Structural diversity and properties of a series of dinuclear and mononuclear copper(II) and copper(I) carboxylato complexes

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The syntheses, crystal structures, magnetic and photoluminescence properties of a series of dinuclear and mononuclear copper(II) and copper(I) *N*-carbazolylacetate [*N*-carbazolylacetic acid = Hcabo] with different carboxylato coordination modes are reported. Although the carboxylato group has different coordination modes, the same carboxylate ligand binding to copper ion *via* four coordinating modes is rare. The crystal structure of complex $[Cu_2(Cabo)_4(dmf)_2]\cdot 2dmf$ (**1**) consists of a symmetrical dimeric Cu(II) carboxylato paddle-wheel core and oxygen atoms from dmf at the apical positions. The dinuclear complex $[Cu_2(Cabo)_3(phen)_2]ClO_4\cdot H_2O\cdot C_2H_5OH$ (**2**) (phen = 1,10-phenanthroline) consists of an unusual dimeric core with two copper atoms bridged by three carboxylates one of which is in the $\eta:\eta:\mu_2$ bridging mode and the other two are in the rarer monoatomic bridging mode. To our knowledge, the present bridging mode has not been reported hitherto. Magnetic susceptibilities were measured in the temperature range 2–300 K. It is found that paddle-wheel copper(II) ions in **1** are strongly coupled antiferromagnetically with $2J = -356.4(6)\ \mathrm{cm^{-1}}$, whereas complex **2** shows weak antiferromagnetic interaction with a $2J$ value of $-12.8(4)\ \mathrm{cm^{-1}}$. Copper(I) *N*-carbazolylacetate with strong fluorescence in the solid state as well as high thermal stability was obtained by reduction of the copper(II) *N*-carbazolylacetate using PPh_3 (triphenylphosphine) in dmf solution.

Introduction

The coordination chemistry of copper complexes with various carboxylates has been investigated for a long time. Dinuclear copper(II) carboxylates 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.[1–16] In general, dinuclear copper(II) carboxylates exhibit a paddle-wheel cage structure, but due to the various coordination modes of the carboxylato ligand, additional interesting structures have been confirmed by X-ray crystallography. The isolation of mononuclear and other dinuclear carboxylates has also confirmed the existence of monodentate and didentate coordinating modes and the coordination modes are dramatically sensitive to ligand steric effects, solvent effects, the medium, participation of counter ions and other factors. Therefore, much work is required to extend the knowledge of the relevant structural types and establish proper synthetic strategies leading to the desired architectures.

It's well known that the carbazole molecule has relatively efficient charge transfer properties. Recently, carbazole-containing compounds have been extensively studied for applications in electroluminescent (EL) devices[17,18] due to their good hole transporting and luminescent properties. However, most of the materials are organic compounds or polymers with low melting points or decomposition temperatures that inhibit the applications of these materials. As far as we know, no carbazole containing metal–organic compound has been crystallographically documented hitherto. We have initiated studies on *N*-carbazolylacetic acid with Cu(II) and d^{10} ions in an attempt to examine their modes of binding and possible properties. In the present paper, we report on the syntheses, crystal structures and properties of a series of complexes with different carboxylato coordination modes.

Experimental

Materials

The chemicals for the syntheses of the compounds were used as purchased (reagent grade) without further purification.

Physical measurements

Elemental analyses were performed with a Perkin-Elmer 240 instrument. I.R. spectrum was recorded with a Nicolet FT-IR 170SX instrument (KBr discs) in the 4000–400 $\mathrm{cm^{-1}}$

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region. UV-vis spectra were recorded with a UV-265 spectrophotometer and corrected by subtracting solvent backgrounds. TGA analyses were recorded with a Perkin-Elmer Pris-1 DMDA-V1 analyzer in a atmosphere of nitrogen at a heating rate of 5 °C min^{-1}. The photoluminescence measurements were carried out on powder samples. The spectrum of Cu(I) *N*-carbazolylacetate was collected with a Perkin-Elmer LS50B spectrofluorimeter using a 357 nm excitation source. Electrospray mass spectra (ES-MS) were determined with a Finnigan LCQ mass spectrograph; the concentration of the samples was about 1.0 mmol L^{-1}. The diluted solution was electrosprayed at a flow rate of 5×10^{-6} L min^{-1} with a needle voltage of 4.5 kV. The mobile phase was an aqueous solution of methanol (1:1, v/v). The samples were run in the positive-ion mode.

