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f-Element/Crown Ether Complexes. 4.[1] Synthesis and Crystal and Molecular Structures of $[MCl(OH_2)_2(18\text{-crown-6})]Cl_2\cdot 2H_2O$ (M = Sm, Gd, Tb)

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Reaction under argon of the hydrated chloride salts of Sm, Gd, or Tb with 18-crown-6 in a 1/3 solution of methanol and acetonitrile yields crystalline $[MCl(OH_2)_2(18\text{-crown-6})]Cl_2\cdot 2H_2O$ (M = Sm, Gd, Tb). X-ray crystallographic studies have been carried out on the three compounds, which belong to an isostructural series. All three crystallize in the orthorhombic space group $P2_12_12_1$ with the following unit cell constants: $a = 7.421$ (1) Å, $b = 15.942$ (3) Å, $c = 18.929$ (5) Å, $D_{calcd} = 1.76$ g cm^{-3}, $Z = 4$ (M = Sm); $a = 7.400$ (1) Å, $b = 15.893$ (4) Å, $c = 18.876$ (4) Å, $D_{calcd} = 1.80$ g cm^{-3}, $Z = 4$ (M = Gd); $a = 7.412$ (7) Å, $b = 15.908$ (8) Å, $c = 18.904$ (8) Å, $D_{calcd} = 1.79$ g cm^{-3}, $Z = 4$ (M = Tb). Least-squares refinement of each led to conventional R values of 0.034 (using 2121 independent observed $[F_o \geq 5\sigma(F_o)]$ reflections) for M = Sm, 0.027 (2083 reflections) for M = Gd, and 0.088 (1506 reflections $[F_o \geq 2\sigma(F_o)]$) for M = Tb. In each case the metal atom is coordinated to the six crown oxygen atoms, one chlorine atom "above" the crown, and two water molecules "below". The remaining chloride ions and water molecules are hydrogen bonded, forming a polymeric network throughout the unit cell. The respective average M–Cl, M–O(crown), and M–O(OH_2) distances are 2.678 (3), 2.55 (2), and 2.45 (3) Å (M = Sm), 2.663 (3), 2.52 (3), and 2.41 (3) Å (M = Gd), and 2.69 (1), 2.53 (5), and 2.36 (4) Å (M = Tb). The Sm analogue studied has an absolute configuration opposite that for M = Gd and Tb.

Introduction

As part of our systematic investigation of the structural chemistry of f-element/crown ether complexes, we have begun to investigate under what conditions (e.g., metal size, crown ether cavity size, anion, solvent, etc.) a crown ether may exclude water molecules from a lanthanide metal's coordination sphere and coordinate to the metal itself. Thus far, we have concentrated on the later (smaller) Ln^{3+} ions and Y^{3+} in order to compare their behavior to some of the earlier lanthanides, for which several structures of crown ether complexes are known. Reaction of 12-crown-4 with $Y(NO_3)_3\cdot nH_2O$ in a methanol/acetonitrile solution produces the anhydrous product $Y(NO_3)_3(12\text{-crown-4})$[2] with direct Y-crown interaction. Under similar conditions using 15-crown-5 and hydrated lanthanide nitrates and chlorides (Gd–Lu, Y), only second-sphere coordination is observed for the crown ether as found in the structures of $[M(OH_2)_8]Cl_3\cdot 15\text{-crown-5}$ (M = Y,[3] Gd,[4] Lu[4]) and $[Y(NO_3)_2(OH_2)_5][NO_3]\cdot 2(15\text{-crown-5})$.[5] This occurs despite the fact that complexes with direct metal/crown interactions are known for 15-crown-5 (La^{3+}–Eu^{3+}).[11] The present study extends our work to 18-crown-6 interactions with hydrated lanthanide chlorides.

The complexation of hydrated lanthanide chlorides with 18-crown-6 in methanolic solution was investigated by Izatt et al.,[6] and more recently the structure of $[GdCl_2(OHEt)(18\text{-crown-6})]Cl$[7] was reported. Izatt et al. reported little or no reaction of 18-crown-6 with any post-Gd^{3+} lanthanides and attributed this in part to a smaller favorable entropy contribution from loss of solvent upon complexation of these elements. It is noted that the Gd complex above was prepared under anhydrous conditions. With these facts in mind and the information from several excellent reviews in this area, including ref 8–11, we have investigated the reaction of 18-crown-6 with several of the hydrated chloride salts of the later lanthanides and Y, which has an ionic radius between those of Dy^{3+} and Ho^{3+}. In those cases thus far studied, direct metal/crown interactions were observed. This paper details the synthesis and structural characterization of $[MCl(OH_2)_2(18\text{-crown-6})]Cl_2\cdot 2H_2O$ (M = Sm, Gd, Tb). Our next contribution will detail the structural changes that occur past Tb^{3+} and the complexes $[M(OH_2)_7(OHMe)][MCl(OH_2)_2(18\text{-crown-6})]_2Cl_7\cdot 2H_2O$ (M = Dy, Y).

Results and Discussion

The three title compounds are isostructural. The metal environment and the atom-labeling scheme for M = Gd are presented in Figure 1. Important bond distances and angles are given for all three compounds in Table I. Each metal center is nine-coordinate, six coordination sites filled by the oxygen atoms of the crown ether, one site "above" the crown ether belt filled by Cl(1), and two water molecules completing the coordination sphere "below" the crown ether. The Tb analogue is the least well determined, and the standard deviations are high due to limitations caused by small crystal size and, consequently, number and quality of observations of data. Although the M = Tb structure does indeed confirm the formation and structure of a Tb^{3+}/18-crown-6 complex, we will for the most part limit our discussion of metal geometry, hydrogen bonding, and crown ether conformation to the Sm and Gd analogues.

