Structure–Magnetism Correlation in Dimeric Copper(II) Carboxylates: Crystal and Molecular Structure of Tetra-μ-(propanoato-*O,O'*)-bis[aquacopper(II)]†

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The dimeric copper(II) carboxylates $[\{Cu(O_2CR)_2(H_2O)\}_2]$ and $[\{Cu(O_2CR)_2\}_2]$ (R = Et or Pr^n) have been prepared and characterized by means of spectroscopic, magnetic, and thermogravimetric analyses. For $[\{Cu(O_2CEt)_2(H_2O)\}_2]$ the crystal and molecular structure has also been determined. The crystals are monoclinic, space group $P2_1/c$, with $a = 15.102(7)$, $b = 17.186(5)$, $c = 15.190(4)$ Å, $\beta = 94.24(3)°$, and $Z = 4$. Full-matrix least-squares refinement, using 1 784 independent reflections converged to a conventional R factor of 0.0561. The unit cell contains four crystallographically independent copper(II) atoms which give rise to three binuclear molecules with copper(II) acetate monohydrate type geometry. Two of these dimers are centrosymmetric with the symmetry centre at the middle of the Cu–Cu bond. Comparison of the present structural data and $|2J|$ values with those of other structurally known dimeric copper(II) alkanoates does not allow an unambiguous determination of a specific ligand parameter to be the major factor in determining the magnitude of $|2J|$, and suggests that it may be the result of several modes of interaction.

A great deal of work on dimeric and polymeric copper(II) carboxylates has already been performed to ascertain the relationship between structural and magnetic parameters.[1] At the same time some theoretical and empirical treatments have been developed in the attempt (*a*) to determine the factors governing the magnitude of the exchange integral $|2J|$, and (*b*) to explain apparently anomalous magnetic data.[2,3] But since these treatments were often initially tested on a very restricted set of complete structural and magnetic data, it is thus hazardous to extend the conclusions of these authors to the wider number of new experimental magnetic data. In fact many difficulties are encountered when we compare dimers in which the bridging carboxylate ligands are not closely related, as well as when the $|2J|$ values are discussed on the basis of magnetic data alone.[4,5]

In this connection, among the hydrated copper(II) alkanoates, only the acetate has been repeatedly investigated by diffractometric,[6,7] spectroscopic,[4,8] and magnetic[9] techniques. On the contrary, for propanoate and butanoate only spectroscopic (e.s.r. and electronic)[10–12] and magnetic data[13] are available, although some doubts as to their validity arise since our thermogravimetric analysis (see later) shows that dehydration begins at a very low temperature, while the temperatures spanned in the magnetic measurements are out of the range for the unquestionable existence of hydrated complexes.

With the aim of filling this gap and supplying more reliable data, we have reinvestigated the magnetic, spectroscopic (e.s.r., electronic, and i.r.), and thermogravimetric properties of the hydrated and anhydrous copper(II) propanoate and butanoate, and rediscuss them in the light of the crystal and molecular structure of tetra-μ-(propanoato-*O,O'*)-bis[aquacopper(II)] here reported.

Experimental

Preparation of Complexes.—$[\{Cu(O_2CEt)_2(H_2O)\}_2]$ *and* $[\{Cu(O_2CPr^n)_2(H_2O)\}_2]$. Both complexes were prepared as reported in ref. 13. By evaporating very dilute solutions several days later, blue-green crystals separated (Found: C, 31.65; H, 5.30; H_2O, 7.95. $[\{Cu(O_2CEt)_2(H_2O)\}_2]$ requires C, 31.65; H, 5.20; H_2O, 7.90%. Found: C, 37.65; H, 6.15; H_2O, 7.00. $[\{Cu(O_2CPr^n)_2(H_2O)\}_2]$ requires C, 37.55; H, 6.30; H_2O, 7.05%).

$[\{Cu(O_2CEt)_2\}_2]$ *and* $[\{Cu(O_2CPr^n)_2\}_2]$. The anhydrous complexes were obtained by recrystallization of the hydrated salts from an ethanolic solution containing a few drops of the appropriate acid (Found: C, 34.15; H, 4.70. $[\{Cu(O_2CEt)_2\}_2]$ requires C, 34.35; H, 4.80%. Found: C, 40.40; H, 5.80. $[\{Cu(O_2CPr^n)_2\}_2]$ requires C, 40.40; H, 5.95%).

