DALTON
FULL PAPER

Synthesis, crystal structure and properties of $[Cu_2(O_2CC_6H_4Me\text{-}p)_3(Me_2NCH_2CH_2NMe_2)_2]PF_6$: an unprecedented $[Cu_2(\mu\text{-}O_2CR)_4]$ into $[Cu_2(\mu\text{-}O_2CR)_3]^+$ core conversion†

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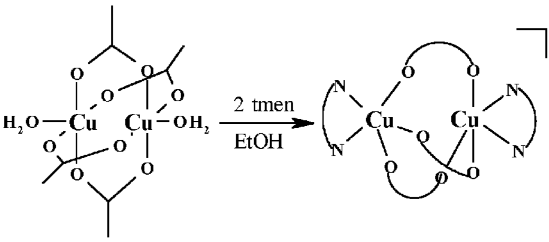
Tris(μ-*p*-methylbenzoato-*O,O′*)bis(*N,N,N′,N′*-tetramethyl-1,2-diaminoethane)dicopper(II) hexafluorophosphate, $[Cu_2(O_2CC_6H_4Me\text{-}p)_3(tmen)_2]PF_6$ **1**, was prepared from a reaction of $[Cu_2(O_2CC_6H_4Me\text{-}p)_4(H_2O)_2]$ with tmen in ethanol at 0 °C and characterized by spectral, electrochemical, magnetic and X-ray crystallographic studies. The cationic complex consists of a dicopper(II) unit having three bridging carboxylates and two bidentate chelating tmen ligands. The co-ordination geometry of the copper centres is distorted square pyramidal (CuO_3N_2). The Cu · · · Cu distance in the core is unusually long, 3.419(2) Å. The Cu–O–C angles at two copper centres are drastically different. Magnetic studies in the temperature range 20–296 K show the presence of an antiferromagnetically coupled dicopper(II) unit giving $-2J = 81.4$ cm^{-1} and $g = 2.081$. Cyclic voltammetric studies have shown a cathodic peak at −0.92 V with an anodic response at 0.10 V *vs.* SCE at 100 mV s^{-1}. The visible electronic spectrum of the complex shows a d–d band at 665 nm ($\varepsilon = 263$ M^{-1} cm^{-1}) in MeCN. The magnetostructural data among the *syn, syn*-carboxylato bridged dicopper(II) systems with a $[Cu_2(\mu\text{-}O_2CR)_m]^{n+}$ (m = 4–1; n = 0–3) core show that while **1** structurally has a tricarboxylato bridged dicopper(II) unit, magnetically it behaves like a dibridged one.

Dinuclear copper(II) carboxylates having a $[Cu_2(\mu\text{-}O_2CR)_m]^{n+}$ (m = 1–4, n = 3–0) core with a pair of copper atoms held by carboxylato-*O,O′* bridges are of interest toward understanding intramolecular magnetic exchange phenomena and for deriving magneto-structural correlations.[1–15] The diaxially bound tetra-μ-carboxylatodicopper(II) complexes with a cage structure exhibit antiferromagnetic interactions between two copper centres giving a singlet ground state. The singlet–triplet separation ($-2J$) ranges between 224 and 555 cm^{-1} depending upon various factors, *viz.* the type of the axial ligands, the R substituent of the carboxylate ligand and the bridging angle at the metal centre.

The $[Cu_2(\mu\text{-}O_2CR)_4L_2]$ complexes (L = unidentate axial ligand) are susceptible to core conversion on reaction with chelating bidentate ligands and the products are often dinuclear copper(II) complexes with a reduced number of carboxylate bridging ligands.[11–19] Earlier work has shown that in the presence of bidentate chelating amines or heterocyclic bases the cage structure converts into $[Cu_2(\mu\text{-}OH/\eta^1\text{-}O_2CR)(\mu\text{-}O_2CR)_x]^{y+}$ ($x = 1, y = 2$; $x = 2, y = 1$) and/or $[Cu_2(\mu\text{-}O_2CR)_2]^{2+}$ cores. While the nature and magnitude of the spin exchange in the asymmetrically di- or tri-bridged dicopper(II) cores depend primarily on the monoatomic Cu–O–Cu bridge angle (φ),[15–18] the spin–spin coupling in the relatively less explored $[Cu_2(\mu\text{-}O_2CR)_2]^{2+}$ core having *syn,syn*-bridging carboxylates is antiferromagnetic in nature and the $-2J$ values range between 86 and 125 cm^{-1}, again depending on the R substituents of the carboxylate and the type of axial ligands.

