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Unprecedented Polycrystal Structure of a New Cadmium Thiolate Containing an Unusually Highly Charged $[\mathrm{ClCd_8\{SCH(CH_2CH_2)_2N(H)Me\}_{16}}]^{15+}$ Core

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Abstract: A new cadmium thiolate with overall composition $[\mathrm{ClCd_8\{SCH(CH_2CH_2)_2N(H)Me\}_{16}}](\mathrm{ClO_4})_{15}\cdot 16[\mathrm{SCH(CH_2CH_2)_2N(H)Me}]\cdot 32\mathrm{H_2O}$ has been obtained in a high ionic strength aqueous medium. The solid is a polycrystal consisting of equally oriented microcrystals of formula $[\mathrm{ClCd_8\{SCH(CH_2CH_2)_2N(H)Me\}_{16}}](\mathrm{ClO_4})_{15}\cdot 16\mathrm{H_2O}$ held together by uncoordinated aminothiolate ligands and water molecules occupying the intercrystal spaces. The composition and structure of the microcrystals is shown by X-ray, XPS, and ^{113}Cd NMR data. The uncoordinated aminothiolate ligands in zwitterionic form and water molecules are essential for the initial formation but not for the continued stability of the microcrystals as their chemical extraction leads to a new microcrystalline powder with essentially the same powder X-ray diffraction pattern. The existence of intercrystal spaces is confirmed by electron and atomic force microscopy techniques, SEM and AFM. The $[\mathrm{ClCd_8\{SCH(CH_2CH_2)_2N(H)Me\}_{16}}]^{15+}$ cage can be described in terms of metal and ligand concentric polyhedra of increasing size as *centro*-Cl-*tetrahedro*-Cd$_4$-*cuboctahedro*-(μ-SRH)$_{12}$-*tetrahedro*-(CdSRH)$_4$, where SRH denotes $^{-}\mathrm{SCH(CH_2CH_2)_2N^{+}(H)Me}$, and thus it constitutes the first example of a metal thiolate cluster where the topology of the bridging ligands is that of a cuboctahedron. Comparison with dimensions predicted by Dance for an idealized topology is made. The structural correspondences between a $[\mathrm{ClCd_4}(\mu\text{-SRH})_4(\mathrm{SRH})_6]$ fragment in $[\mathrm{ClCd_8\{SCH(CH_2CH_2)_2N(H)Me\}_{16}}]^{15+}$ and the Cd$_4$(S-Cys)$_{11}$ cluster in the α domain of metallothioneins, both formed by two fused six-membered cycles, are also discussed.

Introduction

Metal−thiolate chemistry is relevant to the coordination of metals by cysteine in biological systems, cadmium thiolates being particularly related to metallothioneins (MT).[1] The crystal structure of Cd$_5$,Zn$_2$-MT from rat liver has shown that there are two metal clusters in MT, $[\mathrm{M_3(S\text{-}Cys)_9}]^{3-}$ and $[\mathrm{M_4(S\text{-}Cys)_{11}}]^{3-}$, in good agreement with the structures for the α and β domains in solution derived by NMR methods.[2] To our knowledge, no synthetic analogues with close structural parameters have yet been reported. Examples and crystal structures of nonmolecular Cd(SR)$_2$ complexes with one, two, or three dimensionality of the polymeric framework are well-known.[3] Dance has categorized them according to the linked units, which are Cd$_2$(μ-SR)$_2$ quadrilaterals, Cd$_3$(μ-SR)$_3$ rings, and Cd$_4$(μ-SR)$_6$ adamantanoid cages.[4] Cadmium thiolates with molecular structures can be systematized according to two distinctly different structural patterns. That observed for species of general formula $[\mathrm{S}_w\mathrm{M}_x(\mathrm{SR})_y]^{z-}$ is based on fused adamantanoid cages, as found in $[\mathrm{E_4M_{10}(SPh)_{16}}]^{4-}$, (E = S, Se; M = Zn, Cd)[5] and $[\mathrm{S_4Cd_{17}(SPh)_{28}}]^{2-}$.[6] On the other hand, complexes of formula $[\mathrm{XM_8(SR)_{16}}]^{z-}$ (X = Cl, S) have a connectivity pattern comprising a central ligand, a bitetrahedron of four inner and four outer metal atoms, and 12 doubly bridging thiolate ligands. The polyhedron described by the bridging sulfur atoms could be a cuboctahedron or an icosahedron but it is close to an icosahedron in the three aggregates of known structure. These are the $[\mathrm{ClZn_8(SPh)_{16}}]^{-}$ [7] and $[\mathrm{SCd_8(SePh)_{16}}]^{2-}$ [8] complexes and the cyanide-bridged $\{\mathrm{SCd_8(SBu^s)_{12}}\}$ clusters of the $^{3}_{\infty}[\{\mathrm{SCd_8(SBu^s)_{12}}\}(\mathrm{CN})_{4/2}]$ complex.[9] In this second family the series $[\mathrm{XCd_8(SCH_2CH_2OH)_{12}X_3}]$, X = Cl, Br, I,[10] should be included, although half of the thiol ligands behave as bidentate. The main difference from the previous clusters is that in this case the

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polyhedron described by the eight cadmium atoms is a cube instead of a bitetrahedron.

Attempts to obtain a mononuclear cadmium species with the 4-mercapto-1-methylpiperidine ligand, which under appropriate experimental conditions behaves as an unidentate thiol with a solubilizing amine group, have led to a solid of formula $[Cl_{0.125}Cd\{SCH(CH_2CH_2)_2N(H)Me\}_{4.0}](ClO_4)_{1.875}\cdot 4.0H_2O$, which according to analytical data, X-ray, XPS, ^{113}Cd NMR, TGA, SEM, and AFM results should be formulated as $[ClCd_8\{SCH(CH_2CH_2)_2N(H)Me\}_{16}](ClO_4)_{15}\cdot 16[SCH(CH_2CH_2)_2N(H)Me]\cdot 32H_2O$. The structure of the $[ClCd_8\{SCH(CH_2CH_2)_2N(H)Me\}_{16}]^{15+}$ cage can be described in terms of metal and ligand polyhedra as *centro*-Cl-*tetrahedro*-Cd_4-*cuboctahedro*-(μ-SRH)$_{12}$-*tetrahedro*-$(CdSRH)_4$, where SRH denotes $^{-}SCH(CH_2CH_2)_2N^{+}(H)Me$, and thus it constitutes the first example of a metal thiolate cluster where the topology of the bridging ligands is that of a cuboctahedron. No discrete cationic species with such a high positive charge, 15+, has been previously reported. The highest positively charged discrete species known to date is $[Ni_6\{S(CH_2)_3NHMe_2\}_{12}]^{12+}$, where the ligand is also an aliphatic aminothiolate in zwitterionic form.[11] An additional novelty of the cadmium compound lies in its polycrystal nature, where the cations, the perchlorate anions, and half of the water molecules constitute the microcrystals while the noncoordinated ligands together with the remaining water molecules occupy the intercrystal spaces. To our knowledge, no other thiolate complex with these structural features is known to date.