Physical Measurements.—Electronic spectra of the solid compounds were recorded as Nujol mull transmission spectra with a Shimadzu MPS 50L spectrophotometer. I.r. spectra were recorded with a Perkin-Elmer 180 spectrophotometer in KBr pellets and in Nujol mull on KBr discs in the range 4 000—250 cm^{-1}. The room- and low-temperature e.s.r. spectra were recorded with a Varian E-9 spectrometer with *X*-band frequency (9 GHz). Magnetic susceptibility measurements were obtained on a Newport Instruments Magnetic (Gouy) balance, employing a Newport Instruments cryostatic cooling system and $Hg[Co(SCN)_4]$ as calibrant. The molar susceptibilities were corrected for the diamagnetism of all atoms. The diamagnetic corrections were calculated from the appropriate Pascal constants with a value of -12×10^{-6} cm^3 mol^{-1} for copper. The magnetic moments were calculated from the expression $\mu = 2.828 (\chi_M \cdot T)^{\frac{1}{2}}$. Elemental analyses were carried out on the hydrated samples, after the magnetic measurements, as a test for water content. Thermogravimetric analyses were performed at a heating rate of 5 °C min^{-1} with a Mettler TA3000 instrument.

Crystal Structure Determination.—A sample of dimensions 0.23 × 0.33 × 0.52 mm was mounted in a random orientation

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† *Supplementary data available* (No. SUP 56509, 13 pp.): thermal parameters, H-atom co-ordinates, bond distances and angles involving ethyl groups, intermolecular contacts, selected least-squares planes, magnetic susceptibility data. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

Table 1. Fractional atomic co-ordinates (× 10^4)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Cu(1)	4 265(2)	4 784(1)	5 303(2)	C(2)	4 758(18)	7 090(12)	6 145(15)
Cu(2)	2 634(2)	3 739(1)	2 264(1)	C(3)	4 454(19)	7 674(18)	5 526(19)
Cu(3)	2 908(2)	3 018(1)	789(2)	C(4)	5 825(16)	4 432(13)	6 354(13)
Cu(4)	511(2)	4 399(2)	4 954(2)	C(5)	6 295(14)	4 036(14)	7 167(14)
O(1)	4 283(10)	5 821(9)	5 818(9)	C(6)	6 922(25)	3 461(21)	6 917(24)
O(2)	5 534(9)	6 207(7)	5 324(9)	C(7)	2 439(13)	4 560(10)	619(11)
O(3)	6 267(8)	4 776(7)	5 791(8)	C(8)	2 178(21)	5 304(15)	113(19)
O(4)	4 991(10)	4 388(8)	6 284(8)	C(9)	2 197(28)	6 014(25)	460(27)
O(5)	2 372(10)	4 609(7)	1 444(8)	C(10)	1 162(12)	3 058(11)	1 398(13)
O(6)	2 643(11)	3 990(8)	180(8)	C(11)	185(15)	2 899(15)	1 157(15)
O(7)	1 445(9)	3 418(8)	2 045(9)	C(12)	−289(26)	3 200(23)	1 857(27)
O(8)	1 633(9)	2 823(8)	763(9)	C(13)	3 061(12)	2 123(10)	2 350(11)
O(9)	2 918(9)	2 708(7)	2 812(8)	C(14)	3 266(15)	1 339(13)	2 858(15)
O(10)	3 092(9)	2 088(7)	1 537(7)	C(15)	2 368(16)	1 008(16)	2 923(17)
O(11)	3 877(9)	4 013(8)	2 340(8)	C(16)	4 294(13)	3 796(12)	1 705(13)
O(12)	4 099(9)	3 364(9)	1 092(9)	C(17)	5 283(17)	4 123(16)	1 729(18)
O(13)	−693(9)	5 172(8)	6 232(9)	C(18)	5 274(29)	4 697(26)	1 059(30)
O(14)	217(10)	4 177(8)	6 175(9)	C(19)	−310(12)	4 631(11)	6 572(12)
O(15)	−1 452(9)	4 932(8)	4 570(10)	C(20)	−527(19)	4 302(16)	7 485(15)
O(16)	−551(9)	3 906(8)	4 517(11)	C(21)	60(33)	4 536(29)	7 971(33)
O(w1)	3 069(8)	4 377(8)	5 778(8)	C(22)	−1 290(12)	4 233(12)	4 413(13)
O(w2)	2 367(8)	4 275(7)	3 498(7)	C(23)	−2 082(19)	3 722(18)	4 065(19)
O(w3)	3 106(9)	2 295(7)	−346(7)	C(24A)	−1 913(30)	2 999(29)	3 926(29)
O(w4)	1 307(9)	3 451(8)	4 712(15)	C(24B)	−2 202(33)	3 788(28)	3 182(33)
C(1)	4 869(16)	6 308(14)	5 748(15)				

