Synthesis and Characterization of New Mono-, Di-, and Trinuclear Copper(II) Triethanolamine-Carboxylate Complexes

Raphael M. Escovar, John H. Thurston, Teyeb Ould-Ely, Arvind Kumar, and Kenton H. Whitmire*

Houston, TX / USA, Rice University, Department of Chemistry

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Dedicated to Professor Herbert W. Roesky on the Occasion of his 70th Birthday

Abstract. A series of triethanolamine copper(II) carboxylate complexes have been synthesized and characterized both structurally and spectroscopically. The structures of the compounds and the nuclearity of the resulting coordination complexes are influenced both by the stoichiometry of the reagents and the steric and electronic influences of the anionic ligands present in the copper coordination spheres. The complexes can be prepared in high yields and purity as highly crystalline solids. Herein we report the spectroscopic and structural data for $[NaCu(CF_3COO)_3(TEAH_3)]$ (**1**), $[Cu(C_6H_5COO)(TEAH_2)]_2 \cdot 2H_2O$ (**2**), $[Cu_3(CH_3COO)_4(TEAH_2)_2]$ (**3**), $[Cu_3(HCOO)_4(TEAH_2)_2]$ (**4**) and $[Cu_3(CF_3OO)_2(TEAH_2)_2(CH_3OH)_2][CF_3CO_2]_2$ (**5**) ($TEAH_3$ = triethanolamine ($N(CH_2CH_2OH)_3$); $[TEAH_2]^-$ = mono-deprotonated ion; $[TEAH]^{2-}$ = doubly deprotonated ion). Two approaches to these compounds were employed:direct reaction of copper(II) carboxylates with $TEAH_3$ and reaction of the tetrameric compound $[\{Cu(TEAH)\}_4]$ (**6**) with copper(II) carboxylates. Compound **1** is polymeric in the solid state, being a double salt of sodium trifluoroacetate and (triethanolamine)copper(II) trifluoroacetate, while **2** exists as a simple dimer. Compounds **3**, **4** and **5** are trinuclear complexes with Cu_3 chains connected by bridging carboxylate and triethanolamine ligands. **3** was characterized as three crystal modifications: an unsolvated form and as a methanol solvate **3**·2MeOH that was found to exist in both monoclinic and orthorhombic forms. **4** was also found to exist as a methanol solvate, **4**·1.70 MeOH. **5** shows coordination isomerism compared to compounds **3** and **4** in that two of the carboxylate ligands in the metal coordination spheres on the end copper atoms have been replaced by solvent methanol. The magnetic behavior of the di- and trinuclear species has been probed and reveals that at low temperatures the metal centers exhibit strong ferromagnetic coupling, which, on warming, switches to simple paramagnetic behavior.

Keywords: Copper; Copper triethanolamine-carboxylate complexes

Introduction

In the past decade there has been an increasing interest in metal alkoxides because of their application in the sol-gel synthesis of the various homo- and heterometallic oxide materials. Metal alkoxides are easily hydrolyzed or pyrolyzed to give highly pure and homogeneous products, often under far milder conditions than normally possible with conventional solid state methods [1−6]. Using "soft" methods such as this allows better control of the fine structure of the products, and makes possible controlled production of nanoparticle metal oxide materials with narrow polydispersity under the proper conditions. Our work has emphasized the formation of heterometallic complexes of bismuth and other metals for applications as ferroelectric materials, oxide ion conducting materials, and catalysts [7−12]. For highly Lewis acidic metal centers such as bismuth, lead, and the lanthanides, pre-formed metal complexes can simply be attached to the metal center in a donor-acceptor fashion [7−10]. In particular, we and others have had an interest in triethanolamine, $N(CH_2CH_2OH)_3$, complexes of copper and bismuth for their potential application in the production of high T_C superconductors [13−15]. In this paper, we will abbreviate neutral triethanolamine as $TEAH_3$, where H represents the active hydroxyl protons. Deprotonation can therefore lead to metal-bound $TEAH_2{}^-$, $TEAH^{2-}$ and TEA^{3-} ions.

Our previous studies of copper complexes of triethanolamine reported the tetrameric species $[\{Cu(TEAH)\}_4]$ which can be prepared in a variety of solvated forms [14]. This material makes a convenient starting point for the preparation of other copper triethanolamine derivatives that are reported herein. Previous studies of trinuclear copper complexes found three types of molecular structures: isosceles or equilateral triangular arrays of the copper ions, and linearly arranged copper ions. Additionally, magnetic studies have shown that these complexes may display either ferromagnetic, anti-ferromagnetic, or both behaviors. Thus, these exchange-coupled systems are important in the search for molecular ferromagnets.

In this paper we report the new copper triethanolamine complexes $[NaCu(TEAH_3)(CF_3COO)_3]$ (**1**), $[Cu(TEAH_2)(C_6H_5COO)]_2 \cdot 2H_2O$ (**2**), $Cu_3(TEAH_2)_2(CH_3COO)_4$ (**3**), $Cu_3(TEAH_2)_2(HCOO)_4$ (**4**) and $[Cu_3(TEAH_2)_2(CF_3OO)_2(CH_3OH)_2][CF_3CO_2{}^-]_2$ (**5**) prepared by direct reaction of copper(II) carboxylates ($RCO_2{}^-$ = $HCO_2{}^-$, $CH_3CO_2{}^-$, $CF_3CO_2{}^-$, $C_6H_5CO_2{}^-$)

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* Prof. Dr. Kenton H. Whitmire
Department of Chemistry, MS-60, Rice University
6100 Main St.,
Houston TX, 77005 / USA,
e-mail: whitmir@rice.edu
Phone: 713-348-5650, Fax:713-348-5155

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with triethanolamine or reaction of the pre-formed tetrameric complex [{Cu(TEAH)}$_4$] (**6**) with copper(II) carboxylates. The syntheses we describe are readily performed in air and aqueous solutions from common off-the-shelf reagents and produce materials free of excess TEAH$_3$.

Experimental Section

General

The starting materials copper(II) acetate, copper(II) formate, benzoic acid and triethanolamine were purchased and used as received. All solvents employed in the reactions were purified by distillation. Infrared spectra of the complexes were recorded of a Thermo-Nicolet 630 instrument employing ATR techniques with a germanium window. UV-Vis data of the complexes in water was collected on a GBC spectral instrument. Mass spectra were obtained on a Finnigan MAT95 spectrometer using FAB with nitrobenzyl alcohol as the matrix. Magnetic susceptibility data were measured on a Quantum Design MPMS-5S SQUID magnetometer at 1000T from 2 to 300 K. Elemental analyses were obtained from Galbraith Analytical Laboratories.

Syntheses

[NaCu(CF$_3$CO$_2$)$_3${TEAH$_3$}] (1)

Dissolution of Cu(SO)$_4$·5H$_2$0 (1.0 g, 0.004 mol) in methanol (ca. 25 mL) was accomplished with magnetic stirring, yielding a blue-green solution. To this solution was added a solution of Na$_2$CO$_3$ (0.454 g, 0.004 mol) in deionized water (ca. 25 mL). A light blue precipitate developed and was allowed to settle. Without any further purification, trifluoroacetic acid (1.85 g, 0.020 mol) was added and all the precipitate dissolved yielding a clear, pale blue solution. To this mixture was added [{Cu(TEAH)}$_4$] (**6**) (0.947 g, 0.0010 mol) in deionized water (ca. 25 mL) yielding a precipitate. The reaction was then filtered through a medium porosity glass frit with the aid of Celite, and the filtrate was taken to dryness on a rotary evaporator. The product was dissolved in warm methanol (ca. 50 mL) forming a cloudy solution. The precipitate was then allowed to settle and was again filtered through a medium porosity glass frit with the aid of Celite, yielding a blue-green solution. The filtrate was then layered with diethyl ether and the product crystallized over a period of several days. Yield: 17 %. Elemental Analysis: %Found (% Calc.) for [NaCu(CF$_3$CO$_2$)$_3$(TEAH$_3$)]: C, 25.12 (24.35), H, 3.11 (2.72), N, 2.92 (2.37). IR (cm^{-1}): 3401, 1675, 1433, 1202, 1185, 1129, 1092, 1074, 900, 846, 794, 727. UV-Vis: λ_{max} (ε) = 253 nm (8658 M^{-1}), 742 nm (156 M^{-1}). The UV band, for concentrations up to 1 x 10^{-4} M, followed Beer's Law with a correlation coefficient of 0.933, while the visible band, for concentrations up to 6.2 × 10^{-3} M, followed Beer's Law with a R^2 = 0.9995.

