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Mixed-Metal Complexes Containing Unusual Eight-Coordinate [Cu(carboxylato)$_4$] Cores: Structures of $[LiCu(bet)_4]_n(ClO_4)_{3n}$ and $[CaCu(bet)_4(NO_3)_2(H_2O)]_2[Ca(NO_3)_4(H_2O)]_2$ (bet = $Me_3N^+CH_2CO_2^-$)

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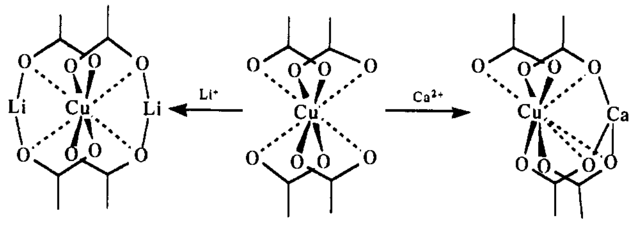
The linkage of Li(I) and Ca(II) ions to the eight-coordinate $[Cu(\eta\text{-}Me_3NCH_2CO_2\text{-}O,O')_4]$ core results in the new complexes $[LiCu(bet)_4]_n(ClO_4)_{3n}$ (**2**) and $[CaCu(bet)_4(NO_3)_2(H_2O)]_2[Ca(NO_3)_4(H_2O)]_2$ (**3**) (bet = $Me_3N^+CH_2CO_2^-$). X-ray structural analysis has revealed that **2** comprises an infinite cationic column with each pair of the eight-coordinate cores bridged by a Li(I) atom, featuring the shortest weak Cu–O(carboxylate) bond [2.705(5) Å] among its type, whereas **3** contains a heterodinuclear Cu–Ca cation consolidated by an uncommmon triple carboxylato-*O,O′* bridge with the Cu(II) atom surrounded by the four chelate groups in a three-up/one-down eight-coordinate arrangement. The dinuclear anion in **3** contains three kinds of nitrato ligands acting in bridging, bidentate chelate, and unidentate modes. Crystal data for **2** (21 °C): tetragonal, space group $P\bar{4}2m$ (No. 111), $a = 12.096(3)$ Å, $c = 6.2330(7)$ Å, $V = 911.8(3)$ Å^3, $Z = 1$; $R = 0.051$ ($R_w = 0.060$) for 613 data with $I > 1.5\sigma(I)$. Crystal data for **3** (21 °C): monoclinic, space group $P2_1/n$ (No. 14), $a = 12.105(2)$ Å, $b = 22.796(9)$ Å, $c = 15.572(4)$ Å, $\beta = 90.63(1)°$, $V = 4297(2)$ Å^3, $Z = 2$; $R = 0.069$ ($R_w = 0.053$) for 4690 data with $I > 3\sigma(I)$.

Introduction

In contrast to the chemistry of the extensively investigated well-known dimeric copper(II) carboxylates, the structural chemistry of copper(II) complexes rich in carboxylate ligands remains virtually undeveloped,[1] which may arise from difficulties with charge compensation and the incorporation of appropriate countercations. Consequently, copper(II) carboxylates of high coordination numbers are rare, and hitherto only a very limited number of structurally characterized eight-coordinate complexes have been reported. The first two examples, namely polymeric $[CaCu(MeCO_2)_4(H_2O)_2]_n\cdot 4nH_2O$[2] and discrete $[Cu(aha)_4](ClO_4)_2$ (aha = 6-aminohexanoic acid),[3] have been subjected to polarized single-crystal electronic and ESR investigations which confirmed that the long Cu···O contact up to 2.88(1) Å reflects a significant though weak metal–ligand bonding interaction.[4] The other two known examples are the double salts $[Rb_2Cu(pht)_2(H_2O)_2]_n$ and $[Li_2Cu(pht)_2(H_2O)_4]_n$ (pht = *o*-phthalate),[5] in which the long Cu–O contacts range from 2.770(4) to 3.072(5) Å.