The metal–chlorine and metal–oxygen distances in these nine-coordinate complexes are not unusual. There is the expected decrease in M–Cl(1), M-O(OH_2), and M–O(crown) separations on going from Sm (2.678 (3), 2.45 (3), 2.55 (2) Å) to Gd (2.663 (3), 2.41 (3), 2.52 (3) Å). At the 3σ level the Tb–Cl(1), Tb–O(OH_2), and Tb–O(crown) distances of 2.69 (1), 2.36 (4), and 2.53 (5) Å also could fit the trend in decreasing ionic radius with increasing atomic number. In a related Gd^{3+} complex of identical geometry, $[GdCl_2(OHEt)(18\text{-crown-6})]Cl$,[7] the two Gd–Cl distances are nonequivalent. One chlorine, in the same coordination site as Cl(1) in the title compounds, is 2.695 (3) Å from the metal; the other (in a site occupied by O(7) or O(8) in the title compounds) is further away at 2.734 (3) Å. It is interesting to note that when water is present, as in our starting material ($MCl_3\cdot 6H_2O$), a tight ion pair at this latter coordination site is prevented, but one tight ion pair (M–Cl(1)) remains intact. The presence of water also prevents coordination or clathration of the solvent used in these studies ($OHMe/CH_3CN$). Water, however, does not totally prevent direct metal/crown interaction as we observed in $[M(OH_2)_8]Cl_3\cdot 15\text{-crown-5}$ (M = Y,[3] Gd,[4] Lu[4]).

The Sm–O(OH_2) (2.45 (3) Å) and Sm–O(crown) (2.55 (2) Å) average distances are comparable to those observed for nine-coordinate Sm^{3+} in $[Sm(OH_2)_4(15\text{-crown-5})][ClO_4]_3\cdot 15\text{-}$

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Table I. Bond Distances (Å) and Angles (deg) for $[MCl(OH_2)_2(18\text{-crown-6})]Cl_2 \cdot 2H_2O$

	distances		
atoms	Sm	Gd	Tb
M–Cl(1)	2.678 (3)	2.663 (3)	2.69 (1)
M–O(1)	2.558 (9)	2.543 (7)	2.50 (3)
M–O(2)	2.531 (9)	2.509 (7)	2.57 (3)
M–O(3)	2.541 (9)	2.523 (6)	2.51 (2)
M–O(4)	2.514 (8)	2.472 (6)	2.45 (3)
M–O(5)	2.549 (8)	2.538 (6)	2.59 (2)
M–O(6)	2.585 (9)	2.565 (7)	2.56 (3)
M–O(7)	2.426 (8)	2.387 (6)	2.39 (2)
M–O(8)	2.467 (8)	2.435 (6)	2.34 (2)
O–C_{av}	1.44 (6)	1.44 (4)	1.4 (1)
C–C_{av}	1.47 (4)	1.45 (4)	1.52 (8)

	angles		
atoms	Sm	Gd	Tb
Cl(1)–M–O(1)	113.2 (2)	114.6 (2)	113.5 (9)
Cl(1)–M–O(2)	77.5 (2)	76.7 (2)	76.2 (6)
O(1)–M–O(2)	62.8 (3)	63.0 (2)	64.3 (9)
Cl(1)–M–O(3)	76.6 (2)	76.4 (2)	76.8 (6)
O(1)–M–O(3)	118.6 (3)	118.7 (2)	120.6 (8)
O(2)–M–O(3)	61.0 (3)	62.0 (2)	62.4 (8)
Cl(1)–M–O(4)	90.5 (2)	90.5 (2)	90.0 (7)
O(1)–M–O(4)	156.3 (3)	154.9 (2)	157 (1)
O(2)–M–O(4)	124.8 (3)	125.9 (2)	126.2 (8)
O(3)–M–O(4)	63.7 (3)	63.9 (2)	63.8 (8)
Cl(1)–M–O(5)	75.1 (2)	74.8 (1)	75.4 (6)
O(1)–M–O(5)	120.4 (3)	120.7 (2)	120.1 (8)
O(2)–M–O(5)	150.9 (3)	149.5 (2)	150.1 (8)
O(3)–M–O(5)	120.6 (3)	120.3 (2)	119.0 (8)
O(4)–M–O(5)	65.4 (3)	65.3 (2)	63.0 (8)
Cl(1)–M–O(6)	80.7 (2)	80.3 (2)	79.1 (6)
O(1)–M–O(6)	61.9 (3)	62.4 (2)	61.4 (9)
O(2)–M–O(6)	104.2 (3)	102.2 (2)	102.2 (8)
O(3)–M–O(6)	155.2 (3)	154.3 (2)	154.0 (8)
O(4)–M–O(6)	127.1 (3)	127.4 (2)	126.2 (8)
O(5)–M–O(6)	61.8 (3)	62.3 (2)	63.2 (8)
Cl(1)–M–O(7)	143.2 (2)	142.6 (2)	141.4 (5)
O(1)–M–O(7)	80.6 (3)	80.3 (2)	79.3 (9)
O(2)–M–O(7)	135.9 (3)	137.2 (2)	137.8 (7)
O(3)–M–O(7)	128.3 (3)	128.4 (2)	129.6 (7)
O(4)–M–O(7)	81.0 (3)	80.2 (2)	81.5 (8)
O(5)–M–O(7)	68.8 (3)	68.3 (2)	67.2 (7)
O(6)–M–O(7)	76.4 (3)	77.2 (2)	76.1 (8)
Cl(1)–M–O(8)	145.5 (2)	145.4 (1)	147.7 (6)
O(1)–M–O(8)	74.7 (3)	74.1 (2)	74.6 (9)
O(2)–M–O(8)	77.1 (3)	78.7 (2)	80.4 (8)
O(3)–M–O(8)	70.7 (3)	70.6 (2)	72.7 (8)
O(4)–M–O(8)	85.0 (3)	84.5 (2)	86.1 (8)
O(5)–M–O(8)	131.9 (3)	131.7 (2)	129.4 (8)
O(6)–M–O(8)	128.3 (3)	129.0 (2)	128.0 (8)
O(7)–M–O(8)	69.7 (3)	70.2 (2)	69.5 (7)
M–O–C_{av}	119 (4)	119 (4)	120 (6)
C–O–C_{av}	113 (6)	113 (5)	112 (7)
O–C–C_{av}	109 (4)	109 (5)	108 (5)

