CRYSTAL STRUCTURES OF SOLID SOLUTIONS
OF $Cs_2HgBr_2(SCN)_2$ and $[Cs_{0.96}(NH_4)_{0.04}]_2HgBr_2(SCN)_2$

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RESUME: Les structures des solutions solides $Cs_2HgBr_2(SCN)_2$ (a = 5.9324(4), b = 6.0363(3), c = 16.6701(9)Å; V = 596.95(6)Å^3; R = 5.7%) et $[Cs_{0.96}(NH_4)_{0.04}]_2HgBr_2(SCN)_2$ (a = 5.9400(5), b = 6.0150(4), c = 16.6560(14)Å; V = 595.10(7)Å^3; R = 4.1%) ont été déterminées par diffraction des rayons-X sur monocristal. Les complexes mixtes cristallisent dans le groupe d'espace Pnmm, leurs structures sont basées sur des chaînes qui s'étendent suivant l'axe b . A l'intérieur des chaînes les bipyramides triangulaires développées autour du mercure sont connectées par des atomes de brome. Les cations Cs^+ (Cs^+/NH_4^+) sont intercalés entre les chaînes dans une géométrie prismatique pyramidée par un atome d'azote . Les complexes mixtes présentent un nouveau arrangement structural différent de celui observé dans le complexe pur Cs_2HgBr_4.

Mots clés: composés mixtes, structure cristalline, arrangement bipyramidale triangulaire.

ABSTRACT: The structure of solid solutions of $Cs_2HgBr_2(SCN)_2$ (a = 5.9324(4),b = 6.0363(3), c = 16.6701(9)Å; V= 596.95(6)Å^3; R = 5.7%) and $[Cs_{0.96}(NH_4)_{0.04}]_2HgBr_2(SCN)_2$ (a = 5.9400(5), b = 6.0150(4), c = 16.6560(14)Å; V = 595.10(7)Å^3; R = 4.1%) have been determined by X-ray diffraction to be in the Pnmm centrosymmetric group. The mixed complexes have a chain-based structure. Chains are stacked along the b axis. Within the stacks, bipyramidal trigonal anions are bridged by Br^- ions. The Cs^+ (Cs^+/NH_4^+) cations are intercalated between chains in a distorted monocapped-triangular prism geometry. The mixed complexes present a new type of structural arrangement from this of pure Cs_2HgBr_4.

Key words : mixed compounds, crystal structure, bipyramidal trigonal arrangement.

INTRODUCTION

As part of our interest concerning mixed compounds, we have been studying mercury complexes with thiocyanate and ammonium as partial substitution respectively for Br and Cs atoms

in Cs_2HgBr_4, resulting in two complexes : $Cs_2HgBr_2(SCN)_2$ (A) and $[Cs_{0.96}(NH_4)_{0.04}]_2HgBr_2(SCN)_2$ (B).

In pure complex Cs_2HgBr_4[1], the structural arrangement is formed by isolated tetrahedra $HgBr_4^{2-}$ and Cs^+ cations in pseudohexagonal environnement. Structural analyses have shown that the crystal could be described, in the room temperature phase by disordered model with the Br atoms occupying two very close positions, allowing the bromine tetrahedron to choose two orientations in the structure. Large atomic displacement parameters that were observed for Br atoms and one of the two independent crystallographic sites of Cs atoms, could be interpreted under considerations of this disorder.

Tetrathiocyanatomercurate (II) complexes [2,3] contain the tetrahedral $Hg(SCN)_4^{2-}$ anion. Since Hg(II) is a soft ion compared to Co(II), Ni(II), Zn(II) and Cd(II), thiocyanate will preferably link to mercury through its S-end according to H. S. A. B. theory[4]. Further support for Hg-SCN linkage is given by the potassium salt $K_2Hg(SCN)_4$[5], in which Hg-SCN linkage is present, where as in $K_2M(NCS)_4$ (M= Cd(II), Ni(II), Zn(II)), M-NCS linkages are present [6, 7].