In the course of our systematic investigation of metal–betaine complexes, we have taken advantage of the zwitterionic betaine ligands to prepare complexes in different metal–ligand stoichiometries.[6] Furthermore, the permanent dipolarity of betaines may facilitate the charge compensation problem in attaching carboxylate-like ligands to metal centers, and accordingly we recently isolated and characterized the discrete eight-coordinate complex $[Cu(bet)_4](NO_3)_2$ (**1**) (bet = betaine, $Me_3N^+CH_2CO_2^-$).[6a] In view of the possibility that the $[Cu(\eta\text{-carboxylato-}O,O')_4]$ core can further coordinate to other group IA and group IIA metal ions through μ-oxygen bridging, our subsequent work has been directed toward the preparation of mixed-metal complexes in the hope of generating new structural varieties and observing concomitant perturbation of the coordination geometry about Cu(II). Although mixed Cu(II)–M complexes [M = Na(I), Mg(II), Zn(II)] cannot be obtained by reacting **1** with the corresponding nitrate salts, repeated attempts have resulted in the successful attachment of two kinds of metal ions, Li(I) and Ca(II), to the $[Cu(\eta\text{-carboxylato-}O,O')_4]$ core, giving rise to two novel mixed-metal complexes, namely $[LiCu(bet)_4]_n(ClO_4)_{3n}$ (**2**) and $[CaCu(bet)_4(NO_3)_2(H_2O)]_2[Ca(NO_3)_4(H_2O)]_2$ (**3**).



2 1 3

Experimental Section

Preparation of $[LiCu(bet)_4]_n(ClO_4)_{3n}$ (2). A mixture of betaine hydrate (0.540 g, 4.0 mmol) and $Cu(ClO_4)_2\cdot 6H_2O$ (0.185 g, 1.0 mmol) was dissolved in hot water (4 mL, 70 °C), forming a clear blue solution. $LiClO_4\cdot 3H_2O$ (0.320 g, 2.0 mmol) was next added and the solution stirred for 5 min. The resulting solution was allowed to stand in air for 5 days to yield deep blue needle-shaped crystals. IR data (KBr pellet; cm^{-1}): 3409 vs (br), 3058 m, 3044 m, 3009 m, 2959 m, 1648 vs, 1497 m, 1476 s, 1455 m, 1398 s, 1321 s, 1244 w, 1110 s, 1096 s, 1082 s, 1061 m, 984 w, 962 w, 927 m, 906 m, 723 m, 625 s, 576 w.

Preparation of $[CaCu(bet)_4(NO_3)_2(H_2O)]_2[Ca(NO_3)_4(H_2O)]_2$ (3). To an aqueous solution (3 mL) containing **1** (0.328 g, 0.50 mmol)[6a] was added $Ca(NO_3)_2\cdot 4H_2O$ (0.236 g, 1.0 mmol). After 10 min of stirring, the resulting clear blue solution was allowed to stand for several days;

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Table 1. Crystallographic Data for Complexes **2** and **3**[a]

	2	**3**
chem formula	$C_{20}H_{44}N_4CuLiCl_3O_{20}$	$C_{20}H_{96}N_{20}Cu_2Ca_4O_{56}$
fw	837.51	2040.96
color and habit	deep-blue needle	deep-blue block
a, Å	12.096(3)	12.105(2)
b, Å	12.096(3)	22.796(9)
c, Å	6.233(1)	15.572(4)
β, deg	90	90.63(1)
V, Å^3	911.8(3)	4297(2)
Z	1	2
space group	$P\bar{4}2m$ (No. 111)	$P2_1/n$ (No. 14)
F(000)	436	2124
ρ(calcd), g/cm^3	1.525	1.577
ρ(obsd), g/cm^3	1.520	1.572
cryst size, mm^3	0.16 × 0.20 × 0.50	0.22 × 0.36 × 0.24
μ, cm^{-1}	8.98	8.40
transm coeff	0.679–0.708	0.663–0.719
collection range; $2\theta_{max}$	h,k,l; 55	$h,k,\pm l$; 50
no. of unique data measd	1124	7568
no. of obsd data,[b] n	613	4690
no. of variables, p	73	551
R[c]	0.053	0.069
R_w[d]	0.062	0.053
S(GOF)[e]	1.670	1.883