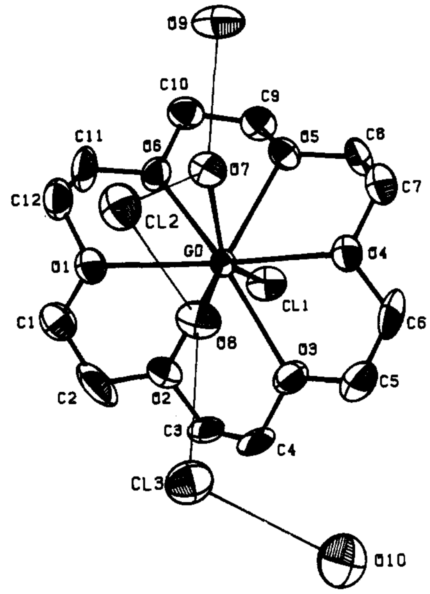

Figure 1. Molecular structure and atom-labeling scheme for $[MCl(OH_2)_2(18\text{-crown-6})]Cl_2 \cdot 2H_2O$ (M = Gd shown). The atoms are represented by their 50% probability ellipsoids for thermal motion. The hydrogen atoms have been omitted.

Table II. Torsion Angles (deg) for $[MCl(OH_2)_2(18\text{-crown-6})]Cl_2 \cdot 2H_2O$

	angles		
atoms	Sm	Gd	Tb
O(1)–C(1)–C(2)–O(2)	45.6	–44.9	–58.6
C(1)–C(2)–O(2)–C(3)	156.8	–158.4	–148.2
C(1)–C(2)–O(2)–C(3)′	–172.2	172.5	–175.4
C(2)–O(2)–C(3)–C(4)	112.1	–113.3	–111.1
C(2)–O(2)–C(3)′–C(4)′	170.6	–163.7	–147.4
O(2)–C(3)–C(4)–O(3)	54.8	–52.1	–50.0
O(2)–C(3)′–C(4)′–O(3)	–41.3	30.1	21.8
C(3)–C(4)–O(3)–C(5)	158.5	–157.4	–156.9
C(3)′–C(4)′–O(3)–C(5)	–146.8	157.2	163.1
C(4)–O(3)–C(5)–C(6)	–164.7	164.3	160.5
C(4)′–O(3)–C(5)–C(6)	–143.8	150.7	147.6
O(3)–C(5)–C(6)–O(4)	–46.2	39.7	44.9
C(5)–C(6)–O(4)–C(7)	–175.4	178.3	172.6
C(6)–O(4)–C(7)–C(8)	–102.1	104.8	108.3
O(4)–C(7)–C(8)–O(5)	–56.9	57.6	45.9
C(7)–C(8)–O(5)–C(9)	–176.0	174.5	–176.9
C(8)–O(5)–C(9)–C(10)	168.5	–170.3	–163.6
O(5)–C(9)–C(10)–O(6)	47.2	–48.2	–55.4
C(9)–C(10)–O(6)–C(11)	176.5	–176.6	–176.3
C(10)–O(6)–C(11)–C(12)	139.2	–135.2	–130.2
O(6)–C(11)–C(12)–O(1)	46.5	–47.5	–47.0
C(11)–C(12)–O(1)–C(1)	91.1	–87.5	–90.7
C(12)–O(1)–C(1)–C(2)	–177.7	173.4	–174.7

crown-5·H_2O[12] (Sm–O(OH_2) = 2.43 (2) Å, Sm–O(15-crown-5) = 2.51 (1) Å). The Gd–O(OH_2) average distance of 2.41 (3) Å is similar to the 2.39 (8) Å average found in $[Gd(NO_3)_3(OH_2)_3] \cdot 18$-crown-6,[13] and the Gd–O(crown) average separation of 2.52 (3) Å is comparable to the 2.54 (4) Å found for similar distances in $[GdCl_2(OHEt)(18\text{-crown-6})]Cl$.

Perhaps the most interesting features of mid- to late-lanthanide complexes of 18-crown-6 involve how the crown ether conformation changes to accommodate the decrease in ionic size. The average C–C and C–O bond lengths and C–C–O and C–O–C bond angles given in Table I are not unusual and would seem to indicate no undue strain on the molecule. However, the crown ether molecules in the title compounds are disordered, and some interesting aspects of the crown geometry may be obscured. Further analysis of least-squares planes results for O(1)–O(6), torsion angles (Table II), and a side-on plot of the complexes (Figure 2) does reveal that some steric strain probably exists and that O(1) and O(4) "absorb" the strain caused by smaller cations in the crown cavity. The crown ether conformation is derived from the D_{3d} conformation found in most of its complexes,[14,15] which tends to equalize $M^{n+} \cdots O$ contacts. The deviations in the torsion angle sequence from that of the D_{3d} crown ether found in the title compounds involve the portions of the crown ether containing O(1) and O(4). In addition, a least-squares analysis of the crown ether reveals that O(1) and O(4) have large deviations of up to 0.93 Å (O(1), M = Gd) out of the plane defined by O(1)–O(6), toward the O(7)–M–O(8) bond angle. There are also significant differences

