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The syntheses, ^{77}Se CP-MAS solid state NMR spectra and crystal structures of adducts of the selenium coronand, 1,5,9,13-tetraselenacyclohexadecane, with copper(I) trifluoromethanesulfonate and mercury(II) cyanide

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Abstract

The preparation, characterization, X-ray crystal structures and ^{77}Se CP-MAS solid state NMR spectra of adducts of 1,5,9,13-tetraselenacyclohexadecane with copper(I)trifluoromethanesulfonate and mercury(II)cyanide are reported. Crystal data: $[(Cu(Se(CH_2)_3)_4)][SO_3CF_3]$ (**1**); orthorhombic; space group $B22_12$; $a = 8.947\ (2)$; $b = 15.184(2)$; $c = 15.918(2)$ Å; $V = 2162.2$ Å^3; $Z = 4$; $FW = 696.77$; $\rho_c = 2.140$ g cm^{-3}; $\lambda = 0.71069$ Å; $R(F) = 0.044$ for 622 data ($I \geqslant 2.5\sigma(I)$). $(Hg(CN)_2)((Se(CH_2)_3)_4)$ (**2**); monoclinic; space group $P2_1/c$; $a = 5.822(1)$; $b = 12.457(2)$; $c = 14.074(2)$ Å; $\beta = 99.07(1)°$; $V = 1008.1$ Å^3; $Z = 2$; $FW = 736.79$; $\rho_c = 2.427$ g cm^{-3}; $\lambda = 0.71069$ Å; $R(F) = 0.038$ for 1153 data ($I \geqslant 2.5\sigma(I)$). **1** displays orientational disorder of the $SO_3CF_3^-$ anion and correlated disorder of the complex cation. The refinement was stabilized using soft restraints. The cation is a three-dimensional polymeric complex with pseudo-tetrahedral coordination about copper to four distinct ligands. **2** consists of linear $Hg(CN)_2$ molecules which interact weakly with four selenium atoms from different ligands to give a tetragonally distorted octahedral arrangement.

Introduction

As part of a program designed to investigate the metal-binding properties of selenium coronands [1], we have recently described [2] the first selenium coronand-metal complex, namely 1,5,9,13-tetraselenacyclohexadecanecopper(II) trifluoromethanesulfonate, $[Cu(16Se4)])[SO_3CF_3]_2$, and its spontaneous electron transfer reaction in organic solvents to give a Cu^I complex as well as the intermediate radical cation $[16Se4]^{\cdot +}$ and the stable dication $[16Se4]^{2+}$. We now report the preparation of adducts of $Cu(SO_3CF_3)$ and $Hg(CN)_2$ with [16Se4] and their characterization, X-ray crystal structures and ^{77}Se CP-MAS solid state NMR spectra.

Experimental

Solid-state NMR spectra were recorded on an instrument (built in-house) operating at a field of 1.4 T. This produces a resonance frequency of 11.4 MHz for ^{77}Se.

Spectra were excited using single-contact Hartmann–Hahn cross-polarization. The matched r.f. field strength was 40 kHz for ^{77}Se. The same field strength was used for proton decoupling during data acquisition. Samples were spun at the magic angle at frequencies of 2–3 kHz. The magic angle was correctly set within ±0.1° by optimizing the linewidth on well crystallized samples of $({}^{t}Bu_2Sn)_2Se_2$ and $H_2C_2O_4 \cdot 2H_2O$. Chemical shifts were measured relative to long cylindrical samples of aqueous H_2SeO_3. These were converted to shifts based on the standard Me_2Se scale, by an independent experiment.

Solvents were distilled before use and were dried, as necessary, by literature procedures. Reactions were performed under nitrogen by use of standard Schlenk-tube techniques.

Microanalyses were performed by Mr. M.K. Yang of the Microanalytical Laboratory of Simon Fraser University.