In this paper we report a tricarboxylato bridged dicopper(II) complex which is obtained from an unprecedented conversion of the tetra(μ-carboxylato)dicopper(II) core, eqn. (1). The tribridged unit is believed to be an intermediate in the hydroxo-carboxylato bridged dicopper(II) core formation from the precursor complex. Herein, we present the synthesis, crystal structure and properties of $[Cu_2(\mu\text{-}O_2CC_6H_4Me\text{-}p)_3(tmen)_2]PF_6$ **1**, where tmen is *N,N,N′,N′*-tetramethyl-1,2-diaminoethane.



(1)

Experimental

All reagents and chemicals were purchased from commercial sources and used without further purification except acetonitrile which was purified by standard procedures before use in electrochemical measurements.

Physical measurements

The elemental analysis was done using a Perkin-Elmer instrument. The electronic spectra were recorded on a Hitachi U-3400 spectrometer. Variable-temperature magnetic susceptibility data in the temperature range 20–296 K were obtained for polycrystalline samples of complex **1** using a George Associates Inc. Lewis-coil-force magnetometer system equipped with a closed-cycle cryostat (Air Products) working in the temperature range 300 to 20 K and a Cahn balance; $Hg[Co(NCS)_4]$ was used as a calibrant. Experimental susceptibilty data were corrected for diamagnetic contributions ($\chi_{dia} = -510.62 \times 10^{-6}$ cm^3 mol^{-1}) and temperature independent paramagnetism ($N_\alpha = 60 \times 10^{-6}$ cm^3 mol^{-1} per copper). The molar magnetic susceptibilities were fitted by the modified Bleaney–Bowers

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† *Supplementary data available*: magnetic susceptibilities at various temperatures. For direct electronic access see http://www.rsc.org/suppdata/dt/1999/1623/, otherwise available from BLDSC (No. SUP 57520, 7 pp.) or the RSC Library. See Instructions for Authors, 1999, Issue 1 (http://www.rsc.org/dalton).

expression,[5] by means of a least-squares computer program. The equation used for theoretical fitting was: $\chi_{Cu} = [Ng^2\beta^2/kT][3 + \exp(-2J/kT)]^{-1}(1 - \rho) + (Ng_1{}^2\beta^2/4kT)\rho + N_\alpha$, where ρ is the fraction of monomeric impurity. The magnetic moments at various temperatures were calculated in μ_B units [$\mu_B \approx 9.274 \times 10^{-24}$ J T^{-1}]. The infrared spectrum of the complex was recorded on a Bio-Rad FTS.7 spectrometer. Cyclic voltammetric measurements were made at 25 °C on a EG&G PAR 253 Versastat Potentiostat/Galvanostat using a three electrode set-up, a glassy carbon working, platinum wire auxiliary and a saturated calomel reference (SCE) electrode. The electrochemical data were uncorrected for junction potentials. Measurements were made in MeCN containing 0.1 M tetrabutylammonium perchlorate as supporting electrolyte. Ferrocene was used as a standard to verify the potentials against the SCE. The $E_{1/2}$ of ferrocene was 0.41 V *vs.* SCE.

