Magnetic Studies of Copper(II) Complexes of Benzoic Acid and Substituted Benzoic Acids

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A study of the magnetic properties (80—310 K) of the complexes $[Cu_3(O_2CC_6H_4R)_6]\cdot3,6NH\text{-od}$ (R = H, *m*-Me, or *o*-NO_2; 3,6NH-od = 3,6-diazaoctane-1,8-diamine) indicates the presence of ferromagnetic interactions. In the cases of R = H and *m*-Me, feeble ferromagnetism appears in the range 80—150 K. The *o*-nitrobenzoato-complex shows only antiferromagnetic interactions leading to diamagnetism in the 80—150 K region. Comparison of the experimental and calculated susceptibilities with the Bleaney–Bowers model with $-2J = 289.2\ cm^{-1}$ for R = H, $311.4\ cm^{-1}$ for R = *m*-Me, and $265.6\ cm^{-1}$ for R = *o*-NO_2 (in each case $g = 2.19$ and $N = 60$ c.g.s. units), indicates that the complexes are polymeric with three binuclear units of benzoatocopper(II) joined by two 3,6NH-od molecules. A spectral band in the 333—425 nm region indicates the presence of metal–metal interactions. Lowering of a band at 1 695 cm^{-1} to 1 620—1 640 cm^{-1} is indicative of carboxylate bridging, and a band in the 800—820 cm^{-1} region is attributed to M–N co-ordination.

THE magnetic properties of copper alkyl and aryl carboxylates with and without different additional ligands have been studied previously.[1,2] Recently, the magnetic and spectroscopic behaviour of copper(II) complexes of 5-substituted 2-salicylidenebiguanides have been reported.[3] The present investigation deals with the preparation of copper(II) benzoate and substituted benzoates with 3,6-diazaoctane-1,8-diamine (3,6NH-od) as additional ligand, $[Cu_3(O_2CC_6H_4R)_6]\cdot3,6NH\text{-od}$ (R = H, *m*-Me, or *o*-NO_2), and with their magnetic and spectroscopic behaviour.

RESULTS

Plots of susceptibility against temperature for benzoato- and *m*-toluato-complexes in the range 70—310 K show that the susceptibility first remains almost constant over the range 275—310 K and then decreases with decreasing temperature having minima at 140—160 K. The susceptibility then increases with decreasing temperature to 80 K (Figures 1 and 2). In the case of the *o*-nitrobenzoato-complex, the susceptibility was almost constant in the 260—310 K region. It sharply decreased with further decrease in temperature to 150 K. Below this temperature the complex became diamagnetic and remained so to 80 K (Figure 3).*

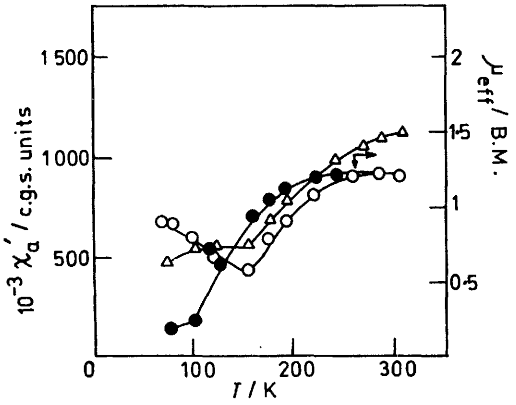

FIGURE 1 Variation of the atomic susceptibility [(○), experimental; (●), calculated] and the effective magnetic moment (△) with temperature for $[Cu_3(O_2CPh)_6]\cdot3,6NH\text{-od}$. 1 B.M. $\approx 9.27 \times 10^{-24}$ A m^2

The decrease in magnetic moments (Figures 1—3) with decreasing temperature over the range 150—310 K indicates antiferromagnetic interactions in the complexes. However, the trend of the magnetic susceptibility with temperature in the 80—150 K region indicates the presence of

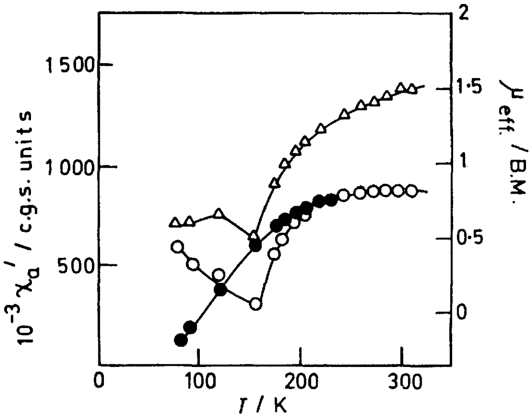

FIGURE 2 Variation of the atomic susceptibility [(○), experimental; (●), calculated] and the effective magnetic moment (△) with temperature for $[Cu_3(O_2CC_6H_4Me\text{-}m)_6]\cdot3,6NH\text{-od}$

