

Crystal engineering with 2,1,3-benzoselenadiazole and mercury(II) chloride

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ABSTRACT

The reactions of HgCl₂ with 2,1,3-benzoselenadiazole (bsd) in methanol afforded the polymeric complexes [HgCl₂(bsd)₂]_n (**1**) and [HgCl₂bsd]_n (**2**) in good yields. The crystal structures of **1** and **2** have been determined by single-crystal X-ray crystallography. Complex **1** is a one-dimensional (1D) polymer and consists of (HgCl₂)_n chains running parallel to the *c*-axes. Complex **2** is a two-dimensional (2D) polymer and consists of (HgCl₂)_n chains running parallel to the *a*-axes and being further bridged by bsd molecules to create a layer lying parallel to the *ab* plane. Both crystal structures are dominated by π...π interactions between the bsd molecules, while the presence of N...Se interactions increases the dimensionality in **1**. Characteristic IR data are discussed in terms of the nature of bonding in the structures of the two complexes.

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1. Introduction

Almost a decade ago, Batten and coworkers noted that the crystal engineering of metal-containing networks was dominated by the first-row transition metals along with Zn, Cd and Ag [1]. The absence of heavier metals in the crystal engineering of metal-containing networks turned his attention toward the synthesis of mercury chloride coordination polymers [1]. Nowadays, a simple search in the Web-of-Science reveals only a handful of papers dealing with the crystal engineering of mercury(II) [1–9] and that in turn prompted us to focus our attention toward the synthesis of coordination polymers with mercury(II) chloride.

Based on our previous experience in crystal engineering with the employment of 2,1,3-benzothiadiazole (btd) [10–12], we decided to study the coordination chemistry of mercury with 2,1,3-benzoselenadiazole (bsd) (Fig. 1), which like btd carries two heterocyclic nitrogen atoms in *meta*-position separated by a heteroatom. Both nitrogen atoms are potentially capable of bridging metal ions while the presence of Se in between them offers the bsd ligand the possibility to assemble with neighboring bsd molecules through the rather exotic N...Se interactions [13–19]. The whole bsd molecule is aromatic offering also the possibility to form π...π stacking interactions like those observed in the crystal structures of the btd analogue. The coordination chemistry of bsd has been sparingly explored [17–19].

By employing bsd with mercury(II) chloride we managed to isolate two coordination polymers namely [HgCl₂(bsd)₂]_n (**1**) and [HgCl₂(bsd)]_n (**2**). Both complexes were characterized by single-crystal X-ray crystallography and IR spectroscopy. Complex **1** is an one-dimensional (1D) coordination polymer while **2** is a two-dimensional (2D) coordination polymer. The structures of both complexes were analyzed to reveal that as well as the coordination between the ligand and the mercury(II) atoms there is a number of other weak interactions stabilizing the crystal structures.

2. Experimental

2.1. General and physical measurements

All manipulations were performed under aerobic conditions. HgCl₂, 2,1,3-benzoselenadiazole and all solvents were obtained from commercial sources and used as received. Microanalyses (C, H, N) were performed with an EA 1108 Carlo Erba analyzer. IR spectra were recorded on a Perkin–Elmer 16 PC FT spectrometer with samples prepared as KBr pellets.

2.2. Compound preparation

2.2.1. Synthesis of [HgCl₂(bsd)₂]_n (**1**)

HgCl₂ (271 mg, 1.0 mmol) and bsd (366 mg, 2.0 mmol) were dissolved in MeOH (40 mL). The resulting pale yellow solution was stirred for 30 min and left undisturbed to evaporate at room

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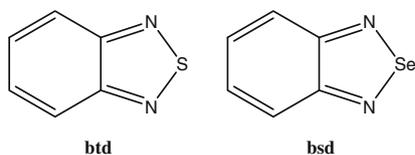


Fig. 1. The structures of 2,1,3-benzothiadiazole (btd) and 2,1,3-benzoselenadiazole (bsd).

temperature. Colorless crystals of **1** were formed over a period of three days. The crystals were isolated by vacuum filtration, washed with Et₂O (2 × 5 mL) and dried in air. Yield ~40%. *Anal. Calc.* for C₁₂H₈HgCl₂N₄Se₂: C, 22.60; H, 1.26; N, 8.79. Found: C, 22.51; H, 1.15; N, 8.87%. Selected IR data (cm⁻¹): 3040 (w), 1602 (m), 1530 (s), 1485 (s), 1460 (s), 1350 (m), 1280 (m), 1130 (m), 924 (s), 870 (vs), 848 (s), 709 (vs), 592 (m), 475 (s).