Synthesis of [Cu(16Se4)][So$_3$CF$_3$] (1)

Copper(I) trifluoromethanesulfonate $(Cu^I(OTf)(C_6H_6)_{1/2})$ (12 mg, 0.0478 mmol) was dissolved in 1 ml of CH_3CN/CH_2Cl_2 (1/1) under a nitrogen atmosphere. A solution of 1,5,9,13-tetraselenacyclohexadecane ≡ (16Se4) (1 eq.) in 1 ml of the same solvent was added, the mixture was stirred for 3h at 50 °C, and the mixture was concentrated to a volume of 1 ml. Vapour diffusion of diethyl ether into this solution resulted in the deposition of white crystals (24 mg, 72%); IR (KBr): 2950, 1445, 1435, 1275, 1235, 1170, 1150, 1040, 650, 550 cm^{-1}; CP-MAS $\delta(^{77}Se)(\pm 1$ ppm; ref.Me_2Se): 112 ($W_{1/2} = 115$ Hz), 159 ($W_{1/2} = 45$ Hz). Anal. Found: C 22.65; H, 3.41. $C_{13}H_{24}F_3O_3SSe_4Cu$ calcd.: C, 22.41; H, 3.47%. These results are indistinguishable from those for the copper(I) salt obtained by the reduction of $Cu(16Se4)(SO_3CF_3)_2$ [2]—crystals of which were used for the X-ray structure determination.

Synthesis of Hg(CN)$_2$(16Se4) (2)

A mixture of 16Se4 (20 mg, 0.0413 mmol) and $Hg(CN)_2$ (1 eq.) in dry acetone (2 ml) was refluxed for 2 h under nitrogen. The mixture was concentrated to a volume of 1 ml and allowed to cool to 0 ° C. The resulting colourless needles were collected by filtration, washed with cold acetone, and dried in vacuo (25.6 mg, 84%); IR (KBr): 2990. 2940, 1445, 1420, 1330, 1290, 1225, 730; CP-MAS $\delta(^{77}Se)(\pm 1$ ppm; ref. Me_2Se): 127 (^1J(Se,Hg) = 123 Hz; ^2J(Se,Se) = 43 Hz), 202 (^1J(Se,Hg) = 110 Hz; ^2J(Se,Se = 43 Hz). Anal. Found: C, 22.73; H, 3.00; N, 3.65. $C_{14}H_{24}Se_4N_2Hg$ calcd.: C, 22.82; H, 3.28; N, 3.80%.

X-Ray crystallography

All crystals were mounted on pyrex filaments using epoxy resin. Measurements were made with an Enraf–Nonius CAD-4F diffractometer using graphite monochromatized radiation. Crystallographic details for both **1** and **2** are given in Table 1.

The unit cell for **1** was determined from 25 well-centred reflections in the range $30 \leqslant 2\theta \leqslant 38°$. Two intensity standards were measured after each 1.33 hours of exposure to the X-rays and showed no systematic variations in intensity throughout data acquisition. Data reduction was performed including corrections for absorption

Table 1

Crystallographic data for the structure determinations at 295 K of $[(Cu(Se(CH_2)_3)_4)][SO_3CF_3]$ (**1**) and $(Hg(CN)_2)((Se(CH_2)_3)_4)$ (**2**)

	1	**2**
Formula	$CuSe_4SF_3O_3C_{13}H_{24}$	$HgSe_4N_2C_{14}H_{24}$
Crystal system	orthorhombic	monoclinic
Space group	$B22_12$	$P2_1/c$
a (Å)	8.947(2)	5.822(1)
b (Å)	15.184(2)	12.457(2)
c (Å)	15.918(2)	14.074(2)
β(°)		99.07(1)
V(Å^3)	2162.2	1008.1
Z	4	2
FW	696.77	736.79
ρ_c (g cm^{-3})	2.140	2.427
μ(Mo-K_α)(cm^{-1})	78.08	147.81
Crystal size (mm)	0.26×0.31×0.31	0.16×0.18×0.23
λ (Å)	0.71069	0.71069
Transmission	0.496–1.000 [a]	0.105–0.179 [b]
Scan mode	$\omega-2\theta$	$\omega-2\theta$
Scan width [c] (°)	$0.75+0.35\tan\theta$	$0.85+0.35\tan\theta$
Scan speed (° min^{-1})	0.6–5.5	1.1–2.8 ($k+l=2n$), 1.1 ($k+1=2n+1$)
Min–max 2θ (°)	4–40 (hkl) 4–30 ($hk-l$)	4–50
Unique data	831	1756
Observed data [d]	622 [e]	1153
Restraints	36	
Refined parameters	86	98
Extinction		$g = 0.162(10)$ [f]
$R(F)$ [g]	0.044	0.038
$R_w(F)$ [h]	0.047 [i]	0.026 [j]
G.O.F. [k]		2.664
Max pk (e Å^{-3})	1.1(2) [l]	1.4(2) [m]
Max |shift/error|	0.04	0.01