Preparation of [Cu$_2$(O$_2$CC$_6$H$_4$Me-*p*)$_3$(tmen)$_2$]PF$_6$ 1

A suspension of [$Cu_2(O_2CC_6H_4Me$-*p*$)_4(H_2O)_2$] (0.45 g, 0.5 mmol) in ethanol (20 cm^3) was treated with tmen (0.116 g, 1.0 mmol) at 0 °C under stirring for 30 min. The resulting solution was filtered and the filtrate treated with an aqueous solution (10 cm^3) of NH_4PF_6 (0.326 g, 2 mmol). The light greenish blue crystalline blocks of the complex were obtained in ≈70% yield on slow evaporation of the solution at ambient temperature. The crystalline product was separated, washed with cold water–ethanol (1 : 1 v/v) and dried *in vacuo* over P_4O_{10} (Found: C, 47.8; H, 5.7; N, 6.3. $C_{36}H_{53}Cu_2F_6N_4O_6P$ requires C, 47.5; H, 5.8; N, 6.2%).

Crystal structure determination

Crystal data. $C_{36}H_{53}Cu_2F_6N_4O_6P$ **1**, $M = 909.9$, monoclinic, space group $P2_1/n$ (no. 1014), $a = 10.269(2)$, $b = 17.713(3)$, $c = 23.903(4)$ Å, $\beta = 91.85(2)°$, $U = 4346(1)$ Å^3, $F(000) = 1888$, $Z = 4$, $D_c = 1.39$ g cm^{-3}, Cu-Kα radiation, $\lambda = 1.5418$ Å, μ(Cu-Kα) = 21.72 cm^{-1}, $T = 293$ K, transmission coefficients 0.36–1.00.

Data collection and processing. A greenish blue rectangular crystal of approximate dimensions 0.55 × 0.18 × 0.18 mm was mounted on a glass fibre with epoxy cement. All geometric and intensity data were collected using an automated Enraf-Nonius CAD4 diffractometer equipped with Cu-Kα radiation. Intensity data, collected using the ω-scan technique for 9273 reflections in the range $3 \leqslant \theta \leqslant 75°$, were corrected for Lorentz-polarization effects and for absorption.[20] Of 8233 unique data, 3035 with $I > 3\sigma(I)$ were used for structure determination.

Structure solution and refinement. The structure was solved by the combination of Patterson and Fourier techniques and refined by full-matrix least squares. Both diamine ligands in the cationic complex showed positional disorders at the carbon centres of the NCH_2CH_2N moiety. The site occupancies of the disordered atoms were refined and three carbon atoms were refined as six centres each with a site occupancy factor of 0.5 and the fourth carbon was refined as two centres with site occupancy factors of 0.7 and 0.3. All non-hydrogen atoms except these positionally disordered ones were refined anisotropically. The positionally disordered carbon atoms and methyl carbons of the tmen ligands also showed higher thermal motions. The disorder which could be a possible reason for the higher residual values had no significant effect on the structural parameters at the co-ordination spheres of the copper atoms as the nitrogens were refined well without showing any disorder. Hydrogen atoms were generated and assigned isotropic thermal parameters, riding on their parent atoms and used for structure factor (F^2) calculation only. The final full-matrix least-squares refinement converged to $R1 = 0.0670$ and $wR2 = 0.1798$ using 503 parameters. All calculations were done using PC versions of SHELXS 86 and SHELXL 93 programs.[21] Atomic scattering factors were taken from ref. 22. The perspective view of the molecule was obtained using ORTEP.[23]