Room-temperature magnetic susceptibilities were measured by the Faraday method using a Cahn 7600 Faraday magnetic balance. Variable temperature magnetic data (2–300 K) were obtained using a Quantum Design MPMS5S SQUID magnetometer using a field strength of 0.1 T. Background corrections for the sample holder assembly and diamagnetic components of the complexes were applied. Calibrations were carried out with a standard palladium cylinder, and temperature errors were determined with [tmen][CuCl$_4$] (tmen = $(CH_3)_2HNCH_2CH_2NH(CH_3)_2{}^{2+}$).

Preparations

Ligand. The *N*-carbazolylacetic acid had been synthesized by several methods before,[19,20] but we used a new method to give the product in a high yield. Carbazole (16.7 g, 0.1 mol) and NaOH (12 g, 0.3 mol) were dissolved in dimethyl sulfoxide (40 mL) and heated to 85 °C to yield a dark-brown solution. After 30 min of stirring, $BrCH_2COOH$ (16.68 g, 0.12 mol) was added in portions during a 30 min time span. The resulting solution was stirred overnight, and then poured into 400 mL cold water. After filtration under vacuum, the pH of the filtrate was adjusted to 3–4, during which time a large quantity of a white product was precipitated. The mixture was filtered under vacuum and the product was washed exhaustively with water and dried in air. Yield: 92%. Anal. Calc. (found) for $C_{14}H_{11}O_2N$: C, 74.65 (74.38); H, 4.92 (4.93); N, 6.22 (6.20%). ES-MS, *m*/*z* 224.3.

[Cu$_2$(Cabo)$_4$(dmf)$_2$]·2dmf (1). HCabo (0.45 g, 2 mmol) and NaOH (0.08 g, 2 mmol) were reacted in water (20 mL) for 30 min at room temperature, and the resulting solution was filtered to remove undissolved HCabo. Copper nitrate (0.24 g, 1 mmol) in water (20 mL) was added with vigorous stirring, the resulting purple precipitation was filtered under vacuum, washed exhaustively with water and dried in air. 0.05 g of the crude product (chemical formula is Cu(Cabo)$_2$·H$_2$O according to elemental analysis) was dissolved in dmf (10 mL) to yield a green solution that was filtered into a large test tube. Ethyl acetate (10 mL) was added slowly to form a separated layer above the dmf solution. After two days, well developed air-stable green crystals suitable for X-ray analysis formed on the sides and bottom of the tube. Anal. Calc. (found) for $Cu_2C_{62}H_{58}O_{10}N_6 \cdot 2C_3H_7NO$: C, 61.85 (62.12); H, 5.50 (5.68); N, 8.49 (8.52%). IR (KBr, pellet) ν_{max}/cm^{-1}: ν_{as}(COO) 1667.4, 1634.4vs; ν_s(COO) 1401.8vs. UV-vis (dmf solution): λ/nm (log ε): 265 (4.44), 292 (4.61), 326.8 (3.94), 340 (3.96).

[Cu$_2$(Cabo)$_3$(phen)$_2$](ClO$_4$)·H$_2$O·C$_2$H$_5$OH (2). **1** (0.11 g, 0.2 mmol) was suspended in ethanol (20 mL) and phen (0.04 g, 0.2 mmol) was added. The mixture was then heated to 80 °C. After stirring for 30 min, NaClO$_4$(0.038 g, 0.2 mmol) in water (10 mL) was added. The resultant mixture was refluxed for 30 min, and then filtered. Dark-green crystals suitable for X-ray analysis were formed from the filtrate after three days standing at room temperature. Anal. Calc. (found) for $C_{66}H_{46}ClCu_2N_7O_{10}H_2OC_2H_5OH$: C, 61.70(61.72); H, 4.11 (4.27); N, 7.41 (7.11%). IR (KBr, pellet) ν_{max}/cm^{-1}: ν_{as}(COO) 1643.9, 1600vs; ν_s(COO) 1401.8vs, 1380vs. UV-vis (dmf solution): λ/nm (log ε): 266 (4.89), 292 (4.79), 310.6 (4.03), 326 (4.03) and 339 (4.00)

Cu(Cabo)$_2$phen (3). **1** (0.11 g, 0.2 mmol) was dissolved in dmf (20 mL) at 90 °C and phen (0.04 g, 0.2 mmol) was added and stirred for 5 min. After cooling of the solution to room temperature, well developed black crystals formed. Anal. Calc. (found) for $CuC_{40}H_{28}O_4N_4$: C, 69.40 (69.02); H, 4.08 (4.35); N, 8.09 (8.10%). IR (KBr, pellet) ν_{max}/cm^{-1}: ν_{as}(COO) 1651vs, 1646.3vs; ν_s(COO) 1425.6vs. UV-vis (dmf solution). λ/nm (log ε): 265.2 (4.77), 282.0 (4.57), 292.4 (4.65), 326.4 (3.92), 340 (3.90)