[a] A Psi absorption correction was applied. Maximum and minimum correction factors are given. [b] The data were corrected analytically for the effects of absorption. The range of the transmission factors is given. [c] The background intensities were estimated by extension of the predetermined scan angle by 25% on either side. [d] $I \geqslant 2.5\sigma(I)$. [e] 461 (hkl), 161 ($hk-l$). [f] A.C. Larson, in *Crystallographic Computing*, Munksgaard, Copenhagen, 1970, p. 291. [g] $R(F) = \sum||F_o|-|F_c||/\sum|F_o|$, for observed data. [h] $R_w(F) = [\sum(w(|F_o|-|F_c|)^2)/\sum(wF_o^2)]^{1/2}$, for observed data. [i] Unit weights ($w=1$). [j] Counter weights ($w = \sigma^2(F_o)+0.0002F_o^2)^{-1}$). [k] G.O.F. $= [\sum w(|F_o|-|F_c|)^2/\text{degrees of freedom}]^{1/2}$. [l] 0.9 Å from Se(11). [m] 0.0 Å from Hg(1).

[3], Lorentz and polarization effects. Problems in the refinement (*vide infra*) led us to carefully consider the possibility of axis doubling, or crystal twinning but no evidence was found to support these hypotheses. Alternate space groups were also considered and rejected. The Laue symmetry was confirmed by measurement of symmetry equivalent reflections over a limited sphere.

The positions of Cu and two Se atoms were determined from the Patterson map, yielding a solution in the space group $B22_12$. An electron density difference map revealed the carbon atoms of the 16Se4 ring and peaks indicating a disordered $SO_3CF_3^-$ anion. The anion was ultimately modeled using two rigid SO_3CF_3 groups of partial occupancy, corresponding to disordered orientations rotated relative to one another about the S–C bond and about the two-fold axis parallel to *a*.

Anisotropic thermal parameters were included for Cu and Se atoms, yielding $R = 0.065$. We considered the anisotropy for Se(1) unreasonably extreme and the thermal parameters for the ring atoms were generally higher than expected. Bond distances ranged: 1.88(5)–2.02(5) Å for Se–C, 1.38(5)–1.64(5) Å for C–C. A model was therefore developed, with the use of soft bond distance and angle restraints to stabilize the refinement, involving two-site disorder for the atoms of the ring (with the exception of Se(5) and C(6) which required only one site each). The Cu atom was also split into two, with one site on the two-fold axis, as a consequence of the unsymmetrical and symmetrical permutations of the Se(1)/Se(11)–Cu–Se(1)/Se(11) arrangement. The fractional occupancy parameter for the complex cation refined independently to a value consistent with a correlation between the disorder of the cation and that of the anion. Subsequently a single occupancy parameter was refined for both. Structures of both polarities were refined and the hand giving the lowest residual was selected for the final refinement.

Final full-matrix least-squares refinement of 86 parameters from 622 observations and 36 restraints included anisotropic thermal parameters for all Cu and Se atoms. Each pair of split atoms (Cu(1) + Cu(11) and Se(1) + Se(11)) were given ellipses that were identical. Those for copper were constrained to two-fold symmetry with the appropriate off-diagonal terms set to zero. Hydrogen atoms were included initially in calculated positions and their coordinate and isotropic temperature factor shifts were included with those of their respective carbon atoms. Refinement converged at $R = 0.044$. The coordinates for the major component (occupancy = 0.686(8)) of the disordered cation only are presented in Table 2.

