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Immobilization of Thallium by Tandem Oxidation/Reduction–Complexation of Thallium(I/III)

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Development of management procedures for toxic superconducting thallium–copper–alkaline earth ceramics and their byproducts requires better understanding of the complexometric chemistry of thallium in the presence of copper and alkaline earth cations. This study reveals that thallium can be immobilized as a thallium-rich mixed-valence solid $[(Tl18c6)_4CuCl_4][TlCl_4]_2{\cdot}nH_2O$ (**1**, $n = 0$; **2**, $n = 0.25$). When either Tl(I) or Tl(III) is treated with 18-crown-6 (18c6) in the presence of copper(II) (or zinc) chloride, tandem oxidation (or reduction) complexation occurs to an extent sufficient to form **1** and/or **2**. The divalent transition metal ion (M) plays a beneficial role of concentrating Tl^+ as a cation $[(Tl18C6)_4MCl_4]^{2+}$, M = Cu or Zn. The template concerted reduction/oxidation–complexation reactions appear to take advantage of the high stability of the $TlCl_4^-$ anions. Similar complexes are obtained if Cl^- is replaced by Br^-, Tl^+ by Rb^+, and Cu^{2+} by Mn^{2+} and Co^{2+}. The crystal structures of **1**, **2**, $(Rb18c6)_2Cu_2Cl_6$ (**5**), and $(Ba18c6)_2(CuCl_4)_2{\cdot}3H_2O$ (**6**) along with solid-state thallium-205 NMR spectra of **1**, **2**, $[(Tl18c6)_4ZnCl_4][TlCl_4]_2$ (**3**), and $[(Rb18c6)_4CuCl_4][TlCl_4]_2$ (**4**) are reported. The cubic ($F23$) complexes **1**, **2**, and **4** feature a room-temperature average T_d geometry for $CuCl_4^{2-}$ anions, and the T_d nature (required by symmetry) of the position it occupies is confirmed by the luminescence of T_d $MnCl_4^{2-}$ and the blue color of T_d $CoCl_4^{2-}$ ions substituting for $CuCl_4^{2-}$ species. Crystal data are as follows. **1**: cubic, space group $F23$ with $a = 20.728$ (2) Å, $V = 8905.1$ (9) Å^3, and $Z = 4$; with 661 reflections having $I > 1\sigma(I)$, $R = 0.038$. **2**: cubic, space group $F23$ with $a = 20.748$ (5) Å, $V = 8932$ Å^3, $Z = 4$; with 549 independent reflections having $|F_o| > 3\sigma(|F_o|)$, $R = 0.043$. **5**: monoclinic, space group $P2_1/c$ with $a = 11.100$ (2) Å, $b = 8.168$ (1) Å, $c = 22.626$ (5) Å, $\beta = 97.55$ (2)°, $V = 2034$ Å^3, and $Z = 2$; with 2456 reflections ($|F_o| > 3\sigma(|F_o|)$), $R = 0.042$. **6**: triclinic $P\bar{1}$ with $a = 8.757$ (3) Å, $b = 17.174$ (5) Å, $c = 17.616$ (6) Å, $\alpha = 66.23$ (3)°, $\beta = 77.31$ (3)°, $\gamma = 75.71$ (2)°, $V = 2327.9$ (13) Å, and $Z = 2$; using 6214 reflections ($I > 3\sigma(I)$), $R = 0.051$.

Introduction

The recent discovery of various thallium-based multicomponent superconducting ceramic oxides with critical transition temperatures (T_c) in the range 73–125 K has stimulated intense research interest in thallium–copper oxides as alternatives to the lanthanide-based superconducting ceramics.[1-6] Whereas the thallium superconducting ceramics, especially those having the stoichiometries $Tl_2Ba_2Ca_2Cu_3O_{10}$ (T_c = 120–125 K)[2] and $Tl_2Ba_2CaCu_2O_8$ (T_c = 100–105 K)[1] have significant advantages over the more popular $YBa_2Cu_3O_7$ ($T \sim 93$ K)[7-9] such as a higher T_c and ease of preparation, the extreme toxicity of thallium is a major concern.[10] Therefore, when large scale or regular usage of thallium compounds in the development, manufacture, and application of superconducting copper oxide ceramics is contemplated, detoxification and clean up procedures for which the feedstocks would be mixtures of many metal ions must also be considered. For this effort, better understanding of the chemistry of thallium in the presence of key metal ions such as Cu^{2+} and the alkaline earth cations is needed.

We have investigated the complexation of thallium cations (Tl^+ and Tl^{3+}) by 18-crown-6 (18c6) in the presence of copper(II) and barium(II) to determine the influence of these cations on the extractibility or immobilization of thallium. Our choice for 18c6 as a complexing agent was inspired by a large volume of studies involving this readily available crown ether which have demonstrated its remarkable versatility for the complexation and transport of M^+ and M^{2+} cations.[11-14] In fact, the 18c6 cavity has recently been bonded on solid polymeric supports and found

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Table I. Crystallography Data

compd	**1**	**2**	**5**	**6**
temp, K	295	297	297	296
empirical formula	$C_{48}Cl_{12}CuH_{96}O_{24}Tl_6$	$C_{48}Cl_{12}CuH_{96.5}O_{24.25}Tl_6$	$C_{24}Cl_6Cu_2H_{48}O_{12}Rb_2$	$Ba_2C_{24}Cl_8Cu_2H_{54}O_{15}$
fw	2772.5	2777.0	1039.4	1268.1
cryst system	cubic	cubic	monoclinic	triclinic
space group	$F23$	$F23$	$P2_1/c$	$P\bar{1}$
lattice consts				
a, Å	20.728 (2)	20.748 (5)	11.100 (2)	8.757 (3)
b, Å			8.168 (1)	17.174 (5)
c, Å			22.626 (5)	17.616 (6)
α, deg				66.23 (3)
β, deg			97.55 (2)	77.31 (3)
γ, deg				75.71 (3)
V, Å^3	8905.1 (9)	8932	2034	2327.9 (13)
d_{calc}, g/mL	2.068	2.066	1.70	1.81
d_{obs}, g/mL	2.048	2.048	1.69	1.82
Z	4	4	2	2
abs coeff (μ), cm^{-1}	115.9	245	84	30.9
radiation (λ, Å)	Mo Kα (0.710 73)	Cu Kα (1.541 78)	Cu Kα (1.541 78)	Mo Kα (0.710 73)
θ limits, deg	$1 < \theta < 30$	$1 < \theta < 58$	$1 < \theta < 58$	$1 < \theta < 25$
no. of unique reflcns	1174	563	2729	8193
no. of obsd reflcns	661 with $I > 1\sigma(I)$	549 with $\lvert F_o\rvert > 3\sigma(\lvert F_o\rvert)$	2456 with $\lvert F_o\rvert > 3\sigma(\lvert F_o\rvert)$	6214 with $I > 3\sigma(I)$
R	0.038	0.043	0.042	0.051
R_w	0.048	0.048	0.046	0.070

to be effective and resilient as a selective metal ion chelate in the purification of water and recovery of several metal ions including Tl^+.[14,15]

We have now found that treatment of Tl^+ with 18c6 in the presence of copper(II) halides leads to tandem oxidation–complexation processes which yield (apparently) thermodynamically more stable mixed-valence complexes: $[(Tl18c6)_4CuCl_4][TlCl_4]_2 \cdot nH_2O$, $n = 0$ (**1**), $n = 0.25$ (**2**). Conversely, when Tl^{3+} is treated with 18c6 in the presence of copper(II) chloride, tanden reduction–complexation reactions occur yielding the same mixed-valence complexes **1** and **2**.