EXPERIMENTAL

In water-acetone solutions, transparent single crystals were grown from a mixture of CsBr, $Hg(SCN)_2$ for complex (A) and CsBr, NH_4SCN, $Hg(SCN)_2$, $HgBr_2$ for complex (B):

$$2CsBr + Hg(SCN)_2 \longrightarrow Cs_2HgBr_2(SCN)_2 \quad (A)$$

$$2(1-x) CsBr+ 2x\ NH_4SCN+ x\ HgBr_2+ (1-x)\ Hg(SCN)_2 \longrightarrow [Cs_{0.96}(NH_4)_{0.04}]_2HgBr_2(SCN)_2\ (B)$$

Chemical analysis were carried out to define complexes contents. The quantitative result was subsequently confirmed by X-ray crystallography.

For the two complexes crystal data collection procedure and refinement of the structures are given in table I. Structure solution and refinement were carried out using Shelx programs [8,9]. A three dimensional Patterson synthesis was used to determine the heavy atoms positions, which phased the data sufficiently enough to permit location of caesium, bromine, sulphur, carbon and nitrogen of (SCN)⁻ groups from Fourier synthesis.

For the double mixed complexe (B), occupancies of Cs and N are refined separately, the total occupancy on the mixed site was unity. The coordinate and thermal parameters for the shared Cs\N site were held identical to avoid problems with correlation. The coordinates resulting from full-

matrix least-squares anisotropic refinements, together with the anisotropic thermal displacement parameters for all non-hydrogen atoms are given in table II and III.

Only one H atom bonded to N of ammonium groups was located from Fourier synthesis and then fixed to generate geometrically calculated positions of the others hydrogen atoms.

Table I. Summary of crystallographic data

	Complex (A)	Complex (B)
Formula	$Cs_2 HgBr_2(SCN)_2$	$[Cs_{0.96}(NH_4)_{0.04}]_2 HgBr_2(SCN)_2$
Formula weight	382.11	366.31
Space group	Pnmm	Pnmm
a(Å)	5.9324(4)	5.9400(5)
b(Å)	6.0363(3)	6.0150(4)
c (Å)	16.6701(9)	16.6560(14)
V(Å^3)	596.95(6)	595.10(7)
Z	4	4
ρ_{calc} (g cm^{-3})	4.252	4.089
ρ_{mes} (g cm^{-3})	4.234	4.125
μ (mm^{-1})	29.055	25.72
Data collection instrument	Enraf-Nonius CAD-4 diffractometer	Enraf-Nonius Kappa-CCD diffractometer
Radiation, graphite monochromator λ(Å)	MoKα(0.71069)	MoKα(0.71069)
Temperature(°C)	20	20
Scan method	ω-2θ	
Data collection range, 2θ(°)	6.8<2θ<60.9	4.9<2θ<54.98
No. Unique reflections measured	904	768
No. Reflections in refinement with I>2σ(I)	815	762
R^a(%)	5.7	4.1
WR$_2^b$(%)	15.15	11.28
Calculated weights	w= 1/[σ²(Fo²)+(0.1163P)²+0.7422P], P= (Fo²+2Fc²)/3	w=1/[σ²(Fo²)+(0.0731P)²+3.7575P], P= (Fo²+2Fc²)/3

$^a R = \sum \left| |F_0| - |F_c| \right| / \sum F_0$, $^b WR_2 = \left[\dfrac{\sum \left[w\left(|F_0|^2 - |F_c|^2 \right) \right]^2}{\sum \left[w\left(|F_0|^2 \right) \right]^2} \right]^{1/2}$

Table II: atomic coordinates and equivalent thermal parameters

$Cs_2HgBr_2(SCN)_2$

Atoms	Multip.	x	y	z	U_{eq}
Hg	1	0.0753(2)	0.2500	0.2500	0.0456(6)
Cs	1	-0.4112(3)	-0.2500	0.38969(11)	0.0409(6)
Br1	1	-0.3703(6)	0.2500	0.2500	0.0353(8)
Br2	1	0.0906(7)	-0.2500	0.2500	0.0404(10)
S	1	0.2033(11)	0.2500	0.3916(3)	0.0343(13)
C	1	-0.041(4)	0.2500	0.4394(16)	0.037(5)
N	1	-0.200(7)	0.2500	0.4710(18)	0.069(9)