[a] Complex **2** = $[LiCu(bet)_4]_n(ClO_4)_{3n}$ and complex **3** = $[CaCu(bet)_4(NO_3)_2(H_2O)]_2[Ca(NO_3)_4(H_2O)]_2$; bet = $Me_3N^+CH_2CO_2^-$. [b] With $I \geq 1.5\sigma(I)$ for **2** and $I \geq 3\sigma(I)$ for **3**. [c] $R = \sum\Delta/\sum|F_o|$. [d] $R_w = (\sum w\Delta^2/\sum w|F_o|^2)^{1/2}$. [e] $S = [w\Delta^2/(n-p)]^{1/2}$, $\Delta = ||F_o| - |F_c||$; weighting scheme $w = [\sigma^2(F_o) + K|F_o|^2]^{-2}$, 10^4K = 2 and 15 for complexes **2** and **3**, respectively.

deep blue block crystals were then deposited. IR data (KBr pellet; cm^{-1}): 3402 s (br), 3051 m, 3042 m, 2995 m, 1634 vs (br), 1496 m, 1476 s, 1406 vs, 1335 vs, 1235 m, 991 w, 963 m, 934 s, 723 s.

X-ray Structural Analysis of 2 and 3. A summary of selected crystallographic data for **2** and **3** is given in Table 1. Data collection was carried out on a Nicolet R3m/V diffractometer using graphite-monochromated Mo Kα (λ = 0.710 73 Å) radiation at 295 K.

For both complexes, determinations of the crystal class, orientation matrix, and cell dimensions were performed according to established procedures.[7] The intensities were collected using the variable ω-scan mode. Two standard reflections were monitored after every 120 data measurements, showing only small random variations. The raw data were processed with the learned-profile procedure,[8] and absorption corrections were applied by fitting a pseudoellipsoid to the ψ-scan data of selected strong reflections over a range of 2θ angles.[9]

Most non-hydrogen atoms in the crystal structures of **2** and **3** were located with the Patterson superposition method, and subsequent difference Fourier syntheses were employed to recover the remaining non-hydrogen atoms. All the non-hydrogen atoms were refined anisotropically except the disordered perchlorate oxygen atoms in **2**, which were subjected to geometric constraints and refined isotropically. Hydrogen atoms of the organic ligands were generated geometrically (C–H bond lengths fixed at 0.96 Å), assigned appropriate isotropic thermal parameters, and allowed to ride on their parent carbon atoms; and hydrogen atoms of the aqua ligands in **3** were located from difference maps and assigned isotropic thermal parameters. All the hydrogen atoms were held stationary and included in structure factor calculations in the final stage of full-matrix least-squares refinement.

All computations were performed with the SHELXTL-PLUS program package on a DEC Micro VAX-II computer.[10] Analytical expressions of neutral-atom scattering factors were employed, and anomalous-dispersion corrections were incorporated.[11] The atomic coordinates of **2** and **3** are given in Tables 2 and 3, respectively. Selected bond lengths and angles for **2** are presented in Table 4, and those for **3**, in Table 5. Additional crystallographic data are available as supplementary material.

Table 2. Atomic Coordinates (×10^4) and Equivalent Isotropic Thermal Parameters (Å^2 × 10^3) for Complex **2**[a]

	x	y	z	U(eq)[b]
Cu(1)	0	0	0	28(1)
Li(1)	0	0	−5000	36(4)
O(1)	1151(3)	1151(3)	85(12)	41(1)
O(2)	961(3)	961(3)	−3454(9)	52(1)
C(1)	1380(4)	1380(4)	−1869(11)	35(1)
C(2)	2266(4)	2266(4)	−2056(10)	38(2)
N(1)	2599(4)	2599(4)	−4300(10)	44(1)
C(3)	3081(6)	1643(7)	−5544(11)	66(2)
C(4)	3471(5)	3471(5)	−3996(17)	77(3)
Cl(1)	5000	5000	0	83(1)
O(01)	4331(6)	4331(6)	1287(18)	148(4)
Cl(2)	5000	0	0	66(1)
O(02)	5237(84)	−1040(30)	906(117)	116(25)
O(03)	6169(8)	0	0	103(8)
O(04)	4532(23)	−434(22)	1863(31)	87(8)
O(05)	4029(19)	−226(30)	−1155(52)	69(9)
O(06)	5111(110)	1171(15)	−177(139)	100(19)
O(07)	5000	0	2247(15)	93(7)