We herein report the syntheses and crystal structures of **1** and **2**. In order to clarify the curious geometry of $CuCl_4^{2-}$, a rare T_d for the d^9 system, in the room-temperature average structures of **1** and **2**, and to check the generality of the beneficial role of MCl_4^{2-} anions as metal ion concentrators, additional compounds of barium, rubidium, zinc, and manganese were prepared and characterized. The thallium-205 solid-state NMR data of **1** and **2** and their zinc and rubidium isomorphs, $[(Tl18c6)_4ZnCl_4][TlCl_4]_2$ (**3**) and $[(Rb18c6)_4CuCl_4][TlCl_4]_2$ (**4**), respectively, as well as the crystal structures of $(Rb18c6)_2Cu_2Cl_6$ (**5**) and $(Ba18c6)_2(CuCl_4)_2 \cdot 3H_2O$ (**6**) are also discussed.

Experimental Details

Materials Used. (1) Thallium(I) chloride was precipitated from aqueous purified thallium(I) nitrate supplied by Fisher Scientific Co. or from neutralization of 99.99% Tl_2CO_3 from Aldrich. (2) 18c6 was 99% pure from Aldrich. (3) Copper(II) and manganese(II) chlorides were Analar quantity $MCl_2 \cdot 2H_2O$ from BDH. (4) Thallium(III) chloride was obtained from 99.99% thallium sesquioxide from Aldrich. (5) Zinc chloride was laboratory reagent grade from BDH. (6) Rubidium chloride was obtained by neutralization of 99.99% rubidium carbonate from Aldrich or 99.9% metallic rubidium from Millmaster Chemical Co. The glass ampule containing the metal was broken under paraffin in the fume hood and small pieces (*caution*: large pieces lead to hydrogen buildup which could ignite) were then transferred to ice cold ethanol. The resulting solution was neutralized with hydrochloric acid, and the resulting crude salt was recrystallized from methanol.

Preparation of the Complexes. $[(Tl18c6)_4MCl_4][TlCl_4]_2 \cdot nH_2O$ (1, M = Cu, n = 0; 2, M = Cu, n = 0.25; 3, M = Zn, n = 0). One millimole of thallium(I) monochloride, TlCl, was suspended in 50 mL of hot methanol, and 18c6 was added in small portions until TlCl dissolved. About 0.2 mmol (or more) of copper or zinc dichloride was added, and the solution was subsequently evaporated slowly over 1–2 days. Higher yields were obtained if one or two drops of hydrochloric acid or ammonium chloride (1 mmol) were added to enhance formation of $CuCl_4^{2-}$ and $TlCl_4^-$ anions. The dark brown crystalline complexes deposited were filtered off hot to give a mixture of **1** and **2** in ~70% yield when excess Cl^- ions are present. Pure **1** can be obtained if crystallization is done in a hot ethanol/butanol mixture. The colorless crystals of the zinc complex **3** were obtained by a similar procedure. When the starting material was thallium(III) trichloride, $TlCl_3 \cdot nH_2O$, the salt (1 mmol) was dissolved in 50 mL of methanol and 18c6 (1 mmol) was added. Copper chloride (0.2 mmol or more) was then added, and the resulting solution was evaporated slowly over 1–2 days to give a crystalline mixture of **1** and **2** in ~60% yield. Anal. Calc for **1**: C, 20.8; H, 3.5; Cl, 15.3. Found: C, 20.77; H, 3.44; Cl, 15.20. Density (by the flotation technique) (g/cm^3): **1**/**2** crystalling mixture, 2.05; **3**, 2.09.

$[(Rb18c6)_4CuCl_4][TlCl_4]_2$ (4). To 2 mmol of rubidium chloride in 50 mL of methanol were added 2 mmol of 18c6 and 0.5 mmol of copper dichloride. The mixture was refluxed for 1 h, and then 1 mmol of thallium trichloride was added. Methanol was then evaporated off and the crude product was recrystallized from ethanol to yield the complex as orange crystals in about 70% yield. Anal. Calc for **4**: C, 25.3; H, 4.2. Found: C, 25.97; H, 4.29. Density (g/cm^3): 1.64.

$(Rb18c6)_2Cu_2Cl_6$ (5). The large dark green crystals of complex **5** are readily obtained by evaporating off a solution containing equimolar quantities of rubidium chloride, copper(II) chloride, and 18c6 in propanol. Yield: ~58%. Anal. Calc for **5**: C, 27.7; H, 4.7. Found: C, 27.68; H, 4.53.

$(Ba18c6)_2(CuCl_4)_2 \cdot 3H_2O$ (6). The orange crystals were obtained by evaporating off a solution containing equimolar quantities of barium chloride and 18c6 and a 50% excess of copper chloride in methanol. Anal. Calc for **6**: C, 22.7; H, 4.3; Cl, 22.4. Found: C, 22.45; H, 4.45; Cl, 22.29.

Absorption Spectra. The absorption spectra of the solid samples in Nujol mulls were recorded on a Hewlett Packard 8452A diode array spectrometer.

Thallium-205 NMR Spectra. The static powder spectra were recorded at room temperature on a Bruker MSL-300 NMR spectrometer using a Bruker 5-mm solenoid wideline probe. The chemical shifts were referenced to dilute aqueous thallium(I) nitrate.

Crystal Structure Determinations. The essential experimental conditions and resulting crystal data are given in Table I. Other details are available as supplementary material.

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Table II. Coordinates[a] and Equivalent Isotropic Thermal Parameters (Å^2) for **1**

atom	x	y	z	U_{eq}[b]
Tl(1)	0.34952 (4)	$1 - x$	x	0.06709 (8)
Tl(2)	0	0	0	0.0628 (1)
Tl(3)	$^1/_4$	$^1/_4$	$^1/_4$	0.0599 (1)
Cu	$^3/_4$	$^1/_4$	$^1/_4$	0.0478 (4)
Cl(1)	0.8114 (2)	$1 - x$	$1 - x$	0.0931 (8)
Cl(2)	0.0665 (2)	x	x	0.0926 (8)
Cl(3)	0.1832 (2)	x	x	0.0930 (8)
O(1)	0.2742 (5)	0.5926 (5)	0.4612 (5)	0.068 (4)
C(2)	0.2542 (7)	0.6455 (8)	0.4984 (9)	0.076 (5)
C(3)	0.3119 (8)	0.6802 (8)	0.5254 (7)	0.072 (5)
O(4)	0.3445 (5)	0.7128 (5)	0.4764 (5)	0.071 (4)
C(5)	0.4007 (9)	0.7477 (9)	0.4991 (7)	0.076 (5)
C(6)	0.4352 (8)	0.7760 (8)	0.4433 (8)	0.084 (6)

[a] These coordinates have been transformed relative to the supplementary material by the axial transformation of *acb*, and the identities of O(1), C(2), C(3), O(4), C(5), and C(6), changed to O(4), C(5), C(6), O(1), C(2), and C(3), respectively, for consistency with the values reported in Table IV. [b] The equivalent isotropic thermal parameter, for atoms refined anisotropically, is defined by the equation $U_{eq} = (^1/_3)\Sigma_i\Sigma_jU_{ij}a_i{}^*a_j{}^*a_ia_j$.