Table 1. Crystal Data, Structure Solution and Refinement

chem formula	$C_{96}H_{240}Cd_8Cl_{16}N_{16}O_{76}S_{16}$
form wt	4814.4
cryst syst	monoclinic
space group	*C*2/*c*
a, Å	30.319(2)
b, Å	24.0998(14)
c, Å	26.257(2)
β, deg	92.707(2)
V, Å^3	19164(2)
Z	4
D_{calcd}, g cm^{-3}	1.669
λ, Å	0.71073 (Mo Kα)
μ, mm^{-1}	1.353
T, K	160
cryst size, mm	0.40 × 0.37 × 0.26
$2\theta_{max}$, deg	50.0
max indices *hkl*	39, 32, 34
reflns measd	48933
indep reflns	16798
R_{int}	0.0454
transm factors	0.426−0.557
refined params	1055
restraints	1636
extinction coeff[a]	0.00014(3)
R^b	0.0901
$R_w{}^c$	0.3047
S^d	1.052
max, min el dens, e Å^{-3}	1.43, −1.02

[a] $F_c' = F_c/(1 + 0.001xF_c^2\lambda^3/\sin 2\theta)^{1/4}$. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$ for 11 851 reflections with $F_o^2 > 2\sigma(F_o^2)$. [c] $R_w = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$ for all data. [d] $S = [\sum w(F_o^2 - F_c^2)^2/(\text{no. of reflns} - \text{no. of params})]^{1/2}$.

Experimental Section

General Details. 4-Mercapto-1-methylpiperidine was prepared according to a known procedure.[12] It was purified by vacuum distillation until its purity achieved 99% (iodometric determination of the SH group). $NaClO_4$, $Cd(ClO_4)_2$, and $HClO_4$ were commercially available. Elemental analyses were performed either on a CE Instruments analyzer (C, H, N, S) or using the ICP technique in a Thermo Jarrell Ash, Polyscan 61E at 182.040 (S) or at 228.802 (Cd) nm. IR spectra were recorded in the range 4000−400 cm^{-1} on a Perkin-Elmer 1710 spectrophotometer. Thermogravimetric analysis was performed on a Rigaku Thermoflex apparatus. The XPS spectrum was measured on a Leybold-Heraeus LHS10 instrument, operating at constant beam mode of 1253.6 eV (Mg Kα) by using as reference the carbon 11 level (284.6 eV). ^{113}Cd NMR spectra were recorded on a Bruker ARX-400 instrument operating at 88.8 MHz. Chemical shift values were referenced to external 0.5 M $Cd(NO_3)_2$ aqueous solution, which resonates at −12.7 ppm relative to 0.1 M aqueous $Cd(ClO_4)_2$. X-ray powder diffraction patterns were performed on a Siemens D500 diffractometer. A Nanoscope III Digital Instruments atomic force microscope and a JSM-840 JEOL scanning electron microscope were used for AFM and SEM measurements, respectively. AFM images were obtained at room temperature and pressure by applying two different stiff cantilever forces of 10 nN (tapping mode) and 1 μN (contact mode).[13] SEM images (BEI and SEI modes, which denote backscattering and secondary electron imaging, respectively) were obtained at −195 °C and 10^{-6} Torr, and the operating voltage was in the range 3−9 kV.[14]

Preparation of the Complex $[ClCd_8\{SCH(CH_2CH_2)_2N(H)Me\}_{16}](ClO_4)_{15}\cdot 16[SCH(CH_2CH_2)_2N(H)Me]\cdot 32H_2O$. To a stirred high ionic strength aqueous solution, 10 M $NaClO_4$ (30 mL), were successively added dropwise the volume corresponding to 2.51 g (19.1 mmol) of 4-mercapto-1-methylpiperidine and then 0.72 mL (3.67 mmol) of 5.1 M $Cd(ClO_4)_2$ in water. The pH was adjusted to 8.3 by using 4 M $HClO_4$. The resulting solution was left to stand in the dark. After a couple of hours a colorless species began to crystallize. Twelve hours later the suspended crystalline solid was filtered off and dried in vacuo, yielding 1.21 g (36.6%). Some crystals were suitable for X-ray diffraction. Anal. Calcd for $C_{192}H_{480}N_{32}O_{92}Cl_{16}S_{32}Cd_8$: C, 31.99; H, 6.72; N, 6.22; S, 14.21; Cl, 7.77; Cd, 12.65. Found: C, 32.29; H, 6.75; N, 6.22; S, 14.27; Cl, 7.66; Cd, 12.20. Two strong and broad bands in the IR region 2800−2400 cm^{-1}, also present in the spectrum of the ligand as hydrochloride, indicated that the amine groups are protonated in the title compound and thus ligand molecules are in zwitterionic form.

The polycrystals are sensitive to moisture but very stable for long periods if kept under strictly anhydrous conditions. Their treatment with water leads to $Cd(OH)_2$, while common organic solvents remove all water molecules and the aminothiolate ligands that do not belong to the cluster, which remains as a powdered solid phase (see below). Accordingly, polycrystals obtained could only be washed with their own mother liquor. This also precluded measurement of crystal density by the traditional flotation method.