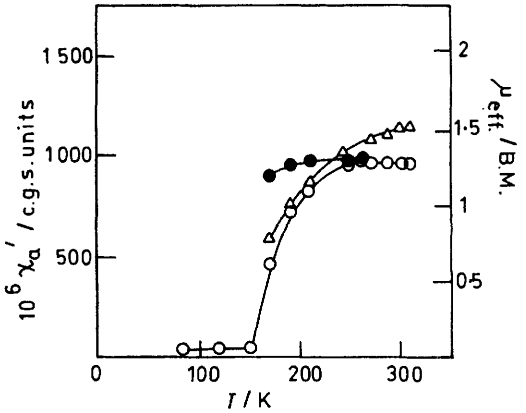

FIGURE 3 Variation of the atomic susceptibility [(○), experimental; (●), calculated] and the effective magnetic moment (△) with temperature for $[Cu_3(O_2CC_6H_4NO_2\text{-}o)_6]\cdot3,6NH\text{-od}$

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* Basic magnetic data are to be found in Supplementary Publication No. SUP 21899 (11 pp.). For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1976, Index issue.

[1] M. Kato, H. B. Jonassen, and J. C. Fanning, *Chem. Rev.*, 1964, **64**, 99.

[2] R. W. Jotham, S. F. A. Kettle, and J. A. Marks, *J.C.S. Dalton*, 1972, 428.

[3] J. Bera, P. Pramanik, and D. Sen, *J.C.S. Dalton*, 1975, 2436.

paramagnetic or ferromagnetic interactions in this system. That the discontinuities observed are not due to any instrumental error follows from the facts that: (*a*) separate samples were prepared from different starting materials for individual runs; (*b*) several compounds have been studied in the same temperature range with the same equipment and this discontinuity was not observed;[3] (*c*) even within the present series, the *o*-nitrobenzoato-complex does not show any ferromagnetic behaviour at this temperature.

Attempts were made to fit the experimental data in the 150—310 K region to the Bleaney–Bowers[4] equation (1).

$$\chi_A = \left[\frac{Ng^2\beta^2}{kT} \cdot \frac{1}{3 + \exp(-2J/kT)}\right] + N\alpha \qquad (1)$$

The experimental susceptibilities agreed very well with the calculated values only in the 200—310 K region; below 200 K the calculated values are increasingly higher than the experimental values with decreasing temperature (Figures 1—3). The use of other known models (*e.g.* Jotham–Kettle[2] and Ising[5]) did not produce a better result. Attempts to correlate the values of the experimental susceptibilities with the open-chain[6] and closed-chain models[7] for copper(II) ions were fruitless. The experimental values can thus be described by the Bleaney–Bowers model[4] only up to 200 K. The deviation of the results from this model in range 80—200 K cannot be ascribed to paramagnetic impurities as suggested by some workers for benzoatocopper(II) complexes, because the experimental values are lower than those predicted by the model.

TABLE 1

Electronic spectral data *

Complex	Band $d_{x^2-y^2}\rightarrow d_{xy}$	$d_{x^2-y^2}\rightarrow d_{z^2}$	$d_{x^2-y^2}\rightarrow d_{zx}, d_{yz}$	*B*	*K*	*E*
$[Cu_3(O_2CPh)_6]\cdot 3,6NH\text{-}od$	700 (14 290)	375 (26 670)	310 (32 250)	290 (34 480)	250 (40 000)	210 (47 620)
$[Cu_3(O_2CC_6H_4Me\text{-}m)_6]\cdot 3,6\text{-}NH\text{-}od$	725 (13 770)	375 (26 670)	310 (32 250)	290 (34 480)	240 (41 670)	210 (47 620)
$[Cu_3(O_2CC_6H_4NO_2\text{-}o)_6]\cdot 3,6NH\text{-}od$	685 (14 600)	390 (25 640)	310 (32 250)	300 (33 340)	240 (41 670)	210 (47 620)

* Given as wavelengths (in nm) with the corresponding wavenumbers (in cm^{-1}) in parentheses.

The electronic spectra of the complexes were recorded in the 200—1 200 nm region (Table 1). The infrared spectra of the complexes, as well as those of 3,6NH-od and *o*-nitrobenzoic acid, were determined in the 625—4 000 cm^{-1} region in order to obtain knowledge of the bonds involved (Table 2).