Cu(Cabo)(PPh$_3$)$_2$ (4). To a solution of **1** (0.11 g, 0.2 mmol) in dmf (10 mL) was added PPh$_3$ (0.16 g, 0.6 mmol). After reaction at 100 °C for 20 min, a colorless solution was obtained. The mixture was cooled to room temperature, and then set aside for 4 h, during which time colorless prism crystals formed. These were collected by filtration and washed with cold dmf and air-dried. Anal. Calc. (found) for $CuC_{50}H_{40}O_2NP_2$: C, 73.93 (74.23); H, 4.96 (5.18); N, 1.72 (1.97%). IR (KBr, pellet) ν_{max}/cm^{-1}: ν_{as}(COO) 1585.6vs, 1434.0vs; ν_s(COO) 1401.4vs. UV-vis (dmf solution). λ/nm (log ε): 266 (4.87), 291.6 (4.55), 325.8 (3.59), 340.2 (3.59)

X-Ray crystal structure determinations

A green prismatic crystal of complex **1**, with approximate dimensions $0.46 \times 0.40 \times 0.34$ mm^3, a dark green prismatic crystal of complex **2**, with approximate dimensions $0.40 \times 0.32 \times 0.30$ mm^3, a black prismatic crystal of complex **3**, with approximate dimensions $0.48 \times 0.40 \times 0.40$ mm^3, and a colorless prismatic crystal of complex **4** with approximate dimensions $0.50 \times 0.14 \times 0.14$ mm^3 were mounted in air.

The data for the complexes were collected on a Siemens SMART CCD area detector diffractometer equipped with Mo-Kα radiation using ω-scan mode. The data collection covered over a hemisphere of reciprocal space by a combination of three sets of exposures; each set had a different ϕ angle (0.88 and 180°) for the crystal and each exposure of 10 s for **1** and 30 s for **2**, **3** and **4** covered 0.3° in ω. The crystal-to-detector distance was 4 cm and the detector swing angle was −35°. Coverage of the unique set is over 99% complete. Crystal decay was monitored by repeating thirty initial frames at the end of data collection and analyzing the duplicate reflections and was found to be negligible.

The unit cell parameters were determined using SMART (Siemens, 1996a).[21] The three sets of data collected were reduced using the program SAINT (Siemens, 1996b).[22] The structure was solved with direct methods using the program SHELXTL (Sheldrick, 1997).[23] All the non-hydrogen atoms were located from the trial structure and then refined anisotropically with SHELXTL using a full-matrix least-squares procedure. The hydrogen atoms were geometrically fixed at calculated positions attached to their parent atoms, and were treated as riding atoms.

The crystal data and data collection parameters are given in Table 1. Selected bond distances and angles are given in Table 2.

CCDC reference numbers 181844–181847.

See http://www.rsc.org/suppdata/nj/b2/b203334h/ for crystallographic data in CIF or other electronic format.

Table 1 The crystal data and parameters of **1**, **2**, **3** and **4**

Complex	**1**	**2**	**3**	**4**
Formula	$C_{68}H_{72}Cu_2N_8O_{12}$	$C_{68}H_{54}ClCu_2N_7O_{12}$	$C_{40}H_{28}CuN_4O_4$	$C_{50}H_{40}CuNO_2P_2$
Formula weight	1320.42	1323.71	692.20	812.31
Colour	Green	Dark-green	Black	Colorless
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Triclinic
Space group	$P2_1/c$	$P2_1/c$	$Pbca$	$P\bar{1}$
a/Å	10.1516(1)	14.2574(4)	16.1794(1)	12.2055(1)
b/Å	13.3088(2)	24.8155(7)	24.1843(1)	13.5557(2)
c/Å	24.2596(2)	21.5853(5)	16.4207(2)	14.4757(1)
α/°	90	90	90	111.532(1)
β/°	96.108(1)	129.630(1)	90	92.833(1)
γ/°	90	90	90	109.639(1)
V/Å^3	3259.00(6)	5881.8(3)	6425.21(9)	2057.11(4)
Z	2	4	8	2
μ/mm^{-1}	0.720	0.842	0.730	0.650
D_c/g cm^{-3}	1.346	1.495	1.431	1.311
F(000)	1380	2820	2856	844
Unique reflections	7875	14221	7933	8338
Reflections observed	22293	39847	42835	13175
R	0.0638	0.1057	0.0402	0.0698
R_w	0.1138	0.2616	0.0715	0.1052
$\Delta\rho_{\max,\ \min}$/e Å^{-3}	0.718, −0.602	1.472, −1.643	0.561, −0.551	0.799,−0.703