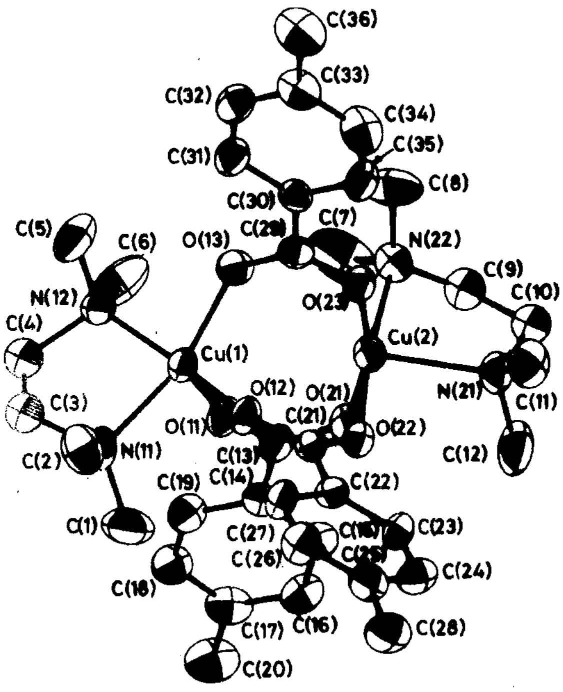


Fig. 1 An ORTEP view of the cation in [Cu$_2$(O$_2$CC$_6$H$_4$Me-*p*)$_3$(tmen)$_2$]PF$_6$ **1** showing the atom labeling scheme and thermal ellipsoids at a 30% probability level. The disorders in the tmen ligands are not shown for clarity.

CCDC reference number 186/1390.

See http://www.rsc.org/suppdata/dt/1999/1623/ for crystallographic files in .cif format.

Results

Synthesis

Dicopper(II) tetracarboxylates form diaxial adducts with unidentate ligands.[1–3] The reactions of $Cu_2(O_2CR)_4(H_2O)_2$ with unidentate ligands proceed through ligand substitution at the axial sites without affecting the cage structure. However, in presence of chelating bidentate ligands, the core undergoes substitution of carboxylates at the equatorial sites in addition to the axial ligands. This results in the conversion of the cage structure into a new core with reduced number of carboxylate ligands. Although there are few reports[11,15] of the formation of a [$Cu_2(\mu$-$O_2CR)_2]^{2+}$ core from [$Cu_2(\mu$-$O_2CR)_4$], core conversion leading to the isolation of complexes with a [$Cu_2(\mu$-$O_2CR)_3]^+$ core is presently unknown. Earlier studies from our laboratory have shown[17] that [$Cu_2(\mu$-$O_2CR)_4(H_2O)_2$] on reaction with tmen in an alcoholic medium forms ferromagnetic [$Cu_2(\mu$-OH)(μ-$O_2CR)_2]^+$ (R = Ph) and antiferromagnetic [$Cu_2(\mu$-OH)(μ-$O_2CR)]^{2+}$ (R = Me or C_6H_4X-*p*: X = Me or OMe) cores under refluxing or ambient temperature reaction conditions. It has now been observed that a reaction of [$Cu_2(\mu$-$O_2CC_6H_4$-Me-*p*$)_4(H_2O)_2$] with tmen in ethanol at 0 °C followed by addition of NH_4PF_6 leads to the formation of a tricarboxylato bridged dicopper(II) species, [$Cu_2(\mu$-$O_2CC_6H_4Me$-*p*$)_3$(tmen)$_2$]PF$_6$ **1**. The reaction proceeds through the substitution of two axial waters and one bridging carboxylate in the precursor complex to form **1** in high yield. Complex **1** is reactive and readily converts into a [$Cu_2(\mu$-OH)(μ-$O_2CR)]^{2+}$ core in MeOH–water medium under refluxing conditions.

Crystal structure

A perspective view of the cationic complex is shown in Fig. 1. Selected bond distances and angles are given in Table 1. The

Table 1 Selected bond lengths (Å) and bond angles (°) for $[Cu_2(O_2CC_6H_4Me\text{-}p)_3(tmen)_2]PF_6$ **1**