on a Siemens AED single-crystal computer-controlled diffractometer using Mo-K_α radiation. Cell dimensions were refined by least squares using 2θ values of 15 accurately measured reflections (36 < 2θ < 48°).

Crystal data. $C_{24}H_{48}Cu_4O_{20}$, $M = 910.3$, monoclinic, $a = 15.102(7)$, $b = 17.186(5)$, $c = 15.190(4)$ Å, $\beta = 94.24(3)°$, $U = 3\,932(2)$ Å^3, $D_m = 1.55$ g cm^{-3}, $Z = 4$, $D_c = 1.539$ g cm^{-3}, $F(000) = 1\,872$, Mo-K_α radiation ($\bar{\lambda} = 0.710\,69$ Å), μ(Mo-K_α) = 22.1 cm^{-1}, space group $P2_1/c$ (from systematic absences).

Intensity data were collected by the ω–2θ scan method (lowest speed 2.5° min^{-1}); the individual reflection profiles were analysed as described by Lehmann and Larsen.[14] A total of 5 429 reflections were measured, 1 784 of which with $I > 3\sigma(I)$ were used in the structural analysis. During the data collection one reflection was measured every 50 reflections as a check of alignment and crystal and instrument stability: no significant changes in their intensities were observed. The structure amplitudes were obtained by the usual Lorentz and polarization reduction and put on an absolute scale by least-squares. An absorption correction was considered unnecessary as the μr values were very low and assuming the cylindrical shape for the crystal the absorption correction coefficients are practically unchanged in the 3—24° θ range.

Solution and refinement of the structure. The structure was solved by the heavy-atom technique: the copper atoms were localized by combining Patterson and direct methods, the successive Fourier syntheses gave all the non-hydrogen atoms. The refinements, carried out isotropically and anisotropically by several full-matrix least-squares cycles, afford the *R* index of 0.060. At this stage the hydrogen-atom co-ordinates, excepting those of the methyl groups and of water oxygens, which were not located, were introduced as fixed contributors in the last refinement: the final *R* indices were $R = 0.0561$ and $R' = 0.0595$. The effects of anomalous dispersion were included in all structure calculations: the function minimized was $\Sigma w|\Delta F^2|$ using the weighting scheme $w^{-1} = \sigma^2(F_o) + 0.0077\,F_o^2$. Atomic-scattering factors were taken from International Tables.[15] Final atomic co-ordinates are quoted in Table 1, some of these, involving terminal carbons show very high thermal motion and/or some disorder [C(24)]. All calculations were performed using a Cyber 76 computer of the Centro di Calcolo dell'Italia Nord-Orientale (Bologna), with the SHELX system of programs,[16] and the ORTEP plotting program,[17] with financial support from the University of Parma.

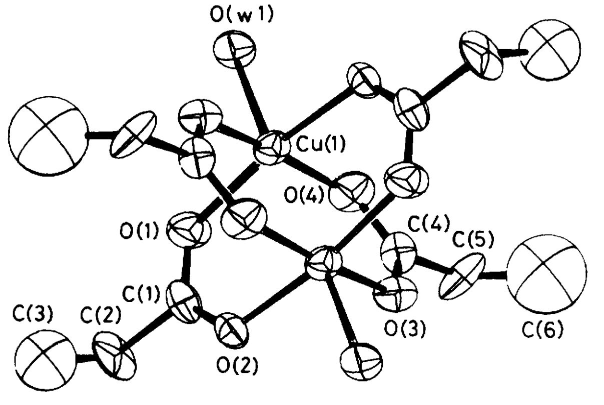

Figure. ORTEP drawing of $[\{Cu(O_2CEt)_2(H_2O)\}_2]$ [Cu(1) dimer] showing the atom numbering and thermal ellipsoids (40%). The hydrogen atoms are omitted for clarity

Analyses.—Carbon and hydrogen were analyzed with a C.Erba Elemental Analyser Instrument, model 1106, by G. Goldoni; the water content was determined gravimetrically by thermal analysis.