$[Cs_{0.96}(NH_4)_{0.04}]_2HgBr_2(SCN)_2$

Atoms	Multip.	x	y	z	U_{eq}
Hg	1	0.57915(9)	0.7500	0.2500	0.0308(3)
Cs	0.96	0.09040(11)	0.2500	0.38953(4)	0.0255(4)
N1	0.04	0.09040(11)	0.2500	0.38953(4)	0.0255(4)
H1	0.04	0.9492	0.2500	0.3717	0.050
H2	0.04	0.1632	0.1304	0.3717	0.050
H3	0.04	0.0904	0.2500	0.4430	0.050
Br1	1	0.1320(2)	0.7500	0.2500	0.0220(4)
Br2	1	0.5926(2)	0.2500	0.2500	0.0258(4)
S	1	0.7074(4)	0.7500	0.39307(13)	0.0223(5)
C	1	0.4561(19)	0.7500	0.4388(6)	0.0246(19)
N	1	0.286(2)	0.7500	0.4712(6)	0.042(3)

$U_{eq} = 1/3 \ \Sigma i \Sigma j \ U_{ij} a^*_i a^*_j a_i a_j$.

Table III: anisotropic displacement parameters$(10^{-3} Å^2)^a$.

$Cs_2HgBr_2(SCN)_2$

Atoms	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Hg	0.0267(8)	0.0873(14)	0.0229(7)	0.000	0.000	0.000
Cs	0.0464(11)	0.0410(10)	0.0352(10)	0.000	0.0047(6)	0.000
Br1	0.0210(15)	0.0453(19)	0.0397(18)	0.000	0.000	0.000
Br2	0.040(2)	0.0287(16)	0.052(2)	0.000	0.000	0.000
S	0.029(3)	0.047(3)	0.027(3)	0.000	-0.003(2)	0.000
C	0.028(11)	0.054(15)	0.031(12)	0.000	0.000(9)	0.000
N	0.07(2)	0.11(3)	0.035(12)	0.000	0.015(14)	0.000

$[Cs_{0.96}(NH_4)_{0.04}]_2HgBr_2(SCN)_2$

Atoms	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Hg	0.0185(4)	0.0603(5)	0.0137(4)	0.000	0.000	0.000
Cs	0.0301(5)	0.0248(5)	0.0218(5)	0.000	0.0030(2)	0.000
N1	0.0301(5)	0.0248(5)	0.0218(5)	0.000	0.0030(2)	0.000
Br1	0.0306(8)	0.0151(6)	0.0318(8)	0.000	0.000	0.000
Br2	0.0156(6)	0.0270(7)	0.0233(7)	0.000	0.000	0.000
S	0.0230(11)	0.0279(11)	0.0161(10)	0.000	-0.0028(9)	0.000
C	0.032(5)	0.025(4)	0.017(4)	0.000	-0.001(4)	0.000
N	0.040(6)	0.064(7)	0.021(4)	0.000	0.016(4)	0.000

^{a} the anisotropic displacement exponent takes the form $(-2\Pi^2[h^2 a^{*2} U_{11} + ... + 2hka^*b^* U_{12}])$.