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Table III. Hydrogen-Bonding-Contact Geometries for $[MCl(OH_2)_2(18\text{-crown-}6)]Cl_2{\cdot}2H_2O$

atoms	distances, Å Sm	Gd	Tb
O(7)–Cl(2)	2.980 (9)	3.001 (6)	3.05 (2)
O(7)–O(9)	2.65 (1)	2.658 (9)	2.58 (3)
O(8)–Cl(2)	3.062 (8)	3.071 (6)	3.04 (2)
O(8)–Cl(3)	3.054 (9)	3.069 (7)	3.20 (2)
O(9)–Cl(3)[a]	3.17 (1)	3.159 (8)	3.17 (3)
O(9)–O(10)[b]	2.77 (1)	2.78 (1)	2.77 (4)
O(10)–Cl(3)	3.12 (1)	3.128 (8)	3.12 (3)
O(10)–Cl(3)[c]	3.14 (1)	3.122 (9)	3.15 (3)

atoms	angles, deg Sm	Gd	Tb
Cl(2)–O(7)–O(9)	108.4 (3)	107.5 (2)	107.9 (9)
Cl(2)–O(8)–Cl(3)	104.1 (3)	103.4 (2)	100.7 (6)
Cl(3)[a]–O(9)–O(10)[b]	113.2 (3)	113.2 (3)	111 (1)
Cl(3)–O(10)–Cl(3)[c]	106.6 (3)	106.5 (2)	106.3 (9)

[a] Atoms related to those in Tables V–VII by $-x-3$, $0.5+y$, $-z-0.5$ (M = Sm) and $3-x$, $y-0.5$, $0.5-z$ (M = Gd, Tb). [b] $-x-2.5$, $-y-1$, $0.5+z$ (M = Sm) and $2.5-x$, $1-y$, $z-0.5$ (M = Gd, Tb). [c] $x-0.5$, $-y-1.5$, $-z-1$ (M = Sm) and $0.5+x$, $1.5-y$, $1-z$ (M = Gd, Tb).

in the M–O(crown) separations. In each case the M–O(4) distance is the shortest of the six crown oxygen atoms. Also, the O(2), O(3), and O(4) to M^{3+} separations are shorter than the M–O interaction trans to them (O(5), O(6), O(1)). Supporting evidence for this type of crown deformation can be found in ref 13, which compares the structures of $[M(NO_3)_3(18\text{-crown-}6)]$ (M = La, Nd).

Besides the metal geometry and crown conformation, the nature of any "supermolecular" structure resulting from hydrogen bonding is important in the complexes we are investigating. These supermolecules usually have a specific energy, geometry, stability, and reactivity. Their use in guest recognition, molecular catalysis, and guest transport deserves serious study.[10] In the absence of water molecule hydrogen atom positions, the hydrogen bonding can be inferred from the geometry of $Cl{\cdots}H_2O$ contacts (Table III). Each of the coordinated water molecules has two hydrogen-bonding interactions: O(7) with O(9) and Cl(2); O(8) with Cl(2) and Cl(3). O(9) is also hydrogen bonded to Cl(3)[a] and O(10)[b] for a total of three such interactions. O(10) also has three hydrogen bonds, one from O(9) and two to Cl(3) and Cl(3)[c]. Cl(1), which is coordinated to the metal, participates in no hy-

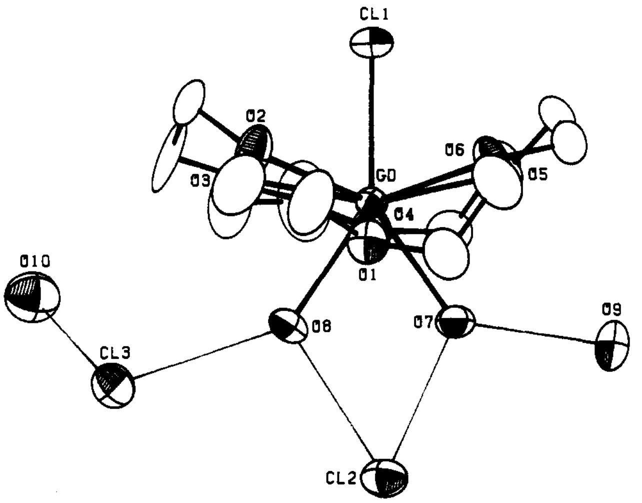

Figure 2. Side view of $[MCl(OH_2)_2(18\text{-crown-}6)]Cl_2{\cdot}2H_2O$ (M = Gd shown). Note the deviations of O(1) and O(4) from the mean plane defined by O(1)–O(6).

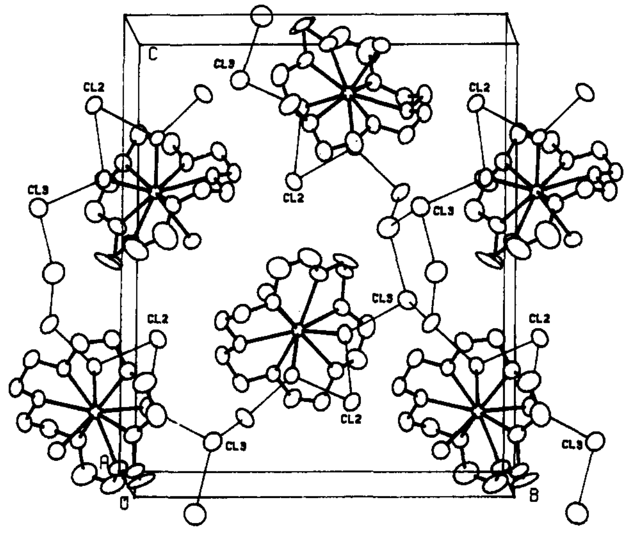

Figure 3. Cell-packing diagram for $[MCl(OH_2)_2(18\text{-crown-}6)]Cl_2{\cdot}2H_2O$ (M = Gd shown) indicating the hydrogen-bonding network.