Crystal Structure Determination. Table 1 lists crystal data and other information on the structure determination. Many attempts were made to collect data over an extended period, using several different crops of crystals, including experiments at room temperature and reduced temperatures with a variety of four-circle diffractometers and area-detector systems and sealed-tube and rotating-anode X-ray sources. From room-temperature data, only the heavy atoms could be located and from most of the experiments the lighter atoms were poorly defined. A satisfactory result was eventually obtained with a Siemens SMART CCD area detector and sealed-tube source, at low temperature. Unusually, an attempt with synchrotron radiation gave no significant improvement on this data set, with essentially the same structural parameters resulting. Cell parameters were refined from the observed ω angles of all strong reflections in the complete data set. Well over a hemisphere of reciprocal space was recorded on a series of 0.3° ω-rotation exposures to give a unique set of data, the high symmetry-equivalent redundancy of which served as the basis of a semiempirical absorption correction and demonstrated that there was no significant intensity decay during data collection. The structure was solved by

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direct methods and refined by full-matrix least-squares on all F^2 values, with weighting $w^{-1} = \sigma^2(F_o^2) + (0.1524P)^2 + (245.69P)$, where $P = (2F_c^2 + F_o^2)/3$. Two-fold disorder of orientation was clearly resolved for one of the crystallographically independent amino thiolate ligands and included in the refinement; high values of anisotropic displacement parameters indicate that other ligands are likely to be disordered, but this could not be resolved. Not all the perchlorate counterions and water molecules of crystallization could be fully identified, and restraints were necessary on various geometrical and displacement parameters; variable occupancy factors were used for some counterions. Water molecules were checked for suitable hydrogen-bonding geometry as a further aid to their identification; they also show high apparent displacement parameters, and so are probably only partially occupied sites. The overall formula most closely fitting the crystallographic results is $[ClCd_8\{SCH(CH_2CH_2)_2N(H)Me\}_{16}](ClO_4)_{15}\cdot 16H_2O$, although the water content is inevitably only approximate and may be an overestimate. Programs used were standard Siemens control and integration software, Siemens SHELXTL, and local programs.

Results and Discussion

Synthesis and Physicochemical Studies. Solution equilibria studies by emf methods on the Cd(II) and 4-mercapto-1-methylpiperidine system at 25 °C and 3 M $NaClO_4$ in H_2O-CH_3OH (10% v/v CH_3OH) indicated formation of the mononuclear $[Cd\{SCH(CH_2CH_2)_2N(H)Me\}_4]^{2+}$ species above pH = 8.[15] With the aim of characterizing structurally this mononuclear species the ionic strength of the titrated solution at pH = 8.5 was progressively increased until crystals appeared. According to this assay, cadmium perchlorate and the mercaptoamine ligand were mixed in water at 1:5 molar ratio, fixed pH, and in the presence of a high concentration of $NaClO_4$ (10 M). This reaction afforded a crystalline solid, hereafter referred to as polycrystal, which analyzed according to the expected $[Cd\{SCH(CH_2CH_2)_2N(H)Me\}_4](ClO_4)_2\cdot 4H_2O$ compound with Cd/mercaptoamine/perchlorate/H_2O = 1:4:2:4 (calcd values for $C_{24}H_{60}CdCl_2N_4O_{12}S_4$: C, 31.74; H, 6.66; N, 6.17; S, 14.12; Cl, 7.81; Cd, 12.38). However, the crystal structure determination revealed the presence of octanuclear $[XCd_8\{SCH(CH_2CH_2)_2N(H)Me\}_{16}]^{15+}$ aggregates and disordered ClO_4^- anions and H_2O molecules with Cd/mercaptoamine/perchlorate/H_2O = 8:16:15:16 ≈ 1:2:2:2. The nature of the X central atom, chlorine or sulfur, could not be unambiguously determined crystallographically. The additional 16 zwitterionic ligands and extra water molecules in the formula $[ClCd_8\{SCH(CH_2CH_2)_2N(H)Me\}_{16}](ClO_4)_{15}\cdot 16[SCH(CH_2CH_2)_2N(H)Me]\cdot 32H_2O$ were not located in the crystal structure and, indeed, there is insufficient space in the unit cell for them, even in highly disordered form; the structure as determined has no significant voids. This discrepancy between the highly reproducible analytical results for the synthesized material and the clear evidence of the crystal structure has prompted us for a considerable period and led to a variety of further experiments in order to explain it.

The different behavior of the 32 zwitterionic ligands in the compound was evidenced in the thermogravimetric analysis (TGA) of the polycrystals, which showed a clear step at about 100 °C corresponding to a mass decrease of 6.8%, in agreement with the loss of the 32 water molecules per formula weight (calcd value, 8.0%) and a second stepwise signal up to 225 °C, corresponding to the 30.4% of the initial mass, indicating the loss of 16 ligand molecules (Calcd value, 29.1%). This clearly suggests that aminothiolate ligands are differently attached in the complex species, exactly half of them being removed before complete thermal decomposition.

Table 2. Ratio of Integrated Peaks, $I \pm 0.1$, in the XPS Spectrum of $[ClCd_8\{SCH(CH_2CH_2)_2N(H)Me\}_{16}](ClO_4)_{15}\cdot 16[SCH(CH_2CH_2)_2N(H)Me]\cdot 32H_2O$[a]

		calculated value	
atomic ratio	experimental value[b]	X = Cl	X = S
S/Cd	7.07/3.77 = 1.90	2.00	2.12
Cl/Cd	6.86/3.77 = 1.85	2.00	1.75
S/Cl	7.07/6.86 = 1.03	1.00	1.21

[a] Experimental values require to assume that the 32 H_2O and 16 $^-SCH(CH_2CH_2)_2N^+(H)Me$ zwitterions are removed in the measurement process. [b] The area of the peak at 161.7 eV corresponds to the 2p level of sulfur. Due to partial decomposition of ClO_4^- anion the total amount of chlorine is distributed among the peaks at 197 and 199 eV (as chloride) and at 204, 207, and 209 eV (as perchlorate and chlorate), all corresponding to the 2p level of chlorine.

To investigate the nature of the extra mercaptoamine molecules we treated the title compound with a chloroform/methanol mixture (2:1) and analyzed the undissolved crystalline powder (Found: C, 24.76; N, 4.78; S, 11.31; Cd, 19.54) as well as the extract (Found: S, 7.48; Cd, 0.13). These results for the remaining solid compare well with the formula $[ClCd_8\{SCH(CH_2CH_2)_2N(H)Me\}_{16}](ClO_4)_{15}$ (calcd values for $C_{96}H_{208}Cd_8Cl_{16}N_{16}O_{60}S_{16}$: C, 25.44; N, 4.95; S, 11.30; Cd, 20.13) and those of the solution indicated that the 16 uncoordinated ligands, which correspond to 7.12% of sulfur in the initial complex species, had been extracted into the solution, with a negligible amount of the octanuclear species also being dissolved (Cd, 0.13%). Solution ^{113}Cd NMR studies, described below, showed that the solids obtained before and after the treatment with $CHCl_3/CH_3OH$ mixture give rise to the same cationic species. Powder X-ray diffraction pattern of the undissolved solid coincided with that measured for the polycrystals (Supporting Information). This confirms that the crystal structure of the octanuclear cadmium aggregate is preserved after removal of uncoordinated ligands and water molecules.