2.2.2. Synthesis of [HgCl₂(bsd)]_n (**2**)

HgCl₂ (271 mg, 1.0 mmol) and bsd (183 mg, 1.0 mmol) were dissolved in MeOH (25 mL). The resulting pale yellow solution was allowed to stir for 20 min and left undisturbed to evaporate at room temperature. Pale yellow crystals of **2** were formed over a period of two days. The crystals were isolated by vacuum filtration, washed with Et₂O (2 × 5 mL) and dried in air. Yield ~30%. *Anal. Calc.* for C₆H₄HgCl₂N₂Se: C, 15.85; H, 0.89; N, 6.16. Found: C, 15.82; H, 0.76; N, 6.18%. Selected IR data (cm⁻¹): 3038 (w), 1598 (m), 1520 (s), 1479 (s), 1465 (s), 1340 (m), 1276 (m), 1128 (m), 930 (s), 878 (vs), 840 (s), 712 (vs), 588 (m), 468 (s).

2.3. Single-crystal X-ray crystallography

2.3.1. Complex **1**

Slow crystallization from MeOH yielded colorless prismatic crystals. A crystal with approximate dimensions 0.05 × 0.14 ×

Table 1
Crystallographic data for complexes **1** and **2**.

Parameter	1	2
Formula	C ₁₂ H ₈ Cl ₂ HgN ₄ Se ₂	C ₆ H ₄ Cl ₂ HgN ₂ Se
Formula weight	637.64	454.56
Crystal colour, habit	colorless, prisms	pale yellow, prisms
Crystal dimensions (mm)	0.05 × 0.14 × 0.50	0.05 × 0.05 × 0.50
Crystal system	triclinic	orthorhombic
Space group	P $\bar{1}$	P212121
<i>Unit cell dimensions</i>		
<i>a</i> (Å)	9.746(6)	3.9231(19)
<i>b</i> (Å)	11.237(7)	14.756(7)
<i>c</i> (Å)	3.857(3)	16.730(7)
α (°)	84.801(16)	90.00
β (°)	80.174(17)	90.00
γ (°)	79.336(17)	90.00
<i>V</i> (Å ³)	408.2(5)	968.5(8)
<i>Z</i>	1	4
ρ_{calc} (g cm ⁻³)	2.594	3.118
Radiation, λ (Å)	Mo K α , 0.71073	Mo K α , 0.71073
<i>T</i> (K)	298(2)	298(2)
θ Range (°)	1.85–25	1.84–24.50
μ (mm ⁻¹)	14.207	20.145
Collected reflections	1659	1897
Independent reflections (<i>R</i> _{int})	1432 (0.0317)	1602 (0.0430)
Observed reflections <i>I</i> > 2 σ (<i>I</i>)	1198	1543
Parameters refined	97	111
($\Delta\rho$) _{max} , ($\Delta\rho$) _{min} (e Å ⁻³)	2.141, -3.727	0.985, -1.050
Goodness-of-fit (GOF) (on <i>F</i> ²)	1.115	1.080
<i>R</i> ₁ ^a , <i>wR</i> ₂ ^b (all data)	0.0840, 0.1959	0.0314, 0.0830
<i>R</i> ₁ ^a , <i>wR</i> ₂ ^b (<i>I</i> > 2 σ (<i>I</i>))	0.0714, 0.1810 ^c	0.0299, 0.0817 ^d

^a $R_1 = \sum(|F_o| - |F_c|) / \sum(|F_o|)$.

^b $wR_2 = \left\{ \frac{\sum[w(F_o^2 - F_c^2)^2]}{\sum[w(F_o^2)^2]} \right\}^{1/2}$.

^c For 1198 reflections with *I* > 2 σ (*I*).

^d For 1543 reflections with *I* > 2 σ (*I*).

0.50 mm was mounted in a capillary. Diffraction measurements were made on a Crystal Logic Dual Goniometer diffractometer using graphite monochromated Mo radiation. Unit cell dimensions were determined and refined by using the angular settings of 25 automatically centered reflections in the range 11 < 2 θ < 23° and they appear in Table 1. Intensity data were recorded using a θ -2 θ scan. Three standard reflections monitored every 97 reflections showed less than 3% variation and no decay. Lorentz, polarization and psi-scan absorption corrections were applied using Crystal Logic software. The structure was solved by direct methods using SHELXS-97 [20] and refined by full-matrix least-squares techniques on *F*² with SHELXL-97 [21]. All hydrogen atoms were introduced at calculated positions as riding on bonded atoms. All non-hydrogen atoms were refined anisotropically.