Table IV. Crystal Data and Summary of Intensity Data Collection and Structure Refinement for $[MCl(OH_2)_2(18\text{-crown-}6)]Cl_2{\cdot}2H_2O$

cmpd	M = Sm	M = Gd	M = Tb
color shape	colorless/rod	colorless/parallelepiped	colorless/needle
mol wt	593.1	600.0	601.7
space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
temp, °C	22	22	22
cell constants			
a, Å	7.421 (1)	7.400 (1)	7.412 (7)
b, Å	15.942 (3)	15.893 (4)	15.908 (8)
c, Å	18.929 (5)	18.876 (4)	18.904 (8)
cell vol, $Å^3$	2239.2	2219.8	2228.8
molecules/unit cell	4	4	4
ρ(calcd), g cm^{-3}	1.76	1.80	1.79
μ(calcd), cm^{-1}	28.5	32.1	36.4
range of rel transmn factors	0.97/0.96	0.92/0.91	0.97/0.96
radiation, graphite monochromator	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)
max cryst dimens, mm	0.10 × 0.13 × 0.40	0.25 × 0.28 × 0.38	0.08 × 0.12 × 0.23
scan width	0.80 + 0.35 tan θ	0.80 + 0.35 tan θ	0.80 + 0.35 tan θ
std reflcns	600, 080, 008	600, 0,14,0, 0,0,10	060, 112, 102, 021
decay of stds, %	±1	±1	±2
no. of reflcns measd	2284	2269	2270
2θ range, deg	$2 < 2\theta < 50$	$2 < 2\theta < 50$	$2 < 2\theta < 50$
range of *h*,*k*,*l*	+8,+18,+22	+8,+18,+22	+8,+18,+22
no. of reflcns obsd	2121 [$F_o \geq 5\,\sigma(F_o)$]	2083 [$F_o \geq 5\sigma(F_o)$]	1506 [$F_o \geq 2\sigma(F_o)$]
no. of params varied	244	244	184
wts	$[\sigma(F_o)^2]^{-1}$	$[\sigma(F_o)^2 + 0.00004F_o^2]^{-1}$	$[\sigma(F_o)^2 + 0.00004F_o^2]^{-1}$
GOF	3.8	2.0	2.3
R	0.034	0.027	0.088
R_w	0.041	0.033	0.090

Table V. Final Fractional Coordinates for $[SmCl(OH_2)_2(18\text{-crown-}6)]Cl_2\cdot 2H_2O$

atom	*x/a*	*y/b*	*z/c*	*U*(eq),^{a} Å^2
Sm	−1.08190 (7)	−0.43135 (3)	−0.36332 (3)	0.025
Cl(1)	−0.8995 (5)	−0.3400 (2)	−0.4581 (2)	0.051
Cl(2)	−1.3646 (4)	−0.5840 (2)	−0.1882 (2)	0.051
Cl(3)	−1.3593 (5)	−0.7271 (2)	−0.4127 (2)	0.057
O(1)	−0.878 (1)	−0.5230 (5)	−0.2864 (4)	0.042
O(2)	−0.893 (1)	−0.5411 (5)	−0.4256 (5)	0.057
O(3)	−1.190 (1)	−0.4891 (6)	−0.4810 (5)	0.049
O(4)	−1.374 (1)	−0.3739 (5)	−0.4090 (4)	0.046
O(5)	−1.143 (1)	−0.2793 (5)	−0.3294 (4)	0.041
O(6)	−0.858 (1)	−0.3575 (5)	−0.2794 (4)	0.044
O(7)	−1.245 (1)	−0.4227 (5)	−0.2526 (4)	0.041
O(8)	−1.254 (1)	−0.5615 (5)	−0.3429 (4)	0.045
O(9)	−1.287 (1)	−0.3017 (5)	−0.1579 (4)	0.063
O(10)	−1.492 (1)	−0.6782 (6)	−0.5635 (5)	0.073
C(1)	−0.748 (2)	−0.573 (1)	−0.3190 (8)	0.080
C(2)	−0.814 (2)	−0.605 (1)	−0.3882 (8)	0.088
C(3)^{b}	−0.905 (4)	−0.548 (1)	−0.503 (1)	0.031
C(4)^{b}	−1.101 (4)	−0.558 (2)	−0.514 (1)	0.069
C(3)′^{b}	−0.979 (5)	−0.590 (2)	−0.492 (2)	iso
C(4)′^{b}	−1.094 (5)	−0.535 (2)	−0.532 (2)	iso
C(5)	−1.360 (3)	−0.472 (1)	−0.506 (1)	0.101
C(6)	−1.410 (3)	−0.393 (1)	−0.4827 (8)	0.106
C(7)	−1.433 (2)	−0.2960 (7)	−0.3793 (7)	0.052
C(8)	−1.278 (2)	−0.2365 (7)	−0.3726 (7)	0.051
C(9)	−0.985 (2)	−0.2264 (7)	−0.3132 (6)	0.047
C(10)	−0.876 (2)	−0.2702 (7)	−0.2571 (6)	0.045
C(11)	−0.747 (2)	−0.4023 (8)	−0.2315 (8)	0.071
C(12)	−0.828 (2)	−0.4862 (9)	−0.2208 (7)	0.063

^{a} *U*(eq) is equal to $(U_{11} + U_{22} + U_{33})/3$. ^{b} C(3), C(4), C(3)′, and C(4)′ are disordered with occupancy factors of 50% each.

drogen bonds. Cl(2) participates in a total of two; Cl(3), in four hydrogen-bond interactions. The result is a polymeric network of hydrogen bonding as seen in the cell-packing diagram (Figure 3).