Cu(1) ··· Cu(2)	3.419(2)	Cu(2)–O(22)	1.973(7)
Cu(1)–N(11)	2.056(10)	Cu(2)–O(23)	1.948(7)
Cu(1)–N(12)	2.056(9)	O(11)–C(13)	1.253(13)
Cu(1)–O(11)	2.190(7)	O(12)–C(21)	1.266(12)
Cu(1)–O(12)	1.951(7)	O(13)–C(29)	1.25(1)
Cu(1)–O(13)	1.948(7)	O(21)–C(13)	1.275(13)
Cu(2)–N(21)	2.262(10)	O(22)–C(21)	1.253(13)
Cu(2)–N(22)	2.089(9)	O(23)–C(29)	1.279(13)
Cu(2)–O(21)	1.945(7)		
N(11)–Cu(1)–N(12)	85.5(4)	N(21)–Cu(2)–O(23)	100.5(3)
N(11)–Cu(1)–O(11)	94.9(4)	N(22)–Cu(2)–O(21)	92.4(3)
N(11)–Cu(1)–O(12)	88.0(3)	N(22)–Cu(2)–O(22)	173.9(3)
N(11)–Cu(1)–O(13)	155.9(3)	N(22)–Cu(2)–O(23)	92.1(3)
N(12)–Cu(1)–O(11)	91.8(4)	O(21)–Cu(2)–O(22)	90.0(3)
N(12)–Cu(1)–O(12)	165.6(3)	O(21)–Cu(2)–O(23)	87.2(3)
N(12)–Cu(1)–O(13)	90.1(3)	O(22)–Cu(2)–O(23)	162.8(3)
O(11)–Cu(1)–O(12)	101.6(3)	Cu(1)–O(11)–C(13)	150.0(7)
O(11)–Cu(1)–O(13)	109.3(3)	Cu(1)–O(12)–C(21)	134.6(6)
O(12)–Cu(1)–O(13)	90.6(3)	Cu(1)–O(13)–C(29)	131.4(7)
N(21)–Cu(2)–N(22)	85.2(4)	Cu(2)–O(21)–C(13)	117.9(7)
N(21)–Cu(2)–O(21)	96.4(3)	Cu(2)–O(22)–C(21)	127.6(7)
N(21)–Cu(2)–O(22)	89.0(3)	Cu(2)–O(23)–C(29)	121.1(6)

structure of **1** consists of a dinuclear $[Cu_2(\mu\text{-}O_2CC_6H_4Me\text{-}p)_3(tmen)_2]^+$ cation and a PF_6^- anion. The copper atoms are held by three bridging carboxylate ligands with the tmen ligands showing the bidentate chelating mode of bonding. The removal of one carboxylate from the cage structure of dicopper(II) tetracarboxylate has resulted in the considerable lengthening of the Cu ··· Cu distance from 2.65 Å in the precursor to 3.419 Å in **1**.

The co-ordination geometry of the copper centres is essentially square pyramidal showing $Cu(1)N_2O_2 \cdots O$ and $Cu(2)NO_3 \cdots N$ chromophores. Severe steric constraint in the carboxylate binding gives distinctly different co-ordination environments for the copper atoms. The deviations of Cu(1) from the N(11), N(12), O(12), O(13) plane and Cu(2) from the O(21), O(22), O(23), N(22) plane are −0.333 and 0.090 Å. The dihedral angle between the planes Cu(1), O(12), O(13), N(11), N(12) and Cu(2), O(21), O(22), O(23), N(22) is 61.7(3)°. The basal planes of the copper atoms show average Cu–N and Cu–O distances of 2.06 and 1.95 Å, respectively. The axial Cu(1)–O(11) and Cu(2)–N(21) distances are 2.190(7) and 2.262(10) Å, respectively. The angle between the bridging carboxylates shows significant variation. Ideally if one carboxylate is removed from the cage structure of the tetracarboxylatodicopper(II) unit the O–Cu–O bond angles should be 90, 90 and 180°. However, the O–Cu(1)–O angles range between 90.6 to 109.3°. The core structure in **1** thus shows considerable rearrangement. The O–Cu(2)–O angles of 90, 163 and 87° in **1** are as expected for the three oxygens lying essentially on a square plane. The angles with the axial atom O(11) at Cu(1), *viz.* O(11)–Cu(1)–O(12), O(13), N(11), N(12) are 101.6, 109.3, 94.9 and 91.8°, respectively. The angles with the axial amine nitrogen N(21) at Cu(2) centre, *i.e.* N(21)–Cu(2)–N(22), O(21), O(22), O(23) range between 85.2 and 100.5°. The structural data indicate the lability of the axially bound carboxylate in the tribridged structure of **1**. The facile conversion of the $[Cu_2(\mu\text{-}O_2CR)_4]$ unit into a $[Cu_2(\mu\text{-}OH/\eta^1\text{-}O_2CR)(\mu\text{-}O_2CR)_m]^{n+}$ ($m = 1, n = 2$; $m = 2, n = 1$) core is likely to involve **1** as a reactive intermediate by cleavage of the weak Cu(1)–O(11) axial bond in **1**.