To verify the nature of the central atom, X, in the $[XCd_8\{SCH(CH_2CH_2)_2N(H)Me\}_{16}]^{(16-x)+}$ aggregate, the XPS spectrum of the polycrystal $[XCd_8\{SCH(CH_2CH_2)_2N(H)Me\}_{16}](ClO_4)_{15}\cdot 16[SCH(CH_2CH_2)_2N(H)Me]\cdot 32H_2O$ was recorded and the S/Cd, Cl/Cd, and S/Cl atomic ratios were calculated from the areas under the corresponding peaks. These were assigned according to the literature[16] and are indicated as a footnote in Table 2, where the experimental values for the atomic ratios are given. From these data two main conclusions can be derived: first, it is required that all water molecules and the noncoordinated SRH are lost during the measurement process, probably due to the ultrahigh vacuum (10^{-9} mmHg) and to the high energy of the incident X-ray radiation; this behavior has also been observed in the SEI studies (see below). Second, the calculated atomic ratios agree better for X = Cl than for X = S in the $XCd_8\{SCH(CH_2CH_2)_2N(H)Me\}_{16}$ core, as shown in Table 2.

^{113}Cd NMR spectra of a DMF solution of $[XCd_8\{SCH(CH_2CH_2)_2N(H)Me\}_{16}](ClO_4)_{15}\cdot 16[SCH(CH_2CH_2)_2N(H)Me]\cdot 32H_2O$ were recorded at variable temperature. The only broad signal observed at 273 K, $\delta = 653$ ppm, split at 220 K into two main signals of approximately equal intensities consisting of two peaks at 669 and 675 ppm and three shoulders at 670, 673 and 678 ppm (Figure 1a). Removal of the uncoordinated ligands and water molecules from the polycrystal, according to the procedure described above, afforded the same spectrum but with much higher resolution (Figure 1b). The observed chemical shift values at 220 K, 669.5, 671.0, 673.0, 675.0 and 677.5

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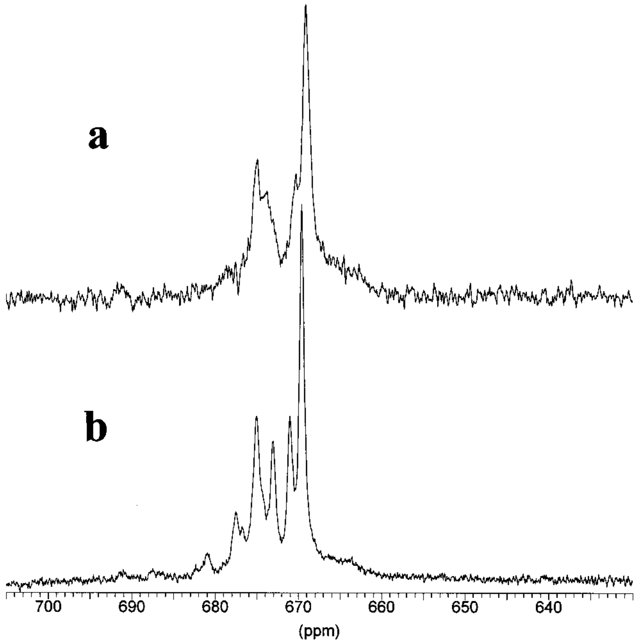

Figure 1. ^{113}Cd NMR spectra of (a) $[ClCd_8\{SCH(CH_2CH_2)_2N(H)Me\}_{16}](ClO_4)_{15}\cdot 16[SCH(CH_2CH_2)_2N(H)Me]\cdot 32H_2O$ and (b) $[ClCd_8\{SCH(CH_2CH_2)_2N(H)Me\}_{16}](ClO_4)_{15}$; both 0.4 M in Cd(II), in DMF solution and 220 K. Cadmium resonance values are given in the text.

ppm, are in the range expected for tetrahedral cadmium thiolates.[17] This spectral pattern agrees with the assumption that the peak at 669.5 is due to the four outer cadmium atoms ($Cd^{o}S^{b}_{3}S^{t}$), while the four inner cadmium atoms ($Cd^{i}S^{b}_{3}X$) give rise to a signal centered at 674 ppm split into four peaks by coupling to a central chlorine atom (^{35}Cl, $I = {}^{3}/_{2}$, 75.5% natural abundance; ^{37}Cl, $I = {}^{3}/_{2}$, 24.5% natural abundance; estimated $^{1}J(Cd-{}^{35}Cl) = 178$ Hz). Values of coupling constants involving quadrupolar nuclei are very scarce in the literature.[18] In the absence of values for J(Cd−Cl), the closest examples are those of ^{1}J(Cd−Se) in $[XCd_8(SePh)_{16}]^{2-}$ (X = S, Se)[8] complexes, which are in the range 120−180 Hz. The coincidence between both ^{113}Cd NMR spectra shows that the corresponding solids give rise to the same soluble cadmium species and clearly suggests that the X-ray structurally characterized $[ClCd_8\{SCH(CH_2CH_2)_2N(H)Me\}_{16}]^{15+}$ cage maintains in both cases its integrity in solution. It is unlikely that fragmentation of two different thiolate complexes would lead to the same soluble species in the presence of such different thiolate-to-metal ratios, 4 in the former and 2 in the latter. Moreover, it is likely that the noncoordinated $^{-}SCH(CH_2CH_2)_2N^{+}(H)Me$ ligands are responsible for the larger broadening of the cadmium resonance lines (Figure 1a) as the same effect has been previously described for the presence of $-NR_2H^{+}$ or RSH in solution.[19] Unfortunately, even though the chlorine site approaches a tetrahedral symmetry, the ^{35}Cl NMR spectrum (39.2 MHz) shows only the predominant ClO_4^- anions, $ClO_4^-/Cl^- = 15{:}1$ ($\delta = 1012$ ppm downfield external 0.5 M NaCl aqueous solution). Among the scarce ^{35}Cl NMR data on related systems, only the chemical shift of Cl in a $ClAg_4$ environment in the Na_8Cl_2 sodalite has been reported.[20] Attempts to record the solid-state ^{113}Cd CPMAS NMR spectrum of $[ClCd_8\{SCH(CH_2CH_2)_2N(H)Me\}_{16}](ClO_4)_{15}\cdot 16[SCH(CH_2CH_2)_2N(H)Me]\cdot 32H_2O$ were unsuccessful as on spinning the polycrystals degenerated into a paste. The sticky nature of the polycrystals, their behavior on rapid centrifugation or attempted grinding, and their conversion to microcrystalline powder on treatment by most organic solvents reinforce the hypothesis that uncoordinated amino thiolate ligands are present, in addition NMR and X-ray powder data indicate that these ligands are not necessary for the stability of the cage.

