8] Peaks occurring in the range 3601-3340 cm^{-1} were assigned to the vibrations of the bridging hydroxide groups. Thus the observations of bands in the region 3600-3560 cm^{-1} for the complexes described here is not inconsistent with the presence of hydroxide bridges in the molecules.

For *p*-cyanobenzoic acid the negligible shift of the $C{\equiv}N$ stretching frequency from 2235 cm^{-1} in the free ligand to 2240 cm^{-1} in the complex indicates that this group is not coordinated. Also, the maxima at 3350 and 3265 cm^{-1} in *p*- and *m*-hydroxybenzoic acids, respectively, which are presumably associated with the vibrations of the hydroxyl groups attached to the phenyl ring, occur with similar frequencies in the spectra of the complexes, implying that the OH groups are not dissociated.

Previously reported compounds which are thought to contain dimeric hydroxide-bridged structural units display subnormal magnetic moments and antiferromagnetic behavior. Thus the room temperature magnetic moments of $[(Et_2NCH_2CH_2NEt_2)Cu(OH)]_2(ClO_4)_2$ and $[(Et_2NCH_2CH_2NHMe)Cu(OH)]_2(ClO_4)_2$ are 1.38 and 1.69 B.M. respectively and these decrease rapidly with decreasing temperature.[9] 2-Aminopyridine[7] and biuret[10] complexes of similar stoichiometry display analogous behavior. Since polymeric copper carboxylates such as copper benzoate tri-hydrate, and certain forms of copper formate are magnetically normal, the formulation of these compounds as polymeric and hydroxide-bridged entities appears more favorable. The insolubility of $[Cu(benzoate)OH]_n$ in common organic solvents is consistent with the presence of polymeric structures since the dimeric compounds are usually soluble.

It is significant that a second preparation of the *p*-iodobenzoic acid complex, using similar experimental conditions, did not afford as satisfactory elemental analyses [C, 30.72; H, 2.28; Cu, 11.03%]. The magnetic moments of this sample were found to be markedly different from those exhibited by the first product and values of 1.70, 1.52 and 1.33 B.M. (based on the mono-ethanolate formulation) were obtained at the three temperatures investigated. Subsequent examination of the infrared spectrum of this compound indicated the presence of a weak peak at 3560 cm^{-1} in addition to the band at 3390 cm^{-1}. Presumably this reffects thc presence of some of the hydroxide containing compound, $[Cu(p\text{-}IC_6H_4CO_2)(OH)]_n$.

Possibly the presence of very small amounts of this material as impurity, in insufficient amounts to significantly affect the elemental analyses, could cause appreciable deviations from the predicted magnetic behavior in systems of this type. It is suggested that our initial investigations of the copper benzoate systems may have been complicated by such factors, also. These conclusions are in agreement with the suggestions of Lewis *et al.*[11]

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(9) W. E. Hatfield, T. S. Piper and U. Klakunde, *ibid.*, 2, 629 (1963).

(10) A. W. McLellan and G. A. Melson, *J. Chem. Soc., Sect. A*, 137 (1967); G. A. Melson, *ibid.*, 669 (1967).

(11) J. Lewis, Y. C. Lin, L. K. Royston and R. C. Thompson, *J. Chem. Soc.*, 6464 (1965).