Table 2 Selected bond distances (Å) and angles (°) of the complexes

1	**2**	**3**	**4**
Cu(1)–O(3) 1.96(2)	Cu(1)–O(5) 1.94(3)	Cu(1)–O(3) 1.91(14)	Cu(1)–O(2) 2.19(3)
Cu(1)–O(4) 1.97(3)	Cu(1)–O(2) 1.97(2)	Cu(1)–O(1) 1.90(12)	Cu(1)–P(1) 2.23(11)
Cu(1)–O(2) 1.97(3)	Cu(1)–O(3) 2.29(4)	Cu(1)–N(2) 2.01(16)	Cu(1)–O(1 2.24(3)
Cu(1)–O(5) 1.99(2)	Cu(2)–O(4) 1.95(3)	Cu(1)–N(1) 2.02(15)	Cu(1)–P(2) 2.25(11)
Cu(1)–O(1) 2.12(3)	Cu(2)–O(3) 2.03(2)	O(3)–C(40) 1.28(2)	O(1)–C(37) 1.26(4)
Cu(1)–Cu(1)# 2.66(8)	Cu(2)–O(2) 2.35(4)	O(4)–C(40) 1.22(2)	O(2)–C(37) 1.25(4)
O(3)–Cu(1)–O(4) 88.3(12)	O(5)–Cu(1)–O(2) 91.3(11)	O(3)–Cu(1)–O(1) 100.0(5)	O(2)–Cu(1)–O(1) 60.0(10)
O(3)–Cu(1)–O(2) 89.7(12)	O(5)–Cu(1)–N(7) 172.2(15)	O(3)–Cu(1)–N(2) 170.5(6)	O(2)–Cu(1)–P(1) 113.0(9)
O(4)–Cu(1)–O(2) 167.5(11)	O(2)–Cu(1)–N(7) 93.2(12)	N(2)–Cu(1)–N(1) 81.5(6)	P(1)–Cu(1)–O(1) 115.2(8)
O(3)–Cu(1)–O(5) 167.7(10)	O(5)–Cu(1)–O(3) 89.9(14)	C(26)–O(1)–Cu(1) 128.3(13)	
O(4)–Cu(1)–O(5) 89.9(12)	O(2)–Cu(1)–O(3) 83.2(12)	O(1)–Cu(1)–N(1) 166.8(6)	

Results and discussion

Description of the structure

Crystal structure of $[Cu_2(Cabo)_4(dmf)_2]\cdot 2dmf$ (1). An ORTEP diagram of the complex **1** is shown in Fig. 1. The structure consists of centrosymmetric dinuclear unit. Each Cu(II) ion has four oxygen atoms of $RCOO^-$ groups in equatorial positions, and a dmf molecule is bound *trans* to the Cu–Cu vector at the apex in a fashion similar to that of the dinuclear structure of $Cu_2(RCOO)_4L_2$.[6,24–26] A further two dmf molecules are loosely held in the lattice.

The individual Cu atom has a Jahn–Teller-distorted, octahedral geometry, with four short Cu–O_{RCOO} (1.963(2)–1.986(2) Å) bond lengths and a long solvent Cu–O(2.121(3) Å) bond length. The two copper atoms in each dimeric unit are separated by a distance of 2.662(1) Å. The distance is similar to that found in other Cu carboxylate dimers.[11,27]

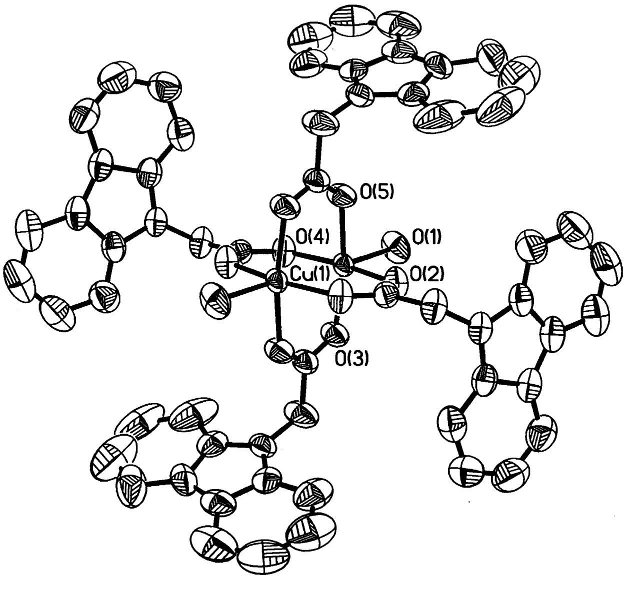

Fig. 1 ORTEP view of complex **1** with 50% thermal ellipsoids showing the atom-labeling scheme around the Cu(1) atom. Hydrogens and solvent molecules have been omitted; for dmf only coordinated oxygen atoms are shown.