For compound **2** two intensity standard reflections were measured after every 1.33 hours of X-ray exposure. Remarkably, these standards increased systematically in intensity by 20 and 27% during the course of data acquisition (to an upper 2θ-limit of 50° for $(h, k, \pm l)$). This change was effected only by exposure of the crystal to the X-rays and no increase is observed in 24 h when the crystal is not exposed. Unit cell parameters determined before and after data acquisition were not

Table 2

Fractional atomic coordinates and isotropic or equivalent isotropic temperature factors (Å^2) for the Cu, Se and C atoms of the major component of the disordered complex cation of $[Cu(Se(CH_2)_3)_4][SO_3CF_3]$ (1) [a]

Atom	*x*	*y*	*z*	*U*(iso)
Cu(1)	0.5000	0.0000	0.7272(8)	0.0547
Se(1)	0.6059(5)	−0.1321(4)	0.6525(3)	0.0531
Se(5)	0.7291(3)	0.0434(2)	0.8059(2)	0.0678
C(2)	0.741(3)	−0.1823(13)	0.7370(13)	0.077(9)
C(3)	0.693(3)	0.2283(12)	0.791(2)	0.051(8)
C(4)	0.817(3)	0.1578(10)	0.784(2)	0.075(10)
C(6)	0.675(2)	0.0478(14)	0.9239(10)	0.076(7)
C(7)	0.797(3)	0.085(3)	0.9840(12)	0.074(9)
C(8)	0.757(3)	−0.081(2)	0.5763(12)	0.073(10)

[a] General equivalent positions: *x*, *y*, *z*; *x*,1/2-*y*,-*z*; -*x*,1/2+ *y*,-*z*; -*x*,-*y*, *z*, plus lattice centring: 1/2,0,1/2.

significantly different, nor was there any noticeable change in the background radiation adjacent to the peaks.

Data acquisition was repeated with the same crystal, in part to test whether the increase in observed intensities was uniform over reciprocal space. The intensity standards continued to grow, increasing in intensity by 10 and 5%. While we can provide no simple explanation for all our observations of this phenomenon, perhaps a secondary phase transition or annealing of the crystal in the X-ray beam was occurring. Independent structure refinement using either data set produced satisfactory results and no substantial difference was observed in the resultant parameters or residual. The second set of data was used in the structure refinement reported here.

The unit cell was determined from 25 well-centred reflections in the range $32 \leqslant 2\theta \leqslant 44°$. The data were corrected for absorption [4], intensity scale variation, and Lorentz and polarization effects and reduced to $|F_o|$'s. Using the varying intensity standards to correct the scale seemed to be more reasonable than not scaling the data, since the stronger reflections are affected similarly to the selected intensity standards.

The mercury and selenium atom positions were determined from the Patterson map. The nitrogen and carbon atoms were found from a subsequent electron density difference map. Coordinates and anisotropic temperature factors were refined for all non-hydrogen atoms while the hydrogen atoms were placed in calculated positions with assigned temperature factors and were repositioned after further refinement of the structure. A weighting scheme was applied such that $< w(|F_o| - |F_c|)^2 >$ was approximately constant as a function of either $|F_o|$ or $(\sin\theta)/\lambda$. Final refinement of 98 variables for 1153 observed data ($I \geqslant 2.5\sigma(I)$) included a refined extinction coefficient. [5] The coordinates of the non-hydrogen atoms are listed in Table 3.

The NRC VAX [6] system of crystallographic programs were used for data reduction and refinement of the structure of **2**. CRYSTALS [7] was used for the restrained refinement of the structure of **1**. The plots of the structures were generated using the program SNOOPI [8]. Complex scattering factors for neutral

Table 3

Fractional atomic coordinates and equivalent isotropic temperature factors (Å^2) for the non-hydrogen atoms of $Hg(CN)_2((Se(CH_2)_3)_4)$

	x	y	z	B [a]
Hg(1)	0	0	0	4.84
Se(1)	0.72022(23)	0.44582(10)	0.27135(9)	4.04
Se(5)	0.91154(22)	0.73888(10)	0.04836(9)	3.89
N(1)	−0.3716(23)	0.1023(9)	0.1151(9)	7.6
C(1)	−0.2484(24)	0.0653(10)	0.0719(9)	4.7
C(2)	0.7201(22)	0.5914(9)	0.2206(8)	5.2
C(3)	0.5688(18)	0.6105(9)	0.1250(8)	3.8
C(4)	0.6040(18)	0.7234(9)	0.0846(8)	4.4
C(6)	0.8343(20)	0.6759(9)	−0.0759(8)	4.6
C(7)	1.0507(23)	0.6325(9)	−0.1156(8)	4.6
C(8)	1.0137(22)	0.6057(10)	−0.2180(8)	5.8

[a] B_{eq} is the mean of the principal axes of the thermal ellipsoid.