[Cu$_2$(C$_6$H$_5$COO)$_2$(TEAH$_2$)$_2$]·2H$_2$O (2)

Method 1: A green, slightly turbid solution of CuSO$_4$·5H$_2$O (5.049 g, 0.020 mol) in methanol was treated with a solution of Na$_2$CO$_3$ (2.3 g, 0.022 mol) in deionized water resulting in the formation of a pale blue precipitate. The slurry was then sequentially treated first with a solution of benzoic acid (9.9 g, 0.081 mol) in methanol, which resulted in the formation of a dark blue precipitate, and then with a solution of **6** (8.96 g, 0.010 mol) suspended in deionized water (ca. 100 mL). Addition of **6** resulted in the solution becoming slightly turbid. The reaction mixture was stirred at room temperature for approximately 30 minutes during which time a pale blue precipitate formed. The precipitate was removed by filtration and the clear blue-green filtrate was concentrated to *ca*. one-quarter of its original volume under reduced pressure. Storage of this solution at reduced temperature resulted in the deposition of blue-green crystals of **2**. Yield: 78 %.

Method 2: A suspension of benzoic acid (5 g, 0.04 mol) in deionized water was treated with a solution of NaOH (1.64 g, 0.041 mol) in deionized water with good stirring. The resulting white flocculent precipitate was taken to dryness using a rotary evaporator. Half of the resulting solid was suspended in deionized water and treated with a solution of CuSO$_4$·5H$_2$O (2.57 g, 0.010 mol) in deionized water. The mixture was stirred and gently heated for approximately 15 minutes to produce a pale blue precipitate. The solid was collected via filtration using a medium porosity Büchner funnel and dried under reduced pressure.

A methanol solution of the copper(II) benzoate prepared as described above was treated sequentially with a solution of benzoic acid (0.57 g, 0.0050 mol) in methanol and an aqueous solution of **6** (0.994g, 0.0010 mol). The reaction mixture was stirred at room temperature for approximately 15 minutes to give a blue-green solution and a pale blue precipitate. The supernatant was removed via filtration and concentrated to ca. one-quarter of its original volume. Storage of the filtrate in a refrigerator resulted in the growth of blue-green crystals that were found to be identical to those described in Method 1 as determined by the crystallographic unit cell parameters. Yield: 71 %. Elemental Analysis: %Found (%Calc.) for [Cu$_2$(TEAH$_2$)$_2$(C$_6$H$_5$COO)$_2$]·2H$_2$O C, 44.33 (44.45); H, 6.15 (6.03); N, 3.99 (3.99). FT-IR (cm^{-1}): 3103(O-H), 1597(COO)$_{asym}$, 1552(COO)$_{sym}$, 1393, 1093, 1070, 1054, 1026, 907, 845, 813, 726, 718. UV-Vis: λ_{max} = 267, 733 with ε = 8350.8, 70.6 mol^{-1}. The UV band, for concentrations up to 2.74 x 10^{-3} M followed Beer's Law with a correlation coefficient of 0.968, while the visible band for concentrations up to 5.4 × 10^{-3} M followed Beer's Law with a R^2 = 0.993.

[Cu$_3$(CH$_3$COO)$_4$(TEAH$_2$)$_2$] (3 and 3·2MeOH)

Method 1: To a solution of Cu(O$_2$CCH$_3$)$_2$ (5.06 g, 0.025 mol) in deionized water, triethanolamine (2.52 g, 0.017 mol) was added. The solution immediately became deep blue. After stirring at room temperature for about an hour, the solvent was removed under reduced pressure. The residue was dissolved in methanol and allowed to recrystallize over a period of three days by slow evaporation. The resulting solid was then redissolved in methanol and the resulting bright blue solution was carefully layered with diethyl ether. Solvent diffusion over the course of several days at room temperature resulted in the deposition of large blue prisms. After crystallization was judged to be complete, the solvent was decanted and the product was washed with acetone (*ca*. 200 mL) then dried *in vacuo*. Yield: 76 %, of a light blue powder or bright blue, clear crystals. These crystals were found to be suitable for X-ray diffraction analyses; however, better crystals were obtained by slow vapor diffusion under vacuum over a period of 4 weeks.

Method 2: A solution of CuSO$_4$·5H$_2$O (5.0 g, 0.020 mol) in deionized water was treated with a solution of Na$_2$CO$_3$ (2.25 g, 0.021 mol) in deionized water, resulting in the immediate formation of a pale blue precipitate. The resulting slurry, was then sequentially treated with acetic acid (0.08 mol), which resulted in the formation of a clear blue solution; and then with [{Cu(TEAH)}$_4$] (8.92 g, 0.010 mol). The reaction mixture was stirred at room temperature for 30 minutes, and then evaporated to dryness under reduced pressure. Extraction of the residue with warm methanol resulted in the formation of a cloudy blue-green solution, which was filtered to remove a white solid. The clear filtrate was carefully layered with diethyl ether, and solvent diffusion was allowed to occur over a period of three days, during which time large, well-formed blue crystals of **1** deposited in the flask. The product isolated in this manner was found to give identical unit cell parameters as that produced by Method 1. Yield: 72 %. Elemental Analysis: %Found (%Calc.) for $Cu_3(TEAH_2)_2(CH_3COO)_4 \cdot 2MeOH$: C, 33.48 (33.56); H, 6.20 (6.15); N, 3.64 (3.56) %. FT-IR (cm^{-1}): 2875(O-H), $1568(COO)_{asym}$, $1443(COO)_{sym}$,1389, 1332, 1266, 1140, 1085, 1060, 1026, 1002, 915, 902, 867, 750. UV-Vis: $\lambda_{max} = 262$ and 741 nm with $\varepsilon = 6038.4$ and 189 mol^{-1}, respectively. The UV band, for concentrations up to 1.02 x 10^{-3} M, followed Beer's Law with a correlation coefficient of 0.963, while the visible band, for concentrations up to 5×10^{-3} M , followed Beer's Law with $R^2 = 0.995$.

$[Cu_3(HCOO)_4(TEAH_2)_2] \cdot 2CH_3OH$ (4)

This complex was produced in a manner analogous to **1**, with the substitution of $Cu(O_2CH)_2$ for $Cu(O_2CCH_3)_2$. Evaporation of the reaction mixture under reduced pressure gave a blue solid, which on recrystallization via diethyl ether/methanol diffusion gave the product as a pale blue powder. Crystals suitable for x-ray diffraction studies were grown by further recrystallization of the product by vapor phase diffusion of diethyl ether into a methanol solution of the complex. Yield: 76 % of a light blue powder or bright blue clear crystals. Elemental Analysis: %Found (%Calc.) For $Cu_3(TEAH_2)_2(HCOO)_4 \cdot CH_3OH$: C, 27.28 (31.10), H, 5.59(5.22), N, 4.10(4.03). FT-IR (cm^{-1}): 3154, 1576, 1458, 1378, 1366, 1337, 1086, 1050, 1024, 1006, 905, 867, 777, 750. UV-vis: λ_{max} (ε) = 253 (8658 M^{-1}), 742 (156 M^{-1}). The UV band, for concentrations up to 1×10^{-4} M, followed Beer's Law with a correlation coefficient of 0.933, while the visible band, for concentrations up to 6.2 x 10^{-3} M, followed Beer's Law with a $R^2 = 0.9995$.