Table III. Selected Interatomic Distances (Å) and Bond Angles (deg) for **1** and **2** (Numbering Schemes in Figures 1 and 2) with Estimated Standard Deviations in Parentheses

	1	**2**
	Distances	
4 × Cu–Cl(1)	2.203 (2)	2.238 (10)
4 × Tl(2)–Cl(2)	2.386 (3)	2.413 (10)
4 × Tl(3)–Cl(3)	2.399 (3)	2.427 (9)
3 × Tl(1)–Cl(1)	3.517 (2)	3.517 (10)
3 × Tl(1)–O(1)	3.040 (10)	3.046 (16)
3 × Tl(1)–O(4)	2.931 (9)	2.941 (16)
mean dists		
C–O	1.409	1.439
C–C	1.491	1.465
	Angles	
Cl(1)–Cu–Cl(1)	109.47 (9)	109.5 (2)
Cl(2)–Tl(2)–Cl(2)	109.47 (8)	109.5 (2)
Cl(3)–Tl(3)–Cl(3)	109.47 (8)	109.5 (2)
mean angles		
C–O–C	114	114
O–C–C	109	108

Absorption corrections for **1** and **6** based on ψ-scans and background, Lorentz, and polarization corrections were applied. In the case of complex **5**, the data were corrected for Lorentz and polarization factors; a numerical absorption correction (face-indexed crystal) was applied for **5**, whereas an empirical absorption correction (ellipsoidal) based on 396 azimuthal measurements was applied for **2**. In **2** a ΔF map also revealed the presence of a partial occupancy water molecule (estimated occupancy 0.25). This atom was refined isotropically. The positions of hydrogen atoms were in all cases idealized with C–H distances constrained to 0.95 Å, assigned isotropic thermal parameters, and allowed to ride on their parent carbon atoms. Refinement was by block-cascade full-matrix least squares using Enraf-Nonius programs[17] in the case of complexes **1** and **6** and an Eclipse S140 computer with the SHELXTL program system in the case of complexes **2** and **5**. The absolute structures of **1** and **2** were determined by R-factor tests.

The structure of **5** shows disorder of the $Cu_2Cl_6{}^{2-}$ anion with the bridging Cl atoms exhibiting 60% occupancy of positions yielding a planar $Cu_2Cl_6{}^{2-}$ geometry and 20% occupancy of positions above and below these planar sites (vide infra). The initial site occupancies for the Cl atoms were determined from the relative residual electron densities in a ΔF map. The final values were obtained by adjusting the occupancies to give equivalent mean isotropic thermal parameters for the three independent sites. Maximum and minimum residual densities in the final ΔF map were 0.72 and −0.34 e Å^{-3}.

The structure of complex **6** exhibits disorder in the position of one barium atom (Ba(2)) with occupancy levels of 84% above and 16% below the crown ether ring. Maximum and minimum residual electron densities in the final ΔF map were respectively 2.35 and −1.50 e Å^{-3}, both being near the disordered Ba(2) atom.

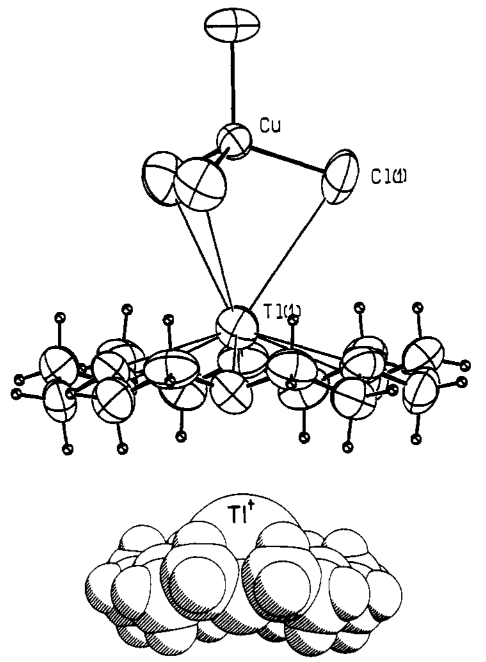

Figure 1. Top: Structure of the Tl18c6$^+$ ion in **1** (40% probability ellipsoids), showing the numbering scheme and the complexation of the large Tl$^+$ cation by the relatively small cavity of 18-crown-6 as well as the 3-fold symmetrical coordination of Tl$^+$ to one of the faces of the $CuCl_4{}^{2-}$ tetrahedron. (b) Bottom: Space-filling view of the "sunrise" coordination of Tl$^+$ by 18c6 typical of **1** and **2**. The Tl18c6$^+$ cation of **2** is shown.

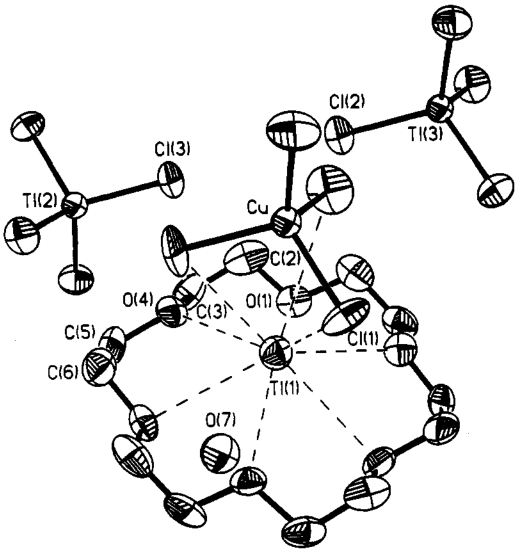

Figure 2. Perspective view, with 40% probability ellipsoids, of the $[(Tl18c6)_4CuCl_4][TlCl_4]_2{\cdot}0.25H_2O$ (**2**) complex, showing the numbering scheme.

Results and Discussion

Treatment of thallium(I) chloride with 18c6 in the presence of copper(II) or zinc(II) chloride leads to tandem oxidation–complexation reactions which yield thallium-rich mixed-valence complexes of stoichiometry $[(Tl18c6)_4CuCl_4][TlCl_4]_2{\cdot}nH_2O$, n = 0, 0.25. Alternatively, when thallium(III) chloride is treated with 18c6 in the presence of copper(II) chloride tandem reduction–complexation reactions occur yielding the same thallium-rich complexes **1** and **2**. The formulation of the complexes is based on carbon, chlorine, and hydrogen analyses, solid-state thallium-

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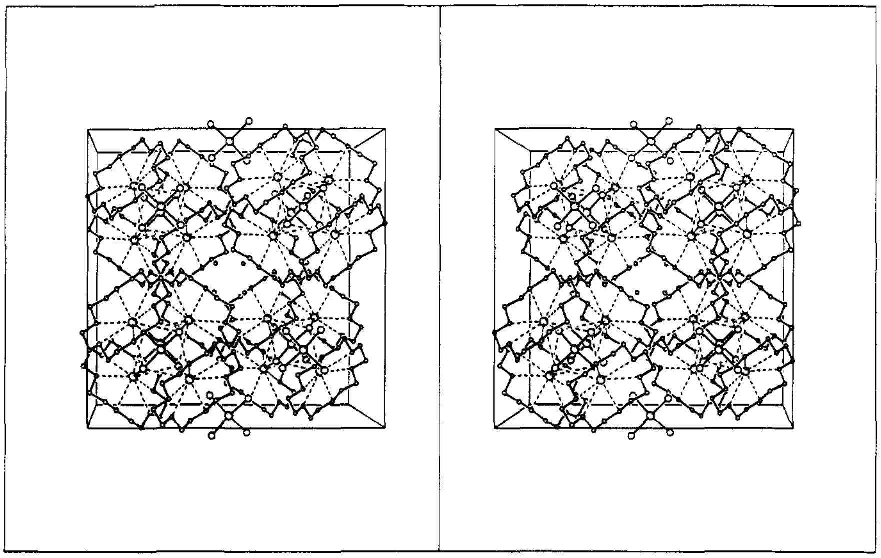

Figure 3. Stereoscopic packing diagram of the cubic unit cell of $[(\mathrm{Tl18c6})_4\mathrm{CuCl_4}][\mathrm{TlCl_4}]_2\cdot 0.25\mathrm{H_2O}$ (**2**), showing, in addition to features of **1**, four water molecules trapped in T_d disposition between concave faces of the $\mathrm{Tl18c6^+}$ units.