RESULTS AND DISCUSSION
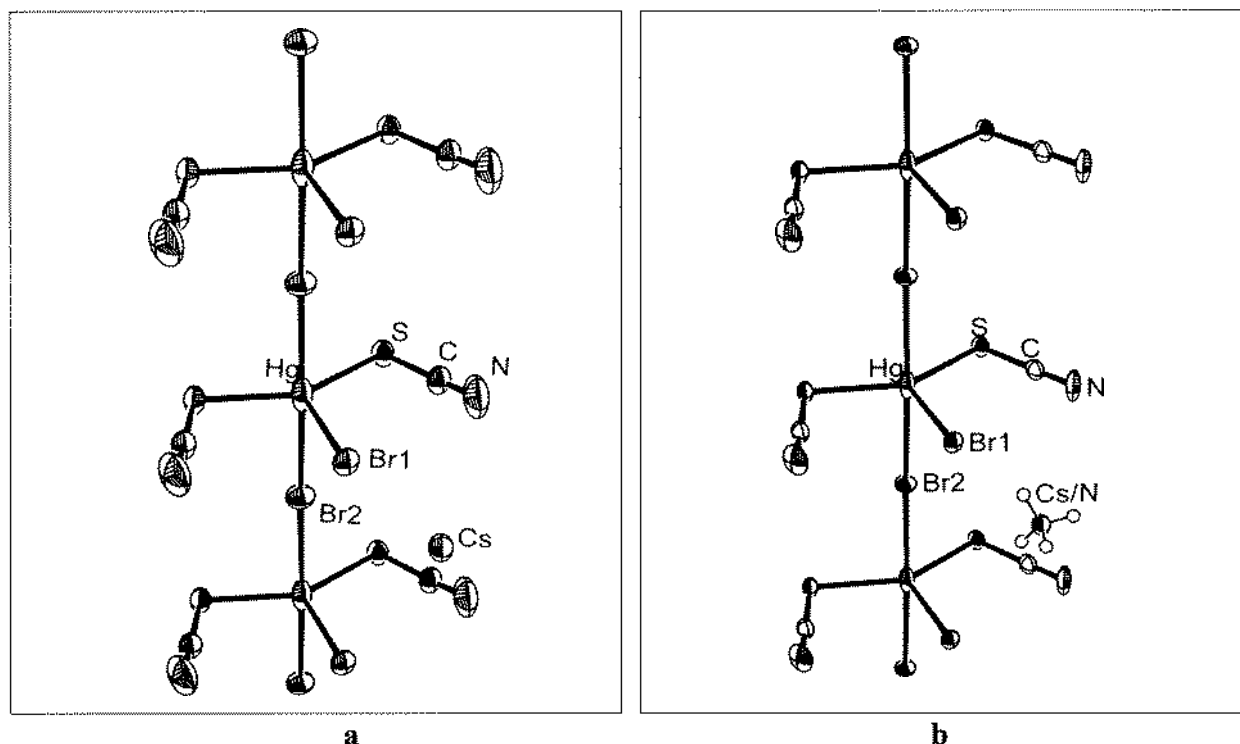
Figure 1: stereoscopic views of the unit cell contents of a) $Cs_2HgBr_2(SCN)_2$ (A)

b) $[Cs_{0.96}(NH_4)_{0.04}]_2HgBr_2(SCN)_2$ (B).

The stereoscopic views of the unit cell contents of $Cs_2HgBr_2(SCN)_2$ (A) and $[Cs_{0.96}(NH_4)_{0.04}]_2HgBr_2(SCN)_2$ (B) are depicted in figure 1. Selected bond angles and distances are listed in table IV. In both complexes we note the presence of one dimensional Hg (II) networks with three Br⁻ ions and two mirror related SCN⁻ groups, acting as S donors.

Separate Cs^+ cations for complex (A) and (Cs^+,NH_4^+) cations for complex (B) are intercalated between chains. The bond lengths and angles are in good agreement with a bipyramidal trigonal coordination polyhedra around Hg(II).

The internal parameters of the bipyramidal chains in the two complexes are quite different. There are three covalent bonds, one Hg-Br and two Hg-S in the equatorial plane parallel to (a,c) yielding to a distorted trigonal symmetry. Hg(II) is also linked to two Br⁻ ions in the axial direction, Hg-Br distances in this direction are clearly elongated when compared with the equatorial distances so they are considered as coordination type, and complete the symmetry around Hg(II), thus with respect to the equatorial and axial angles, the effective coordination is bipyramidal trigonal. The polyhedra have two common Br⁻ ions and are stacked into chains which develop along the b axis (figure 2).

Table IV: selected bond lengths (Å) and angles (°).

$Cs_2HgBr_2(SCN)_2$				$[Cs_{0.96}(NH_4)_{0.04}]_2HgBr_2(SCN)_2$			
Hg	S		2.480(6)	Hg	S		2.502(2)
Hg	S^i		2.480(6)	Hg	S^{vi}		2.502(2)
Hg	Br1		2.644(4)	Hg	Br1		2.6559(14)
Hg	Br2		3.0195(2)	Hg	Br2		3.0086(2)
Hg	Br2^{ii}		3.0195(2)	Hg	Br2^{ii}		3.0086(2)
S	C		1.65(3)	S	C		1.676(12)
C	N		1.08(4)	C	N		1.144(16)
Cs	N^{iii}		3.27(3)	Cs	N^{vii}		3.223(10)
Cs	N		3.538(19)	Cs	N		3.500(6)
Cs	N^{iv}		3.538(19)	Cs	N^{iv}		3.500(6)
Cs	Br2^v		3.763(4)	Cs	Br2^v		3.7608(13)
Cs	Br2		3.780(4)	Cs	Br2		3.7817(13)
Cs	Br1^{iv}		3.8198(12)	Cs	Br1^{iv}		3.8089(5)
Cs	Br1		3.8198(12)	Cs	Br1		3.8089(5)
S	Hg	S	144.3(3)	S	Hg	S^{vi}	144.53(12)
S	Hg	Br1	107.83(16)	S	Hg	Br1	107.73(6)
S^i	Hg	Br2	89.47(3)	S	Hg	Br2	89.535(9)
Br1^i	Hg	Br2	91.72(8)	Br1	Hg	Br2	91.53(3)
Br2	Hg	Br2^{ii}	176.56(17)	Br2	Hg	Br2^{ii}	176.95(6)
C	S	Hg	101.0(10)	C	S	Hg	99.3(4)
N	C	S	180(3)	N	C	S	178.8(10)