$[Cu_3(CF_3CO_2)_2(TEAH_2)_2(CH_3OH)_2][CF_3CO_2]_2$ (5)

A deep turquoise solution of $Cu(O_2CCH_3)_2$ (3.00 g, 0.015 mol) in methanol was prepared with gentle heating and stirring. The solution was treated with trifluoroacetic acid (3.43 g, 0.030 mol), resulting in a color change to pale blue. The mixture was stirred at room temperature for 10 minutes and dried under reduced pressure. The residue was dissolved in a minimal amount of methanol and subsequently treated with triethanolamine (1.50 g, 0.010 mol), which resulted in a color change to deep blue. The reaction mixture was stirred at room temperature for 15 minutes and then again evaporated to dryness under reduced pressure. The residue was extracted into a minimal amount of methanol and carefully layered with diethyl ether. Solvent diffusion over a period of days at room temperature resulted in the deposition of large, well-formed, blue-green crystals. When crystallization was judged to be complete, the solvent was decanted and the product was dried under reduced pressure. Yield: 28 % of large, blue-green, clear crystals. The yield could be improved by allowing the product to crystallize over a longer period of time. FT-IR (cm^{-1}): 3156(O-H), $1672(COO)_{asym}$, $1567(COO)_{sym}$, 1483, 1439, 1354, 1203, 1132, 1086, 1066, 1046, 1026, 1006, 904, 854, 796, 754, 733, 717. UV-Vis: $\lambda_{max} = 267$ nm, 760 with $\varepsilon = 7743.3$, 188.8 mol^{-1}. The UV band for concentrations up to 1.44 x 10^{-4} M followed Beer's Law with a correlation coefficient of 0.997, while the visible band for concentrations up to 5.3 $\times 10^{-3}$ M followed Beer's Law with a $R^2 = 0.999$.

Single-Crystal X-ray Diffraction Studies

Data for compounds **1**, **3**·2MeOH, **4**·1.70MeOH and **5** were studied on a Bruker Smart 1000 diffractometer equipped with a CCD area

Table 1 Selective Crystallographic Data Collection and Refinement Parameters for Compounds **1** and **2**

	1	2
Composition	$[NaCu(CF_3CO_2)_3(TEAH_3)]_\infty$	$[Cu(C_6H_5CO_2)(TEAH_2)]_2 \cdot 2H_2O$
Chemical Formula	$C_{12}H_{15}CuF_9NNaO_9$ (empirical)	$C_{26}H_{42}Cu_2N_2O_{12}$
Formula wt /g·mol^{-1}	574.78	701.70
Z	4	2
Cell dimensions:		
a /Å	12.505(3)	7.5920(15)
b /Å	10.834(2)	27.018(5)
c /Å	15.031(3)	8.0400(16)
β /°	98.69(3)	111.05(3)
Cell Volume /Å^3	2012.9(7)	1539.2(5)
Temperature /K	293(2)	293(2)
Crystal system	monoclinic	monoclinic
Space Group	$P2_1/n$ (#14)	$P2_1/n$ (#14)
ρ /g·cm^{-3}, calc	1.897	1.514
F000	1148	732
R_{int}	0.0427	0.0300
Data Collection Ranges	$-13 \le h \le 7$	$0 \le h \le 9$
	$-12 \le k \le 11$	$0 \le k \le 35$
	$-16 \le l \le 16$	$-10 \le l \le 9$
Number of reflections	2903	3549
Number of Paramaters	296	190
R (all reflections)	0.0949	0.1210
R ($I \ge 2\sigma(I)$)	0.0726	0.0601
R_w (all reflections)	0.2215	0.2057
Goodness of fit, *S*	1.129	1.132
Max shift/error	0.001	0.000
Residual peaks max/min /e/Å^3	1.463/−0.843	1.246/−1.974

Table 2 Selective Crystallographic Data Collection and Refinement Parameters the Trinuclear Copper Compounds **3**, **3**·2MeOH, **4**, and **5**

	3	**3**·2 MeOH **monoclinic**	**3**·2 MeOH **orthorhombic***	**4**·1.70 MeOH	**5**
Composition	$Cu_3(CH_3CO_2)_4(TEAH_2)_2$	$Cu_3(CH_3CO_2)_4(TEAH_2)_2 \cdot$ 2 MeOH	$Cu_3(CH_3CO_2)_4(TEAH_2)_2 \cdot$ 2 MeOH	$Cu_3(HCO_2)_4(TEAH_2)_2 \cdot$ 1.70 MeOH	$[Cu_3(CH_3CO_2)_2(TEAH_2)_2$-$(MeOH)_2][CF_3CO_2]_2$
Chemical Formula	$C_{20}H_{40}Cu_3N_2O_{14}$	$C_{22}H_{48}Cu_3N_2O_{16}$	$C_{22}H_{48}Cu_3N_2O_{16}$	$C_{17.0}H_{38.80}Cu_3N_2O_{15.70}$	$C_{22}HCu_3N_2O_{16}$
Formula wt /g·mol^{-1}	723.16	787.24	787.24	721.53	997.10
Z	1	2	4	1	1
Cell dimensions:					
a /Å	7.7550(16)	7.8969(17)	19.545(4)	7.9418(16)	8.4906(17)
b /Å	9.791(2)	10.599(2)	7.9530(16)	8.6198(17)	10.637(2)
c /Å	10.235(2)	10.732(4)	20.724(4)	11.412(2)	11.035(2)
α /°	69.74(3)			72.15(3)	112.51(3)
β /°	82.81(3)	92.216(4)		85.02(3)	98.95(3)
γ /°	78.36(3)			69.33(3)	98.24(3)
Cell Volume /Å^3	712.8(2)	1650.2(6)	3222.9(11)	695.6(2)	886.8(3)
Temperature /K	293(2)	293(2)	293(2)	293(2)	293(2)
Crystal system	triclinic	monoclinic	orthorhombic	triclinic	triclinic
Space Group	$P\bar{1}$(#2)	$P2_1/n$(#14)	Pbca	$P\bar{1}$(#2)	$P\bar{1}$(#2)
ρ /g·cm^{-3}, calc	1.685	1.584		1.722	1.867
F000	373	818		372	499
R_{int}	0.012	0.0669		0.0196	0.0119
Data Collection Ranges	$-8 \le h \le 8$ $-9 \le k \le 0$ $-9 \le l \le 10$	$-8 \le h \le 7$ $-11 \le k \le 9$ $-21 \le l \le 19$		$-8 \le h \le 8$ $-8 \le k \le 9$ $-12 \le l \le 12$	$-9 \le h \le 9$ $-7 \le k \le 11$ $-12 \le l \le 11$
# Reflections	1353	2373		1942	2530
# Paramaters	179	196		191	238
R (all reflections)	0.0582	0.0598		0.0555	0.0742
R ($I \ge 2\sigma(I)$)	0.0506	0.0496		0.0457	0.0713
R_w (all reflections)	0.1982	0.1528		0.1306	0.2155
Goodness of fit, S	1.228	1.053		1.055	1.111
Max shift/error	0.000	0.001		0.000	0.000
peaks max/min /e/Å^3	0.744/−0.821	0.696/−0.498		1.033/−0.637	1.693/−1.435

* This data set refined poorly but sufficiently to establish the identity of the compound, thus only minimal data are provided.

detector. Data for compounds **2** and unsolvated **3** were collected on a Rigaku AFC5S diffractometer. In all cases, graphite-monochromated MoK$_\alpha$ radiation was employed. The stability of the crystals during data collections was monitored through three standard reflections which were collected every 75 frames on the Bruker Smart 1000 while standards were measured for intensity variations after every 150 reflections measured on the Rigaku AFC5S. No significant decay of the reflection intensities were detected during the data collections for any of the crystals. Pertinent details of the data collections and refinements are supplied in Tables 1 and 2. The data were corrected for Lorentz and polarization effects. Absorption corrections for the data measured on the Bruker Smart 1000 system were applied using the program SADABS [16]. The data for compounds **2** and unsolvated **3** that were collected on a Rigaku AFC5 diffractometer were corrected for absorption using psi scans. Data collection and reduction for the AFC5S data were performed using TEXSAN v. 5.0 [17], while those collected on the Bruker system were performed using the SHELXTL package [18]. Pertinent details of the data collections are supplied in Tables 1 (compounds **1** and **2**) and 2 (compounds **3** − **5**). For **4**, the lattice methanol was found in the electron density difference maps and refined at partial occupancy to give an over formula of **4**·1.70MeOH.

Table 3 Selected Bond Distances/Å and Angles/° for Compound **1**.