[a] sof = 0.6, 0.7, 0.9, 0.6, 0.6, and 0.6 for O(02), O(03), O(04), O(05), O(06), and O(07), respectively. [b] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Results and Discussion

As expected, the crystal structure of **2** is similar to that of the polymeric Cu(II)–Ca(II) complex,[2] featuring an infinite cationic column in which each pair of adjacent Cu(II) and Li(I) atoms are doubly bridged by a pair of bet ligands (Figure 1), with disordered perchlorate anions filling the intercolumnar space in the crystal packing. As in the case of **1**, the Cu(II) atom, occupying Wyckoff position 1(a) of site symmetry $\bar{4}2m$ (D_{2d}), is coordinated by four carboxylate groups of the bet ligands with four short Cu–O bonds [Cu–O = 1.970(4) Å] in an idealized square-planar fashion, the most distorted angle being O(1)–Cu(1)–O(1b) at 176.2(6)°. The coordination sphere of the metal atom is completed by the remaining four caroboxylate O(2) atoms at much longer contacts of Cu(1)–O(2) = 2.706(5) Å. The bet ligands, as located at Wyckoff positions 4(n) of symmetry m, coordinate the Cu(II) atom in an alternatively up/down fashion; thus the coordination geometry about the Cu(II) atom can be described as a (4+4*) distorted dodecahedron. Analogous stereochemistry has been found in **1** and the polymeric Cu–Ca acetato complex.[2] The most striking feature in **2** is that its long Cu–O bond [2.705(5) Å] is significantly shorter than the corresponding values [≥2.770(4) Å] for all other related complexes possessing analogous [Cu(carboxylato)$_4$] units.[6a]

As depicted in Figure 1, two pairs of the long-bonded oxygen atoms of the *trans*-related carboxylate groups from adjacent $[Cu(bet)_4]^{2+}$ cores chelate to a Li(I) ion located at Wyckoff position 1(c) of symmetry $\bar{4}2m$, resulting in tetrahedral coordination about the Li(I) atom with Li–O = 1.905(5) Å and O–Li–O = 104.8(1)–119.1(3)°. The Li–O distance is significantly shorter than the mean value (1.957 Å) for known tetrahedral lithium(I) carboxylates.[13] As the coordination geometry of the $[Cu(bet)_4]^{2+}$ core in **2** is similar to that of the discrete $[Cu(bet)_4]^{2+}$ ion in **1**, the polymeric structure can be considered primarily as an assembly of alternate discrete $[Cu(bet)_4]^{2+}$ cations and Li(I) ions with a nonbonded Cu(I)···Li(I) spacing of $c/2$ = 3.116(1) Å.

The main difference between the $[Cu(bet)_4]^{2+}$ core in **2** and the discrete $[Cu(bet)_4]^{2+}$ in **1** is that the long Cu–O bonds in the former are much shorter, concomitant with significantly smaller Cu–O–C angles. These changes in the geometrical parameters

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Table 3. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters (Å^2; $\times 10^4$ for Cu and Ca; $\times 10^3$ for Others) for Complex **3**