i) x, y, -z+1/2; ii) x, y+1, z; iii) –x-1, -y, -z+1; iv) x, y-1, z; v) x-1, y, z; vi)x, -y+3/2, -z+1/2; vii) -x, -y+1, -z+1.

It is noted that the Hg-Br bonds, which are involved in the chains along [0 1 0], show a decrease in the length from 3.0195(2) to 3.0086(2)Å as a function of the introduction of NH_4^+. It is this decrease of bond lengths that also contribute to the increase in the Hg-S and Hg-Br equatorial bond lengths from 2.480(6) to 2.502(2) and 2.644(4) to 2.6559(14) Å, respectively, as do the S-C and C-N bond lengths, which increase from 1.65(3) to 1.676(12)Å and 1.08(4) to 1.144(16)Å, respectively. the internal thiocyanate S-C-N groups are close to linear in all cases (176.56(17)° for (A) and 176.95(6)for (B)). The mean value of the Hg-S-C angle is slightly distorted in the complex (B) and with good agree for the compound (A) from accustomed for many thiocyanate mercury complexes [10]. Hg-S bond length values are comparable with those observed in Bis(thiocyanato)(triphenylphosphine)mercury II[11]. In fact, Hg-S distances in this complex are of 2.539 and 2.469Å. The Hg-Br distance values are typical for a bipyramidal trigonal coordination like those observed in the imidomercuricbromide complex [12]. Thermal parameters of the two compounds were carefully examined. A systematic decrease was found for all atoms as NH_4^+ is incorporated. This observation suggested that partial occupancy of NH_4^+ should gives more stability in the room temperature structure.