Na(1)-O(11)#2	2.607(6)	Cu(1)-N(1)	2.032(6)
Na(1)-O(21)	2.717(6)	Cu(1)-O(11)	2.642(6)
Na(1)-O(31)	2.570(6)	Cu(1)-O(21)	1.967(5)
Na(1)-O(42)	2.374(6)	Cu(1)-O(31)	2.391(5)
Na(1)-O(52)#1	2.404(7)	Cu(1)-O(41)	1.942(5)
Na(1)-O(61)	2.298(6)	Cu(1)-O(51)	1.936(6)
		O(51)-Cu(1)-O(41)	90.7(2)
O(61)-Na(1)-O(42)	162.4(3)	O(51)-Cu(1)-O(21)	178.0(2)
O(61)-Na(1)-O(52)#1	111.9(2)	O(41)-Cu(1)-O(21)	90.5(2)
O(42)-Na(1)-O(52)#1	83.9(2)	O(51)-Cu(1)-N(1)	93.8(2)
O(61)-Na(1)-O(31)	87.8(2)	O(41)-Cu(1)-N(1)	171.0(2)
O(42)-Na(1)-O(31)	79.1(2)	O(21)-Cu(1)-N(1)	84.8(2)
O(52)#1-Na(1)-O(31)	110.5(2)	O(51)-Cu(1)-O(31)	93.3(2)
O(61)-Na(1)-O(11)#2	93.8(2)	O(41)-Cu(1)-O(31)	109.3(2)
O(42)-Na(1)-O(11)#2	89.9(2)	O(21)-Cu(1)-O(31)	87.8(2)
O(52)#1-Na(1)-O(11)#2	102.6(2)	N(1)-Cu(1)-O(31)	78.3(2)
O(31)-Na(1)-O(11)#2	143.6(2)	O(51)-Cu(1)-O(11)	87.8(2)
O(61)-Na(1)-O(21)	90.1(2)	O(41)-Cu(1)-O(11)	97.1(2)
O(42)-Na(1)-O(21)	74.47(19)	O(21)-Cu(1)-O(11)	90.5(2)
O(52)#1-Na(1)-O(21)	158.0(2)	N(1)-Cu(1)-O(11)	75.2(2)
O(31)-Na(1)-O(21)	70.09(18)	O(31)-Cu(1)-O(11)	153.55(18)
O(11)#2-Na(1)-O(21)	73.54(18)		

Symmetry transformations used to generate equivalent atoms: #1 −x, −y+3, −z+2 #2 −x+1/2, y+1/2, −z+5/2 #3 −x+1/2, y−1/2, −z+5/2

In addition to the unsolvated form of compound **3**, methanol solvated forms in both monoclinic and orthorhombic settings were observed. The latter orthorhombic setting was solved sufficiently to confirm the composition as being the same as for the monoclinic form, but the data were not as good and a number of shadow peaks remained near the heavy atoms in the final refinements possibly indicating a less-than-optimal absorption correction or some irresolvable disorder. Since the monoclinic form refined well, it was not deemed worthwhile to pursue further study on the orthorhombic form; however, the crystal parameters of that form are presented in Table 2 for comparison purposes. Plots of the structures are given in Figures 1−9. For all thermal displacement parameter plots, the ellipsoids are drawn at the 50 % probability level.

Heavy atoms in all six compounds were located using direct methods with the SHELXTL software package [18]. All other atoms were located by successive Fourier difference maps and were refined

Table 4 Selected Bond Distances/Å and Angles/° for Compound **2**.

Cu(1)-N(1)	2.053(4)	Cu(1)-O(21)#1	1.946(3)
Cu(1)-O(11)	2.474(5)	Cu(1)-O(31)	2.570(4)
Cu(1)-O(21)	1.951(3)	Cu(1)-O(1)	1.966(4)
O(21)#1-Cu(1)-O(21)	82.69(16)	O(1)-Cu(1)-O(11)	85.71(16)
O(21)#1-Cu(1)-O(1)	95.16(16)	N(1)-Cu(1)-O(11)	76.38(16)
O(21)-Cu(1)-O(1)	177.28(15)	O(21)#1-Cu(1)-O(31)	114.71(15)
O(21)#1-Cu(1)-N(1)	161.62(17)	O(21)-Cu(1)-O(31)	90.71(15)
O(21)-Cu(1)-N(1)	84.66(16)	O(1)-Cu(1)-O(31)	88.68(15)
O(1)-Cu(1)-N(1)	97.82(17)	N(1)-Cu(1)-O(31)	78.66(15)
O(21)#1-Cu(1)-O(11)	91.72(15)	O(11)-Cu(1)-O(31)	153.39(13)
O(21)-Cu(1)-O(11)	95.99(16)		

Symmetry transformation used to generate equivalent atoms: #1 −x+1, −y, −z+2

Table 5 Comparison of Bond Distances/Å and Angles/° for the Trinuclear Compounds **3**, **3**·2 MeOH, **4** and **5**

Distances to the central copper atoms:				
	3	**3**·2 MeOH **monoclinic**	**4**·1.70 MeOH	**5**
Cu(1)-O(21)	1.929(6)	1.915(3)	1.964(3)	1.956(4)
Cu(1)-O(31)	2.730(7)	2.764(4)	2.523(4)	2.557(6)
Cu(1)-O(41)	1.950(7)	1.961(4)	1.969(4)	1.976(5)
Distances to the end copper atoms:				
Cu(2)-O(11)	2.508(7)	2.563(4)	2.429(4)	2.391(5)
Cu(2)-O(21)	1.916(6)	1.924(3)	1.950(4)	1.950(5)
Cu(2)-O(31)	2.535(7)	2.467(3)	2.528(4)	2.437(5)
Cu(2)-O(42)	1.945(7)	1.958(4)	1.953(4)	1.951(5)
Cu(2)-O(51)	1.969(7)	1.987(3)	1.958(4)	2.008(5)
Cu(2)-N(1)	2.058(8)	2.046(4)	2.024(4)	2.035(6)
Bond angles involving the central copper atoms:				
O(21)-Cu(1)-O(21)#Symm	180.0(3)	180.000(1)	180.000(1)	180.000(1)
O(21)-Cu(1)-O(31)	78.9(2)	78.06(12)	83.54(13)	81.63(18)
O(21)#Symm-Cu(1)-O(31)	101.1(2)	101.94(12)	96.46(13)	98.37(18)
O(21)-Cu(1)-O(41)	89.6(3)	89.52(15)	88.75(15)	90.9(2)
O(21)-Cu(1)-O(41)#Symm	90.4(3)	90.48(15)	91.25(15)	89.1(2)
O(31)-Cu(1)-O(41)	93.9(3)	92.25(14)	91.30(16)	88.7(2)
O(31)-Cu(1)-O(41)#Symm	86.1(3)	87.75(14)	88.70(16)	91.3(2)
O(41)-Cu(1)-O(41)#Symm	180.0(3)	180.0(2)	180.000(1)	180.000(1)
Bond angles involving the end copper atoms:				
N(1)-Cu(2)-O(11)	76.5(3)	76.04(15)	76.81(15)	77.5(2)
N(1)-Cu(2)-O(21)	85.8(3)	85.40(15)	86.65(16)	86.7(2)
N(1)-Cu(2)-O(31)	76.1(3)	77.79(14)	77.14(15)	78.6(2)
N(1)-Cu(2)-O(42)	177.7(3)	178.16(14)	177.24(16)	177.8(2)
N(1)-Cu(2)-O(51)	94.2(3)	94.48(16)	93.19(18)	92.9(2)
O(11)-Cu(2)-O(21)	92.8(2)	91.86(14)	95.02(14)	97.44(19)
O(11)-Cu(2)-O(31)	152.6(2)	153.82(14)	153.95(13)	155.80(19)
O(11)-Cu(2)-O(42)	102.0(3)	105.66(15)	103.28(15)	104.6(2)
O(11)-Cu(2)-O(51)	92.5(2)	92.09(14)	88.27(17)	85.7(2)
O(21)-Cu(2)-O(31)	84.3(2)	85.94(13)	83.68(14)	84.98(19)
O(21)-Cu(2)-O(42)	92.6(3)	93.80(15)	90.60(15)	92.4(2)
O(21)-Cu(2)-O(51)	174.5(3)	175.90(13)	176.57(16)	176.64(19)
O(31)-Cu(2)-O(42)	105.4(3)	100.51(14)	102.75(15)	99.3(2)
O(31)-Cu(2)-O(51)	90.3(2)	90.03(13)	92.94(17)	91.7(2)
O(42)-Cu(2)-O(51)	87.5(3)	86.20(15)	89.58(17)	87.8(2)