Results and Discussion

Bond distances and angles involving the copper atoms and carboxylate groups and water molecules are reported in Table 2, with atoms labelled as in the Figure.

The unit cell contains four crystallographically independent

Table 2. Bond distances (Å) and angles (°) with e.s.d.s in parentheses, involving the copper atoms and carboxylate groups and water molecules*

Cu(1)–O(1)	1.95(2)	Cu(1)–O(4)	1.91(1)	C(7)–O(5)	1.27(2)	C(13)–O(9)	1.25(2)
Cu(1)–O(2^{i})	1.99(1)	Cu(1)–O(w1)	2.11(1)	C(7)–O(6)	1.24(2)	C(13)–O(10)	1.24(2)
Cu(1)–O(3^{i})	1.94(1)	Cu(1)–Cu(1^{i})	2.575(4)	C(10)–O(7)	1.21(2)	C(16)–O(11)	1.25(2)
Mean Cu(1)–O(equatorial)	1.95(1)			C(10)–O(8)	1.30(2)	C(16)–O(12)	1.21(2)
C(1)–O(1)	1.23(3)	C(4)–O(3)	1.27(3)	Cu(4)–O(13^{ii})	1.98(1)	Cu(4)–O(16)	1.89(1)
C(1)–O(2)	1.24(3)	C(4)–O(4)	1.26(3)	Cu(4)–O(14)	1.98(1)	Cu(4)–O(w4)	2.07(1)
Cu(2)–O(5)	1.97(1)	Cu(3)–O(6)	1.94(1)	Cu(4)–O(15^{ii})	1.93(1)	Cu(4)–Cu(4^{ii})	2.589(5)
Cu(2)–O(7)	1.88(1)	Cu(3)–O(8)	1.95(1)	Mean Cu(4)–O(equatorial)	1.95(1)		
Cu(2)–O(9)	1.99(1)	Cu(3)–O(10)	1.97(1)	C(19)–O(13)	1.19(2)	C(22)–O(15)	1.25(2)
Cu(2)–O(11)	1.93(1)	Cu(3)–O(12)	1.92(1)	C(19)–O(14)	1.29(2)	C(22)–O(16)	1.25(2)
Cu(2)–O(w2)	2.15(1)	Cu(3)–O(w3)	2.16(1)				
Cu(2)–Cu(3)	2.620(3)						
Mean Cu(2)–O(equatorial)	1.94(1)						
Mean Cu(3)–O(equatorial)	1.95(1)						
O(1)–Cu(1)–O(2^{i})	168.6(6)	O(3^{i})–Cu(1)–O(w1)	96.4(6)	Cu(3)–Cu(2)–O(w2)	176.8(3)	Cu(2)–Cu(3)–O(6)	87.7(4)
O(1)–Cu(1)–O(3^{i})	88.9(6)	O(4)–Cu(1)–O(w1)	94.1(6)	Cu(3)–Cu(2)–O(5)	81.7(4)	Cu(2)–Cu(3)–O(8)	83.1(4)
O(1)–Cu(1)–O(4)	91.3(6)	Cu(1^{i})–Cu–O(w1)	177.3(4)	Cu(3)–Cu(2)–O(7)	85.4(4)	Cu(2)–Cu(3)–O(10)	85.1(3)
O(1)–Cu(1)–O(w1)	98.8(6)	Cu(1^{i})–Cu(1)–O(1)	83.8(5)	Cu(3)–Cu(2)–O(9)	83.9(4)	Cu(2)–Cu(3)–O(12)	81.5(4)
O(2^{i})–Cu(1)–O(3^{i})	89.5(5)	Cu(1^{i})–Cu(1)–O(2^{i})	84.8(4)	Cu(3)–Cu(2)–O(11)	87.3(4)	Cu(2)–Cu(3)–O(w3)	173.2(3)