	x	*y*	*z*	*U*(eq)[a]
Cu(1)	2073(1)	2540(1)	649(1)	279(3)
Ca(1)	4869(1)	3078(1)	497(1)	290(4)
Ca(2)	5595(1)	389(1)	1186(1)	355(5)
O(1w)	5717(4)	2154(2)	654(3)	60(2)
N(1)	6360(6)	3518(3)	–836(4)	47(3)
O(1)	5447(5)	3731(2)	–737(3)	70(2)
O(2)	6578(6)	3110(3)	–382(5)	143(4)
O(3)	7027(5)	3690(3)	–1361(4)	81(3)
N(2)	6064(5)	3830(3)	1696(4)	45(2)
O(4)	5260(5)	4020(2)	1277(3)	66(2)
O(5)	6330(4)	3311(3)	1568(4)	70(2)
O(6)	6568(5)	4141(2)	2206(3)	68(2)
O(11)	2497(4)	1745(2)	1075(3)	33(2)
O(12)	673(4)	1716(2)	967(3)	46(2)
C(11)	1557(6)	1493(3)	1171(4)	30(2)
C(12)	1680(5)	915(3)	1644(4)	39(3)
N(11)	639(5)	546(2)	1710(3)	42(2)
C(13)	–283(6)	855(3)	2152(4)	53(3)
C(14)	280(7)	352(4)	855(5)	93(4)
C(15)	931(8)	20(3)	2258(6)	96(5)
O(21)	2134(3)	2273(2)	–531(3)	35(2)
O(22)	3947(3)	2441(2)	–481(3)	42(2)
C(21)	3096(6)	2268(3)	–849(4)	28(2)
C(22)	3106(5)	2001(3)	–1746(4)	31(2)
N(21)	4201(4)	1993(2)	–2206(3)	32(2)
C(23)	5061(5)	1639(3)	–1743(4)	48(3)
C(24)	4004(6)	1719(4)	–3070(4)	65(3)
C(25)	4610(6)	2609(3)	–2341(4)	49(3)
O(31)	2101(3)	2797(2)	1853(3)	35(2)
O(32)	3942(4)	2827(2)	1801(3)	46(2)
C(31)	3057(6)	2817(3)	2181(4)	30(2)
C(32)	2986(5)	2835(3)	3170(4)	42(3)
N(31)	4049(5)	2785(3)	3675(3)	42(2)
C(33)	4785(6)	3303(3)	3527(5)	62(3)
C(34)	3740(6)	2774(4)	4614(4)	73(4)
C(35)	4639(7)	2228(3)	3469(5)	76(4)
O(41)	1459(4)	3291(2)	291(3)	39(2)
O(42)	3197(4)	3608(2)	219(3)	41(2)
C(41)	2190(6)	3673(3)	148(4)	31(2)
C(42)	1682(5)	4258(3)	–125(4)	37(2)
N(41)	2468(5)	4761(2)	–297(3)	38(2)
C(43)	3172(7)	4633(3)	–1073(5)	67(3)
C(44)	3174(6)	4895(3)	470(5)	65(3)
C(45)	1781(6)	5293(3)	–492(5)	55(3)
O(2w)	4343(3)	1118(2)	572(3)	41(2)
N(3)	6933(7)	1472(4)	2337(6)	70(3)
O(7)	6259(6)	1130(3)	2126(5)	120(4)
O(8)	7274(6)	1553(3)	3049(4)	110(3)
O(9)	7330(6)	1799(4)	1772(5)	128(4)
N(4)	7469(5)	–431(3)	1007(4)	46(2)
O(13)	7607(4)	65(2)	1331(5)	88(3)
O(14)	6477(4)	–594(2)	918(3)	46(2)
O(15)	8241(5)	–739(2)	787(3)	69(2)
N(5)	4549(7)	121(4)	2786(5)	83(4)
O(16)	4121(5)	473(3)	2290(4)	78(3)
O(17)	5403(5)	–144(2)	2541(3)	70(2)
O(18)	4191(7)	27(5)	3502(5)	177(5)
N(6)	3432(5)	–636(3)	599(4)	45(2)
O(23)	4199(4)	–277(2)	452(3)	51(2)
O(24)	3156(5)	–935(3)	–24(4)	100(3)
O(25)	3028(5)	–700(3)	1290(4)	83(3)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for **2**[a]

(A) Lengths			
Cu(1)–O(1)	1.970(5)	Cu(1)–O(2)	2.706(5)
Li(1)–O(2)	1.902(6)	C(1)–O(1)	1.280(10)
C(1)–O(2)	1.228(9)		
(B) Angles			
O(1)–Cu(1)–O(1a)	90.1(2)	O(1)–Cu(1)–O(1b)	176.9(5)
O(1)–Cu(1)–O(2)	54.2(6)	O(2)–Li(1)–O(2d)	104.9(2)
O(2)–Li(1)–O(2b)	119.1(3)	Cu(1)–O(1)–C(1)	106.5(5)
Li(1)–O(2)–C(1)	156.8(6)	O(1)–C(1)–O(2)	125.6(7)