Symmetry transformations used to generate equivalent atoms for compound **3**: #Symm = −x−1, −y+1, −z; Compound **3**·2 MeOH monoclinic form: #Symm = −x, −y+2, −z+1; Compound 4: Symm = −x−1, −y+2, −z+1; Compound **5**: #Symm = −x+1, −y+1, −z+1

using the full-matrix least squares technique on F^2. Hydrogen atoms were placed in calculated positions and allowed to ride on the adjacent atom. Refinement of positional and anisotropic displacement parameters for all non-hydrogen atoms (except for those described below for **1** and **5**) led to convergence in all cases. A list of relevant bond lengths and angles of the molecules are supplied in Tables 3−5.

For **1** and **5**, the CF_3 groups were found to be disordered. Anisotropic refinement of a single position, or even two disordered positions, led to unsatisfactory thermal displacement ellipsoids even when the CF_3 groups were refined with restraints to give nearly ideal tetrahedral geometries at the C atoms. For **1**, one CF_3 group was found to be ordered, while the other two were refined with three orientations of idealized CF_3 groups (total population of 1). During the final stages of refinement, these populations were fixed and a common isotropic thermal parameter for all fluorine atoms was refined. For **5**, two orientations of each CF_3 group were employed with total occupancies summing to 1, and with a common isotropic thermal parameter for each fluorine atom. The formate derivative **4** also exhibits disorder in one of the formate ligands. The terminal HCO_2^- group shows two sites with roughly equal populations for the non-metal-bound O atom.

Results and Discussion

Syntheses

The triethanolamine ligand readily binds to the copper(II) ion [14], and in the absence of coordinating ligands such as carboxylate ions produces tetrameric $[\{Cu(TEAH)\}_4]$ (**6**). In pursuing other synthetic routes to **6**, we attempted to treat copper(II) acetate directly with $TEAH_3$, with the idea that removal of volatile acetic acid would drive the reaction to completion. Upon heating, solutions of copper(II) acetate and $TEAH_3$ emitted a strong smell of acetic acid. Characterization of crystals from the first attempt at this reaction showed, that the acetate ligands were not completely replaced. Instead mixed complexes containing both triethanolamine residues and carboxylate were obtained. Based upon these observations, a variety of heteroleptic copper(II) carboxylate complexes of $[TEAH_2]^-$ or $[TEAH]^{2-}$ were prepared via syntheses in aqueous or methanolic solutions by either the addition of $TEAH_3$ to a copper(II) carboxylate solution or the addition of a copper(II) carboxylate to **6**. In the first method, the reaction is an equilibrium between free $TEAH_3$ and metal-bound carboxylate, versus metal-bound $[TEAH_{3-x}]^{x-}$ and free carboxylic acid. This equilibrium can be shifted by the removal of the volatile carboxylic acid product (Equation (1)).

$$TEAH_3 + Cu(O_2CR)_2 \rightarrow [Cu(O_2CR)\,(TEAH_2)] + RCO_2H\uparrow \quad (1)$$

Because this approach depends upon the removal of the carboxylic acid, it does not work well for the heavier carboxylates due to their lower volatility, and therefore a different route to synthesize complexes of the less volatile carboxylic acids was sought. This was accomplished by the stoichiometric addition of $[\{Cu(TEAH)\}_4]$ to an *in situ*-prepared copper(II) carboxylate. The latter was synthesized by first producing a slurry of '$Cu(OH)_2$' via the reaction of aqueous copper(II) sulfate and sodium carbonate followed by treatment with an appropriate carboxylic acid. In the case of trifluoroacetic acid, if residual sodium ions from the sodium carbonate employed are not removed, a double salt of sodium trifluoroacetate and copper(II) acetate coordinated by $TEAH_3$ is obtained.

The formulations of the compounds observed show different degrees of displacement of the anionic carboxylate ligands by a triethanolamine-derived ligand. For Compounds **1** and **2** the ratio of $TEAH_3$ to Cu is 1:1. Compound **1** shows a neutral, non-deprotonated form of the $TEAH_3$ ligand, based upon the charge balance (one Na^+ ion, one Cu^{2+} ion and three $CF_3CO_2^-$ ions). This simple coordination of $TEAH_3$ is unique for this series of compounds as the other compounds show either single or double deprotonation of $TEAH_3$ upon complexation. The dinuclear benzoate derivative is also a 1:1 complex between copper and a $TEAH_3$-derived ligand, but here the single deprotonation of $TEAH_3$ allows for the elimination of one carboxylate ligand producing $[Cu(C_6H_5CO_2)(TEAH_2)]_2$ (**2**). The known tetranuclear complex **6** is also a 1:1 complex, but here the amine ligand is doubly deprotonated so that the copper valence is completely satisfied by the chelating ligand and no other ligands are present. For the trinuclear species **3**, **4**, and **5**, the stoichiometry is 3:2 (Cu: $TEAH_2^-$), so the complexes may be viewed as triethanolamine poor relative to **1** and **2**. One way of viewing these compositions is as 2:1 adducts of $TEAH_2^-$/carboxylate complexes analogous to **2** with an additional equivalent of copper(II) carboxylate:$[Cu(O_2CR)(TEAH_2)]_2[Cu(O_2CR)_2]$.

Structures

Compound **1** is a double salt of sodium trifluoroactetate and copper(II) trifluoroacetate, with a neutral triethanolamine ligand, $TEAH_3$, coordinated to the copper atom. The asymmetric unit of the structure is shown in Figure 1. The overall composition is $[NaCu(CF_3CO_2)_3(TEAH_3)]_\infty$. For ease of discussion, the three acetate units will be described as trifluoroacetate(x), where x = 4, 5, or 6, corresponding to the atom labels C(x1), C(x2), O(x1) and O(x2). This compound is polymeric in the solid state forming an infinite 2-dimensional sheet (Figure 2). Trifluoroacetate(6) is bound in a terminal fashion only to the sodium ion, while trifluoroacetates(4) and (5) bridge between the Na^+ ions and the Cu^{2+} centers. Two oxygen atoms (O(21) and O(31)) of the $TEAH_3$ ligand on one copper center also bridge to one sodium ion, while O(11) bridges to a different Na^+ ion.

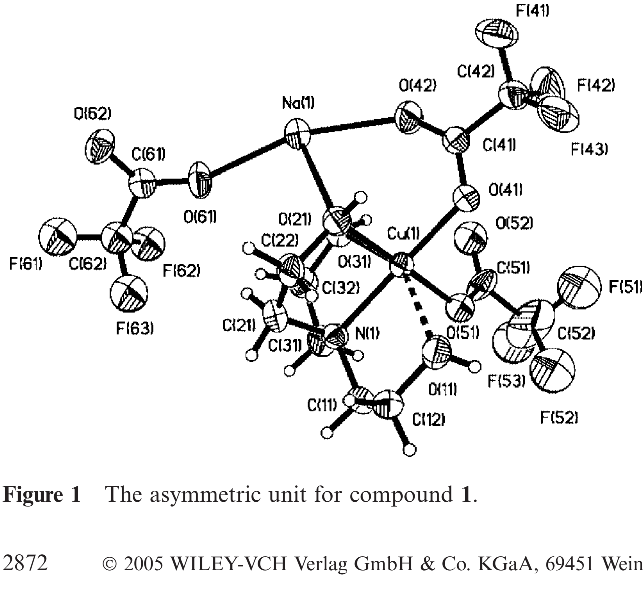


Figure 1 The asymmetric unit for compound **1**.