Experimental Section

Synthesis of $[SmCl(OH_2)_2(18\text{-crown-}6)]Cl_2\cdot 2H_2O$. Under Ar, 5 mmol of 18-crown-6 in 30 mL of CH_3OH/CH_3CN (1/3) was added to a stirring solution of 5 mmol of $SmCl_3\cdot 6H_2O$ in 30 mL of the corresponding solvent. The reaction was heated to 60 °C for 5 h, allowed to cool to 20 °C, and stored at 5 °C for 36 h. Carbon tetrachloride was used as a crystallizing agent. Mp: 66–68 °C. Anal. Calcd for $[SmCl(OH_2)_2(18\text{-crown-}6)]Cl_2\cdot 2H_2O$: C, 24.30; H, 5.44. Found: C, 22.01; H, 4.65.

$[GdCl(OH_2)_2(18\text{-crown-}6)]Cl_2\cdot 2H_2O$. Under Ar, 5 mmol of 18-crown-6 in 15 mL of CH_3OH/CH_3CN (1/3) was added to a stirring solution of 5 mmol of $GdCl_3\cdot 6H_2O$ in 15 mL of the same solvent. The reaction mixture was heated to 60 °C for 24 h, allowed to cool to 20 °C, and stored at 5 °C for 5 days. To this solution 25 mL of pentane was added, and the resultant solution was evaporated slowly. Clear rodlike crystals deposited along the walls of the flask. Mp: 68–70 °C. Anal. Calcd for $[GdCl(OH_2)_2(18\text{-crown-}6)]Cl_2\cdot 2H_2O$: C, 24.02; H, 5.38. Found: C, 24.16; H, 5.39.

$[TbCl(OH_2)_2(18\text{-crown-}6)]Cl_2\cdot 2H_2O$. Under Ar, 1.2 mmol of 18-crown-6 in 8 mL of CH_3OH/CH_3CN (1/3) was added to a stirring solution of 1.2 mmol of $TbCl_3\cdot 6H_2O$ in the same solvent. The mixture was heated to 60 °C for 1 h and allowed to cool to 20 °C. Microcrystals formed after 5 days at 5 °C. The reaction mixture was than heated until the product went back into solution and slowly cooled to −45 °C, at which time small crystals suitable for the X-ray diffraction study formed. Mp: 70–74 °C. Anal. Calcd for $[TbCl(OH_2)_2(18\text{-crown-}6)]Cl_2\cdot 2H_2O$: C, 23.95; H, 5.36. Found: C, 25.63; H, 5.40.

After formation of the title compounds, small shifts of 5–35 cm^{-1} in the vibrational bands due to the crown ether were observed compared to those for the free crown.

X-ray Data Collection, Structure Determination, and Refinement for $[MCl(OH_2)_2(18\text{-crown-}6)]Cl_2\cdot 2H_2O$ (M = Sm, Gd, Tb). Clear single crystals of the title complexes were mounted in air on a glass pin placed on the goniometer head. Final lattice parameters as determined from a least-squares refinement of $[(\sin\theta)/\lambda]^2$ values for 25 reflections ($\theta > 18°$ (M = Gd, Sm); $\theta > 10°$ (M = Tb)) accurately centered on the diffractometer are given in Table IV. The space group was determined to be acentric $P2_12_12_1$ from the systematic absences.

Data were collected on an Enraf-Nonius CAD-4 diffractometer by the θ–2θ scan technique. A summary of data collection parameters is given in Table IV. The intensities were corrected for Lorentz, polarization, and absorption effects. (An empirical absorption correction using ψ scans of χ = 90° reflections was employed.)

Table VI. Final Fractional Coordinates for $[GdCl(OH_2)_2(18\text{-crown-}6)]Cl_2\cdot 2H_2O$

atom	*x/a*	*y/b*	*z/c*	*U*(eq),^{a} Å^2
Gd	1.08087 (5)	0.43114 (2)	0.36359 (2)	0.024
Cl(1)	0.9003 (4)	0.3400 (2)	0.4585 (1)	0.049
Cl(2)	1.3670 (3)	0.5823 (2)	0.1883 (1)	0.049
Cl(3)	1.3609 (4)	0.7268 (2)	0.4128 (1)	0.056
O(1)	0.883 (1)	0.5238 (4)	0.2856 (3)	0.043
O(2)	0.887 (1)	0.5381 (4)	0.4250 (3)	0.054
O(3)	1.1884 (9)	0.4884 (4)	0.4809 (3)	0.045
O(4)	1.3705 (8)	0.3744 (4)	0.4080 (3)	0.043
O(5)	1.1419 (8)	0.2790 (3)	0.3303 (3)	0.036
O(6)	0.854 (1)	0.3580 (4)	0.2814 (3)	0.044
O(7)	1.2434 (8)	0.4207 (4)	0.2547 (3)	0.039
O(8)	1.2533 (9)	0.5594 (4)	0.3436 (3)	0.046
O(9)	1.285 (1)	0.2995 (4)	0.1591 (3)	0.064
O(10)	1.497 (1)	0.6777 (5)	0.5641 (4)	0.075
C(1)	0.752 (2)	0.5729 (8)	0.3189 (6)	0.070
C(2)	0.808 (2)	0.6013 (7)	0.3870 (6)	0.081
C(3)^{b}	0.894 (2)	0.5457 (9)	0.5039 (7)	0.045
C(4)^{b}	1.089 (3)	0.554 (1)	0.5149 (8)	0.076
C(3)′^{b}	0.957 (4)	0.583 (2)	0.489 (1)	iso
C(4)′^{b}	1.089 (6)	0.543 (2)	0.532 (2)	iso
C(5)	1.360 (2)	0.4692 (8)	0.5059 (6)	0.081
C(6)	1.417 (2)	0.3911 (8)	0.4799 (7)	0.095
C(7)	1.431 (1)	0.2947 (6)	0.3788 (5)	0.048
C(8)	1.275 (1)	0.2363 (5)	0.3742 (5)	0.044
C(9)	0.986 (1)	0.2275 (5)	0.3144 (5)	0.044
C(10)	0.876 (1)	0.2720 (5)	0.2596 (5)	0.045
C(11)	0.741 (2)	0.4038 (6)	0.2337 (6)	0.058
C(12)	0.828 (1)	0.4854 (6)	0.2203 (5)	0.052