205 NMR spectra, and single-crystal X-ray diffraction crystallography studies.

Crystal Structure of 1. The crystal structure of **1** is cubic, space group *F*23; atomic positions are given in Table II. The cubic unit cell of **1** contains four equivalent $[(\mathrm{Tl18c6})_4\mathrm{CuCl_4}]^{2+}$ and eight $\mathrm{TlCl_4^-}$ ions. The four $[(\mathrm{Tl18c6})_4\mathrm{CuCl_4}]^{2+}$ cations are tetrahedrally disposed in four octants about the center of the cube, the other four octants in the cube being occupied by four $\mathrm{TlCl_4^-}$ anions (central atom Tl(3)). The positions occupied by the $\mathrm{TlCl_4^-}$ (Tl(3)) and $\mathrm{CuCl_4^{2-}}$ anions have site symmetry 23(*T*); thus, the apparent average room-temperature geometry of $\mathrm{TlCl_4^-}$ and $\mathrm{CuCl_4^{2-}}$ anions is perfect tetrahedral, T_d. The faces and corners of the cube, also *T* sites, are occupied by other $\mathrm{TlCl_4^-}$ anions (central atom Tl(2)). Each of the four triangular faces of the $\mathrm{CuCl_4}$ tetrahedron is individually and symmetrically capped by the large $\mathrm{Tl^+}$ cation which lies on a crystallographic 3-fold axis. This $\mathrm{Tl^+}$ ion, Tl(1), is in "sunrise coordination" to 18c6 (Figure 1), which is typical of large cations coordinating to small ligand cavities.[12] The crown ether, 18c6, has crystallographic C_3 symmetry and exists in the D_{3d} conformation most typical of this species in metal ion complexes.[11,12] The $\mathrm{Tl^+}$ ion is 0.92 Å above the least-squares plane of the six crown ether oxygens. Selected interatomic distances and angles are given in Table III. The Tl–O(crown) distances, 2.931 (9) Å for O(1) and 3.039 (10) Å for O(4), are within the range found in structures of other $\mathrm{Tl18c6^+}$ species.[12,18] The Tl–Cl bond distances in the crystallographically independent $\mathrm{TlCl_4^-}$ are equivalent (2.39 (1) Å). The Cl–Tl–Cl angle in both $\mathrm{TlCl_4^-}$ ions is by symmetry tetrahedral. These parameters are comparable to those found in other $\mathrm{TlCl_4^-}$ compounds such as $\mathrm{KTlCl_4}$ and $\mathrm{TlTlCl_4}$[19] after allowing for the distortion of T_d geometry in $\mathrm{KTlCl_4}$.

The equivalent Cu–Cl distances in the $\mathrm{CuCl_4^{2-}}$ anions are equal to 2.203 (3) Å, and the Cl–Cu–Cl angle is by symmetry tetrahedral. The Cu–Cl distances in **1** are on the shorter side of Cu–Cl distances found in other tetrachlorocuprate anions[20-22] for which the averages range from 2.20 to 2.27 Å. These literature Cu–Cl distances being referred to are for variously distorted D_{2d} tetrachlorocuprates; no perfect T_d $\mathrm{CuCl_4^{2-}}$ has been reported.

Crystal Structure of 2. The crystal structure of **2** (Figure 2) is cubic, space group *F*23; *a* = 20.748 (5) Å (Figure 3), and atomic positions are given in Table IV. The disposition of the $[(\mathrm{Tl18c6})_4\mathrm{CuCl_4}]^{2+}$ and $\mathrm{TlCl_4^-}$ ions is similar to the one adopted by **1** (vide supra). The four partial weight water (O(7)) molecules in the cubic unit cell are trapped between the concave faces of the Tl18c6 units and are tetrahedrally disposed about the center of the cube (Figure 2).

Table IV. Atom Coordinates and Temperature Factors (Å^2) with Estimated Standard Deviations in Parentheses for $[(\mathrm{Tl18c6})_4\mathrm{CuCl_4}][\mathrm{TlCl_4}]_2\cdot 0.25\mathrm{H_2O}$ (**2**)

atom	*x*	*y*	*z*	U_{eq}[a]
Tl(1)	0.34905 (4)	1 – *x*	*x*	0.061 (1)*
Tl(2)	0	0	0	0.051 (1)*
Tl(3)	1/4	1/4	1/4	0.050 (1)*
Cu	3/4	1/4	1/4	0.044 (1)*
Cl(1)	0.8123 (2)	1 – *x*	1 – *x*	0.097 (2)*
Cl(2)	0.0671 (3)	*x*	*x*	0.089 (2)*
Cl(3)	0.1825 (3)	*x*	*x*	0.081 (2)*
O(1)	0.2761 (6)	0.5931 (6)	0.4625 (6)	0.060 (4)*
C(2)	0.2531 (12)	0.6472 (10)	0.4985 (12)	0.079 (7)*
C(3)	0.3108 (13)	0.6797 (11)	0.5251 (9)	0.069 (8)*
O(4)	0.3432 (6)	0.7119 (6)	0.4769 (5)	0.056 (4)*
C(5)	0.4003 (10)	0.7469 (10)	0.4995 (11)	0.070 (6)*
C(6)	0.4299 (11)	0.7759 (11)	0.4432 (11)	0.077 (8)*
O(7)	0.4471 (40)	0.0529 (40)	0.0529 (40)	0.102 (39)

[a] An asterisk indicates an equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Selected interatomic distances are given in Table III. The Tl–O(crown) distances of **2**, Tl(1)–O(1) (3.046 Å) and Tl(1)–O(4) (2.941 Å), are also within the range known for other Tl18c6 units.[12,18] The Tl–Cl distances in the two crystallographically

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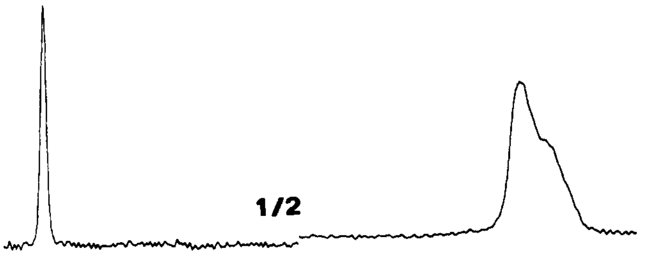

Figure 4. Thallium-205 NMR spectra of solid samples: **1/2** hydrate mixture $[(Tl18c6)_4CuCl_4][TlCl_4]_2\cdot nH_2O$, n = 0, 0.25; **3**, $[(Tl18c6)_4ZnCl_4][TlCl_4]_2$; **4**, $[(Rb18c6)_4CuCl_4][TlCl_4]_2$.

independent $TlCl_4^-$ anions are the same (2.42 (1) Å). This distance is comparable to that found in $TlCl_4^-$ species in other environments.[19] The Cu–Cl distances are by symmetry equal (2.24 (1) Å). Similarly, the Cl–Cu–Cl and Cl–Tl–Cl angles are again by symmetry tetrahedral.