2.3.2. Complex **2**

Slow crystallization from MeOH yielded yellow prismatic crystals. A crystal with approximate dimensions 0.05 × 0.05 × 0.50 mm was mounted in air and covered with epoxy glue. Diffraction measurements were made on a Crystal Logic Dual Goniometer diffractometer using graphite monochromated Mo radiation. Unit cell dimensions were determined and refined by using the angular settings of 25 automatically centered reflections in the range 11° < 2 θ < 23° and they appear in Table 1. Intensity data were recorded using a θ -2 θ scan. Three standard reflections monitored every 97 reflections showed less than 3% variation and no decay. Lorentz, polarization and psi-scan absorption corrections were applied using Crystal Logic software. The structure was solved by direct methods using SHELXS-97 [20] and refined by full-matrix least-squares techniques on *F*² with SHELXL-97 [21]. All hydrogen atoms were introduced at calculated positions as riding on bonded atoms. All non-hydrogen atoms were refined anisotropically.

3. Results and discussion

3.1. Brief synthetic comments

Reaction of one mol of HgCl₂ with one and two mol of bsd in MeOH results in yellow crystals of [HgCl₂(bsd)]_n (**2**) and colorless crystals of [HgCl₂(bsd)₂]_n (**1**), respectively and therefore, the identity of the products is ratio depended. Higher HgCl₂/bsd mole ratios than 1:2 (i.e. 1:3, 1:4) always result in the formation of **1**, while mole ratios of 1:1 or 2:1 result in **2**. The HgCl₂/bsd reaction system is not temperature depended since refluxing the reaction mixtures always resulted in the formation of **1** or **2** according to the HgCl₂/bsd molar ratio.

3.2. Description of structures

Selected bond distances and angles for compound **1** are listed in Table 2. The structure of **1** consists of 1D {Hg(μ -Cl)₂]_n linear chains running along the *c*-axis (Fig. 2), with intrachain Hg...Hg separations of 3.857(3) (*c*-axis). The shortest interchain Hg...Hg separation is 9.746(6) Å (*a*-axis). The Hg^{II} atom sits on an inversion

Table 2
Selected bond distances (Å) and angles (°) in **1**.

Hg–Cl	2.427(7)	Hg–N1	2.627(1)
Hg–Cl ^a	3.100(1)		
Cl–Hg–N1	91.6(3)	Cl ^a –Hg–N1	81.7(3)
Cl–Hg–Cl ^a	92.4(3)	Cl ^c –Hg–N1	98.3(3)
Cl–Hg–Cl ^b	180.00	Cl ^a –Hg–Cl ^c	180.00
Cl–Hg–Cl ^c	87.6(3)	N1–Hg–N1 ^b	180.00
Cl–Hg–N1 ^b	88.4(3)		

Symmetry codes: a: -*x*, -*y*, 1-*z*; b: -*x*, -*y*, -*z*; c: *x*, *y*, 1 + *z*.

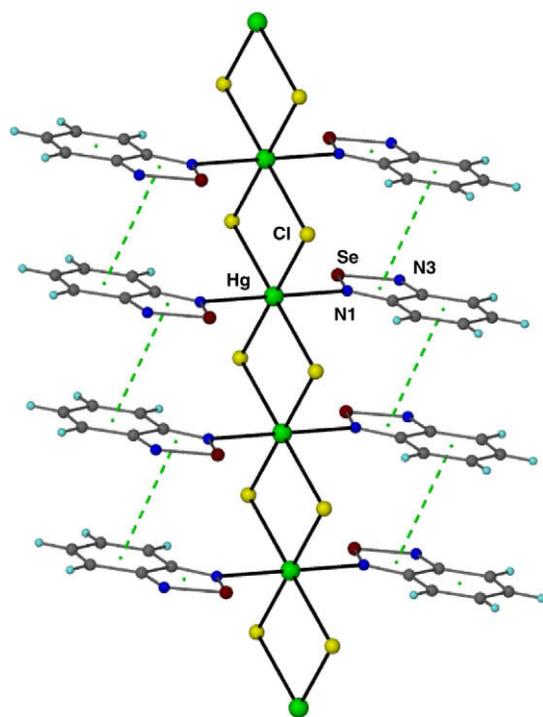


Fig. 2. Ball and stick representation of **1** showing a single chain and the $\pi\cdots\pi$ interactions (green dashed lines) between the bsd molecules. Color code: Hg green, Cl yellow, N blue, Se dark-red, C grey, H cyan, centroids small green spheres. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