^{a} *U*(eq) is equal to $(U_{11} + U_{22} + U_{33})/3$. ^{b} C(3) and C(4) have occupancy factors of 65%; C(3)′ and C(4)′, 35%.

Table VII. Final Fractional Coordinates for $[TbCl(OH_2)_2(18\text{-crown-}6)]Cl_2\cdot 2H_2O$

atom	*x/a*	*y/b*	*z/c*	*U*(eq),^{a} Å^2
Tb	1.0818 (2)	0.43153 (9)	0.36353 (9)	0.032
Cl(1)	0.898 (2)	0.3391 (6)	0.4585 (5)	0.056
Cl(2)	1.365 (1)	0.5846 (5)	0.1882 (5)	0.054
Cl(3)	1.362 (1)	0.7281 (6)	0.4122 (6)	0.057
O(1)	0.883 (6)	0.519 (1)	0.286 (1)	0.083
O(2)	0.882 (4)	0.540 (2)	0.427 (1)	0.053
O(3)	1.191 (3)	0.488 (2)	0.480 (1)	0.047
O(4)	1.365 (4)	0.373 (1)	0.408 (1)	0.062
O(5)	1.153 (3)	0.277 (1)	0.330 (1)	0.044
O(6)	0.855 (4)	0.357 (2)	0.283 (1)	0.051
O(7)	1.238 (3)	0.419 (1)	0.253 (1)	0.042
O(8)	1.247 (3)	0.554 (1)	0.340 (1)	0.039
O(9)	1.287 (4)	0.302 (1)	0.161 (1)	0.060
O(10)	1.490 (4)	0.680 (2)	0.564 (2)	0.087
C(1)	0.737 (6)	0.575 (3)	0.322 (2)	iso
C(2)	0.826 (6)	0.602 (2)	0.384 (2)	iso
C(3)^{b}	0.890 (9)	0.549 (3)	0.499 (3)	iso
C(4)^{b}	1.103 (9)	0.548 (3)	0.510 (3)	iso
C(3)′^{b}	0.96 (1)	0.589 (6)	0.498 (5)	iso
C(4)′^{b}	1.12 (2)	0.537 (6)	0.532 (6)	iso
C(5)	1.353 (6)	0.466 (2)	0.505 (2)	iso
C(6)	1.407 (8)	0.380 (3)	0.483 (3)	iso
C(7)	1.438 (5)	0.294 (2)	0.381 (2)	iso
C(8)	1.292 (5)	0.237 (2)	0.367 (2)	iso
C(9)	0.993 (5)	0.230 (2)	0.315 (2)	iso
C(10)	0.886 (6)	0.274 (2)	0.258 (2)	iso
C(11)	0.742 (6)	0.402 (2)	0.233 (2)	iso
C(12)	0.836 (7)	0.488 (3)	0.218 (2)	iso

^{a} *U*(eq) is equal to $(U_{11} + U_{22} + U_{33})/3$. ^{b} C(3) and C(4) have occupancy factors of 60%; C(3)′ and C(4)′, 40%.

Calculations were carried out with the SHELX[16] system of computer programs. Neutral-atom scattering factors for Tb, Gd, Sm, Cl, O, C,

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[16] Sheldrick, G. M. "SHELX", a system of computer programs for X-ray structure determination as locally modified, 1976.

and H were taken from ref 17, and the scattering was corrected for the real and imaginary components of anomalous dispersion.[17]