Crystal structure of $[Cu_2(Cabo)_3(phen)_2](ClO_4)\cdot H_2O\cdot C_2H_5OH$ (2). An ORTEP diagram of the complex **2** with atom numbering scheme around the copper atoms is shown in Fig. 2. The crystal of **2** consists of a dinuclear $[Cu_2(Cabo)_3(phen)_2]^+$ cation and a well-separated perchlorate anion. The copper(II) ions are bridged by three carboxylate groups. Two of the *N*-carbazolylacetates are in the rare monoatomic

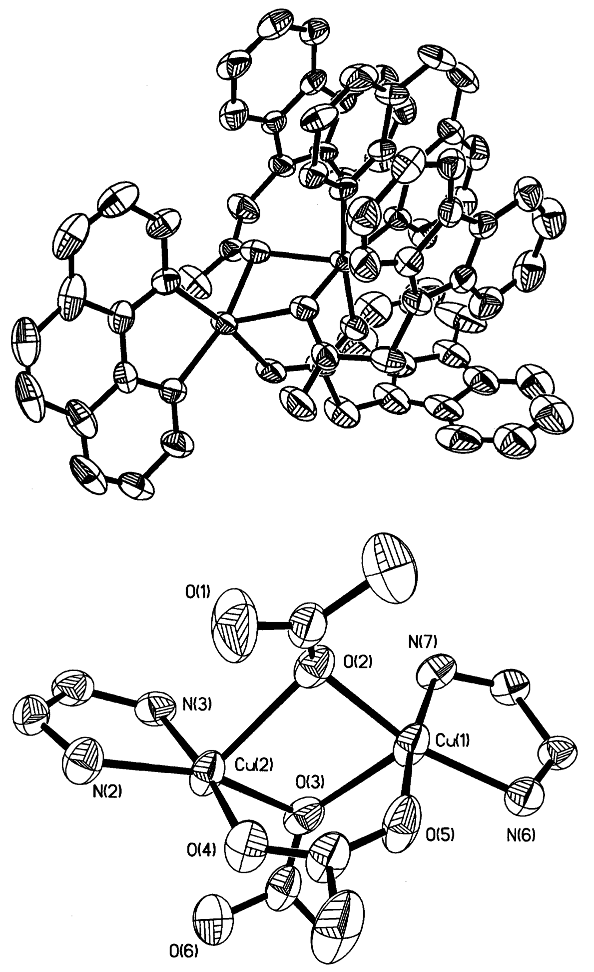

Fig. 2 ORTEP view of complex **2** with 50% thermal ellipsoids (top) and the atom-labeling scheme around the Cu atoms (bottom). Hydrogen atoms, anion and solvent molecules have been omitted for clarity.

bridging mode, and the third is in the didentate η:η:μ_2 bridging mode; a terminal phen molecule completes the five-coordination at each copper(II) ion. Fig. 2 (bottom) shows that the copper atoms are orthogonally bridged to the monodentate bridging carboxylates and equatorially bridged to the didentate carboxylate and have significantly longer Cu–O bond distances [Cu(1)–O(3) 2.290 Å, Cu(2)–O(2) 2.345 Å] than those of $[Cu_2(O_2CMe)_3(bpy)_2](ClO_4)$.[28] Although dinuclear copper carboxylates have been investigated extensively, this kind of bridging mode has not been reported according to the summary of Psomas *et al.*[29] Since many five-coordinate structures with geometries, intermediate between regular trigonal bipyramidal and rectangular pyramidal, a method[30] has been developed which attempts to quantify the structure. The relevant angles in $[Cu_2(Cabo)_3(phen)_2]^+$, $\theta_1 = 172.31°$ and $\phi_1 = 165.09°$; $\theta_2 = 172.14°$ and $\phi_2 = 160.72°$, yield τ values of 0.12 and 0.19. The data indicate geometries closer to rectangular pyramidal for Cu(1) and Cu(2) in $[Cu_2(Cabo)_3(phen)_2]^+$, respectively. The cations of **2** form infinite chains as a result of H-bonding interaction with ClO_4^- anions and a water molecule.