Thallium-205 NMR Studies. The simultaneous presence of thallium(I) and thallium(III) in complexes **1**–**4** is readily confirmed by thallium-205 NMR spectra of the powder samples. The thallium(III) resonance is sharp and symmetrical reflecting the high symmetry of the crystallographic *T* site it occupies and occurs at ~2900 ppm in the spectra of complexes **1**–**4** (Figure 4). The observed chemical shifts of Tl(III) in $TlCl_4^-$ are comparable to the values obtained for the $TlCl_4^-$ species in solid environments, for example the value 2712 ppm found in $KTlCl_4$;[23] the relatively smaller chemical shift value reflects the distortion of the $TlCl_4^-$ ion from T_d geometry and the resulting electron redistribution.[19] The resonance of Tl(I) is broad with almost axial symmetry, chemical shift anisotropy of –438 ppm, principal components at –599, –613, and –1042 ppm, and a true chemical shift of –782 ppm for complexes **1** and **2**. By contrast, the spectrum of the diamagnetic cubic zinc complex **3**, which is isostructural with **1**, shows the anisotropic axial Tl(I) resonance at lower field with principal components at –63, –71, and –250 ppm, a chemical shift anisotropy of –183 ppm, and a true chemical shift of –117 ppm. The appearance of the Tl(I) resonance at high field in copper complexes is consistent with the proximate positions of $Tl18c6^+$ and paramagnetic $CuCl_4^{2-}$ ions (Tl(1)–Cu = 3.5728 (4) Å for **1**). Interactions (through space and Tl–Cl–Cu bonds) between the Tl(I) nucleus and the Cu^{2+} unpaired electrons is expected to lead to paramagnetic shielding, hence, a shift of the Tl(I) resonance. Interactions among proximate Tl(I) nuclei in $[(Tl18c6)_4CuCl_4]^{2+}$ species e.g. thallium-205 and thallium-203 could lead to the Tl^+ chemical shift anisotropy in both copper and zinc complexes. The sharp resonance at 376 ppm is probably due to TlCl impurities present in the mother liquor trapped in the crystals.[23–25] The sensitivity of the thallium-205 nucleus to a changing environment demonstrated above and the broad chemical shift range are major attributes fueling interest in the use of thallium-205 as an NMR structural probe.[23–27]

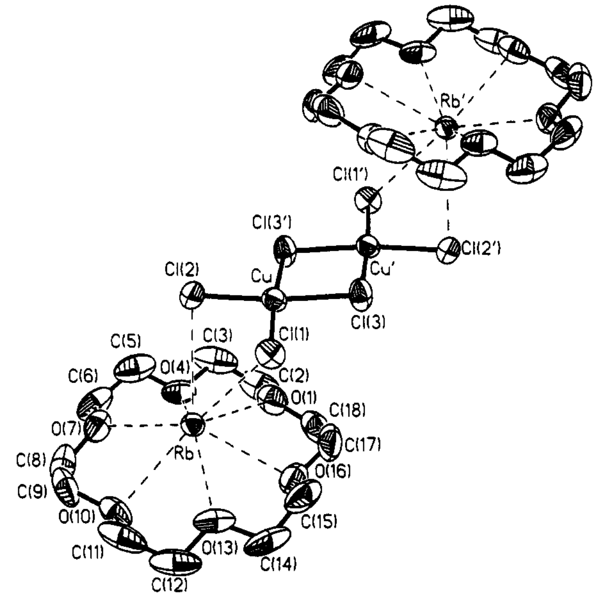

Figure 5. Molecular structure of $(Rb18c6)_2Cu_2Cl_6$ in **5** with 40% probability ellipsoids.

Rubidium Complexes 4 and 5. The rubidium complex **4** was synthesized to determine if metal ion enrichment through coordination to $ZnCl_4^{2-}$ or $CuCl_4^{2-}$ anions was restricted to thallium(I). Rb^+ and Tl^+ cations have similar cation radii of ~1.50 Å in 6-fold coordination.[28] If the significance of the lone pair on Tl^+, covalence contributions in Tl–Cl bonds of $[(Tl18c6)_4MCl_4]^{2+}$ cations, or the moderately greater stability[13] of $Tl18c6^+$ over $Rb18c6^+$ is minimal, then Rb^+ should behave more like Tl^+. The $[(Rb18c6)_4CuCl_4]^{2+}$ cations are indeed readily formed and stabilized in the presence of $TlCl_4^-$ despite prolonged reflux in ethanol over about 4 days. The rubidium complex $[(Rb18c6)_4CuCl_4][TlCl_4]_2$ is by X-ray powder diffraction analyses cubic and isostructural with the isostoichiometric Tl^+ complex **1**; the structural similarity is also indicated by thallium-205 NMR spectroscopy (Figure 4) (Tl(III) resonance at 2900 ppm). The anions $TlCl_4^-$ appear to be well shielded from the paramagnetic effects of $CuCl_4^{2-}$ ions.

However, when Rb^+ interacts with 18c6 and copper chloride in the absence of thallium(III) chloride, a different complex with lower rubidium levels (relative to **4**) is formed. The compound, $(Rb18c6)_2Cu_2Cl_6$ (**5**), features a dimeric and disordered $Cu_2Cl_6^{2-}$ species coordinated in trans fashion to the $Rb18c6^+$ ions through the terminal Cl atoms (Figure 5). Atomic positions are given in Table V. The Rb^+ cations are in typical "sunrise" coordination[12] to 18c6 (0.81 Å above the best plane of the six crown oxygen), which has D_{3d} symmetry. The distances and angles (Table VI) in $Cu_2Cl_6^{2-}$ are comparable to those found in similar compounds

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Table V. Atom Coordinates and Temperature Factors (Å^2) with Estimated Standard Deviations in Parentheses for $(Rb18c6)_2Cu_2Cl_6$ (**5**)

atom	*x*	*y*	*z*	U_{eq}[a]
Rb	0.3520 (1)	0.1629 (1)	0.1742 (1)	0.054 (1)*
Cu	0.1138 (1)	–0.0467 (1)	0.0548 (1)	0.057 (1)*
Cl(1)	0.1172 (2)	–0.0941 (2)	0.1512 (1)	0.068 (1)*
Cl(2)	0.3106 (1)	–0.0933 (2)	0.0555 (1)	0.068 (1)*
Cl(3)	–0.0944 (2)	–0.0168 (4)	0.0446 (1)	0.075 (1)*
O(1)	0.1836 (4)	0.3523 (5)	0.0887 (2)	0.092 (1)*
C(2)	0.2299 (8)	0.4380 (9)	0.0419 (3)	0.121 (2)*
C(3)	0.3340 (8)	0.3451 (9)	0.0232 (3)	0.115 (1)*
O(4)	0.4309 (4)	0.3508 (5)	0.0699 (2)	0.082 (1)*
C(5)	0.5317 (7)	0.2620 (9)	0.0552 (3)	0.112 (1)*
C(6)	0.6360 (6)	0.2826 (9)	0.1027 (4)	0.107 (1)*
O(7)	0.6046 (4)	0.2116 (5)	0.1570 (2)	0.087 (1)*
C(8)	0.6926 (6)	0.2390 (9)	0.2065 (4)	0.116 (1)*
C(9)	0.6572 (6)	0.1585 (8)	0.2585 (4)	0.114 (1)*
O(10)	0.5497 (4)	0.2364 (5)	0.2758 (2)	0.085 (1)*
C(11)	0.5101 (8)	0.1607 (8)	0.3280 (3)	0.117 (1)*
C(12)	0.4010 (8)	0.2471 (9)	0.3427 (3)	0.118 (1)*
O(13)	0.3033 (5)	0.2133 (5)	0.2970 (2)	0.093 (1)*
C(14)	0.1897 (7)	0.2837 (10)	0.3088 (3)	0.120 (2)*
C(15)	0.0991 (7)	0.2585 (10)	0.2559 (4)	0.119 (2)*
O(16)	0.1335 (4)	0.3483 (5)	0.2078 (2)	0.095 (1)*
C(17)	0.0413 (8)	0.3468 (9)	0.1577 (4)	0.135 (2)*
C(18)	0.0863 (7)	0.4395 (9)	0.1087 (4)	0.125 (2)*
Cl(3a)	–0.0806 (6)	–0.1102 (9)	0.0350 (3)	0.069 (2)
Cl(3b)	–0.0785 (7)	0.0825 (10)	0.0424 (3)	0.076 (2)