O(2^{i})–Cu(1)–O(4)	88.2(6)	Cu(1^{i})–Cu(1)–O(3^{i})	84.0(4)	Cu(2)–O(5)–C(7)	123(1)	Cu(3)–O(6)–C(7)	119(2)
O(2^{i})–Cu(1)–O(w1)	92.6(6)	Cu(1^{i})–Cu(1)–O(4)	85.5(5)	Cu(2)–O(7)–C(10)	125(1)	Cu(3)–O(8)–C(10)	122(1)
O(3^{i})–Cu(1)–O(w4)	169.4(6)			Cu(2)–O(9)–C(13)	121(1)	Cu(3)–O(10)–C(13)	121(1)
Cu(1)–O(1)–C(1)	125(2)	Cu(1^{i})–O(3)–C(4)	124(1)	Cu(2)–O(11)–C(16)	115(1)	Cu(3)–O(12)–C(16)	123(1)
Cu(1^{i})–O(2)–C(1)	121(1)	Cu(1)–O(4)–C(4)	124(1)	O(5)–C(7)–O(6)	129(2)	O(9)–C(13)–O(10)	128(2)
O(1)–C(1)–O(2)	124(2)	O(3)–C(4)–O(4)	123(2)	O(7)–C(10)–O(8)	125(2)	O(11)–C(16)–O(12)	132(2)
O(5)–Cu(2)–O(7)	88.1(6)	O(6)–Cu(3)–O(8)	88.3(6)	O(13^{ii})–Cu(4)–O(14)	168.4(6)	O(15^{ii})–Cu(4)–O(w4)	95.6(6)
O(5)–Cu(2)–O(9)	165.5(6)	O(6)–Cu(3)–O(10)	172.4(6)	O(13^{ii})–Cu(4)–O(15^{ii})	88.4(6)	O(16)–Cu(4)–O(w4)	94.2(6)
O(5)–Cu(2)–O(11)	90.1(6)	O(6)–Cu(3)–O(12)	90.2(6)	O(13^{ii})–Cu(4)–O(16)	91.1(6)	Cu(4^{ii})–Cu(4)–O(13^{ii})	82.9(4)
O(5)–Cu(2)–O(w2)	100.6(6)	O(6)–Cu(3)–O(w3)	98.7(5)	O(13^{ii})–Cu(4)–O(w4)	90.6(6)	Cu(4^{ii})–Cu(4)–O(14)	85.8(4)
O(7)–Cu(2)–O(9)	89.2(6)	O(8)–Cu(3)–O(10)	88.2(6)	O(14)–Cu(4)–O(15^{ii})	88.5(6)	Cu(4^{ii})–Cu(4)–O(15^{ii})	86.0(4)
O(7)–Cu(2)–O(11)	172.6(6)	O(8)–Cu(3)–O(12)	164.7(6)	O(14)–Cu(4)–O(16)	90.0(6)	Cu(4^{ii})–Cu(4)–O(16)	83.3(4)
O(7)–Cu(2)–O(w2)	92.4(6)	O(8)–Cu(3)–O(w3)	94.6(5)	O(14)–Cu(4)–O(w4)	100.8(6)	Cu(4^{ii})–Cu(4)–O(w4)	172.9(5)
O(9)–Cu(2)–O(11)	90.8(6)	O(10)–Cu(3)–O(12)	91.3(6)	O(15^{ii})–Cu(4)–O(16)	169.2(6)	Cu(4^{ii})–O(15)–C(22)	120(1)
O(9)–Cu(2)–O(w2)	93.7(6)	O(10)–Cu(3)–O(w3)	88.4(5)	Cu(4^{ii})–O(13)–C(19)	126(1)	Cu(4)–O(16)–C(22)	125(1)
O(11)–Cu(2)–O(w2)	95.0(6)	O(12)–Cu(3)–O(w3)	100.8(6)	Cu(4)–O(14)–C(19)	121(1)	O(15)–C(22)–O(16)	126(2)
				O(13)–C(19)–O(14)	124(2)		

* i = 1 − x, 1 − y, 1 − z; ii = $\bar{x}$, 1 − y, 1 − z.