Spectral and electrochemical properties

Complex **1** exhibits a visible band at 665 nm ($\varepsilon = 263\ M^{-1}\ cm^{-1}$) in MeCN. The broad spectral features are typical for square-pyramidal structures of copper(II) centres with a CuN_2O_3 chromophore.[15] The IR spectrum shows carboxylate bands at 1613, 1561 cm^{-1} for ν_{asym}(OCO) and 1458, 1392 cm^{-1} for ν_{sym}(OCO). A band at 835 cm^{-1} is assignable to PF_6^-. Cyclic voltammetry of **1** in MeCN–0.1 M NBu_4ClO_4 at a glassy carbon working electrode shows a cathodic peak at −0.92 V with a large anodic response at 0.10 V *vs.* SCE at 100 mV s^{-1}. The cathodic peak is broad at scan rates between 100 and 400 mV s^{-1}. The anodic peak is well defined and gives a $i_{pa} : i_{pc}$ ratio between 1.5 and 2.0 : 1 suggesting the formation of an electrochemically active copper species adsorbed on the electrode. The electrochemical behaviour of **1** indicates that the reduced copper(I) species is susceptible to disproportionation thus giving a higher anodic current. With a ΔE_p value of *ca.* 1.0 V, the electron transfer is sluggish and is quasireversible.

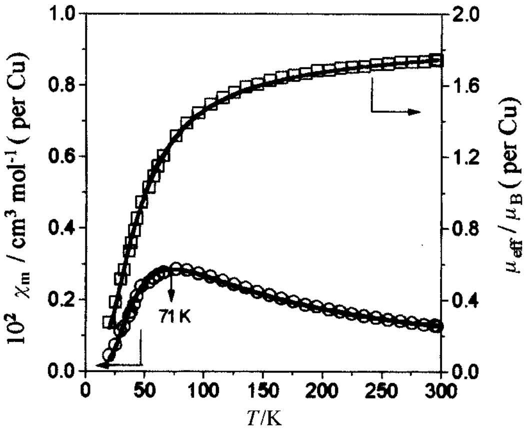


Fig. 2 Plots of molar magnetic susceptibilty and effective magnetic moment (per copper) *vs.* temperature for a polycrystalline sample of $[Cu_2(O_2CC_6H_4Me\text{-}p)_3(tmen)_2]PF_6$ **1**. The solid line shows a theoretical fit to the experimental data.

Magnetic behaviour

Magnetic susceptibility in the temperature range 20–296 K for complex **1** were obtained using a George Associates Inc. Lewis-coil-force magnetometer equipped with a close-cycle cryostat (Air Products) and a Cahn balance (supplementary data is available, SUP 57520); $Hg[Co(NCS)_4]$ was used as a calibrant. The molar susceptibility value increases with lowering of temperature to a maximum at 71 K and then decreases steadily indicating the antiferromagnetic nature of the complex. The effective magnetic moment (μ_{eff}) per copper(II) decreases from 1.74 at 296 K to 0.27μ_B at 20 K. A theoretical fit of the experimental data by the modified Bleaney–Bowers susceptibility expression gave the fitting parameters $2J = -81.4\ cm^{-1}$, $g = 2.081$, $g_1 = 2.055$ and $p = 0.4\%$ (Fig. 2). The low magnitude of J indicates a weak antiferromagnetic interaction in the $[Cu_2(\mu\text{-}O_2CR)_3]^+$ core.