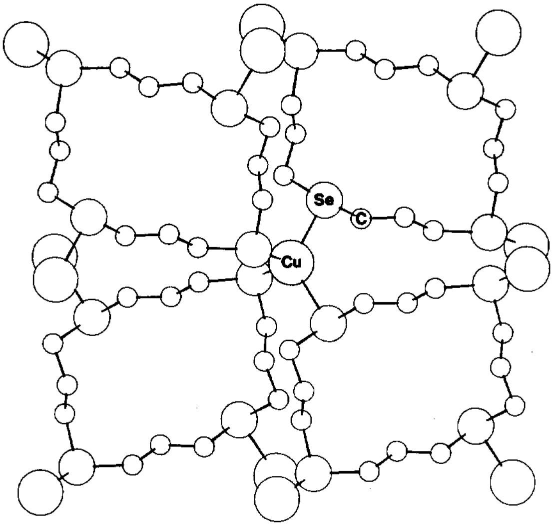

Fig. 1. A section of the three-dimensionally polymeric complex cation of **1**; rotated by 5° about *c* (horizontal axis) from the projection on (1 0 0).

atoms [9] were used in the calculations. All computations were performed with a MicroVAX-II computer.

Results and discussion

In the structure of **1** (Fig. 1) the 16Se4 ring does not chelate as might be expected based on previous work on cyclic polythiaether complexes of Cu^I [10–14] and the Cu^{II} complex of 16Se4 [2]. In **1** each Se atom of the 16Se4 ring forms a coordinate bond to a different, though symmetry related, Cu^+ ion. Each Cu^+ ion is pseudo-tetrahedrally coordinated by Se atoms from four different 16Se4 rings. The Cu^+ ion is located on a crystallographic 2-fold axis running parallel to *c*, while another crystallographic 2-fold axis, parallel to *a*, passes through the centre of mass of the 16Se4 ring. The space between adjacent rings along this axis is occupied by the disordered $SO_3CF_3^-$ anion. There are almost no significant contacts between anion and complex cation and the few observed (slightly below Van der Waals distances) are entirely consistent with the proposed correlation between the disorder of the cation and anion.

The predominant conformation of the 16Se4 ring approximates a [3535] quadrilateral (Fig. 2), as was also found for the uncomplexed ring [1], although the disorder of the structure implies considerable flexibility or conformational interconversion. This disorder and the imposed soft restraints on the structure refinement preclude detailed quantitative discussion of most of the structural parameters *. Nevertheless, the Cu–Se bond lengths are slightly longer than Cu–S bonds in Cu^I

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* Cu–Se: 2.42–2.52 Å; Se–C: 1.93–1.98 Å; C–C: 1.54–1.56 Å; Se–Cu–Se: 98.0(1)–125.0(7)°; Cu–Se–C: 91(1)–124(1)°; C–Se–C: 97.1–104.3°; C–C–Se: 102.7–115.6°; C–C–C: 105.8–110.8°.

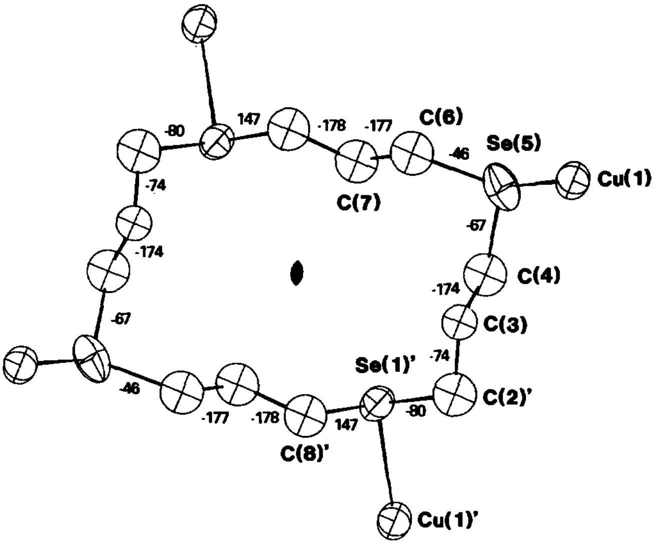

Fig. 2. Structure of the predominant (disordered) 16Se4 conformer in **1**, including bonds to copper; bond torsion angles (°) of the ring are shown.