[a] Symmetry codes: (a) $-x, y, -z$. (b) $-x, -y, z$. (c) $x, -y, -z$. (d) $x, -y, -1 - z$. (e) $-x, y, -1 - z$. (f) $0.5 - x, 0.5 - y, z$.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for **3**[a]

(A) Lengths			
Cu(1)–O(11)	1.994(4)	Cu(1)–O(21)	1.938(4)
Cu(1)–O(31)	1.965(4)	Cu(1)–O(41)	1.946(4)
Cu(1)–O(12)	2.582(4)	Cu(1)–O(42)	2.872(4)
Cu(1)–O(32)	2.945(4)	Cu(1)–O(22)	2.895(4)
Ca(1)–O(1w)	2.355(5)	Ca(1)–O(1)	2.536(6)
Ca(1)–O(2)	2.494(7)	Ca(1)–O(4)	2.508(5)
Ca(1)–O(5)	2.474(6)	Ca(1)–O(22)	2.374(5)
C(11)–O(11)	1.285(8)	C(11)–O(12)	1.224(8)
C(21)–O(21)	1.271(8)	C(21)–O(22)	1.238(8)
C(31)–O(31)	1.261(8)	C(31)–O(32)	1.230(8)
C(41)–O(41)	1.263(8)	C(41)–O(42)	1.231(8)
(B) Angles			
O(11)–Cu(1)–O(21)	91.0(2)	O(11)–Cu(1)–O(31)	87.2(2)
O(31)–Cu(1)–O(21)	176.7(2)	O(11)–Cu(1)–O(41)	72.2(2)
O(21)–Cu(1)–O(41)	91.4(2)	O(41)–Cu(1)–O(31)	90.8(2)
O(41)–Cu(1)–O(42)	50.8(2)	O(31)–Cu(1)–O(32)	48.2(2)
O(21)–Cu(1)–O(22)	50.3(2)	O(11)–Cu(1)–O(12)	56.1(2)
O(1w)–Ca(1)–O(1)	118.7(2)	O(4)–Ca(1)–O(22)	156.7(2)
O(1w)–Ca(1)–O(2)	73.8(2)	O(2)–Ca(1)–O(1)	47.9(2)
O(13)–Ca(2)–O(14)	49.6(2)	O(17)–Ca(2)–O(24a)	150.8(2)
Cu(1)–O(21)–C(21)	114.6(4)	Cu(1)–O(11)–C(11)	102.8(4)
Cu(1)–O(41)–C(41)	113.0(4)	Cu(1)–O(31)–C(31)	113.8(4)
Ca(1)–O(32)–C(31)	146.0(4)	Ca(1)–O(22)–C(21)	151.0(4)
O(11)–C(11)–O(12)	123.5(6)	Ca(1)–O(42)–C(41)	155.7(4)
O(31)–C(31)–O(32)	127.3(6)	O(21)–C(21)–O(22)	125.4(6)
		O(41)–C(41)–O(42)	126.6(6)

[a] Symmetry code: (a) $-x, -y, -z$.

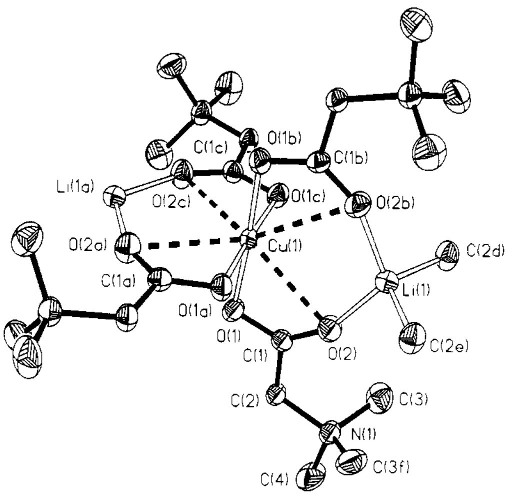

Figure 1. ORTEP (35% thermal ellipsoids) drawing of the coordination environment about the metal atoms in $[LiCu(bet)_4]_n(ClO_4)_{3n}$ (**2**) and atom-numbering scheme. Symmetry codes are given in Table 4.

can be rationalized in the same manner as discussed later for the heterodinuclear cation of **3**.