copper atoms which give rise to three binuclear molecules with copper(II) acetate monohydrate type geometry; two of these dimers are centrosymmetric [Cu(1) and Cu(4)], the symmetry centre being located at the middle of the Cu–Cu bond. In each dimer the two copper atoms are held together through four carboxylate bridges. The Figure shows the ORTEP drawing of the dimer referred to Cu(1) as an example of the metal-ion co-ordination. The Cu atoms are co-ordinated by four carboxylic oxygens, as equatorial ligands, and by a water molecule, occupying the apex of a distorted square pyramid. The Cu–O(carboxylic) bond distances in each of the three dimers are similar [1.91(1)—1.99(1) for Cu(1), 1.88(1)—1.99(1) for Cu(2), 1.92(1)—1.97(1) for Cu(3), and 1.89(1)—1.98(1) Å for Cu(4)] and comparable with literature values.[1a,d–g] All the apical bonds are longer than the basal ones, as is usually found, but in the centrosymmetric dimers they are significantly shorter than in the non-centrosymmetric dimer [2.11(1) Å and 2.07(1) Å for Cu(1) and Cu(4) in comparison to 2.15(1) and 2.16(1) Å for Cu(2) and Cu(3) respectively]; the same consideration can also be applied to the Cu–Cu intradimer distances [Cu(1)–Cu(1^{i}) = 2.575(4) Å (i = 1 − x, 1 − y, 1 − z), Cu(4)–Cu(4^{ii}) = 2.589(5) Å (ii = x, 1 − y, 1 − z), and Cu(2)–Cu(3) = 2.620(3) Å]. The '*cis*' O–Cu–O angles around the copper atoms show only slight displacements from the 90° ideal value [88.1(6)—91.3(6)°]. The distortion of the co-ordination polyhedra may be better evaluated from the '*trans*' O–Cu–O angles which range from 164.7(6) to 172.6(6)° and particularly from the planarity analyses for the basal CuO_4 groups (SUP 56509) which are tetrahedrally distorted for Cu(2) and Cu(3); all the copper atoms are displaced out of the mean planes towards the apical ligands [0.185(4) for Cu(1), 0.190(2) for Cu(2), 0.184(3) for Cu(3), and 0.188(4) Å for Cu(4)]. All angles involving the water molecules are greater than 90°, except O(10)–Cu(3)–O(w3) = 88.4(5)°, with the maximum value being 100.8(6)°. The structural parameters of the carboxylate groups are in the range expected, but the ethyl chains are affected by high thermal motion and disorder [C(24A) and C(24B)]; consequently their bond distances and angles are less reliable. In all the dimers the planes of the adjacent carboxylic groups are near mutually normal and perpendicular to their CuO_4 equatorial planes. The lengths of Cu–O–C–O–Cu bridges are 6.41 and 6.38 for Cu(1), 6.42, 6.34, 6.45, and 6.31 for Cu(2) and Cu(3), and 6.44 and 6.32 Å for Cu(4); some of these are shorter than those reported for analogous systems and denote distortions in the 'acetic cages'. The dimers are packed in the structure with short contacts, the shortest of these, involving water molecules and carboxylic oxygens, can be interpreted as hydrogen bonds [O(2)···O(w3^{i}) = 2.78(2), O(3)···O(w2^{i}) = 2.78(2), O(8)···O(w4^{ii}) = 2.73(2), O(9)···O(w3^{ii}) = 2.79(2), O(10)···O(3w^{ii}) = 2.77(2), O(13)···O(w2^{iii}) = 2.76(2), O(15)···O(wl^{iii}) = 2.73(2), and O(w4)···O(w3^{iv}) = 3.01(2)

Table 3. Magnetic parameters, room-temperature electronic and i.r. spectral data, low- and room-temperature e.s.r. parameters, and dehydration temperature ranges