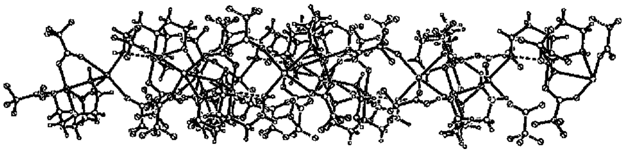


Figure 2 A partial packing diagram of **1** showing the 2-dimensional sheet-like structure.

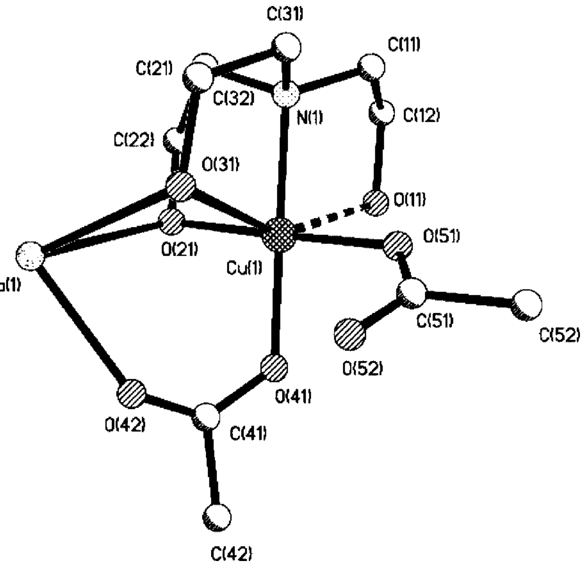


Figure 3 A ball and stick plot showing the Cu^{2+} coordination environment in **1**.

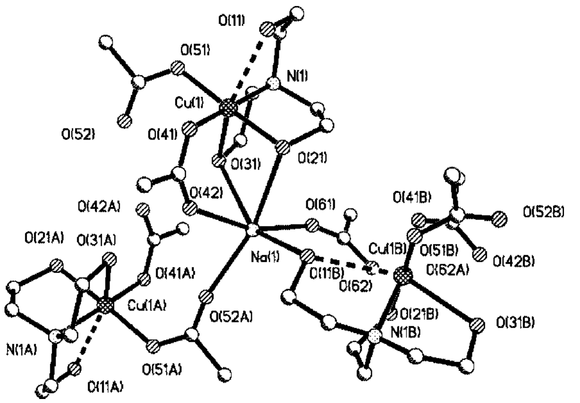
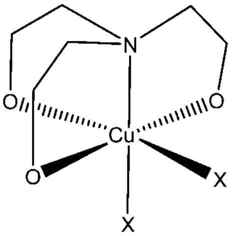


Figure 4 A ball and stick plot showing the Na^+ coordination environment in **1**.

Overall, this provides distorted octahedral coordination for both Cu^{2+} (Figure 3) and Na^{+} ions (Figure 4). The Cu^{2+} ion is thus coordinated by the nitrogen and three oxygen atoms of the $TEAH_3$ ligand as well as two carboxylate oxygen atoms. As with all of the copper $TEAH_{3-x}^{x-}$ ($x = 0 - 2$) complexes observed to date, the $N(CH_2CH_2O)_3$ unit coordinates the metal with the oxygen atoms in a meridional configuration, **I**. The $Cu\text{-}O_{TEAH_3}$ distances, as with other $TEAH_3$ derivatives such as **6** are highly asymmetric, ranging from 1.967(5) to 2.642(6) Å [14]. The $Cu^{2+}\text{-}O_{trifluoroacetate}$ distances are shorter at 1.936(6) and 1.942(5) Å. The $Na^{+}\text{-}O_{TEAH_3}$ distances range from 2.570(6) to 2.717(6) Å, while the $Na^{+}\text{-}O_{trifluoroacetate}$ distances are shorter, lying between 2.298(6) and 2.404(7) Å. As seen in Table 3, the angles about Na^{+} and Cu^{2+} are also highly distorted from the idealized 90 and 180° values expected for a regular octahedron.



I

The benzoate derivative **2** can be viewed as a dimer of two neutral $Cu(TEAH_2)(C_6H_5CO_2)$ units. The dimerization is achieved through the bridging of one oxygen atom of each $TEAH_2^{-}$ unit to the adjacent Cu^{2+} ion, and the molecule possesses crystallographic inversion symmetry. The carboxylate groups are bound in a terminal fashion to each copper atom. As indicated in Table 4 and Figure 5, the $Cu\text{-}O_{TEAH_3}$ distances are highly asymmetric (Table 4) ranging from 1.951(3) to 2.570(4) Å. With all interactions to copper included, the metal center can be viewed as a highly distorted octahedron similar to **1**.

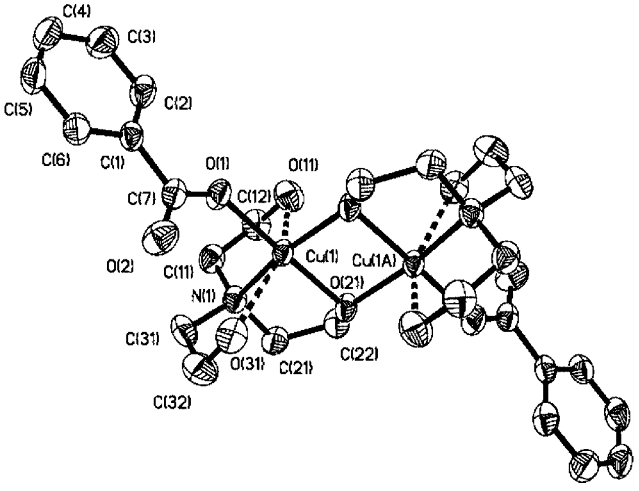


Figure 5 Thermal ellipsoid plot of compound **2**. Hydrogen atoms have been omitted for clarity.

The linear trinuclear motif appears to be a favored arrangement, and such compositions have been observed for the acetate, formate, and trifluoroacetate ligands. The core structure has been observed previously for related complexes based upon N,N-2-diethylaminoethanol: $[Cu_3(RCO_2)_4(Et_2NCH_2CH_2O)_2]$ although those compounds were found to have C_2 symmetry rather than *i* as found here [19−24]. All of these compounds have very simi-

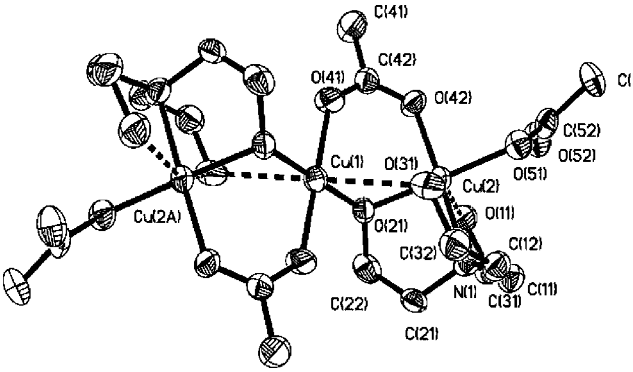


Figure 6 Thermal ellipsoid of unsolvated compound **3**. Hydrogen atoms have been omitted for clarity.

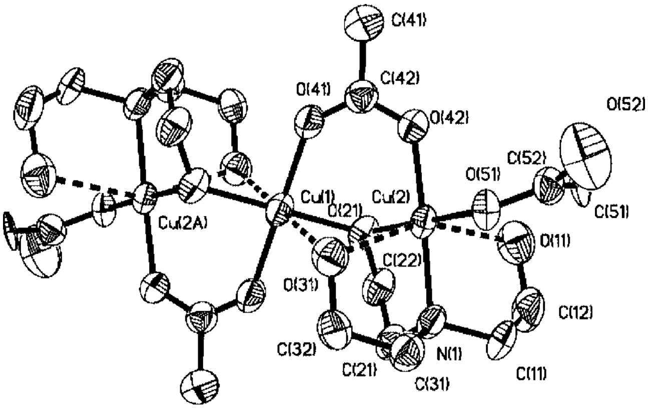


Figure 7 Thermal ellipsoid of monoclinic version of methanol solvated compound **3**·2MeOH. Hydrogen atoms have been omitted for clarity.