Discussion

A comparison of the magneto-structural data on representative *syn, syn*-carboxylato bridged dicopper(II) complexes with a $[Cu_2(\mu\text{-}O_2CR)_m]^{n+}$ core ($m = 4$–1; $n = 0$–3) has been made in Table 2. The dicopper(II) cores with reduced number of carboxylate ligands are generally obtained from the tetra(μ-carboxylato)dicopper(II) cage structure. The copper(II) centres with a d^9–d^9 configuration generate a singlet and a triplet state. The extent of the exchange interaction is obtained using the isotropic form of the Heisenberg–Dirac–van Vleck (HDvV) model giving $H = -2JS_1S_2$, where $S_1 = S_2 = 1/2$ in a dicopper(II) system. The energy separation between these two states ($-2J$) with the singlet being the ground state for copper(II) carboxylates primarily depends on the following factors: (i) the electron donating nature of the R substituent of the carboxylate bridging ligands, (ii) the σ-donor ability of the axial ligand, (iii) the planarity of the basal planes at the copper

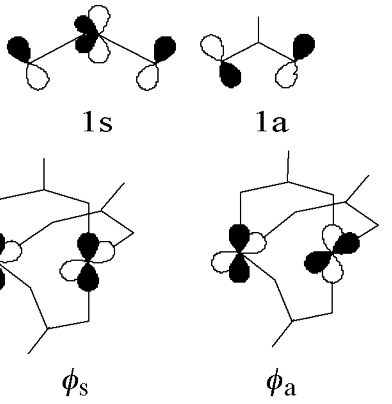
Table 2 Structural and magnetic parameters of selected dicopper(II) complexes with a $[Cu_2(\mu\text{-}O_2CR)_m]^{n+}$ core (m = 1–4, n = 3–0)

Complex	Cu···Cu/Å	$-2J$/cm^{-1}	Ref.
$m = 4$			
$[Cu_2(O_2CMe)_4(H_2O)_2]$	2.616(1)	284	15(*a*)
$[Cu_2(O_2CMe)_4(py)_2]$	2.630(3)	333	15(*b*)
$[Cu_2(O_2CPh)_4(quin)_2]$	2.671(2)	267	15(*c*)
$[Cu_2(O_2CPh)_4(py)_2]$	2.681(1)	328	15(*d*)
$[Cu_2(O_2CCCl_3)_4(PhCN)_2]$	2.732(1)	224	15(*e*)
$m = 3$			
$[Cu_2(O_2CC_6H_4Me\text{-}p)_3(tmen)_2]PF_6$	3.419(2)	81.4	This work
$m = 2$			
$[Cu_2(O_2CMe)_2(phen)_2(H_2O)_2][NO_3]_2\cdot 4H_2O$	3.063(3)	86	11
$[Cu_2(O_2CH)_2(phen)_2(H_2O)_2][NO_3]_2\cdot 4H_2O$	3.103(2)	125	11
$[Cu_2(O_2CEt)_2(salN\text{-}p\text{-}tolyl)_2]$	3.122(1)	101	15(*h*)
$m = 1$			
$[Cu_2(O_2CPh)Cl_2L_2]ClO_4$	3.565(2)	2.4	15(*i*)

L = 1,4,7-Trimethyl-1,4,7-triazacyclononane, quin = quinoline, salN-p-tolyl = *N*-*p*-tolylsalicylidene amine.

centres and (iv) the dihedral angle between the two metal containing planes. The Cu···Cu distance in the tetracarboxylato bridged core ranges between 2.58 and 2.73 Å. On removal of one carboxylato bridge, the Cu···Cu separation increases to 3.419 Å in **1**. A lengthening of *ca.* 0.8 Å of the Cu···Cu separation results in distortion in the $[Cu_2(\mu\text{-}O_2CR)_3]^+$ core structure making one carboxylate ligand bonded at the axial–equatorial positions. Such a ligation has major effect on the magnetic exchange interaction between two copper centres. The Cu···Cu separation in $[Cu_2(\mu\text{-}O_2CR)_2]^{2+}$ cores is *ca.* 3.0 Å. The shorter Cu···Cu distances in the dibridged cases compared to that in **1** may be due to the stacking interaction between two chelating equatorial ligands like 2,2′-bipyridine and 1,10-phenanthroline in the dibridged structure.[11,12]