XPS and ^{113}Cd NMR results, indicating that chlorine rather than sulfur was responsible for holding the $Cd_4\{\mu\text{-}SCH(CH_2CH_2)_2N(H)Me\}_4$ rings together (the structure is described below), were corroborated by using $NaClO_4$ recrystallized five times and ultrapure water in a repeat of the synthesis. In this case the complex $[Cd\{SCH(CH_2CH_2)_2N(H)Me\}_2](ClO_4)_2\cdot 2H_2O$ of known polymeric structure was obtained[21] instead of the title compound. This was checked by elemental analyses and X-ray powder diffraction. Moreover, the reaction of MX_2 (M = Zn, Cd, Hg; X = Cl, Br, I) with 4-mercapto-1-methylpiperidine in aqueous solution had already allowed the structural characterization of dinuclear sulfur-bridged $[M_2X_4\{\mu\text{-}SCH(CH_2CH_2)_2N(H)Me\}_2]$ neutral species.[22] On the other hand, in a parallel reaction with highly purified $NaClO_4$ but in the presence of a few millimoles of chloride ion the $[ClCd_8\{SCH(CH_2CH_2)_2N(H)Me\}_{16}](ClO_4)_{15}\cdot 16[SCH(CH_2CH_2)_2N(H)Me]\cdot 32H_2O$ polycrystal was again isolated. Its synthesis is totally reproducible if either commercial $NaClO_4$ or purified $NaClO_4$ together with additional chloride ions are used, and chemical analysis results are always consistent. Attempts to use PF_6^- as anion gave instead a different cluster cation[23] with the familiar adamantane-like structure,[24] so the preparation does seem to be dependent on the anion.

The difficulties in obtaining and characterizing metal thiolate complexes with macromolecular octanuclear cages of general formula $XM_8(ER)_{16}$, where X denotes a central chlorine or sulfur monatomic ligand, M = Zn or Cd, E = S or Se, R = alkyl or aryl group (charges are omitted for clarity), are well reflected in the literature, as of the three aggregates of known structure, $[ClZn_8(SPh)_{16}]^{-}$,[7] $\{SCd_8(SBu^{s})_{12}\}^{2+}$,[9] $[SCd_8(SePh)_{16}]^{2-}$,[8] only for the latter has a reproducible synthesis been reported. Attempts to reproduce the original preparations of the two other examples has frequently led to crystals containing other species. In addition, in complex $[ClZn_8(SPh)_{16}]^{-}$, identification of the central atom as Cl^{-} rather than the possible alternative S^{2-} is not definite. The synthetic problems are then followed by the drawbacks usually encountered in the structural characterization of macromolecular aggregates, which in this case are enhanced by the fact that crystalline products are often unsuitable for diffraction analysis.[8]

To gain insight into the distribution of the noncoordinated ligands throughout the polycrystal structure, SEM (BEI and SEI) and AFM techniques were applied. The images derived from BEI (at −195 °C) showed main areas with intense electron scattering separated from each other by channels or zones with

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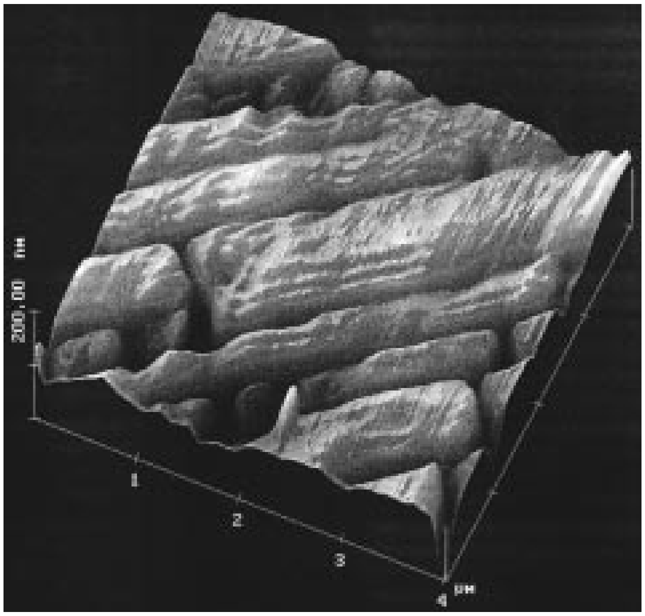

Figure 2. AFM image of the polycrystal $[ClCd_8\{SCH(CH_2CH_2)_2N(H)Me\}_{16}](ClO_4)_{15}\cdot 16[SCH(CH_2CH_2)_2N(H)Me]\cdot 32H_2O$. Lighter zones represent microcrystals; dark zones, channels occupied by the noncoordinating ligands and half of the water molecules.

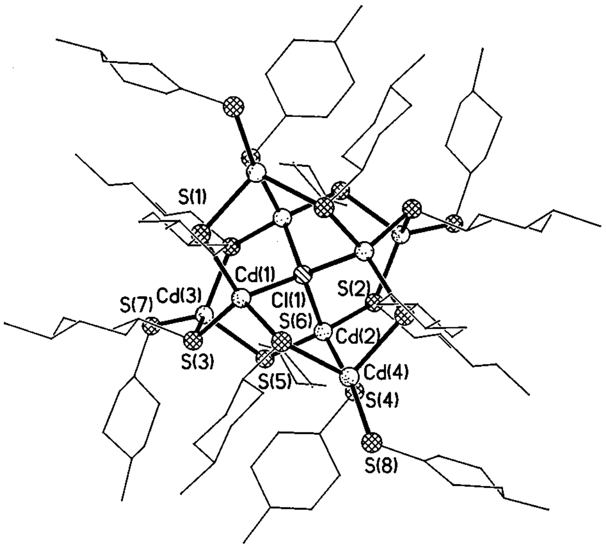

Figure 3. The structure of the $[ClCd_8\{SCH(CH_2CH_2)_2N(H)Me\}_{16}]^{15+}$ cation in the solid state. H atoms and the minor disorder components are not shown. The view is along the crystallographic C_2 axis through the central Cl atom.