[a] An asterisk indicates an equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table VI. Selected Interatomic Distances (Å) and Bond Angles (deg) for $(Rb18c6)_2Cu_2Cl_6$ (**5**) with Atom Labels According to Figure 5 and Estimated Standard Deviation in Parentheses[a]

	Distances		
Cu–Cl(1)	2.211 (2)	Rb–Cl(1)	3.334 (2)
Cu–Cl(2)	2.216 (2)	Rb–Cl(2)	3.389 (2)
Cu–Cl(3)	2.305 (2)	Rb–O(1)	2.945 (4)
Cu–Cl(3a)	2.207 (7)	Rb–O(4)	3.038 (4)
Cu–Cl(3b)	2.365 (7)	Rb–O(7)	2.908 (4)
Cu′–Cl(3)	2.291 (2)	Rb–O(10)	3.022 (4)
Cu′–Cl(3a)	2.389 (7)	Rb–O(13)	2.929 (4)
Cu′–Cl(3b)	2.202 (8)	Rb–O(16)	3.039 (5)
Cu–Cu′	3.386 (1)	Rb–Cu	3.917 (1)
	Angles[b]		
Cl(1)–Cu–Cl(2)	94.3 (1)	Cl(1)–Cu–Cl(3)	91.1 (1)
Cl(3)–Cu–Cl(3′)	83.2 (1)	Cu–Cl(3)–Cu′	96.8 (1)
Cl(1)–Cu–Cl(3′)	173.6 (1)	Cu–Cl(1)–Rb	87.4 (1)
Cl(2)–Cu–Cl(3)	172.7 (1)	Cu–Cl(2)–Rb	86.0 (1)
Cl(2)–Cu–Cl(3′)	91.7 (1)	Cl(1)–Rb–Cl(2)	57.7 (1)

[a] Primes on atom names refer to symmetry operation –*x*, –*y*, –*z*. [b] Only angles involving the $Cu_2Cl_6^{2-}$ anion were selected; the rest are available as supplementary material.

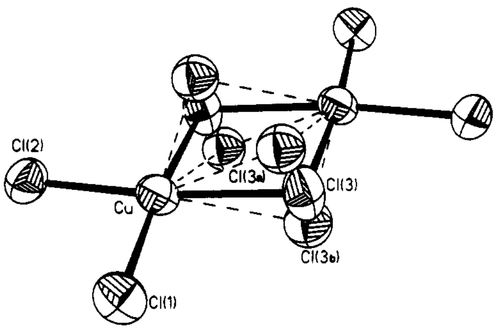

Figure 6. Structure of the Cu_2Cl_6 unit in $(Rb18c6)_2Cu_2Cl_6$ (**5**) (with 40% probability ellipsoids), showing the disorder in the positions of bridging Cl(3) atoms. Occupancies: 60% Cl(3) and 20% each Cl(3a) and Cl(3b).

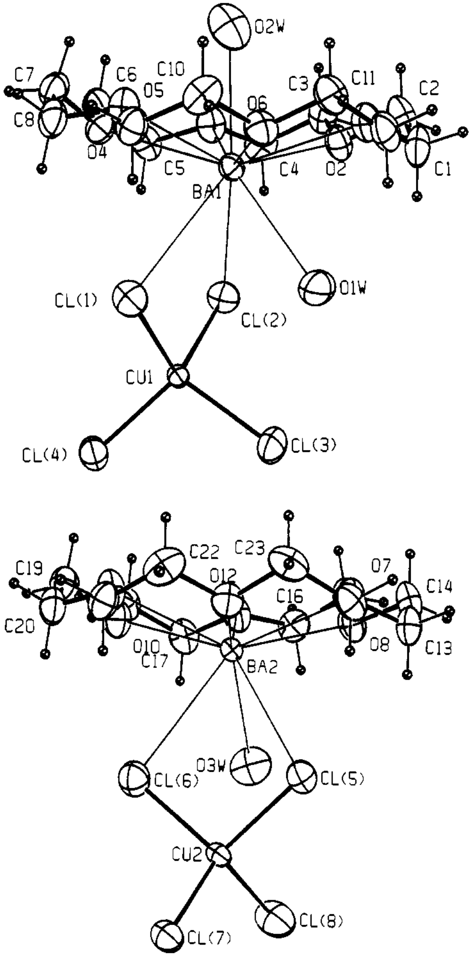

Figure 7. Molecular structures of the independent $(Ba18c6)CuCl_4{\cdot}2H_2O$ (a, top) and $(Ba18c6)CuCl_4{\cdot}H_2O$ (b, bottom) molecules constituting the complex $(Ba18c6)_2(CuCl_4)_2{\cdot}3H_2O$ (**6**) at 40% probability ellipsoids.

having 4 + 0 coordination.[29] There is disorder in the bridging chlorine atoms (Cl(3)) as shown by the large thermal parameters in Table V and detailed in Figure 6. The major occupancy Cl(3) is 60% whereas the minor occupancies Cl(3a) (above Cl(3)) and Cl(3b) (below Cl(3)) are 20% each (Figure 6).

Structure of the Barium Complex 6. Further, we have studied the behavior of Ba^{2+} which is large (radius 1.36 Å[28] in coordination number 6) and coordinates to 18c6[30a] in the sunrise fashion like Rb^+ and Tl^+. In the absence of $TlCl_3$, a reaction between 18c6, barium chloride, and copper(II) chloride yields the complex $[(Ba18c6)(CuCl_4){\cdot}2H_2O][(Ba18c6)(CuCl_4)(H_2O)]$ (**6**) (Figure 7). Atomic coordinates are given in Table VII. $Ba18c6^{2+}$ has the expected sunrise structure in the two independent molecules, but coordination of the complex cations to the tetrachlorocuprate anions is much less efficient compared to that found in $[(M18c6)_4CuCl_4]^{2+}$, M = Tl and Rb (vide supra). Besides the six crown oxygens, the Ba^{2+} cation Ba(1), of the dihydrate $(Ba18c6)CuCl_4{\cdot}2H_2O$ (Figure 7a), is coordinated to two water molecules, one above and another below the crown, and two Cl^- species of the D_{2d} $CuCl_4^{2-}$ anion to give a 10-fold coordination. Ba(1) is positioned 0.79 Å above the best plane of the six crown oxygens. The large angles of $CuCl_4^{2-}$ are 130 and 131°, while the small ones are 102 and 97°, which therefore define a distorted D_{2d} $CuCl_4^{2-}$ geometry.[20-22]

The monohydrated molecule of Ba(2), $(Ba18c6)CuCl_4{\cdot}H_2O$, features a nanocoordinated Ba(2) atom having six Ba–O(crown), one Ba–O(water), and two Ba–Cl bonds (Figure 7b). The Ba(2)