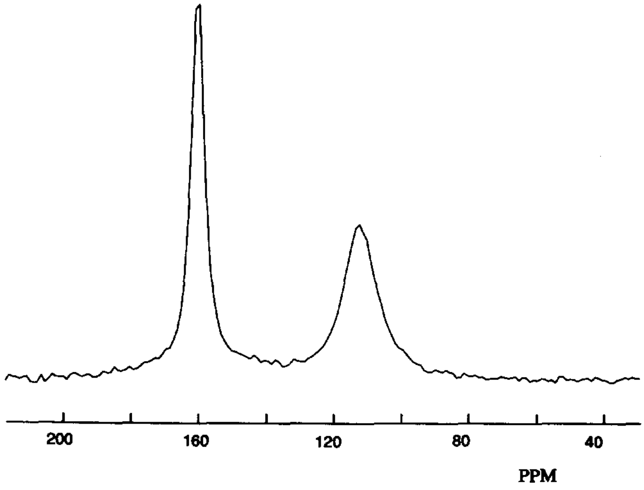

Fig. 3. Solid state CP-MAS ^{77}Se NMR spectrum of **1**.

complexes of cyclic polythiaethers * [10–14], and thus reasonably represent single coordinate covalent bonds. For further comparison, the Cu–Se bond length in CuHgSeCl is 2.379(3) Å. [15] In all of the reported structures of Cu^{I} complexes of cyclic polythiaethers the ligands chelate. The 15S5 [11], 16S6 [12] and 18S6 [13] coronands all form monomeric complexes with Cu^{I} in which the Cu^{+} ion is pseudotetrahedrally coordinated by four S atoms from one ring. In Cu(14S4)(ClO_4) [10] the complex cation forms a chain polymer.

The unique type of complexation found in **1**, as opposed to the expected tetrahedral encapsulation of Cu^{I} by the ligand, probably results from the combined

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* Cu–S: 2.243(5)–2.360(2) Å.

Table 4

Selected interatomic distances (Å) and angles (°) for $Hg(CN)_2((Se(CH_2)_3)_4$ (2)

Hg(1)–C(1)	2.059(13)	N(1)–C(1)	1.11(2)
Se(1)–C(2)	1.949(11)	C(7)–C(8)	1.46(2)
Se(1)–C(8) ^{a}	1.935(12)	C(6)–C(7)	1.55(2)
Se(5)–C(4)	1.947(10)	C(3)–C(4)	1.54(2)
Se(5)–C(6)	1.906(12)	C(2)–C(3)	1.51(2)
Hg(1)···Se(1) ^{b}	3.4370(14)	Hg(1)···Se(5) ^{c}	3.3793(12)
C(1)–Hg(1)–C(1) ^{d}	180.0	Hg(1)–C(1)–N(1)	175.7(13)
C(2)–Se(1)–C(8) ^{a}	96.9(5)	C(4)–Se(5)–C(6)	96.1(5)
Se(1)–C(2)–C(3)	116.1(8)	Se(1) ^{a}–C(8)–C(7)	117.1(9)
Se(5)–C(4)–C(3)	111.6(7)	Se(5)–C(6)–C(7)	112.7(8)
C(6)–C(7)–C(8)	115.6(10)	C(2)–C(3)–C(4)	112.3(9)
Se(1) ^{b}···Hg(1)···Se(1) ^{e}	180.0	Hg(1) ^{g}···Se(1)–C(2)	97.6(4)
Se(5) ^{c}···Hg(1)···Se(5) ^{f}	180.0	Hg(1) ^{g}···Se(1)–C(8) ^{a}	97.9(4)
Se(1) ^{b}···Hg(1)···Se(5) ^{c}	71.77(3)	Hg(1) ^{h}···Se(5)–C(4)	108.9(3)
Se(1) ^{b}···Hg(1)–C(1)	83.3(4)	Hg(1) ^{h}···Se(5)–C(6)	103.5(3)
Se(5) ^{c}···Hg(1)–C(1)	98.0(3)		

$^{a} = 2-x, 1-y, -z$; $^{b} = 1-x, -1/2+y, 1/2-z$; $^{c} = -1+x, -1+y, z$; $^{d} = -x, -y, -z$; $^{e} = -1+x, 1/2-y, -1/2+z$; $^{f} = 1-x, 1-y, -z$; $^{g} = 1-x, 1/2+y, 1/2-z$; $^{h} = 1+x, 1+y, z$.