Of more structural interest is complex **3**, which comprises discrete $[CaCu(bet)_4(NO_3)_2(H_2O)]^{2+}$ cations and $[Ca(NO_3)_4(H_2O)]_2{}^{4-}$ dimeric anions in a 2:1 molar ratio. In the heterodinuclear cation (Figure 2), the Cu(II) atom is coordinated by four bet ligands with four short Cu–O(carboxylate) bonds in the range 1.938(4)–1.994(4) Å and four long Cu–O(carboxylate) bonds ranging from 2.582(4) to 2.945(4) Å. The three-up/one-down arrangement of the carboxylato groups of the bet ligands gives rise to a very irregular and hitherto unobserved eight-coordinate environment about the Cu(1) atom, which is linked to the Ca(1) atom by an unusual tris(carboxylato-*O,O'*)-bridge at a nonbonded Cu⋯Ca separation of 3.610(2) Å. The Ca–O(carboxylate) bond lengths [2.374(5)–2.400(5) Å] and the Ca–O–C bond angles [146.0(4)–155.7(4)°] are both compatible with those found for other calcium(II) carboxylates.[13] The coordination sphere about the Ca(1) atom is completed by four oxygen atoms from a pair of chelating nitrato ligands [Ca–O = 2.474(6)–2.536(6) Å], as well as one aqua ligand [Ca–O = 2.355(5) Å], in a distorted-

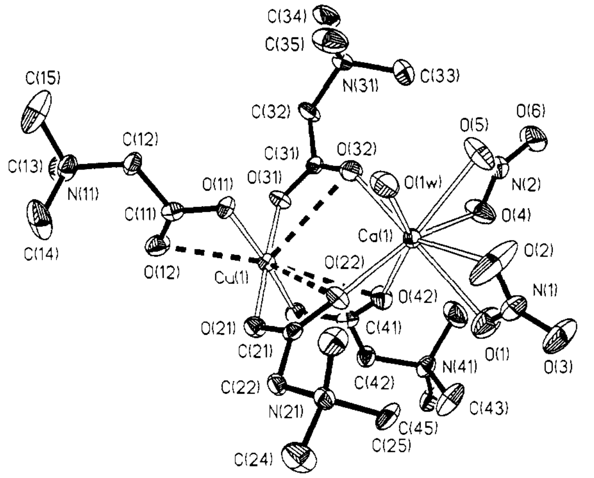

Figure 2. ORTEP (35% thermal ellipsoids) drawing of the heterodinuclear cation $[CaCu(bet)_4(NO_3)_2(H_2O)]^{2+}$ in **3** and atom-numbering scheme.

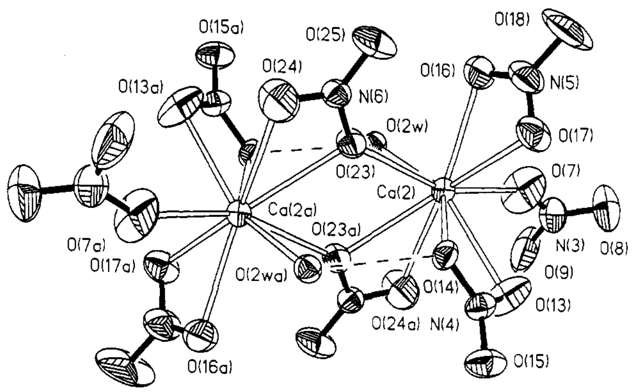

Figure 3. ORTEP (35% thermal ellipsoids) drawing of the homonuclear dimeric anion $[Ca(NO_3)_4(H_2O)]_2^{4-}$ in **3** and atom-numbering scheme. Symmetry code: (a) $-x, -y, -z$.