a **b**
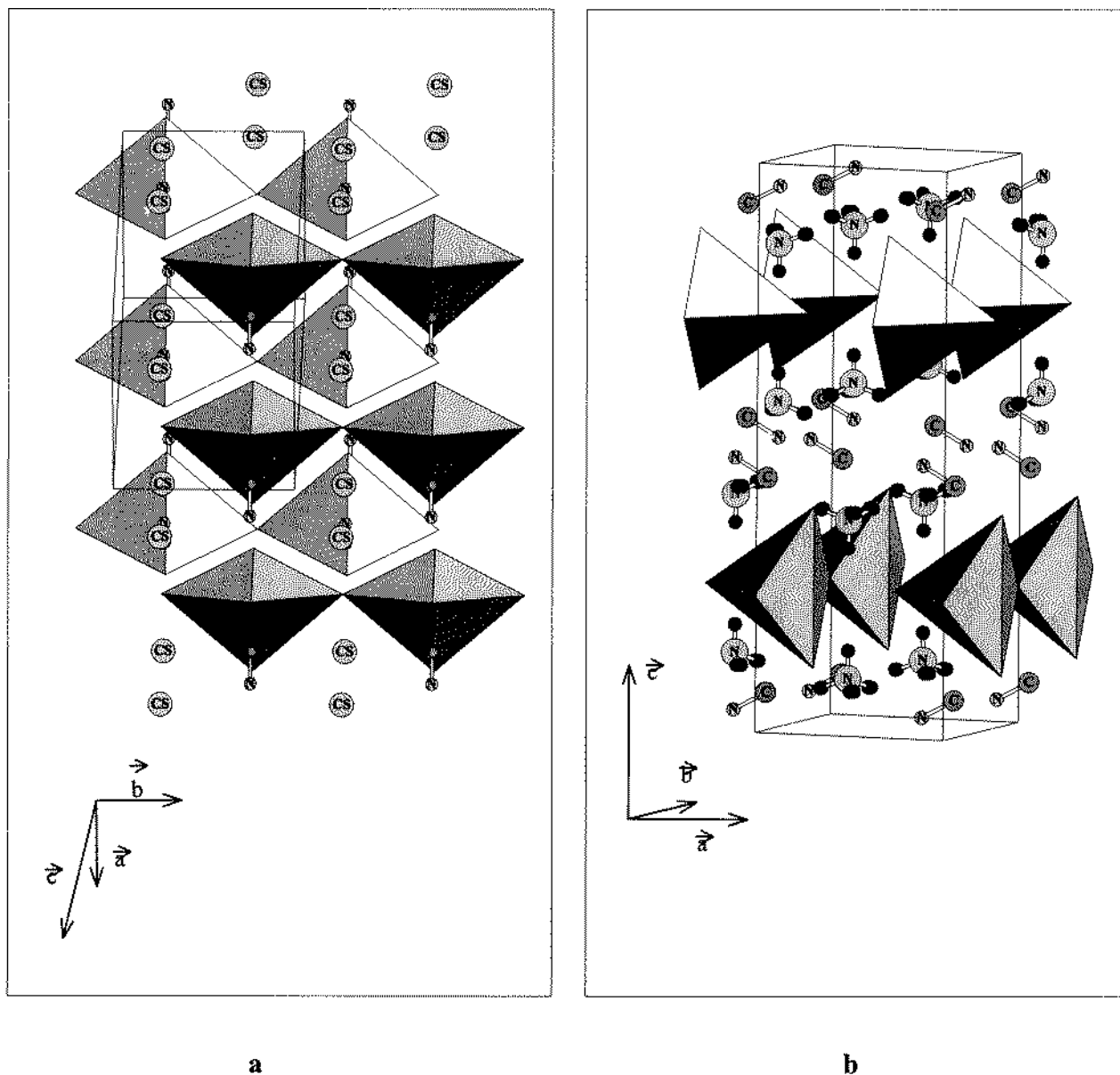
Figure 2: perspective views of structures of a) $Cs_2HgBr_2(SCN)_2$ (A)

b) $[Cs_{0.96}(NH_4)_{0.04}]_2HgBr_2(SCN)_2$ (B).

The Cs^+ (Cs^+/NH_4^+) site are enclosed by seven atoms in a distorted monocapped-triangular prism geometry as seen in figure 3. The seven atoms forming this coordination sphere are distributed as three nitrogen atoms and four bromine ones. Table IV also shows Cs-N and Cs-Br distances, The Cs^+ (Cs^+/NH_4^+) cages decrease in size as NH_4^+ is incorporated, this is can be related first to the small size of NH_4^+ cations toward Cs^+ one (r (Cs^+) = 1.65Å, r (NH_4^+) = 1.42Å) **[13]**, second to the electrostatic interactions with neighbours that increase because of the hydrogen bonding. In $[Cs_{0.96}(NH_4)_{0.04}]_2$ $HgBr_2(SCN)_2$ short distances are found between N atoms of NH_4^+

groups and N atoms of SCN groups or Br atoms. Values seen in table V are suggestive of hydrogen

bonding that assure cohesion between $[HgBr_2(SCN)_2]_n^{2n-}$ chains.

Table V: hydrogen bonding lengths (Å) and bond angles (°) (A= Br, N).

N-H... A	d(N-H)	d(H..A)	<NHA	d(N..A)
N1-H1... Br1	0.890	2.932	155.73	3.761
N1-H2... Br2 [i]	0.890	3.063	142.65	3.809
N1-H3... N[ii]	0.890	2.656	122.57	3.223