Crystal structure of Cu(Cabo)$_2$(phen) (3). An ORTEP diagram of complex **3** with atom numbering scheme is shown in Fig. 3. The copper(II) ion is coordinated by two oxygen atoms of two monodentate carboxylates and two nitrogen atoms of a phen forming a four-coordinate planar geometry. The N(1), C(1), C(12) and N(2), atoms are almost in one plane (largest deviation: 0.0048 Å) which forms a dihedral angle of 9.6° with the Cu(1), O(1), O(3) plane. Each carboxylate group acts as monodentate ligand in an *anti* manner. The monomeric structure is extended into an infinite two-dimensional network *via* the C–H···O hydrogen bonds and aromatic π–π stacking

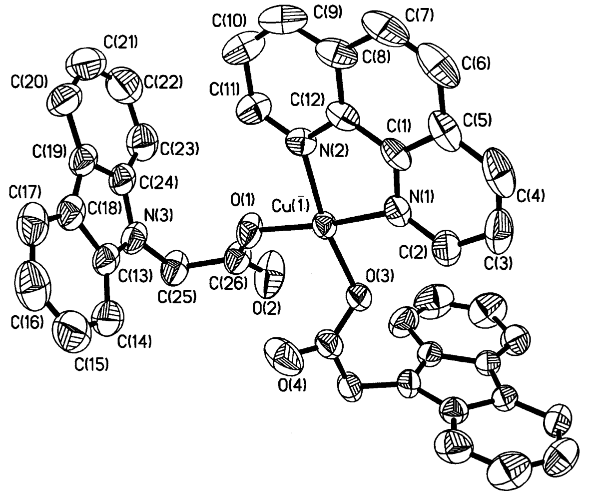

Fig. 3 ORTEP view of complex **3** with 50% thermal ellipsoids showing the atom-labeling scheme. Hydrogen atoms have been omitted for clarity.

Crystal structure of Cu(Cabo)(PPh$_3$)$_2$ (4). As shown in Fig. 4, the copper atom is in a distorted tetrahedral CuO_2P_2 geometry, being coordinated by two P atoms of two PPh_3 ligands, two oxygen atoms of one chelating didentate *N*-carbazolylacetato group. The C(37), C(38), O(1), O(2) and Cu(1) atoms are almost in one plane (largest deviation: 0.0176 Å) which forms a dihedral angle of 78.1° with the carbazole ring. The three benzene rings of PPh_3 are almost perpendicular to each other (C(1)–P(1)–C(13) 103.65°, C(1)–P(1)–C(7): 106°). Although the formation of a four-membered Cu–O–C–O ring,[5,31,32] with the high angular strains involved, is not expected to be energetically favorable, this type of structure is more stable than that in which carboxylato group adopts a monodentate mode with three bulky triphenylphosphine ligands to complete four-coordination geometry of the Cu(I) ion.

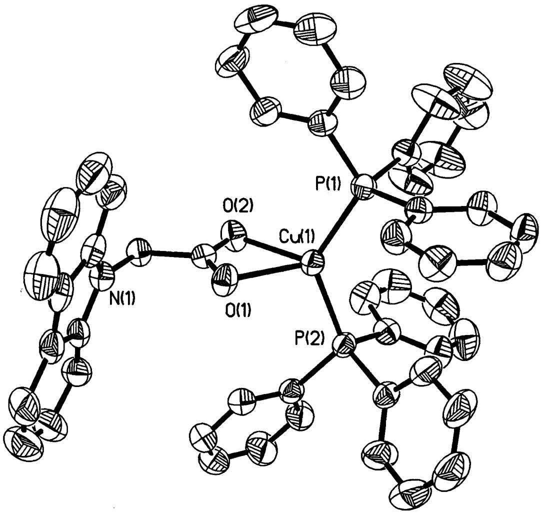

Fig. 4 ORTEP view of complex **4** with 50% thermal ellipsoids showing the atom-labeling scheme around the Cu atom. Hydrogen atoms have been omitted for clarity.

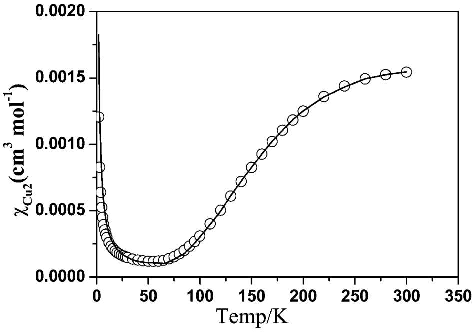

Fig. 5 The magnetic susceptibility of **1**. See the text for fitting parameters.