effect of a special lattice stability associated with the choice of anion, as well as the fact that the 16Se4 ring remains in a low-energy conformation. A Cu^{I} complex with 16S4 (the thiather-analogue of **1**) has not been reported, however 1,3,6,9,11,14-hexathiacyclohexadecane (16S6) is capable of encapsulating Cu^{I} with four of the six S atoms coordinating in a tetrahedral arrangement [12]. 1,5-diaza-9,13-dithiacyclohexadecane also forms a coronand complex with Cu^{I} in which Cu has a tetrahedral N_2S_2 environment [18]. In $[Cu(16Se4)][SO_3CF_3]_2$ [2] the ligand encapsulates Cu^{II} to form a centrosymmetric tetragonally distorted octahedral complex in which oxygen atoms of the trifluoromethanesulfonate ions are weakly bound in the axial positions.

The solid state CP-MAS ^{77}Se NMR spectrum of **1** (Fig. 3) displays two rather broad resonances of equal integrated intensity. This broadening may be largely attributable to coupling to the quadrupolar Cu nucleus, although the disorder of the structure must also contribute. The broader peak at high field may be assigned to the disordered Se(1)/Se(11) (see above) while the other is presumably associated with Se(5).

In compound **2** the closest Se···Hg distances (3.3793(12) and 3.4370(14) Å) represent rather weak interactions *, as compared with the Hg–Se bond distances in CuHgSeCl: 2.477(2), 2.486(3). [15] Selected interatomic distances and angles are given in Table 4 and the geometry of the 16Se4 ring is shown in Fig. 4. Both the Hg atom and the centre of mass of the ring are located on different crystallographic centres of inversion. The $Hg(CN)_2$ molecules in **2** are approximately linear and have bond distances comparable to those found in $Hg(CN)_2$ itself [16]. The molecules pack such that four Se atoms from four different rings most closely approach Hg in a plane approximately perpendicular to the molecular axis of $Hg(CN)_2$, forming an extended two-dimensional structure in the (100) plane (Fig. 5). The Hg atom thus has a tetragonally distorted octahedral ligand environment.

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* cf. Sum of the covalent radii (Hg+Se): 2.67 Å; Sum of Van der Waals radii (Hg+Se): 3.45 Å.

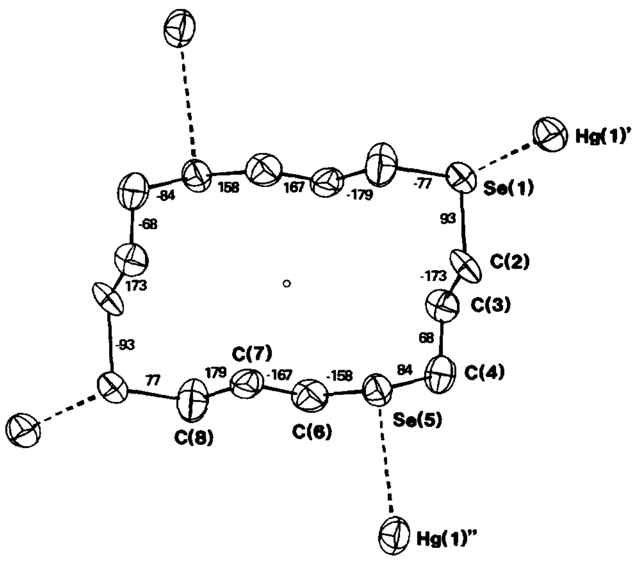

Fig. 4. Structure of 16Se4 in **2**, showing Hg atom contacts; bonds labelled with torsion angles (°), esds range 0.7–1.2°.