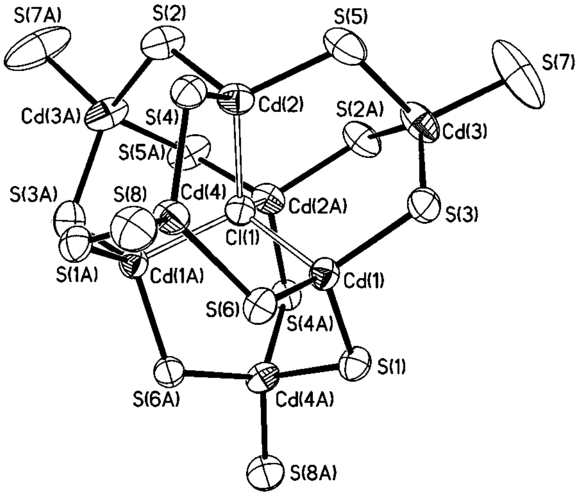

Figure 4. The inner core of the $[ClCd_8\{SCH(CH_2CH_2)_2N(H)Me\}_{16}]^{15+}$ cation with a view direction slightly inclined to one of the approximate C_3 axes, which lie along the four Cl−Cd bonds. Only Cd, Cl, and S atoms are shown, with 30% probability ellipsoids.

weaker scattering. Accordingly, the former indicated the presence of atoms with high atomic number, and the latter that of either lighter atoms or empty spaces. The SEI technique, which is sensitive to the electrons ejected from the sample, showed at −195 °C a uniform image devoid of channels, thus confirming the presence of lighter atoms in the channels. Furthermore, when heating the sample progressively up to room temperature, the initial uniform picture evolved to a channeled image, as in BEI mode, which indicated that the material filling the channels had evaporated. Independently, AFM images at room temperature fully confirmed the previous results; both main areas and channels are apparent in Figure 2, obtained in the contact mode.

All experimental data lead us to propose a polycrystal structure for the $[ClCd_8\{SCH(CH_2CH_2)_2N(H)Me\}_{16}](ClO_4)_{15}\cdot 16[SCH(CH_2CH_2)_2N(H)Me]\cdot 32H_2O$ complex where $[ClCd_8\{SCH(CH_2CH_2)_2N(H)Me\}_{16}](ClO_4)_{15}\cdot 16H_2O$ constitutes the microcrystals, while the noncoordinating ligands and the remaining water molecules occupy the intercrystal spaces. According to X-ray crystallography results, the structure of $[ClCd_8\{SCH(CH_2CH_2)_2N(H)Me\}_{16}](ClO_4)_{15}\cdot 16H_2O$ consists of $[ClCd_8\{SCH(CH_2CH_2)_2N(H)Me\}_{16}]^{15+}$ cationic species, ClO_4^- counterions and H_2O molecules, the two latter being partially disordered. The role played by the uncoordinated ligands and water molecules can be easily understood by combining the information provided by NMR and powder diffraction data. NMR results indicate that irrespective of the presence of free aminothiolate ligands the octanuclear aggregates are present in both solid phases, which, according to powder diffraction data, have essentially the same crystal structure.

Description of the Structure of the $[ClCd_8\{SCH(CH_2CH_2)_2N(H)Me\}_{16}]^{15+}$ Cation. Figure 3 shows the complete cation (without hydrogen atoms), and Figure 4 shows the central core of Cd, S, and Cl atoms. Main bond lengths and angles are given in Table 3. The structure of the cationic $[ClCd_8\{SCH(CH_2CH_2)_2N(H)Me\}_{16}]^{15+}$ species can be described as formed by two $Cd_4(\mu\text{-}SRH)_4$ rings linked by a central chlorine atom, which sits on a crystallographic 2-fold axis perpendicular to the plane of the paper in Figure 3, and by four additional sulfurs that bridge the cadmium atoms in the two rings. The chlorine atom is surrounded by two pairs of Cd atoms in near tetrahedral geometry, each pair belonging to a different $Cd_4(\mu\text{-}SRH)_4$ ring, which contains two crystallographically independent cadmium atoms. Thus, Cd(1) in one ring and Cd(2) in the other, and their symmetry-related Cd(1A) and Cd(2A), achieve tetrahedral coordination by two sulfur atoms of their respective rings, the central chlorine and an additional sulfur of a mercaptoamine ligand. As a consequence, S(3), S(4) and their symmetry-related equivalents reinforce the link between the two rings as they bridge the four Cd atoms of one ring with those of the other. In contrast, Cd(3), Cd(4), and their symmetry equivalents accomplish tetrahedral coordination by means of two sulfur atoms of their own ring, a third sulfur of the connecting S(3), S(4), S(3A), or S(4A) atoms, and a fourth one from a terminal aminothiolate ligand through the S(7), S(8), S(7A), or S(8A) atoms. Because of the high effective symmetry of the central core of the cation, the same description could be based on two other pairs of $Cd_4(\mu\text{-}SRH)_4$ rings.