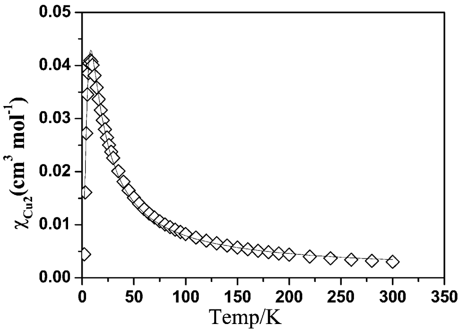

Fig. 6 The magnetic susceptibility of **2**. See the text for fitting parameters.

Magnetic susceptibility

The magnetic susceptibility for **1** decreases with decreasing temperature from 300 to 65 K, below which there is a rapid increase in magnetic susceptibility as the temperature is lowered further to 2 K (Fig. 5), typical of a dinuclear copper(II) complex exhibiting intramolecular antiferromagnetic exchange.[33–35] The large increase in χ at very low temperatures is attributed to a small fraction (ρ) of a monomeric $S = 1/2$ Cu(II) spin impurity being present.[36] The magnetic data were fitted to modified Bleaney-Bowers susceptibility expression[37,38] (based on the exchange Hamiltonian $H_{ex} = -2J\{S_1 \cdot S_2\}$) within MAGMUN4.0[39] to give $g = 2.245(3)$, $2J = -356.4(6)$ cm^{-1}, TIP $= 71 \times 10^{-6}$ emu mol^{-1}, $\rho = 0.0024$, $\theta = -2.15$ K ($10^2R = 0.62$); $R = [\Sigma(\chi_{obs} - \chi_{calc})^2/\Sigma\chi_{obs}{}^2]^{1/2}$; ρ = fraction paramagnetic impurity, TIP = temperature independent paramagnetsim, θ = Weiss-like temperature correction), as the best fit result. The solid line in Fig. 5 was calculated with these parameters. The fitted parameters for **1** are comparable to those for $[Cu(OAc)_2H_2O]_2$ [$2J = -296$ cm^{-1}, $g_{Cu} = 2.16$ and $\rho = 0.05$],[40,41] but exchange is somewhat stronger. Although the magneto-structural relations of various copper(II) carboxylates with $[Cu_2(RCOO)_4L_2]$ structure have been studied, the finer details remain obscure. The exchange integral ($-2J$) depends primarily 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, and (iii) the Cu–Cu distances.

The $-2J$ value obtained for **1** is significantly higher than the average value of 316 cm^{-1} for a dinuclear compound with CuO_5 coordination in a similar bridging situation.[42] A comparison of the magneto-structural data on representative *syn, syn*-carboxylato bridged dicopper(II) complexes with a $[Cu_2(RCOO)_4L_2]$ core[5,6,43] has been made in Table 3. All four dinuclear complexes in Table 3 have the same axial coordinating molecules whereas complex $[Cu_2(Cabo)_4(dmf)_2]\cdot 2dmf$ (**1**) has the largest Cu–Cu distance and the largest $-2J$ value. This indicates that the carboxylate constituents play a key role in this system, and the large $-2J$ value may be a consequence of the efficient charge transfer ability of the carbazole moiety. This is supported by the fact that the carbazole moiety is a strong electron donor, having been used in nonlinear optical applications.[44]

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

Complex	Cu···Cu /Å	$-2J$	Ref.
$m = 4$			
$Cu_2(O_2CPh)_4(dmf)_2$	2.630	305	5
$Cu_2(Indo)_4(dmf)_2$	2.630	286	6
$Cu_2(O_2CCHCHMe)_4(dmf)_2$	2.613	305	43
$Cu_2(Cabo)_4(dmf)_2$	2.663	353	This work
$m = 3$			
$[Cu_2(O_2CC_6H_4Me\text{-}p)_3]PF_6$	3.419	81	46
$m = 2$			
$Cu_2(O_2CMe)_2(phen)_2(H_2O)(NO_3)_2$	3.063	86	11
$Cu_2(O_2CH)_2(phen)_2(H_2O)(NO_3)_2$	3.103	125	11
$Cu_2(O_2CEt)_2(saln\text{-}p\text{-}tolyl)_2$	3.122	101	47