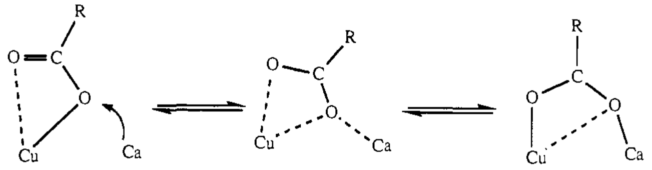

Figure 4. Schematic drawing of the proposed "carboxylate shift" mechanism in the formation of the heterodinuclear cation in **3**.

dodecahedral environment with O(42), O(4), O(2), and O(1w) constituting an elongated tetrahedron and the remaining ligand O atoms its companion flattened tetrahedron.

The stereochemistry of the present heterodinuclear cation differs markedly from those of the only two known examples, *viz.* the polymeric Cu(II)–Ca(II) complex[2] and discrete $[CaCu(2\text{-}ClC_6H_4OCH_2CO_2)_4(H_2O)_5]$.[14] In the polymeric complex, the eight-coordinate Cu(II) atom surrounded by four acetato groups in an alternate up/down arrangement is linked to the Ca(II) atom in the octahedral $CaO_4(OH_2)_2$ moiety through a bis(carboxylato-*O,O′*) bridge, giving rise to a one-dimensional polymer. In the heterodinuclear molecule, the Cu(II) atom is linked to the Ca(II) atom by a tetrakis(carboxylato-*O,O′*) bridge, and the coordination number of the Cu(II) atom is increased to 9 by the addition of an aqua ligand, while the coordination sphere about the Ca(II) atom is completed by four aqua ligands in a square-antiprismatic geometry. Thus the present heterodinuclear cation constitutes a new structural variety among mixed Cu(II)–Ca(II) dinuclear complexes.

In the present dimeric anion (Figure 3), a pair of Ca(II) atoms are linked by two nitrato μ-1,1-*O* bridges to form a centrosymmetric dimer, in which each Ca(II) atom is coordinated by three chelating nitrato groups, one unidentate nitrato group, and one aqua ligand, as well as the bridging oxygen atom from one nitrato ligand chelating to the other Ca(II) atom. Thus the nine-coordinate Ca(2) atom is enclosed in a distorted tricapped-trigonal prism. The Ca–O bond lengths range from 2.370(7) to 2.677(7) Å, and the O–Ca–O bond angles, from 49.6(2) to 155.7(4)°. The aqua ligand in this dimeric anion forms an intradimer hydrogen bond [2.782(8) Å] with a chelate nitrato ligand coordinated to the adjacent Ca(2a) atom. In addition, the aqua ligands in both ions form three intermolecular hydrogen bonds, which play a significant role in consolidating the crystal structure.

In the heterodinuclear cation of **3**, rearrangement of the four carboxylato groups coordinating to the Cu(II) atom may be ascribed to the fact that Ca(II) ion has a strong tendency for seven- and eight-coordination.[13] With reference to the "carboxylate shift" mechanism proposed by Lippard and co-workers,[15] a similar process may be used to describe the geometric changes caused by the introduction of the Ca(II) ion into the neighborhood of the original eight-coordination system. As seen in Figure 4, the approach of the Ca(II) atom may weaken one of the short Cu–O bonds in the chelate ring, with the corresponding long Cu–O bond becoming accordingly shorter. Finally, the previous shorter Cu–O bond now becomes a longer bond, while the previous long Cu–O bond of the same carboxylate group becomes a short bond, resulting in the three-up/one-down arrangement of the bet ligands.

In summary, the present study has shown that the coordination geometry of the eight-coordinate $[Cu(bet)_4]^{2+}$ core can be perturbed by the presence of Li(I) and Ca(II) ions. The large ionic radius and coordination flexibility of Ca(II) and the very small radius and tetrahedral coordination tendency of Li(I) play important roles in the formation of the heterometallic complexes. The perturbation can be slight, resulting in only minor changes of the structural parameters of the core, as in the case of **2**, or it can be very drastic, leading to a rearrangement of the carboxylate groups in the core, as in the case of **3**. Further exploration of $[Cu(bet)_4]^{2+}$ as a metallo ligand in the generation of heterometallic Cu(II)–M aggregates [M = Na(I), Mg(II), Zn(II), etc.] is in progress.

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Supplementary Material Available: Tables of anisotropic thermal parameters and hydrogen atomic coordinates for **2** and **3** (3 pages). Ordering information is given on any current masthead page.

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