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Table VII. Atomic Coordinates and Temperature Factors (Å) with Estimated Standard Deviations in Parentheses for **6**

atom	x	y	z	U_{eq}
Ba(1)	0.04162 (6)	0.04993 (3)	0.70547 (3)	0.0325 (1)
Ba(2)	0.55341 (6)	0.54075 (3)	0.20880 (3)	0.0253 (1)[a]
Ba(2′)	0.4705 (4)	0.4262 (2)	0.3144 (3)	0.0924 (11)[a]
Cu(1)	0.1849 (1)	0.23489 (6)	0.47760 (6)	0.0241 (3)
Cu(2)	0.8189 (1)	0.73303 (7)	0.04827 (7)	0.0293 (4)
Cl(1)	0.3166 (3)	0.1004 (2)	0.5432 (1)	0.0532 (8)
Cl(2)	-0.0624 (3)	0.2131 (1)	0.5422 (1)	0.0474 (6)
Cl(3)	0.1740 (3)	0.3602 (1)	0.4938 (1)	0.0618 (8)
Cl(4)	0.2937 (3)	0.2628 (1)	0.3440 (1)	0.0519 (8)
Cl(5)	0.7104 (3)	0.7088 (1)	0.1828 (1)	0.0536 (8)
Cl(6)	0.8356 (3)	0.5990 (1)	0.0496 (1)	0.0565 (8)
Cl(7)	1.0638 (3)	0.7639 (1)	-0.0140 (1)	0.0494 (8)
Cl(8)	0.6558 (3)	0.8563 (2)	-0.0139 (2)	0.0735 (10)
O(1)	-0.0078 (7)	0.0754 (4)	0.8602 (3)	0.053 (3)
O(2)	-0.2642 (7)	0.1265 (4)	0.7696 (3)	0.049 (2)
O(3)	-0.2564 (7)	0.0367 (4)	0.6692 (3)	0.048 (2)
O(4)	0.0282 (7)	-0.0583 (3)	0.6196 (3)	0.044 (2)
O(5)	0.2721 (7)	-0.1029 (3)	0.7157 (3)	0.049 (2)
O(6)	0.2828 (7)	-0.0154 (4)	0.8168 (3)	0.049 (2)
O(7)	0.5071 (7)	0.5649 (4)	0.3657 (3)	0.052 (2)
O(8)	0.2494 (7)	0.6128 (4)	0.2811 (3)	0.051 (3)
O(9)	0.2569 (7)	0.5223 (4)	0.1784 (3)	0.054 (3)
O(10)	0.5344 (7)	0.4317 (3)	0.1224 (3)	0.052 (2)
O(11)	0.7809 (7)	0.3857 (4)	0.2151 (3)	0.054 (3)
O(12)	0.7956 (7)	0.4715 (3)	0.3184 (3)	0.048 (2)
C(1)	-0.131 (1)	0.1481 (6)	0.8608 (5)	0.057 (3)
C(2)	-0.281 (1)	0.1323 (7)	0.8505 (6)	0.063 (4)
C(3)	-0.406 (1)	0.1088 (6)	0.7577 (6)	0.053 (3)
C(4)	-0.381 (1)	0.1062 (6)	0.6719 (6)	0.052 (3)
C(5)	-0.232 (1)	0.0203 (6)	0.5931 (5)	0.048 (3)
C(6)	-0.124 (1)	-0.0636 (5)	0.6058 (5)	0.053 (3)
C(7)	0.133 (1)	-0.1398 (5)	0.6401 (5)	0.053 (3)
C(8)	0.292 (1)	-0.1294 (5)	0.6456 (5)	0.054 (3)
C(9)	0.419 (1)	-0.0995 (5)	0.7358 (5)	0.049 (3)
C(10)	0.391 (1)	-0.0937 (5)	0.8188 (6)	0.053 (3)
C(11)	0.240 (1)	-0.0101 (6)	0.8988 (5)	0.052 (3)
C(12)	0.134 (1)	0.0713 (6)	0.8927 (5)	0.054 (3)
C(13)	0.391 (1)	0.6401 (5)	0.3649 (5)	0.052 (3)
C(14)	0.236 (1)	0.6256 (6)	0.3573 (5)	0.056 (3)
C(15)	0.111 (1)	0.5866 (5)	0.2750 (5)	0.049 (3)
C(16)	0.123 (1)	0.5849 (6)	0.1910 (6)	0.051 (3)
C(17)	0.274 (1)	0.5108 (6)	0.1015 (5)	0.052 (3)
C(18)	0.383 (1)	0.4272 (6)	0.1087 (5)	0.049 (3)
C(19)	0.640 (1)	0.3523 (6)	0.1363 (5)	0.053 (3)
C(20)	0.798 (1)	0.3628 (6)	0.1445 (5)	0.054 (3)
C(21)	0.928 (1)	0.3864 (5)	0.2362 (6)	0.051 (3)
C(22)	0.899 (1)	0.3923 (6)	0.3207 (6)	0.059 (4)
C(23)	0.754 (1)	0.4748 (6)	0.4010 (5)	0.056 (3)
C(24)	0.649 (1)	0.5590 (6)	0.3947 (5)	0.051 (3)
O(1W)	0.1609 (9)	0.2094 (4)	0.6894 (4)	0.066 (3)
O(2W)	-0.0700 (8)	-0.0900 (5)	0.8199 (4)	0.081 (3)
O(3W)	0.4281 (8)	0.6935 (5)	0.0650 (5)	0.077 (3)

[a] Ba(2) has a population of 0.84; Ba(2′) has a population of 0.16.

atom is disordered above (0.83 Å) and below (1.41 Å) the crown with occupancies of 84% and 16%, respectively. The large angles in the $CuCl_4^{2-}$ anion (Cu(2)) are 128 and 129°, while the small ones are 99 and 103°, which are normal for a distorted D_{2d} $CuCl_4$ polyhedron.[20-22] The Ba–O(crown) distances (Table VIII) which fall in the range 2.855–2.906 Å are normal.[30a]

M18c6···Cl Contacts. The M18c6···Cl interactions in all of the compounds we have studied so far appear to be mainly electrostatic. The average Ba–Cl bond length is 3.246 Å for Ba(1) and 3.312 Å for Ba(2) (the difference arising from the greater uncertainty in Ba(2) parameters). Both values are closer to the ionic radii sum for Ba^{2+} (coordination number 9 or 10) and Cl^- (coordination number 6) of about 3.30 Å.[28] The Rb–Cl distances (average 3.36 Å) in $(Rb18c6)_2Cu_2Cl_6$ are slightly shorter than the ionic radii sum of 3.41 Å for Rb^+ in 8-fold coordination. The three equivalent Tl(1)–Cl(1) distances in **1** and **2** (~3.52 Å) are rather longer than the ionic radius sum (3.46 Å using the radius of Tl^+ in 9-fold coordination) presumably because of steric repulsions. There are four $Tl18c6^+$ ions per $CuCl_4$ polyhedron of **1** and **2** as opposed to one $M18c6^{n+}$ per $CuCl_4$ unit in the barium (**6**) and the dimeric rubidium (**5**) complexes.

Table VIII. Selected Interatomic Distances (Å) and Bond Angles (deg) for $(Ba18c6)_2(CuCl_4)_2 \cdot 3H_2O$ (**6**) with Atom Labels According to Figure 7 and Estimated Standard Deviations in Parentheses