As the superexchange interaction is operative through the carboxylate bridge, the magnitude of antiferromagnetic interaction ($-2J$) is expected to be dependent on the number of bridging carboxylate ligands.[24] Complex **1** with $m = 3$ is expected to have a $-2J$ value between those having m = 4 and 2 (Table 2). Instead, the $-2J$ value of 81.4 cm^{-1} in **1** is close to the range observed for the dibridged core. Such an observation can be explained by the fact that although **1** has a $[Cu_2(\mu\text{-}O_2CR)_3]^+$ core, the carboxylate ligand involved in the axial/equatorial ligation makes the superexchange interaction through this bridge weak in comparison to the superexchange pathways involving two other carboxylate ligands having oxygens lying on the basal planes of the copper centres. A notable observation is the significant variation of the Cu–O–C angles (a) of **1**. These angles are of importance as the superexchange between two copper(II) centres giving symmetric (φ_s) and antisymmetric (φ_a) combinations of the $d_{x^2-y^2}$ orbitals can occur through the carboxylato bridges *via* the symmetry adapted **1s** and **1a** combinations of the lone pair orbitals of the carboxylate group. The Cu(2)–O–C angles in **1** range between 117.9(7) and 127.6(7)°. Similar angles at the Cu(1) centre show major variations. The Cu(1)–O(11)–C(13) angle is 150.0(7)°; Cu(1)–O(12)–C(21) and Cu(1)–O(13)–C(29) are 134.6(6) and 131.4(7)°, respectively. The axial ligation of O(11) to Cu(1) makes this angle much higher than the corresponding Cu(2)–O(21)–C(13) angle [117.9(7)°]. It is expected that the overlap between the $d_{x^2-y^2}$ orbital of copper(II) and the p orbital of the bridging carboxylato oxygen will primarily involve two equatorial carboxylate ligands. As shown in the magneto-structural data in Table 2, the magnitude of coupling between two $d_{x^2-y^2}$ magnetic orbitals reduces with a reduction of the number of bridging carboxylato ligands.



The energy difference $\varepsilon_s - \varepsilon_a$, arising from φ_s and φ_a *via* the **1s** and **1a** combinations, is likely to be maximal in tetracarboxylato cage structures.[25] The extent of superexchange antiferromagnetic (AF) coupling may be directly related to the extent of $\varepsilon_s - \varepsilon_a$ splitting. Consequently, the AF interactions are likely to be reduced on gradual removal of the *syn,syn*-bridging carboxylates from the equatorial positions. An axial/equatorial combination of bridging carboxylates in complex **1** suggests the non-involvement of one carboxylate ligand in the spin coupling between the two copper centers. The structural results show that while atom O(11) is ligated along the d_{z^2} orbital of Cu(1), the corresponding O(21) atom is involved in binding with the $d_{x^2-y^2}$ orbital of the Cu(2) atom. As the d_{z^2} and $d_{x^2-y^2}$ orbitals are orthogonal to each other, the effect of axial/equatorial bridging of one carboxylate ligand in **1** has no significant impact on the energy difference between the ε_s and ε_a levels. In addition, the large displacement of Cu(1) from the basal plane by 0.333 Å and a dihedral angle of 62° between the two copper containing square planes are likely to reduce the magnitude of AF coupling between the two copper centres.

In summary, complex **1** with a $[Cu_2(\mu\text{-}O_2CR)_3]^+$ core is obtained from an unprecedented core conversion of the tetracarboxylatodicopper(II) cage structure. The μ-tricarboxylatodicopper(II) unit represents a new structural motif in copper(II) carboxylate chemistry. The magnetic properties of **1**, however, resemble those of μ-dicarboxylatodicopper(II) cores.

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