The gadolinium analogue was solved first, and the position of the gadolinium atom was determined from a Patterson map. The remaining non-hydrogen atoms were located from successive difference Fourier maps. These coordinates were used for the solution of the Sm and Tb analogues. Higher than normal thermal motion was observed for carbon atoms C(1), C(2), C(3), C(4), C(5), and C(6). Inspection of a difference Fourier around these atoms revealed what appeared to be a disordered conformation, indicated in Tables V-VII as C(3)′, C(4)′. No other resolvable peaks near C(1), C(2), C(5), or C(6) were observed. Refinement of the occupancy factors for C(3), C(4) and C(3)′, C(4)′ converged at 65%/35% for M = Gd, 50%/50% for M = Sm, and 60%/40% for M = Tb. Due to the disorder, C(3)′ and C(4)′ were only refined isotropically in all three compounds. Least-squares refinement with isotropic thermal parameters led to $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.075$ (M = Gd), 0.057 (M = Sm), and 0.089 (M = Tb). The hydrogen atoms of the crown ether were placed in calculated positions 0.95 Å from the bonded carbon atom and allowed to ride on that atom with *B* fixed at 5.5 Å^2. Due to the proximity of C(3), C(4) and C(3)′, C(4)′, no attempt was made to place hydrogen atoms around these atoms. The hydrogen atoms associated with the water molecules were not located. Refinement of the non-hydrogen atoms with anisotropic temperature factors led to final values of $R = 0.027$ and $R_w = 0.033$ for the Gd analogue. No systematic variation of $w(|F_o| - |F_c|)$ vs. $|F_o|$ or $(\sin\theta)/\lambda$ was noted. The Sm and Tb analogues were refined similarly. The final values of the positional parameters are given in Table V (M = Sm), Table VI (M = Gd), and Table VII (M = Tb). Due to the limited data resulting from the small crystal size, only the Tb, Cl, and O atoms were refined anisotropically for M = Tb. An investigation of absolute configuration revealed the M = Sm complex to have an absolute configuration opposite to that for the M = Gd or M = Tb complex. *R* factors for the inverse configurations (from those in Tables V-VII) were 0.038 (M = Gd), 0.044 (M = Sm), and 0.092 (M = Tb). Final values for M = Sm were $R = 0.034$ and $R_w = 0.041$ and for M = Tb $R = 0.088$ and $R_w = 0.090$.

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Supplementary Material Available: Tables SI-SX, listing derived hydrogen positions, thermal parameters, complete bond distances and angles, and least-squares planes results (8 pages); Tables SXI-SXIII, giving observed and calculated structure factor amplitudes (22 pages). Ordering information is given on any current masthead page.

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[17] *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1972; Vol. IV, pp 72, 99, 149.

Contribution from the Laboratoire de Chimie de Coordination du CNRS,
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Assembling Potentialities of an Anionic Tripod Ligand: Trirhodium and Triiridium Complexes of 1,1,1-Tris(sulfidomethyl)ethane.[1] Molecular Structure and Crystal Packing of $Ir_3(CH_3C(CH_2S)_3)(CO)_6$

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Reaction of $CH_3C(CH_2SLi)_3$ with $M_2(\mu\text{-}Cl)_2(C_8H_{12})_2$ gives quantitatively trimetallic complexes, $M_3(CH_3C(CH_2S)_3)(C_8H_{12})_3$ (**1**, M = Rh; **2**, M = Ir). Reaction of **1** and **2** with carbon monoxide gives $M_3(CH_3C(CH_2S)_3)(CO)_6$ derivatives (**3**, M = Rh; **4**, M = Ir). The structure of **4** has been determined by single-crystal X-ray diffraction. Compound **4** crystallizes in the monoclinic space group $P2_1/c$ with four molecules in a unit cell of dimensions $a = 10.304$ (3) Å, $b = 14.712$ (2) Å, $c = 12.270$ (3) Å, and $\beta = 104.17$ (2)° ($V = 1803$ (1) Å^3). Least-squares refinement leads to a value of 0.037 for the conventional *R* index for 2082 reflections having $I > 3\sigma(I)$. The crystallographic investigation confirms the formulation of **4** as a hexacarbonyl trimetallic species in which the trithiolato group acts as a 12-electron-donor ligand bridging a triangle of three nonbonded iridium atoms (Ir-Ir = 3.315 (1), 3.366 (1), 3.336 (1) Å) giving a trithiatrimetallaadamantane-like structure. Short intermolecular Ir···Ir distances (3.471 (1), 3.506 (1), 3.506 (1) Å) lead to a description of the packing of adamantane units as a stacking of bidimensional networks. Spectroscopic investigations of **3** and **4**, i.e. IR ν(CO) absorption and ^{1}H NMR, indicate that the molecular structure of **4** remains unchanged in solution while that of **3** is quite similar to that determined for **4**. Substitution of tertiary phosphine ligands for carbonyl on **3** leads to trisubstituted derivatives, $Rh_3(CH_3C(CH_2S)_3)(CO)_3(PR_3)_3$, of C_3 symmetry (**5**, R = OMe; **6**, R = Ph). Identical complexes may be prepared by reaction of $CH_3C(CH_2SLi)_3$ with $Rh_2(\mu\text{-}Cl_2)(CO)_2(PR_3)_2$. $Rh_3(CH_3C(CH_2S)_3)(P(OMe)_3)_6$ (**7**) has similarly been prepared by the reaction of $CH_3C(CH_2SLi)_3$ with $Rh_2(\mu\text{-}Cl_2)(P(OMe)_3)_4$. Reaction of dimethyl acetylenedicarboxylate with **2** yields quantitatively a 1:1 adduct, $Ir_3(CH_3C(CH_2S)_3)(CO)_6(\mu\text{-}(CH_3COOC)_2)$, in which the added alkyne is assumed to bridge two bonded metallic centers, leading to a formally "d^8, d^7-d^7" derivative.

Introduction

A few years ago, we[3] and others[4] claimed that the synthesis of polymetallic compounds in which the metallic reactive sites are kept close to each other by means of bridging ligands may be used as one of the most convenient experimental approaches to polymetallic activation.

In this context, we extensively studied the reactivity of thiolato-bridged bimetallic complexes, and we have shown that, among these, dirhodium and diiridium complexes exhibit rich stoichiometric reactivity (oxidative addition of a variety of small molecules including molecular hydrogen,[5] iodine,[6] tetracyanoethylene,[7] hexafluoro-2-butyne,[8] dihalomethane,[9] methyl iodide[10]) as well as outstanding catalytic activities (hydrogenation[11] and hydroformylation[12] of alkenes).

Moreover, from a more fundamental point of view, we were able to establish clearly, following the example of bimetallic activation of dihydrogen over diiridium species, a relationship between the reactivity of these complexes and the deformability

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