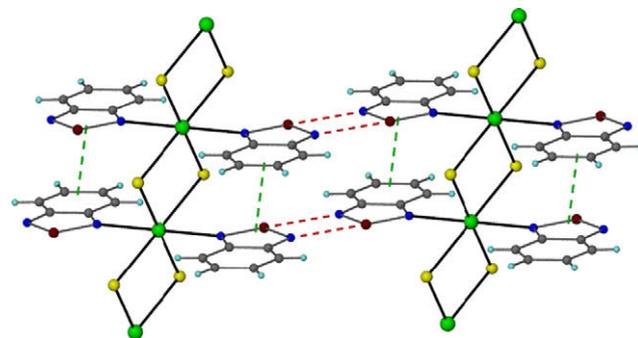


Fig. 3. Ball and stick representation of **1** showing two chains and the N...Se interactions (red dashed lines) between the bsd molecules. Color code: Hg green, Cl yellow, N blue, Se dark-red, C grey, H cyan. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 3

Selected bond distances (Å) and angles (°) in **2**.

Hg–Cl1	2.352(3)	Hg–Cl2 ^b	3.059(3)
Hg–Cl2	2.348(3)	Hg–N1	2.666(9)
Hg–Cl1 ^a	3.050(3)	Hg–N3 ^c	2.718(9)
Cl1–Hg–Cl2	179.11(10)	Cl2–Hg–N3 ^c	85.9(2)
Cl1–Hg–N1	82.8(2)	Cl1 ^a –Hg–N1	81.4(2)
Cl1–Hg–Cl1 ^a	92.24(9)	Cl2 ^b –Hg–N1	99.3(2)
Cl1–Hg–Cl2 ^b	87.70(9)	N1–Hg–N3 ^c	164.4(3)
Cl1–Hg–N3 ^c	93.3(2)	Cl1 ^a –Hg–Cl2 ^b	179.33(8)
Cl2–Hg–N1	98.1(2)	Cl1 ^a –Hg–N3 ^c	83.8(2)
Cl1 ^a –Hg–Cl2	87.99(9)	Cl2 ^b –Hg–N3 ^c	95.6(2)
Cl2–Hg–Cl2 ^b	92.07(10)		

Symmetry codes: a: $-1 + x, y, z$; b: $1 + x, y, z$; c: $-x, -1/2 + y, 3/2 - z$.

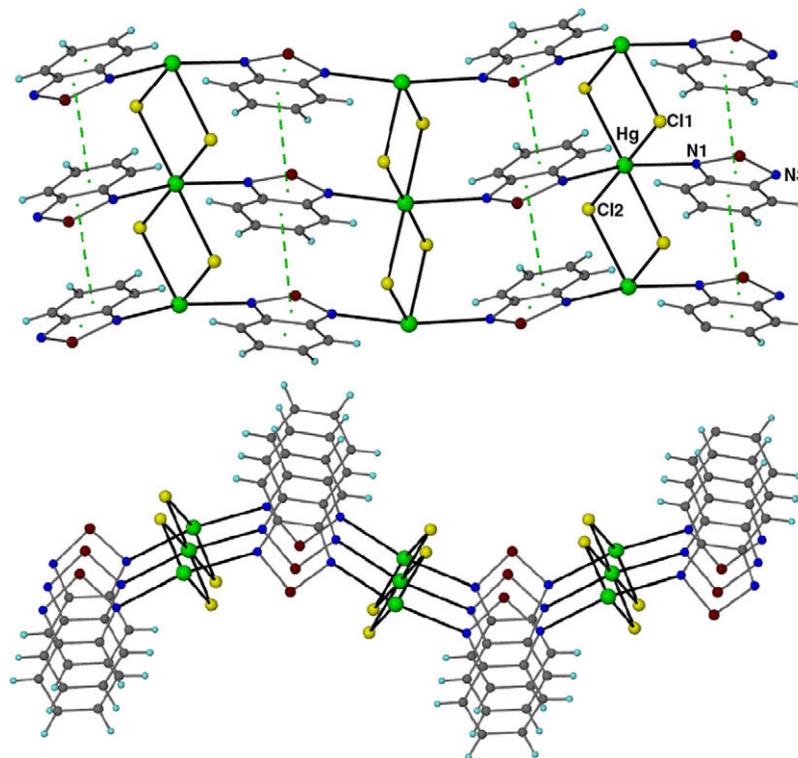


Fig. 4. Ball and stick representation of **2** showing the top and side view of the undulated layer and the $\pi\cdots\pi$ interactions (green dashed lines) between the bsd molecules. Color code: Hg green, Cl yellow, N blue, Se dark-red, C grey, H cyan, centroids small green spheres. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

center. Each Hg^{II} atom is octahedrally coordinated to four Cl⁻ ligands and two terminal bsd molecules. The Hg–Cl distances are 2.427(7) and 3.100(7) Å and the Hg–N bond length is 2.627(1) Å, in good agreement with those of other similar Hg(II) complexes [1].