	$[\{Cu(O_2CEt)_2(H_2O)\}_2]$	$[\{Cu(O_2CEt)_2\}_n]$	$[\{Cu(O_2CPr^n)_2(H_2O)\}_2]$	$[\{Cu(O_2CPr^n)_2\}_n]$
$g_{\parallel}$ (298 K)	2.389	—	2.354	—
$g_{\parallel}$ (123 K)	2.359	2.349	2.337	2.355
$g_{\perp}$ (298 K)	2.084	—	2.076	—
$g_{\perp}$ (123 K)	2.075	2.062	2.066	2.059
$<g>^a$ (298 K)	2.19		2.17	
$<g>^a$ (123 K)	2.17	2.16	2.16	2.16
D/cm^{-1} (298 K)	0.345	—	0.344	—
D/cm^{-1} (123 K)	0.338	0.335	0.338	0.342
E/cm^{-1} (123 K)		0.0101		0.0086
$\|2J\|^b$/cm^{-1}	311	304	324	330
d–d_1 band max./cm^{-1}	14 100	14 900	14 400	14 900
C.t. band^c/cm^{-1}	26 170	26 700	27 300	26 900
$\nu(OH)_{asym}$(water)/cm^{-1}	3 550m	—	3 530m	—
$\nu(OH)_{sym}$(water)/cm^{-1}	3 400ms	—	3 380ms	—
$\nu(OCO)_{asym}$/cm^{-1}	1 610vs	1 585vs	1 605vs	1 585vs
$\nu(OCO)_{sym}$/cm^{-1}	1 425vs	1 420vs	1 420vs	1 420vs
Temp. range for loss of water (K)	320—397	—	309—378	—

[a] $<g> = [(g_{\parallel}^2 + 2g_{\perp}^2)/3]^{\frac{1}{2}}$. [b] The g value used in the fitting process for the calculation of $|2J|$ is the mean value between the e.s.r. parameters calculated at 298 and 123 K for the hydrated complexes (2.18 for propanoate and 2.165 for butanoate).

Å; i = $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$; ii = $x, \frac{1}{2} - y, z - \frac{1}{2}$; iii = $\bar{x}, 1 - y, 1 - z$; iv = $x, \frac{1}{2} - y, \frac{1}{2} + z$].*

Thermogravimetric analysis shows that both the hydrates begin to lose the co-ordinated water molecule at a very low temperature (Table 3) despite a Cu–L(axial) bond length comparable to or slightly shorter than that of tetra-μ-(propanoato-*O*,*O*′)-bis[(3-methylpyridine)copper(II)][18] and copper(II) acetate monohydrate.[6,7]

The electronic data, in agreement with the CuO_5 chromophore in all the complexes, show differences between the hydrated and anhydrous complexes in accordance with the shorter Cu–O(axial) bond in the former than in the latter compounds. Furthermore the i.r. spectra of the anhydrous complexes reflect the different bonding mode of the carboxylate groups,[1f,19] with displacement of the $\nu(OCO)_{asym}$ stretching frequency to lower values due to the reduction in the C–O bond order.

Only the e.s.r. spectra of the anhydrous complexes present a marked temperature dependence, being roughly resolved only at 123 K. A very weak absorption at $g = 2.1$, due to the presence of a monomer, is detected for $[\{Cu(O_2CEt)_2(H_2O)\}_2]$. The g values and zero-field splitting parameters, D and E, are slightly different from the literature values[10–12] probably due to the presence of inequivalent dimer molecules in the unit cell.

The magnetic interaction between spins $\vec{S}_A$ and $\vec{S}_B$ for atoms A and B is usually written as $\mathscr{H} = -2J\vec{S}_A \cdot \vec{S}_N$, where the coupling constant is negative for antiferromagnetic interactions. The molar susceptibilities are well described by the Bleaney–Bowers equation for exchange-coupled dimers,[20] using in the fitting process as constants g values obtained from e.s.r. spectra and $N\alpha = 60 \times 10^{-6}$ cm^3 mol^{-1} (Table 3). The agreement between experimental and calculated molar susceptibilities, better for the present work than for those of ref. 13, makes the $|2J|$ values calculated more reliable, although no marked differences are observed with the $|2J|$ values of ref. 13.