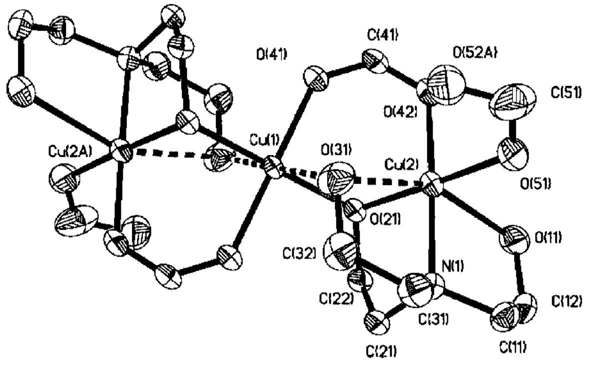


Figure 8 Thermal ellipsoid of the formate derivative compound **4**. Hydrogen atoms have been omitted for clarity.

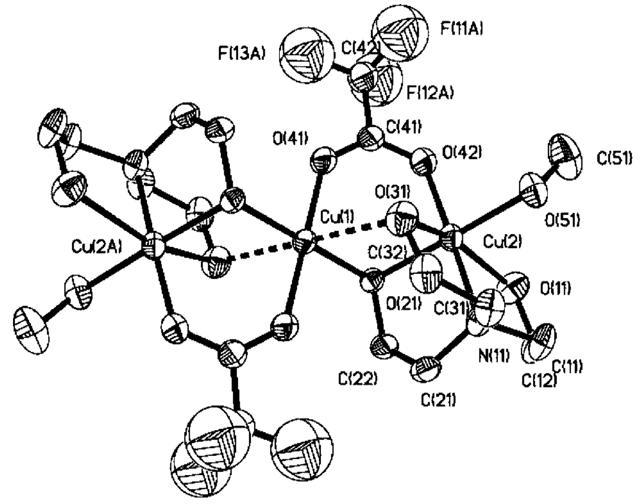
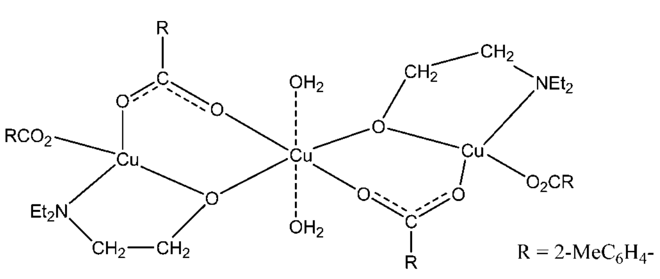


Figure 9 Thermal ellipsoid plot of the trinuclear trifluoroacetate derivative **5**. Hydrogen atoms have been omitted for clarity.

lar structural features and trends in bond distances and angles. A comparison of all the compounds is found in Table 5. The compounds all possess a central Cu atom that is bridged to two other Cu atoms through carboxylate ions as well as via two oxygen atoms of the TEAH$_2^-$ ligand attached to the end copper atoms, with distances to O(31) are very long in each case (Figures 6 − 9), although these distances are very much longer (~0.2 Å) for the acetate structures as compared to both the formate and trifluoroacetate structures. This may arise from the weaker acidity of acetic acid (pK_a = 4.75) than for formic acid (pK_a = 3.75) and trifluoroacetic acid (pK_a = 0), which in turn is related to the electron donating/withdrawing capability of R in the RCO$_2$H. One might expect even stronger bonding of the triethanolamine oxygen atoms to copper for the trifluoroacetate derivative as compared to the formate compound; however, compound **5** differs in the number of carboxylate ions bound directly to the metals (*vide infra*) making comparisons less clear. As with **1** and **2** the central copper atoms Cu(1) in all compounds can be viewed as highly distorted octahedral centers considering the binding of O(31), or as square planar copper centers if those long interactions are neglected. This situation is similar to that encountered for the long interactions as in the related trinuclear ethanolamine complexes [Cu$_3$(OCH$_2$CH$_2$NEt$_2$)$_2$(O$_2$C$_6$H$_4$Me-2)$_4$](H$_2$O)$_2$ [19] (**II**) in which the central copper atom is ligated by two water molecules in addition to the two carboxylate and two ethanolamine oxygen atoms.



II

The end copper atoms are also roughly octahedral but there is a substantial difference between the acetate and formate complexes as compared to the trifluoroacetate derivative. For both acetate and formate, the end copper atoms have their coordination spheres completed by bonding to the four donor atoms of the TEAH$_2^-$ ligands, a carboxylate ligand, which bridges to the central copper center and a terminal carboxylate. Both of these molecules show crystal morphologies that include in the lattice two molecules (when considered at full occupancy) of methanol per trinuclear copper complex. In the case of the trifluoroacetate derivative, however, the end copper atoms are not bound to a terminal carboxylate ligand. Instead, these atoms are attached to methanol solvent and the additional trifluoroacetate ions are located in the crystal lattice. One can consider these as examples of coordination isomerism: [Cu$_3$(RCO$_2$)$_2$(TEAH$_2$)$_2$(solvent)$_2$][RCO$_2$]$_2$ versus [Cu$_3$(RCO$_2$)$_4$(TEAH$_2$)$_2$]·2(solvent). Given the ability of triethanolamine to exist with several degrees of protonation coupled with the coordination isomerism, there could be some ambiguity about whether the CF$_3$CO$_2$ units in the lattice are present as CF$_3$CO$_2^-$ or CF$_3$CO$_2$H given the difficulty of identifying hydrogen atoms in the X-ray structure; however, it appears unlikely that a relatively strong acid such as trifluoroacetic acid would exist simultaneously with a metal bound-alkoxide ligand, as would be required if the CF$_3$CO$_2$H were the species present in the lattice.

Magnetic Data for Compound 2

The temperature dependence of the magnetic susceptibility of **2** in the temperature range 2-300 K is shown in Figure 10. As expected, the magnetic behavior of **2** resembles that of related dinuclear compounds. At room temperature χ_MT is 0.91 cm^3·mol^{-1}·K. This value is slightly larger than that expected for a magnetically uncoupled dinuclear Cu^{II} compound (0.82 cm^3·mol^{-1}·K, given a g = 2.1). Upon cooling the sample, χ_MT increases and reaches a maximum at 8 K of 1.3 cm^3·mol^{-1}·K. This behavior is characteristic of strong ferromagnetic exchange coupling between the ad-

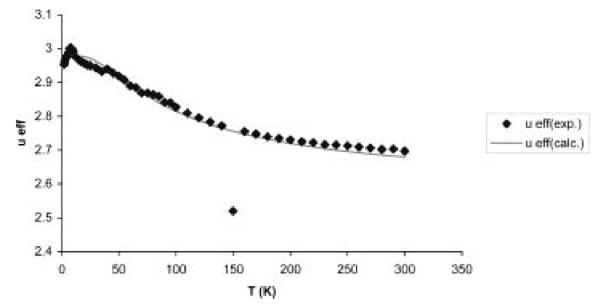


Figure 10 Magnetic data for Compound **2·2H$_2$O** showing a fitted plot of μ_{eff} versus T(K).

jacent Cu^{II} atoms [19, 25]. Below this maximum the $\chi_M T$ product decreases rapidly down to 1.09 $cm^3 \cdot mol^{-1} \cdot K$.

The appropriate Heisenberg-Hamiltonian for two paramagnetic centers is the simple isotropic:

$$\hat{H} = -J\hat{S}_1\hat{S}_2$$

where $S_1 = S_2 = 1/2$, and zero field splitting (ZFS) effects have again been ignored [25]. The exchange parameter J refers to the interaction between both copper centers. The resulting spin levels $|S_T = S_1+S_2,\ S^+ = S_1+S_2\rangle$ for two interacting $S_i = 1/2$ centers gives two doublets $|1, 1\rangle$ and $|0, 0\rangle$. From this Hamiltonian the following version of the Bleaney-Bowers expression for the temperature dependence of χ is derived:

$$\chi_{calcd}(T) = \frac{2N_A\mu_B^2 g^2}{3k(T-\theta)}\left[1 + \frac{1}{3}\exp\left(\frac{-2J}{kT}\right)\right]^{-1}$$

where θ, the Weiss constant, is included to account for the decrease in magnetic moments at low temperatures which is caused by ZFS [19, 26]. Fitting the experimental data with equation (**4**) using MAGMUN afforded J = 70.5 (4.6) cm^{-1}, $g = 2.11$ (0.006), TIP = 0, $\theta = -0.02$, and R = 1.6 E −7 (where R is calculated from the expression $R = \{\Sigma_i[(\chi_M T)_{obs,i} - (\chi_M T)_{calcd,i}]^2 / \Sigma_i[(\chi_M T)_{obs,i}]^2\}$) [25, 27]. The *g* tensor values evaluated from the fits are comparable to those found in similar dinuclear compounds, and the coupling constant J is indicative of strong ferromagnetic coupling, albeit at low temperatures.