A characteristic structural feature common to free bsd and **1** is the existence of strong face-to-face stacking interactions between the bsd ligands. The bsd molecules form columns within the crystal lattice, with the *interplanar* distances being 3.576 and 3.474 Å for free bsd [13] and **1**, respectively. In **1** the columns of the bsd molecules are orientated on alternating sides of each {Hg(μ-Cl)₂}_n chain. The bsd molecules within a column in **1** stack off set such that the five-membered ring (C₂N₂Se) of one molecule forms a π...π stacking interaction with the phenyl ring of a neighboring molecule [centroid...centroid 3.622 Å] (Fig. 2). The centroid...centroid distance between the five-membered ring of one molecule and the phenyl ring of a neighboring molecule in the structure of the free ligand is 3.621 Å. This structural feature has also been observed in the crystal structures of btd [22] and its complexes [10,11].

Neighboring layers of **1** are further bridged in the second dimension via N...Se interactions (Fig. 3). Each bsd molecule forms two complementary N...Se interactions [N...Se 2.876(1) Å] with a bsd molecule belonging to a neighboring chain giving rise to an undulated layer running parallel to the *bc* plane. Similar N...Se contacts are observed in the crystal structure of the free ligand with the N...Se distance being 3.155(6) Å [13].

Selected bond distances and angles for complex **2** are listed in Table 3. Complex **2** consists of 1D {Hg(μ-Cl)₂}_n linear chains running along the *a*-axis and linked via μ-bsd ligands along the *b*-axis to afford an extended undulated (4,4) 2D layered network (Fig. 4), with *intralayer* Hg...Hg separations of 3.923 Å (via chlorides) and 7.480 Å (via bsd). The shortest *interlayer* Hg...Hg separation is 7.773 Å. The Hg^{II} atom is octahedrally coordinated to four Cl⁻ ligands and two bsd molecules. There are two kinds of Hg–Cl bonds, short and long. The short Hg–Cl distances are 2.352(3) and 2.348(3) Å, while the long Hg–Cl distances are 3.050(3) and 3.059(3) Å. The Hg–N bond lengths are 2.666(9) and 2.718(9) Å. Complex **2** has a similar structure with [CuCl₂(btd)]_n [10], [CoCl₂(btd)]_n and [CoBr₂(btd)]_n [11].

Complex **2** is dominated by the existence of strong face-to-face *intralayer* stacking interactions between the bsd ligands along the *c*-axis (Fig. 4). Like in **1**, the bsd molecules in **2** form columns within the crystal lattice, with the *interplanar* distances being 3.516 Å. The columns of the bsd molecules in **2** are orientated on alternating sides of each sheet. The bsd molecules within each column in **2** stack off set such that the five-membered ring (C₂N₂Se) of one molecule forms a π...π stacking interaction with the phenyl ring of a neighboring molecule [centroid...centroid 3.624 Å] (Fig. 4).

3.3. Spectroscopic characterization

3.3.1. IR Spectroscopy

The IR spectra of both complexes are similar and exhibit the typical bands of the disubstituted benzene ring and bands assignable to vibrations of the selenadiazole ring. The bands in the 1600–1520 cm⁻¹ region are associated with the ν(C=N) and ν(C=C) of the phenyl ring while the bands at ca. 1480 and 470 cm⁻¹ are associated with the ν(CN) and ν(SeN) vibrational modes of the selen-

adiazole ring, respectively. Due to coordination these bands are shifted compared to those in free bsd.

4. Conclusions and perspectives

The employment of 2,1,3-benzoselenadiazole in the coordination chemistry of mercury(II) chloride afforded two coordination polymers. Both polymers feature 1D {Hg(μ-Cl)₂}_n linear chains, while bsd molecules act as terminal ligands in **1** and as bridging ligands in **2** to create a 2D layer in the latter case. The linear chains in **1** are further bridged via N...Se interactions to create a 2D layer. A structural feature observed in the crystal structures of the free ligand and of both complexes is the present of π...π stacking interactions between the bsd molecules. The same feature has been observed in the crystal structures of the similar ligand btd and its complexes [10,11] and seems to be persistent regardless of the different heteroatom in the five-membered ring. Efforts to employ other mercury salts and bsd are continuing.

Supplementary data

CCDC 723314 and 723315 contain the supplementary crystallographic data for **1** and **2**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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