i) x, y-1, z; ii) -x, -y+1, -z+1.
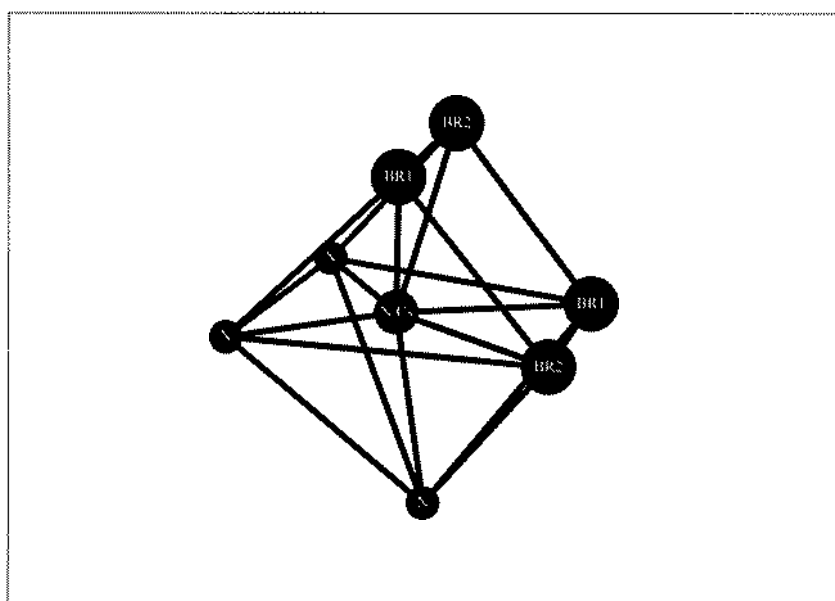
Figure 3: coordination sphere of Cs^+ (Cs^+/NH_4^+).

Structural arrangement in both compounds which crystallise in the same space group Pnmm

differs considerably from the Cs_2HgBr_4 one that crystallise in the space group Pnma. Because of the

lowest symmetry for the mixed complexes, we have observed a large decrease of the cell volume

(table VI) by an important decrease of b and essentially a lattice parameters and a small increase of

the c lattice parameter. This effect is essentially due to the environment of Hg(II) that depend on the

steoechiometry of the complex.

Generally it has been found that the electronegativity difference $[\chi(Hg)-\chi(L)]$ is most

suitable for a rational classification of the crystal structures of mercury complex. With respect to

results resumed by GRDENIĆ [14], the value 2.5 for ligand electronegativity is a critical one. For

Br atoms with electronegativity less than 2.5 the effective coordination is tetrahedral. The

tetrahedral coordination is also observed for tetrathiocyanate (II) mercury complexes in spite of the

electronegativity of sulphur that is above 2.5 . This may be the result of steric factors and essentially of the fact that mercury prefer to link to (SCN) group through its S-end and ever through the N-end, so it was not possible to observe structural arrangement in which (SCN) group bridge two mercury atoms from S and N end, the coordination of mercury for $Hg(SCN)_4^{2-}$ complexes is then tetrahedral.

In the mixed complexes $[HgBr_2(SCN)_2]^{2-}$, Br atoms and (SCN) groups act to change the coordination from tetrahedral. Br atoms can assure the linkage between polyhedra and (SCN) groups impose a non tetrahedral coordination with respect to the electronegativity of the sulphur. The coordination of Hg(II) change from tetrahedral to bipyramidal trigonal chains .

Using the conventional disordered model for the Cs_2HgBr_4 structure [1], it was found that the new structural arrangement in mixed complexes is exclude from disordered models. While bromide tetrahedron present two orientations in the Cs_2HgBr_4 structure, bipyramidal polyhedra are stacked with the intermediate of Br atoms into chains with only one orientation in mixed complexes. All atoms occupy only one position with appreciable reduced thermal parameters, specially Br and Cs ones.

This examination lead us to conclude that the substitution of Br⁻ ions by (SCN)⁻ groups stabilises the room temperature structure of Cs_2HgBr_4 by changing the coordination of mercury in a new one that have the advantage of not being subject to systematic disorder.

Table VI: cell parameters of pure and substituted compounds

Compounds	a (Å)	b (Å)	c(Å)	V(Å³)
Cs_2HgBr_4[1]	10.270(2)	7.946(1)	13.935(2)	1137.1(3)
$Cs_2HgBr_2SCN_2$	5.9324(4)	6.0363(3)	16.6701(9)	596.95(6)
$[Cs_{0.96}(NH_4)_{0.04}]_2HgBr_2SCN_2$	5.9400(5)	6.0150(4)	16.6560(14)	595.10(7)

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