The solid state CP-MAS ^{77}Se NMR spectrum (Fig. 6) of **2** displays two sharp resonances consistent with the observed symmetry of the structure. These display satellites of appropriate relative intensity for ^{77}Se–^{199}Hg couplings of 110 Hz and 123 Hz and natural abundance of the ^{199}Hg isotope. These couplings suggest a very weak bonding interaction between Hg and Se; cf. the magnitude of the one-bond ^{77}Se–^{199}Hg coupling for $[HgSe_2]^{2-}$ is 2258 Hz [17]. The resonances also have

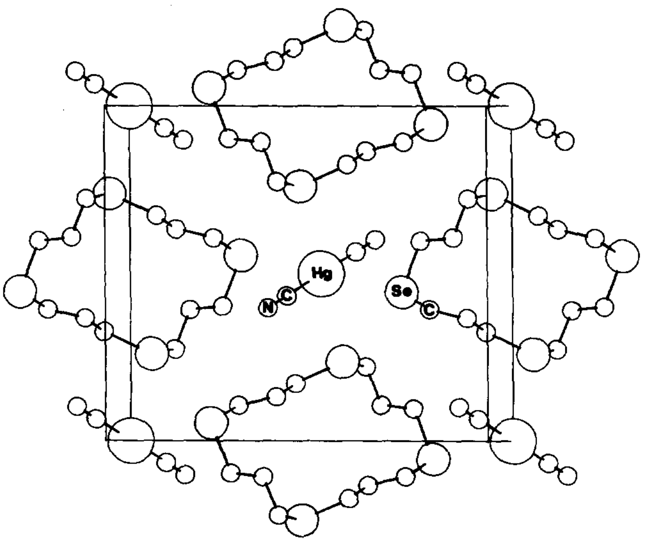

Fig. 5. Crystal structure of **2**; projected on (1 0 0); *c*-axis horizontal.

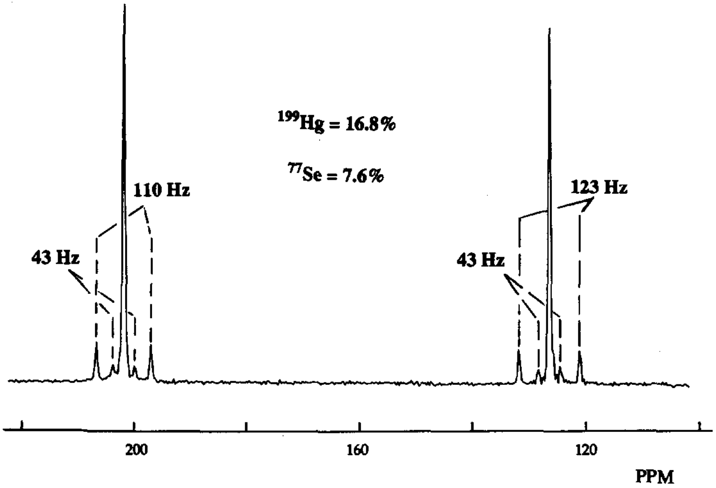

Fig. 6. Solid state CP-MAS ^{77}Se NMR spectrum of **2**.

satellites indicating a ^{77}Se–^{77}Se coupling of 43 Hz. Since no four bond ^{77}Se–^{77}Se couplings have been observed in the course of our work on selenium coronands, we conclude that the observed 43 Hz coupling occurs between Se atoms from different rings which are *cis*-related in their arrangement about the Hg atom. It is interesting to note that the intensity of these satellites requires that the observed coupling could arise from only one of the two geometrically different *cis* Se–Hg–Se relationships. (i) Se–Hg–Se 71.77(3)°, or (ii) Se–Hg–Se 108.23(3)°.

The quadrangular conformation of the ring in **2** differs from that apparently predominating in **1** and in the uncomplexed ligand [1] in that the corners occupied by selenium atoms are formed by two consecutive *gauche* bond torsion angles of opposite sign (denoted G^-G^+). Considering the weakness of the Hg · · · Se interactions, it must be concluded that the energy difference between these two types of ring conformation is small. A similar relationship was found between the two conformers of 1,3,7,9-tetraselenacyclododecane which cocrystallize [1]. The crystal structure of 1,3,6,9,11,14-hexathiacyclohexadecane [12] also contains two different conformers, one of which is analogous to that in **2**. The preference for G^+G^+ over G^-G^+ corners in cycloalkanes [19] must be considerably diminished when the corner atom is replaced by selenium since the distance between the cross-corner hydrogen atoms effectively increases. The consequent choice of corner types results in the coexistence of different highly flexible low-energy conformers which have similar overall physical dimensions. This is presumably the cause of the disorder evidenced in the structures of 16Se4 [1] and **1**. Finally, the apparent greater stability of such conformations over, for example, the [4444] conformation has been attributed [1] to their relative compactness.

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