DISCUSSION

In all these complexes the decrease in magnetic moments indicates antiferromagnetic coupling between the copper(II) ions. The constancy of the singlet–triplet separation energy ($-2J$) from the Bleaney–Bowers model at 200—310 K indicates a good binuclear model. Thereafter the experimental values show variation. This can only be due to the development of new types of interactions with decreasing molecular dimensions at low temperature. Although the experimental susceptibilities of the complexes indicate binuclear spin–spin coupling, chemical analysis shows that three molecules of bis(benzoato)copper(II) are bound to one molecule of 3,6NH-od. Thus the structures of the complexes are suggested to comprise three binuclear copper units joined together by two molecules of 3,6NH-od. The co-ordination of 3,6NH-od and the bridging carboxylates are such that the structure as a whole is sufficiently flexible to undergo changes in the molecular dimensions, resulting in increasing spin–spin coupling in each binuclear unit and closer approach of the three units with decreasing temperature. A comparison of *X*-ray powder diffraction patterns at room and at liquid-nitrogen temperatures shows no change in the position of lines, indicating no structural transformation in this temperature range.

In all these complexes at higher temperatures, the spin–spin antiferromagnetic coupling is attributed mainly to superexchange through the carboxylate bridges with little or no overlap of the metal *d* orbitals in the binuclear units. As the temperature decreases, interdimer superexchange interactions may develop through normalised and orthogonal overlap of the metal *d* orbitals and the 2*s* and 2*p* orbitals of oxygen atoms of the carboxylate group, leading simultaneously to antiferromagnetic and weak ferromagnetic interactions. However, the ferromagnetism is not sufficient to nullify the antiferromagnetism within and between the binuclear units. As a result, the overall interaction prevailing in the complexes is antiferromagnetic. No ferromagnetic effect was observed for the *o*-nitrobenzoato-complex. This is probably due to the high steric hindrance of the nitro-group at the *ortho*-position, keeping one binuclear unit away from the other. Inter-

TABLE 2

Infrared spectral data (cm^{-1})

	CO_2^-	C_3N
$o\text{-}NO_2\cdot C_6H_4\cdot CO_2H$	1 695	830
3,6NH-od		
	CO_2 bridge	M–N
$[Cu_3(O_2CPh)_6]\cdot 3,6NH\text{-}od$	1 620	820
$[Cu_3(O_2CC_6H_4Me\text{-}m)_6]\cdot 3,6NH\text{-}od$	1 630	800
$[Cu_3(O_2CC_6H_4NO_2\text{-}o)_6]\cdot 3,6NH\text{-}od$	1 640	820

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unit interaction under these circumstances will not be perceptible.

For all the complexes, two bands in the visible region at 685—700 and 275 nm indicate the presence of direct copper–copper interaction.[1] The bands at 700 and 375 nm are assigned to the $d_{xy} \rightarrow d_{x^2-y^2}$ and $d_{xz},d_{yz} \rightarrow d_{x^2-y^2}$ transitions. The band at 310 nm is assigned to a charge-transfer band of the type $CO_2^- + Cu^{2+} \longrightarrow CO_2 + Cu^+$. In the hydrated copper(II) benzoate only one band was observed at 702 nm, whereas two bands, at 667—714 and 333—415 nm, were recorded for the pyridine adduct of the benzoato-complex. Since the hydrated complex is a normal paramagnetic compound, while its pyridine analogue is antiferromagnetic, it is argued that the band at 333—425 nm is indicative of metal–metal interaction in copper(II) carboxylates.

In the ultraviolet region three bands were observed and are probably due to the benzene ring. The presence of the benzene ring in the ligand give rises to E and B bands representing π–π^* transitions. Band E is assigned to the overlapping symmetry-allowed transition, whereas B represents the symmetry-forbidden transition. The presence of the carboxyl group in the ligand extends the conjugation, and this results in another π–π^* transition (termed K) at 250 nm.

In the i.r. spectra it is difficult to assign all the bands due to the complicated nature of the molecules. However, the shift of the asymmetric and symmetric bands of the carboxylate groups in the same direction to lower energy clearly indicates the presence of carboxylate bridging.[8] The asymmetric stretching for C_3N in pure 3,6NH-od at 830 cm^{-1} shifts to lower energy in the complexes. This shift is attributed to M–N bond formation.

EXPERIMENTAL

The complexes were prepared as described in the literature.[9]

	Analyses (%)			
	Found		Calc.	
Complex	Cu	N	Cu	N
$[Cu_3(O_2CPh)_6]\cdot$3,6NH-od	17.9	5.25	18.05	5.30
$[Cu_3(O_2CC_6H_4Me\text{-}m)_6]\cdot$3,6NH-od	16.05	4.85	16.7	4.90
$[Cu_3(O_2CC_6H_4NO_2\text{-}o)_6]\cdot$3,6NH-od	14.3	10.45	14.35	10.55

Spectra in the range 200—1 200 nm were recorded on a Cary 14 spectrophotometer and i.r. spectra (625—4 000 cm^{-1}) were obtained on a Perkin-Elmer 237B spectrophotometer from Nujol mulls. Magnetic measurements were made on a Gouy balance as described previously.[3] The measurements were repeated with samples prepared separately. Reproducible results (within 2%) were obtained.

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[5/590 *Received, 27th March,* 1975]

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