The variable temperature magnetic susceptibility data for **2** are plotted in Fig. 6 along with the line of best fit. On cooling from room temperature the molar susceptibility value reaches a maximum at 8 K, and then decreases rapidly, as the temperature is lower further to 2 K indicating the antiferromagnetic nature of the complex. The magnetic data were also fitted to the modified Bleaney–Bowers susceptibility expression[37,38] within MAGMUN4.0[39] to give $g = 2.166(1)$, $2J = -12.8(4)$ cm^{-1}, TIP $= 150 \times 10^{-6}$ emu mol^{-1}, $\rho = 0$, $\theta = -6$ K ($10^2R = 1.62$), as the best fit result. The low magnitude of $-2J$ indicates a weak antiferromagnetic interaction in the $[Cu_2(RCOO)_3]^+$ core. As the superexchange interaction is operative only through the carboxylate bridges, the magnitude of the antiferromagnetic interaction ($-2J$) might be expected to be dependent on the number of bridging carboxylate ligands.[45] An examination of the structure of complex **2** shows that only one carboxylate bridge links the copper magnetic orbitals directly. Cu(1) and Cu(2) have $d_{x^2-y^2}$ ground states, but connections to O(2) and O(3) (Cu(1)–O(3) 2.290 Å, Cu(2)–O(2) 2.345 Å) are long and axially oriented relative to the magnetic planes, thus creating orthogonal bridging connections, which would lead to insignificant antiferromagnetic exchange. The single *syn-syn*-carboxylate bridge is therefore associated with the weak net intramolecular exchange situation ($-2J = 12.8$ cm^{-1}), which is quite reasonable.[28,46]

Photoluminescence

The strong emission spectrum of **4** in the solid state at room temperature with two kinds of emissions is shown in Fig. 7. The maximum is at *ca.* 376 nm with a shoulder at *ca.* 390 nm. The other emission is at *ca.* 415 nm with a shoulder at 439 nm (357-nm excitation), which can be assigned to the excimeric emissions due to the weak ligand–ligand interactions between the molecules in solid state. The emission at 376 nm can be assigned to the intraligand $\pi^* \rightarrow \pi$ charge transfer similarly to the emission of carbazole in dilute solution.

Most carbazole compounds emit at wavelengths >400 nm in solid state[48–50] due to the aromatic π–π stacking. The reason for the unusual short wavelength emissions for **4** can be explained according to its structure. As shown by Fig. 4, the two bulky PPh_3 ligands both with three benzene rings almost perpendicular to one another significantly decrease the symmetry of the molecule. The strong emission at short wavelength may be caused by the energy increase resulting from the symmetry decrease of **4** compared to that of the ligand and the high angular strain of the four-membered chelating ring. Few metal–organic compounds showing intense fluorescence

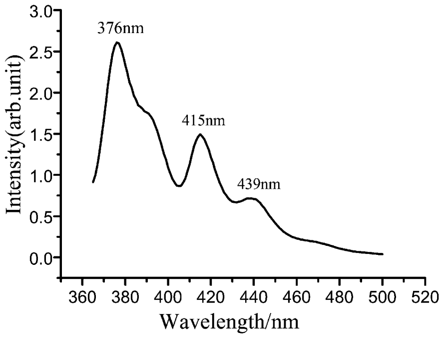

Fig. 7 The photoluminescence spectrum of **4** in solid state

or phosphorescence at wavelengths < 450 nm are reported in the literature.[51] Thus complex **4** may be used as an advanced material for a light emitting diode device owing to its strong short-wavelength emission and reasonable thermal stability (no weight loss occurred below 272 °C according to TGA).

In conclusion, a series of *N*-carbazolylacetates with different carboxylato coordination modes were synthesized and magnetic and/or PL properties have been studied. In this paper, for the first time, a novel motif of a dinuclear tricarboxylato copper(II) complex with one η:η:μ_2 bridge and two unusual monoatomic bridges is reported. Complex **4** shows unusual emissions in the solid state. The high UV intraligand emission together with the visible emission arising from intermolecular ligand–ligand interactions suggest a future in the design of photoluminescent materials for light-emitter applications by tailoring their structures.

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39 MAGMUN4.0 is available free of charge. It has been developed by Dr Zhiqiang Xu (zxu@hpower.com) and Kathy Minzhen He (heminzhen@yahoo.com) in collaboration with Prof. L. K. Thompson (lthomp@mun.ca), and Dr O. Waldmann (waldmann@physik.uni-erlangen.de), who wrote the energy state routine (Ow01.exe). We do not distribute the source codes. The programs may be used only for scientific purposes, and economic utilization is not allowed. If either routine is used to obtain scientific results, which are published, the origin of the programs should be quoted.
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