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

Cl(1)−Cd(1)	2.518(2)	Cl(1)−Cd(2)	2.505(2)
Cd(1)−S(1)	2.519(3)	Cd(1)−S(3)	2.511(3)
Cd(1)−S(6)	2.517(3)	Cd(2)−S(2)	2.511(3)
Cd(2)−S(4)	2.521(3)	Cd(2)−S(5)	2.517(4)
Cd(3)−S(2A)	2.557(3)	Cd(3)−S(3)	2.565(4)
Cd(3)−S(5)	2.547(4)	Cd(3)−S(7)	2.458(4)
Cd(4)−S(1A)	2.578(3)	Cd(4)−S(4)	2.548(3)
Cd(4)−S(6)	2.538(3)	Cd(4)−S(8)	2.482(4)
Cd(2A)−Cl(1)−Cd(2)	106.34(13)	Cd(2A)−Cl(1)−Cd(1)	110.69(3)
Cd(2)−Cl(1)−Cd(1)	108.96(2)	Cd(1A)−Cl(1)−Cd(1)	111.10(13)
S(3)−Cd(1)−S(6)	113.53(11)	S(3)−Cd(1)−Cl(1)	110.27(10)
S(6)−Cd(1)−Cl(1)	98.38(8)	S(3)−Cd(1)−S(1)	109.28(10)
S(6)−Cd(1)−S(1)	114.91(10)	Cl(1)−Cd(1)−S(1)	109.97(7)
Cl(1)−Cd(2)−S(2)	105.97(9)	Cl(1)−Cd(2)−S(5)	112.37(9)
S(2)−Cd(2)−S(5)	111.87(14)	Cl(1)−Cd(2)−S(4)	111.60(9)
S(2)−Cd(2)−S(4)	108.88(11)	S(5)−Cd(2)−S(4)	106.18(11)
S(7)−Cd(3)−S(5)	114.3(2)	S(7)−Cd(3)−S(2A)	104.4(2)
S(5)−Cd(3)−S(2A)	102.51(13)	S(7)−Cd(3)−S(3)	117.6(2)
S(5)−Cd(3)−S(3)	92.60(12)	S(2A)−Cd(3)−S(3)	124.03(10)
S(8)−Cd(4)−S(6)	111.10(11)	S(8)−Cd(4)−S(4)	110.84(11)
S(6)−Cd(4)−S(4)	120.83(9)	S(8)−Cd(4)−S(1A)	112.79(11)
S(6)−Cd(4)−S(1A)	101.99(9)	S(4)−Cd(4)−S(1A)	98.13(9)
Cd(1)−S(1)−Cd(4A)	105.38(10)	Cd(2)−S(2)−Cd(3A)	114.13(12)
Cd(1)−S(3)−Cd(3)	106.45(11)	Cd(2)−S(4)−Cd(4)	106.52(9)
Cd(2)−S(5)−Cd(3)	108.02(12)	Cd(1)−S(6)−Cd(4)	115.03(11)

[a] Symmetry transformations used to generate equivalent atoms: A, $-x, y, -z + {}^{3}/_{2}$.

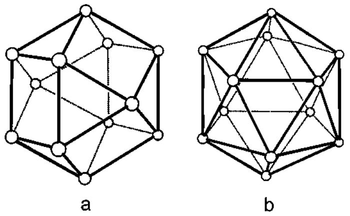

Figure 5. Idealized polyhedra: (a) S_{12} cuboctahedron and (b) S_{12} icosahedron.

The core of $[ClCd_8\{SCH(CH_2CH_2)_2N(H)Me\}_{16}]^{15+}$ can be alternatively described in terms of concentric polyhedra of increasing size, as *centro*-Cl-*tetrahedro*-Cd$_4$-*cuboctahedro*-(μ-SRH)$_{12}$-*tetrahedro*-(CdSRH)$_4$ and thus it is the first example with this topology for the bridging thiolate ligands. This description of the structure by its constituent polyhedra takes into account that the four Cd(1), Cd(2), Cd(1A), and Cd(2A) atoms are on the vertexes of an inner tetrahedron (Cd^i), while the other four Cd(3), Cd(4), Cd(3A), and Cd(4A) atoms are on those of an outer tetrahedron (Cd^o), both centered by the Cl(1) atom. In the bitetrahedron thus constituted, where the 12 Cd^i-Cd^o and the six Cd^i-Cd^i distances average 4.12 Å (standard deviation, 0.08 Å), the sets formed by Cl(1), two Cd^i, and two Cd^o are nearly coplanar. Maximum deviation of atoms from the corresponding mean planes is 0.12 Å and the dihedral angle between planes is in the range 90.3−91.2°, which shows the essential regular geometry of the bitetrahedron.

The arrangement of the 12 bridging sulfur atoms [S(1) to S(6) and their symmetry equivalents] describes a cuboctahedron rather than an icosahedron. The former can be defined as the polyhedron obtained by linking the vertexes of a regular hexagon with those of two equilateral triangles, which are rotated 60° to each other and are parallel to the hexagon, located above and below it, as shown in Figure 5a. In agreement with this figure, the sulfur atoms that define the four possible S^b_6 hexagons are at an average distance of 0.30 Å from the corresponding mean plane (standard deviation, 0.28 Å); maximum deviation 0.61 Å. All these planes contain the central chlorine atom. The mean value of the dihedral angles formed by each hexagon and the corresponding upper and lower triangles is of 6.05° (standard deviation, 1.1°). Alternatively, an icosahedron should be described as consisting of two regular parallel pentagons rotated 36° to each other with two additional vertexes on the rotation axis above and below the parallel planes, respectively, as shown in Figure 5b. On this assumption, the sulfur atoms that may define the 12 possible S^b_5 pentagons are at an average distance of the corresponding mean planes of 0.38 Å (standard deviation, 0.58 Å); maximum deviation results much larger under this analysis, 2.10 Å. Mean value of the dihedral angles formed by each pair of pentagons would be 9.6° with a standard deviation of 7.9°. These figures show how the S^b_{12} skeleton approaches more closely to a cuboctahedron. Mean values of geometric parameters of the octanuclear cadmium cluster are given in Table 4. Comparison of these values with those calculated by Dance for the four idealized possible geometries of $Zn_8(\mu\text{-}S)_{12}$ frameworks also shows that, despite the different nature of the metal atoms, the observed dimensions are closer to those predicted for an idealized *centro*-X-*tetrahedro*-M$_4$-*cuboctahedro*-(SR)$_{12}$ topology than to the three other alternatives.[7] This agrees with our previous calculations and allows consideration of the $[ClCd_8\{SCH(CH_2CH_2)_2N(H)Me\}_{16}]^{15+}$ cation as formed by an inner tetrahedron of four Cd atoms and a cuboctahedron of 12 S atoms, both centered on the Cl atom.