The present structural and magnetic data confirm that the Cu–Cu distance, the bridging pathway (the Cu–O–C–O–Cu distance), and the Cu–$L_{ax.}$ bond length do not affect the magnitude of $|2J|$ which is mainly determined by the nature of the RCO_2H bridging ligand itself. A less important effect is also produced by the type of axial ligand L. The fundamental role of the RCO_2H ligand was formerly expressed by its pK_a value[4] and recently by the polarizability of the R group[1b,3a] or by its inductive effect. However, if we test the relationship between $|2J|$ and group polarizability[1b] for other structurally known copper(II) alkanoates,[1f,19] such as the propanoates and butanoates or halogenoacetates, the order of increasing group polarizability with decreasing $|2J|$ values is no longer obeyed (as was anticipated by Porter and Doedens[1b]). Indeed for copper(II) alkanoates, within the related series of R groups CH_3, Et, Pr^n (Table 4) the increase in group polarizability is accompanied by a slight increase in $|2J|$ rather than a decrease. Now the importance of this behaviour is emphasized by the knowledge of the crystal structure of hydrated copper(II) proponate (and in part by the corresponding butanoate) and the redetermination of their $|2J|$ values (not markedly different from literature values given by Martin and Waterman[13]), thus furnishing for alkanoates a set of well correlated structural and magnetic data which throw doubt on a prevailing dependence of $|2J|$ on group polarizability. Also, for structurally known halogenoacetates no satisfactorily agreement between group polarizability and $|2J|$ values is found (Table 4). On the other hand, no better agreement was observed when the $|2J|$ values are correlated with pK_a of the parent acids.

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* The structure of the analogous butanoate compound $[\{Cu(O_2CPr^n)_2(H_2O)\}_2]$ was determined in a similar way to the propanoate derivative [$C_{32}H_{64}Cu_4O_{20}$, M = 1 023.0, monoclinic, a = 26.924(8), b = 14.615(5), c = 25.151(8) Å, β = 110.22(5)°, U = 9 287(5) Å^3, D_c = 1.463 g cm^{-3}, D_m = 1.45 g cm^{-3}, Z = 8, Mo-K_α radiation, λ = 0.710 69 Å, $F(000)$ = 4 255, μ(Mo-K_α) = 17.98 cm^{-1}, space group $C2/c$ (from systematic absences and structure determination)]. A crystal of dimensions 0.58 × 0.58 × 0.68 mm was employed for collecting a total of 6 081 reflections of which 3 363 with $I > 2\sigma(I)$ were used in the subsequent analysis. A standard reflection measured every 50 observations showed a decay of 16.6% of the initial value: the data were scaled accordingly. The copper atoms were located by Patterson and direct methods, the subsequent Fourier syntheses gave the non-hydrogen atoms, but several of those belonging to the hydrocarbon chains were affected by disorder. Final refinement gave an R index of 0.1021. The structure is closely similar to that of the propanoate with Cu–O(carboxylic) = 1.939(5) (average), Cu–O(water) = 2.16(1) (average), and Cu–Cu = 2.608(3) Å.

Table 4. Magnetic parameters of selected $[\{Cu(O_2CR)_2L\}_2]$ dimers[a]

R	L[b]	χ^c	$\lvert 2J\rvert/cm^{-1}$	Ref.
CH_3	H_2O	2.19	284	9
Et	H_2O	3.96	311	This work
Pr^n	H_2O	5.73	324	This work
CF_3	quin	2.07	310	*d*
CH_2F	quin	2.15	364	*e,f*
CH_3	quin	2.19	320	*g*
CH_2Cl	quin	4.05	331	*f,g*
CCl_3	2Cl-py	7.77	217	3(*a*)

[a] quin = Quinoline, 2Cl-py = 2-chloropyridine. [b] The choice of different axial ligands L does not significantly alter the trend of $\lvert 2J\rvert$. [c] The reported group polarizabilities are evaluated from the data reported in ref. 1*b* and P. Chiorboli, 'Fondamenti di Chemica,' Unione Tipografico Editrice Torinese, Torino, Italy, 1975, pp. 503—504. [d] J. A. Moreland and R. J. Doedens, *J. Am. Chem. Soc.*, 1975, **97**, 508. [e] A. Yu. Simonov, A. A. Dvorkii, V. Yu. Yablokov, L. N. Milkova, and A. V. Ablov, *Zh. Strukt. Khim.*, 1978, **19**, 175. [f] A. Yu. Yablokov, L. N. Mosina, A. Yu. Simonov, L. N. Milkova, A. V. Ablov, and V. I. Ivanov, *Zh. Strukt. Khim.*, 1978, **19**, 42. [g] A. Yu Simonov, V. I. Ivanov, A. V. Ablov, L. N. Milkova, and T. I. Malonovskii, *Zh. Strukt. Khim.*, 1976, **17**, 516 and refs. therein.

As a result it does not seem easy to find a specific ligand parameter on which the magnitude of $\lvert 2J\rvert$ alone depends, since it is likely that several modes of interaction contribute significantly to the coupling in these dimers.[2a]

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