# Dimeric Copper(II) Carboxylate Complexes with Unusually Low Magnetic Moments

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*Summary* The $+I$ inductive effect of the metalloid can account for the unusually low magnetic moments of the copper(II) complexes of triphenylsilane- and triphenylgermane-carboxylic acid.

WE have observed that the magnetic properties of the copper(II) salts of triphenylsilane- and triphenylgermane-carboxylic acid are quite different from those of their carbon analogue. The magnetic data for the complexes, $Cu(O_2CMPh_3)_2,nH_2O$† are, for M = C: $n = 2$, $\chi_M + 543 \times 10^{-6}$, $\chi_A + 921 \times 10^{-6}$, $\mu$ 1·48 B.M.; M = Si: $n = 1$, $\chi_M - 93{\cdot}4 \times 10^{-6}$, $\chi_A + 300 \times 10^{-6}$, $\mu$ 0·84 B.M.; M = Ge: $n = 1$, $\chi_M - 151{\cdot}6 \times 10^{-6}$, $\chi_A + 254 \times 10^{-6}$, $\mu$ 0·78 B.M.‡

The complexes, $Cu(O_2CMPh_3)_2,H_2O$ (M = Si and Ge) although diamagnetic, exhibit small permanent magnetic moments which are much lower than any previously reported moments for dimeric copper(II) alkanoates, while the moment observed for the carbon analogue, $Cu(O_2CCPh_3)_2,2H_2O$, is consistent with previous studies. This observation is significant since the magnetic moments of *ca.* 100 copper(II) alkanoate complexes are reported to be in the range 1·30—2·05 B.M.;[2–5] those of a few formates are *ca.* 1·0 B.M.[6–8]

These copper(II) carboxylate complexes are assigned a dimeric structure of the copper(II) acetate monohydrate type[9] on the basis of structural studies of similar complexes,[3,7,8] the subnormal magnetic moments[2,5] and a preliminary $X$-ray diffraction study on $Cu(O_2CGePh_3)_2,H_2O$: triclinic: $a = 14{\cdot}717$, $b = 9{\cdot}447$, $c = 15{\cdot}392$ Å; $\alpha = 77° \ 28'$, $\beta = 66° \ 22'$, $\gamma = 89° \ 55'$; $U = 1869{\cdot}3$ Å$^3$; $D_m = 1{\cdot}50$ g cm$^{-3}$, $D_c = 1{\cdot}38$ g cm$^{-3}$; $Z = 2$ for $C_{38}H_{32}CuGe_2O_5$.

The electronic spectral data, solid state and ethereal solution, for the compounds, $Cu(O_2CMPh_3)_2,nH_2O$, along with the data for solid $Cu(O_2CMe)_2,H_2O$, are given in the Table. As previously reported,[3] a maximum of three absorption bands occur in the region 10,000—35,000 cm$^{-1}$ which are designated I, II, and III in the order of increasing energy. These data indicate that similar species are present in the ethereal solution and the solid state.

The lowest energy absorption, band I, assigned to the $d$–$d$ transitions of copper(II)[10–12] is shifted to higher energy in the silicon and germanium compounds by *ca.* 0·2 eV. This hypsochromic shift undoubtedly results from the greater ligand-field splitting of the $d$-orbitals of copper(II) due to the greater electropositive nature of the metalloids compared to carbon, the most important effect arising from the raising of the energy of the $d_{x^2-y^2}$ level. The effect on the energy levels of the other $d$-orbitals is probably relatively small owing to their position relative to the ligands.

The higher energy bands, II and III, which undergo a bathochromic shift, 0·5—0·6 eV, when silicon or germanium replaces carbon, are undoubtedly charge-transfer bands of the ligand-to-metal[10,12] or metal-to-ligand type. $\pi(\pi^* \rightarrow d)$ bonding in the ligand may be responsible for this observed shift to lower energy.[13]

† M = C: $n = 2$, m.p. > 150°; M = Si: $n = 1$, m.p. 99·5—101·5°; M = Ge: $n = 1$, m.p. 84·5—86°. All analyses (Cu, C, and H) are consistent with the empirical formulae.

‡ Magnetic susceptibilities (c.g.s. units) were determined by the Faraday method at four different field strengths, at 23 °C, using a platinum wire standard. Pascal's constants were used to correct for the diamagnetic component.[1,3]

TABLE. Electronic spectral data[a]

| Compound | Solid[b] | Ether solution[c] | |
|---|---|---|---|
| | $\nu_{max}$/cm$^{-1}$ | $\nu_{max}$/cm$^{-1}$ | $\epsilon$ |
| $Cu(O_2CCPh_3)_2,2H_2O$ .. | 14,400 | 14,400 | — |
| | 32,300 | 34,400 | — |
| $Cu(O_2CSiPh_3)_2,H_2O$ .. | 16,300 | 16,000 | 495 |
| | 24,500sh | 22,500sh | 321 |
| | 29,400 | 30,500 | 9,360 |
| $Cu(O_2CGePh_3)_2,H_2O$ .. | 15,600 | 15,700 | 612 |
| | 22,000sh | 21,600sh | 354 |
| | 28,800 | 29,000 | 11,260 |
| $Cu(O_2CMe)_2,H_2O$[d] .. | 14,300 | | |
| | 27,000sh | | |
| | 34,200 | | |

[a] Except for solvent shifts, similar spectra are obtained in benzene and ethyl bromide media; the complexes are decomposed in pyridine and dimethyl sulphoxide media; [b] Determined on a Beckman model DU spectrophotometer equipped with a reflectance attachment, MgO reference. [c] Cary model 14 spectrophotometer, 1·0 and 10·0 cm quartz cells. [d] Ref. 3 and refs. therein.

The magnetic and spectral data given indicate that direct metal–metal bonding is an important factor in explaining the exchange interaction which give rise to the antiferromagnetic behaviour of copper(II) carboxylate complexes.[5,11] Greater energy differences between the singlet and triplet states, $-J = ca.\ 600\ cm^{-1}$ (*cf.* ref. 5), for the silicon and germanium compounds are expected owing to the increased electron density on the two copper(II) ions resulting from the inductive effect, $+I$, of the metalloid. This effect would be largest for the $d_{x^2-y^2}$ orbitals which are directed toward the carboxylate ligands, and thus supports the $\delta$-bonding approach.[11]

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