Table 4. Mean Geometric Parameters of the Cd_8S_{12} Core in $[ClCd_8\{SCH(CH_2CH_2)_2N(H)Me\}_{16}]^{15+}$

dimension	Å, deg (std dev)
Cd−S	2.53 (0.03)
$Cl-Cd^i$	2.51 (0.01)
$Cl-Cd^o$	4.22 (0.06)
$Cl-S^b$	4.07 (0.17)
S^b-S^b	4.12 (0.22)
S^b-S^t [a]	4.16 (0.11)
Cd^i-Cd^i	4.10 (0.06)
Cd^i-Cd^o	4.13 (0.09)
S−Cd−S	109.8 (7.7)
$Cd^i-S^b-Cd^o$	109.3 (4.0)
$Cl-Cd^i-S^b$	108.1 (5.0)
$Cd^i-Cl-Cd^i$	109.7 (7.7)

[a] Average of the 12 shortest values.

The crystallographic symmetry imposes a C_2 molecular symmetry on the $[ClCd_8\{SCH(CH_2CH_2)_2N(H)Me\}_{16}]^{15+}$ cation. However, if the C, H, and N atoms are ignored, a virtual T_d symmetry is found (T symmetry including the C_α atoms of the ligands). Accordingly, the four 3-fold axes are coincident with the four $Cl(1)-Cd^i$ vectors and the three 2-fold axes with the bisectors of the six bond angles at Cl(1). The view for Figure 4 is a little displaced from one of these approximate C_3 axes.

The cage skeleton of the $[ClCd_8\{SCH(CH_2CH_2)_2N(H)Me\}_{16}]^{15+}$ cation shows interesting similarities with the Cd_4(S-Cys)$_{11}$ cluster of the α domain of mammalian MT,[2] which could be formulated as $[Cd_4(\mu\text{-S-Cys})_5(\text{S-Cys})_6]$ and described as an eight-membered ring of alternating Cd and S atoms with two opposite cadmium atoms additionally bridged by a S-Cys residue. As shown in Figure 6 there are two different environments for tetrahedrally coordinated cadmium atoms in this cluster: $CdS^b_3S^t$ and $CdS^b_2S^t_2$. At this point it is worth noting that the structure of the $[ClCd_8\{SCH(CH_2CH_2)_2N(H)Me\}_{16}]^{15+}$ cation has been described as consisting of two $[Cd_4(\mu\text{-SRH})_4]$ rings connected by a central Cl atom. Considering the fragment formed by this Cl atom and one of the two $[Cd_4(\mu\text{-SRH})_4]$ rings, the topological correspondences between the Cd_4(S-Cys)$_{11}$ and the $[ClCd_4(\mu\text{-SRH})_4(SRH)_6]$ aggregates become apparent as both are formed by two fused six-membered rings. The assumption that the S atom of the S-Cys residue that bridges two opposite

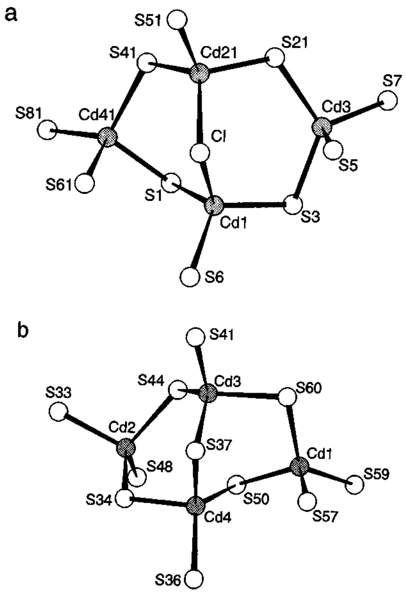

Figure 6. Comparison of a fragment of the cage skeleton of the $[ClCd_8\{SCH(CH_2CH_2)_2N(H)Me\}_{16}]^{15+}$ cation (a) with the $Cd_4(S\text{-}Cys)_{11}$ cluster of the α domain of rat liver Cd_5,Zn_2-MT (b). In both, the right hand side ring adopts a boat conformation.

Cd atoms in α-MT is replaced by Cl atom in the fragment has to be made. Their comparison, Figure 6, evidences that one of these six-membered rings adopts a boat conformation in both the fragment and the α domain. Distances between pairs of cadmium atoms bound to the same sulfur are within a comparable range (4.1−4.3 Å in the title complex, 3.9−4.4 Å in the α-MT cluster). The only main difference lies in the position of one cadmium atom, which forces the conformation of the other six-membered ring to be a distorted boat in the title compound and a chair in the $Cd_4(S\text{-}Cys)_{11}$ cluster. Accordingly, the Cd3−Cd41 distance is 6.93 Å in our complex and the corresponding distance in α-MT, Cd1−Cd2, is 5.2 Å.

The absence of synthetic analogues of the two metal clusters $[M^{II}_3(S\text{-}Cys)_9]^{3-}$ and $[M^{II}_4(S\text{-}Cys)_{11}]^{3-}$ in MT, despite their well-known occurrence in mammalian species, is still unresolved. It seems likely that the highly conserved polypeptide chain embodying both clusters plays an essential role for the stability of these cores. Consideration of the few examples of $XM_8(ER)_{16}$ species with reproducible synthesis evidences the low stability of macromolecular metal−thiolate complexes containing $[Cd_4(\mu\text{-}SRH)_4]$ rings connected by a central monatomic ligand. A fragment of this cage shows close structural features to the $Cd_4(S\text{-}Cys)_{11}$ cluster in MT. However, we presume that in the highly charged $[ClCd_8\{SCH(CH_2CH_2)_2N(H)Me\}_{16}]^{15+}$ cationic species, not only the central chlorine atom but the presence of extra uncoordinated aminothiolate ligands in zwitterionic form and water molecules in the initial product has allowed isolation and characterization of an otherwise elusive species.

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Supporting Information Available: Tables of atomic coordinates, thermal parameters, bond distances and angles, and hydrogen atom positions for $[ClCd_8\{SCH(CH_2CH_2)_2N(H)Me\}_{16}](ClO_4)_{15}\cdot 16H_2O$ and powder X-ray diffraction patterns of $[ClCd_8\{SCH(CH_2CH_2)_2N(H)Me\}_{16}](ClO_4)_{15}\cdot 16[SCH(CH_2CH_2)_2N(H)Me]\cdot 32H_2O$ and $[ClCd_8\{SCH(CH_2CH_2)_2N(H)Me\}_{16}](ClO_4)_{15}$ (17 pages). See any current masthead page for ordering and Internet access instructions.

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