Distances			
Ba(1)–Cl(1)	3.275 (2)	Ba(2)–O(3W)	2.991 (6)
Ba(1)–Cl(2)	3.217 (2)	Ba(2′)–Cl(4)	3.341 (5)
Ba(1)–O(1)	2.855 (6)	Ba(2′)–O(7)	2.971 (9)
Ba(1)–O(2)	2.883 (5)	Ba(2′)–O(8)	3.206 (6)
Ba(1)–O(3)	2.900 (7)	Ba(2′)–O(9)	3.037 (7)
Ba(1)–O(4)	2.866 (7)	Ba(2′)–O(11)	2.982 (7)
Ba(1)–O(5)	2.856 (5)	Ba(2′)–O(12)	3.153 (8)
Ba(1)–O(6)	2.906 (6)	Cu(1)–Cl(1)	2.262 (2)
Ba(1)–O(1W)	2.982 (8)	Cu(1)–Cl(2)	2.259 (2)
Ba(1)–O(2W)	2.680 (7)	Cu(1)–Cl(3)	2.259 (2)
Ba(2)–Ba(2′)	2.241 (3)	Cu(1)–Cl(4)	2.238 (2)
Ba(2)–Cl(5)	3.324 (3)	Cu(2)–Cl(5)	2.259 (2)
Ba(2)–Cl(6)	3.299 (2)	Cu(2)–Cl(6)	2.262 (2)
Ba(2)–O(7)	2.885 (6)	Cu(2)–Cl(7)	2.268 (3)
Ba(2)–O(8)	2.897 (5)	Cu(2)–Cl(8)	2.246 (3)
Ba(2)–O(9)	2.878 (7)	av dist	
Ba(2)–O(10)	2.902 (7)	C–O[a]	1.43 (1)
Ba(2)–O(11)	2.883 (6)	C–O[b]	1.42 (1)
Ba(2)–O(12)	2.889 (6)	C–C[a]	1.47 (1)
		C–C[b]	1.48 (1)
Angles[c]			
Ba(1)–Cl(1)–Cu(1)	95.46 (8)	Cl(6)–Ba(2)–O(3W)	68.2 (1)
Ba(1)–Cl(2)–Cu(1)	97.15 (7)	Ba(2)–Cl(5)–Cu(2)	95.9 (1)
Cl(1)–Cu(1)–Cl(2)	97.70 (8)	Ba(2)–Cl(6)–Cu(2)	96.47 (8)
Cl(1)–Cu(1)–Cl(3)	130.2 (1)	Cl(5)–Cu(2)–Cl(6)	98.24 (9)
Cl(1)–Cu(1)–Cl(4)	102.28 (9)	Cl(5)–Cu(2)–Cl(7)	128.2 (1)
Cl(2)–Cu(1)–Cl(3)	97.1 (1)	Cl(5)–Cu(2)–Cl(8)	98.8 (1)
Cl(2)–Cu(1)–Cl(4)	131.3 (1)	Cl(6)–Cu(2)–Cl(7)	102.8 (1)
Cl(3)–Cu(1)–Cl(4)	102.75 (9)	Cl(6)–Cu(2)–Cl(8)	129.4 (1)
Cl(5)–Ba(2)–Cl(6)	62.14 (7)	Cl(7)–Cu(2)–Cl(8)	103.04 (9)
Cl(5)–Ba(2)–O(3W)	70.9 (2)		

[a] Molecule of Ba(1). [b] Molecule of Ba(2). [c] Only angles involving the $CuCl_4^{2-}$ anions have been selected; the rest are available as supplementary material.

It appears, therefore, that enrichment of thallium as $[(Tl18c6)_4MX_4]^{2+}$ (M = Cu, Zn; X = Cl, Br) is a template process requiring the participation of a very stable counteranionic complex such as TlX_4^- (X = Cl, Br; stability constant ~10^{19}, 10^{26}, respectively).[23] Studies attempting to generalize this conclusion to other potential M^{2+} and M^{3+} cation templates are in progress. The structure of the $[(Tl18c6)_4CuBr_4][TlBr_4]_2$ complex is also cubic, *F*23.[30b]

Electronic Evidence for the T_d Nature of the 23*T* Site Occupied by $CuCl_4^{2-}$. Caution in the interpretation of average room-temperature structures, especially of copper which frequently adopts static or dynamic distortions in its coordination geometry,[20] is important. For example, the complexes $[M(NH_3)_6][CuCl_5]$, M = Co and Cr, were for a while believed to constitute a unique case of copper(II) in an unusual perfect trigonal bipyramidal geometry,[31] but this turned out to be a dynamic average of several thermodynamically stable square pyramidal structures.[32] We have therefore recorded the absorption spectra of some of the compounds discussed above.

The absorption spectra of the complexes in the region 12 200–43 500 cm^{-1} are dominated by charge-transfer bands in the energy regions 33 000–37 000, 27 000–30 000 and 21 000–23 000 cm^{-1}. The peak at 33 000–37 000 cm^{-1} is associated with $TlCl_4^-$ as it is present in the spectra of **3** and **4** but not **6**. The peaks in the 27 000–30 000 cm^{-1} ($^2E \leftarrow {}^2B_2$) and 21 000–23 000 cm^{-1} ($^2A_2 \leftarrow$

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$^2B_2$ and $^2E \leftarrow {}^2B_2$) regions are charge-transfer bands due to $CuCl_4^{2-}$ and appear in positions generally predicted for D_{2d} $CuCl_4^{2-}$.[33] The spectrum of **5** was of poor quality and not informative. Further, with the aid of MCl_4^{2-} anions which have a stable and readily diagnosable T_d geometry, it is possible to electronically establish unequivocally the T_d nature of the $23T$ site occupied by $CuCl_4^{2-}$ in complexes **1** and **2**. We therefore prepared the complexes $[(Rb18c6)_4MnCl_4][TlCl_4]_2$, $[(Tl18c6)_4MnCl_4][TlCl_4]_2$, and $[(Tb18c6)_4Mn_{1-x}Cu_xCl_4][TlCl_4]_2$. The complexes are from X-ray powder diffraction studies isostructural with **1**, **2**, and **4** and exhibit $^4T_1$ (^4G) $\rightarrow$ $^6A_1$ luminescence characteristics of tetrahedral $MnCl_4^{2-}$ species (manuscript in preparation). The complexes $[(Rb18c6)_4Mn_{1-x}Co_xCl_4][TlCl_4]_2$ are also similar to **1** and **2** and exhibit the blue color typical of tetrahedral $CoCl_4^{2-}$ species. Clearly the $23T$ site occupied by $CuCl_4^{2-}$ anions in **1** and **2** is, as required by symmetry, of authentic T_d geometry not an average of structures of other symmetry, but the issue of the local geometry of $CuCl_4^{2-}$ is unresolved. Therefore, theoretical and experimental studies similar to those carried out[32] on the compound $[Co(NH_3)_6][CuCl_5]$ would be helpful in establishing the degree of distortion of $CuCl_4^{2-}$ from T_d symmetry and should in light of the foregoing yield interesting conformational information on $CuCl_4^{2-}$ geometry.

Conclusion

This study has therefore demonstrated that thallium can be immobilized in the presence of copper(II), Cu^{2+} playing a beneficial role of concentrating thallium in the solid phase as $[(Tl18c6)_4CuCl_4]^{2+}$. The formation of the $[(Rb18c6)_4CuCl_4]^{2+}$ complex cations in the presence but not absence of $TlCl_4^-$ ions suggests that the overall formation of the $[(M18c6)_4CuCl_4][TlCl_4]_2 \cdot nH_2O$ complexes is a template process taking advantage of the simultaneous stabilization of M^+ as $(M18c6)^+$, M^+ = large monovalent cation, and Tl^{3+} as $TlCl_4^-$. Through a series of concerted reactions, oxidation of Tl(I) or reduction of Tl(III) occurs only to an extent sufficient to yield the apparently thermodynamically more stable phases $[(Tl18c6)_4CuCl_4][TlCl_4]_2 \cdot nH_2O$. Stable T_d MCl_4^{2-} anions such as those of M = Mn, Co, and Zn show similar ability of concentrating thallium. The average T_d room-temperature geometry of $CuCl_4^{2-}$ observed in the $[(M18c6)_4CuCl_4][TlCl_4]_2 \cdot nH_2O$ complexes is intriguing since its existence would contradict theoretical predictions[20–23,33,34] and has so far not been observed. However, resolution of this important question must await the benefit of the low-temperature structural studies, which are in progress, as well as detailed variable-temperature spectroscopic and thermoanalytical data and concomitant theoretical studies.

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Supplementary Material Available: Tables of experimental details for X-ray data collection, simulated C–H positions, bond and torsion angles, and positional and anisotropic thermal parameters (13 pages). Ordering information is given on any current masthead page.

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