Magnetic Data for Compounds 3, 4 *and* 5

The appropriate isotropic Heisenberg-Hamiltonian for three paramagnetic centers in C_{2v} symmetry has the form which should also appropriate for the inversion-symmetric compounds reported here [19]:

$$\hat{H} = -2J_{12}(\hat{S}_1\hat{S}_2 + \hat{S}_2\hat{S}_3) - 2J_{13}(\hat{S}_1\hat{S}_3),$$

where the occurrence of axial ZFS between the Kramer doublets has not been included [25]. The exchange parameters J_{12} and J_{13} refer to the interaction between the two adjacent centers and the interactions between the terminal centers, respectively. The resulting spin levels $|S_T = S_1+S_2+S_3,\ S^+ = S_1+S_3\rangle$ for three interacting $S_i = 1/2$ centers are one quartet $|3/2, 1/2\rangle$, and two doublets, $|1/2, 0\rangle$ and $|1/2, 1\rangle$, with energies of $E(3/2,1/2) = -J_{12} - 1/2J_{13}$, $E(1/2,0) = 3/2J_{13}$, and $E(1/2,1) = 2J_{12} - 1/2J_{13}$, respectively. Applying this to the van Vleck equation, the following theoretical expression for the temperature dependence of χ is obtained [19]:

$$\chi_{calcd}(T) = \frac{N_A g^2\mu_B^2}{12k(T-\theta)} \cdot \frac{10\exp(J_{12}/kT) + \exp(-2J_{12}/kT) + \exp(-2J_{13}/kT)}{2\exp(J_{12}/kT) + \exp(-2J_{12}/kT) + \exp(-2J_{13}/kT)} + N\alpha$$

where θ, the Weiss constant, is included to account for the decrease in magnetic moments at low temperatures which is caused by ZFS. Fitting the experimental data with equation (**2**) using MAGMUN afforded the J_{12}, J_{13}, *g*, TIP, and θ parameters [27]. These parameters and R (where R is calculated from the expression $R = \{\Sigma_i[(\chi_M T)_{obs,i} - (\chi_M T)_{calcd,i}]^2 / \Sigma_i[(\chi_M T)_{obs,i}]^2\}$) are summarized in Table 6 for compounds **3**, **4**, and **5**[25].

Table 6 Magnetic Parameters for Compounds **3**·2MeOH, **4**·1.70MeOH, and **5**.

Compound	J_{12} /cm^{-1}	*g*	θ /K	R
1	65(2)	2.21(0.07)	−0.6	8.2 E-6
4	88.9(3.6)	2.07(0.01)	−1.4	1.7 E-6
5	70.8 (1.5)	2.25 (0.003)	−0.2	4.6 E-7

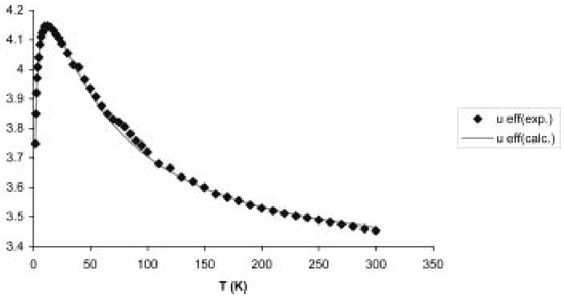


Figure 11 Magnetic data for Compound **3**·2MeOH showing a fitted plot of μ_{eff} versus T(K).

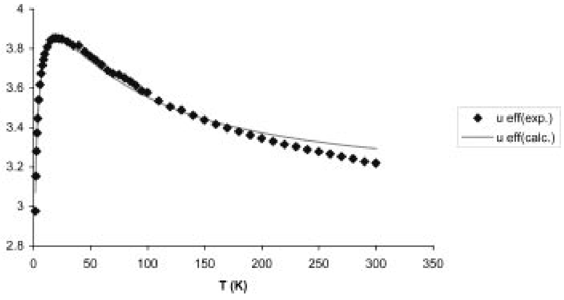


Figure 12 Magnetic data for Compound **4**·1.70MeOH showing a fitted plot of μ_{eff} versus T(K).

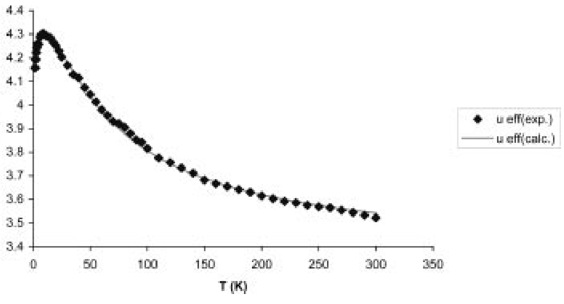


Figure 13 Magnetic data for Compound **5** showing a fitted plot of μ_{eff} versus T(K).

Fits were conducted both by fixing the terminal coupling parameter at $J_{13} = 0$ and by allowing it to vary freely. In the latter case the free fit parameter was insignificantly small, converging to $J_{13} \approx 0\ \mathrm{cm}^{-1}$, and did not improve the quality of the fits. The *g* tensor values evaluated from the fits are comparable to those found in similar trimeric compounds [25]. The J_{12} exchange parameters in Table 6 are indicative of strong ferromagnetic coupling, albeit at low temperatures [19, 24, 25].

The temperature dependence of the molar magnetic susceptibility $\chi_M T$ of **3**, **4**, and **5** in the temperature range 2-300 K are shown in Figures 11−13. As expected, the magnetic behavior of compounds **3**, **4**, and **5** resembles that of related trinuclear compounds [19−24]. At room temperature $\chi_M T$ is 1.49, 1.30 and 1.55, $\mathrm{cm^3 \cdot mol^{-1} \cdot K}$ for **3**, **4** and **5**, respectively. These values are somewhat larger than those expected for a magnetically uncoupled trinuclear $\mathrm{Cu^{II}}$ compound (1.23 $\mathrm{cm^3 \cdot mol^{-1} \cdot K}$, given a $g = 2.1$). Upon cooling the samples, $\chi_M T$ increases and reaches a maximum at 12.5 K of 2.15 $\mathrm{cm^3 \cdot mol^{-1} \cdot K}$ for **3**, at 20 K of 1.86 $\mathrm{cm^3 \cdot mol^{-1} \cdot K}$ for **4** and at 9 K of 2.32 $\mathrm{cm^3 \cdot mol^{-1} \cdot K}$ for **5**. This behavior is characteristic of strong ferromagnetic exchange coupling between the adjacent $\mathrm{Cu^{II}}$ atoms in trinuclear $\mathrm{Cu^{II}}$ species. Below these maxima the $\chi_M T$ product decreases rapidly down to 1.76 $\mathrm{cm^3 \cdot mol^{-1} \cdot K}$ (**3**), 1.11 $\mathrm{cm^3 \cdot mol^{-1} \cdot K}$ (**4**) and 2.16 $\mathrm{cm^3 \cdot mol^{-1} \cdot K}$ (**5**),which is most likely due to ZFS within the quadruplet ground state.

Conclusions

Heteroleptic complexes of copper(II) carboxylates with triethanolamine are readily obtained by direct reaction of $\mathrm{Cu(O_2CR)_2}$ with $\mathrm{TEAH_3}$ or $[\{\mathrm{Cu(TEAH)}\}_4]$ in stoichiometric amounts. By control of the reaction conditions, mononuclear, dinuclear or trinuclear complexes may be obtained.

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