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FULL PAPER

Synthesis, structure, luminescence, and electrochemical properties of polynuclear mercury(II) chalcogenolate complexes

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A series of novel polynuclear mercury(II) diimine complexes with bridging chalcogenolate ligands have been synthesized and characterized and their luminescence and electrochemical properties studied. The crystal structures of $[Hg(\mu\text{-}SC_6H_4OCH_3\text{-}p)(bpy)]_n[PF_6]_n$ and $[Hg(\mu\text{-}SeC_6H_5)(bpy)]_n[PF_6]_n$ have also been determined (bpy = 2,2′-bipyridine).

Introduction

The synthesis, structure and luminescence properties of transition metal complexes of chalcogenolate ligands have attracted growing attention in the past two decades. Chalcogenolate ligands such as thiolates are well known as a basic type of ligands and a huge number of transition metal chalcogenolates have been obtained up to now.[1–10] Owing to the highly flexible bonding modes of the ligands, the transition metal–chalcogenolate complexes represent an important aspect in structural chemistry, adopting various nuclearities and great structural complexities.

Mercury organometallics have long been used in organic synthesis,[11] but studies on the species themselves are relatively few.[12] Although there have been many reports on mercury(II) thiolate systems,[10] they are limited to those of their structures, with only few studies on luminescence behaviour.[13] The closed-shell d^{10} zinc(II) and cadmium(II) systems[14,15] with mixed diimine chalcogenolate ligands have been reported to exhibit ligand-to-ligand charge transfer (LLCT) transition in the visible region without the involvement of the metal centre. In an attempt to elucidate further the nature of the electronic excited states of these interesting molecules, the investigations have been extended to mercury(II) chalcogenolate complexes. Herein is reported the synthesis of a series of mercury(II) diimine complexes with bridging chalcogenolate ligands. The tunabilities of the luminescence and electrochemical properties of these complexes through variation of the chalcogenolate and diimine ligands have been examined. The crystal structures of two examples have also been determined.

Experimental

Materials and reagents

Benzenethiol and sodium tetrahydroborate were obtained from Aldrich Chemical Co., mercury acetate, *p*-toluenethiol, 4-methoxybenzenethiol, 4-chlorobenzenethiol, 2,2′-bipyridine and 1,10-phenanthroline from Lancaster Synthesis Ltd and diphenyl diselenide and ammonium hexafluorophosphate (99.5%) from Strem Chemicals Inc. 4,4′-Di-*tert*-butyl-2,2′-bipyridine (^{t}Bu$_2$bpy) was prepared by the modification of a literature procedure.[16] 4′-Sulfanylmonobenzo-15-crown-5 (CrSH) was synthesized according to a published procedure.[17] Tetrabutylammonium hexafluorophosphate (^{n}Bu$_4$NPF$_6$) (Aldrich, 98%) was purified by recrystallization with ethanol three times before use. Acetonitrile was distilled over calcium hydride before use. All other reagents were of analytical grade and used as received.

Preparations

$[Hg(\mu\text{-}SC_6H_5)(bpy)]_n[PF_6]_n$ 1. 2,2′-Bipyridine (50 mg, 0.32 mmol) in methanol (20 mL) was added to a solution of $Hg(OAc)_2$ (100 mg, 0.31 mmol) in methanol (20 mL) and the resultant mixture stirred at room temperature for 30 minutes under a nitrogen atmosphere. Benzenethiol (35 mg, 0.32 mmol) was dissolved in a large amount of methanol (60 mL) so as to make a very dilute solution and then added to the reaction mixture very slowly with rigorous stirring during which the solution changed from colourless to pale yellow. After the mixture was stirred for an hour, some white precipitates came out which could not be dissolved in any common organic solvents. They were filtered off and ammonium hexafluorophosphate was added to the filtrate to isolate the PF_6^- salts as white solids, which were then filtered off, washed with methanol and dried. Recrystallization by slow vapour diffusion of diethyl ether into an acetonitrile solution of the complex gave **1** as white crystals. Yield: 88 mg (46%). ^{1}H NMR (300 MHz, CD_3CN, 298 K, relative to Me_4Si): δ 7.25 (m, 3H, aryl H *ortho* and *para* to S), 7.60 (m, 2H, aryl H *meta* to S), 7.85 (t, 2H, bpy H), 8.30 (t, 2H, bpy H), 8.44 (d, 2H, bpy H) and 8.56 (d, 2H, bpy H). Positive FAB-MS (*m*/*z*): 467 {M}$^+$. Calc. for $C_{16}H_{13}F_6HgN_2PS$: C, 31.46; H, 2.14; N, 4.59. Found: C, 31.45; H, 2.01; N, 4.54%.

$[Hg(\mu\text{-}SC_6H_4CH_3\text{-}p)(bpy)]_n[PF_6]_n$ 2. The procedure was similar to that described for the preparation of complex **1**, except *p*-toluenethiol (40 mg, 0.32 mmol) was used to give white crystals of **2**. Yield: 75 mg (38%). ^{1}H NMR (300 MHz, CD_3CN, 298 K, relative to Me_4Si): δ 2.30 (s, 3H, CH_3), 7.15 (d, 2H, aryl H *ortho* to S), 7.45 (d, 2H, aryl H *meta* to S), 7.78 (t, 2H, bpy H), 8.25 (t, 2H, bpy H), 8.36 (d, 2H, bpy H) and 8.50 (d, 2H, bpy H). Positive FAB-MS (*m*/*z*): 481 {M}$^+$. Calc. for $C_{17}H_{15}F_6HgN_2PS$: C, 32.67; H, 2.42; N, 4.48. Found: C, 32.62; H, 2.27; N, 4.36%.

$[Hg(\mu\text{-}SC_6H_4OCH_3\text{-}p)(bpy)]_n[PF_6]_n$ 3. The procedure was similar to that described for the preparation of complex **1**, except 4-methoxybenzenethiol (45 mg, 0.32 mmol) was used to give opaque white crystals of **3**. Yield: 90 mg (45%). ^{1}H NMR (300 MHz, CD_3CN, 298 K, relative to Me_4Si): δ 3.80 (s, 3H, OCH_3), 6.88 (d, 2H, aryl H *ortho* to S), 7.55 (d, 2H, aryl H *meta* to S), 7.83 (t, 2H, bpy H), 8.30 (t, 2H, bpy H), 8.40 (d, 2H,

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bpy H) and 8.55 (d, 2H, bpy H). Positive FAB-MS (*m*/*z*): 497 {M}$^+$. Calc. for $C_{17}H_{15}F_6HgN_2OPS$: C, 31.86; H, 2.36; N, 4.37. Found: C, 31.89; H, 2.22; N, 4.24%.

$[Hg(\mu\text{-}SC_6H_4Cl\text{-}p)(bpy)]_n[PF_6]_n$ 4. The procedure was similar to that described for the preparation of complex **1**, except 4-chlorobenzenethiol (48 mg, 0.33 mmol) was used to give white crystals of **4**. Yield: 82 mg (41%). ^{1}H NMR (300 MHz, CD_3CN, 298 K, relative to Me_4Si): δ 7.30 (d, 2H, aryl H *ortho* to S), 7.60 (d, 2H, aryl H *meta* to S), 7.87 (t, 2H, bpy H), 8.33 (t, 2H, bpy H), 8.40 (d, 2H, bpy H) and 8.52 (d, 2H, bpy H). Positive FAB-MS (*m*/*z*): 501 {M}$^+$. Calc. for $C_{16}H_{12}ClF_6HgN_2PS$: C, 29.78; H, 1.87; N, 4.34. Found: C, 29.79; H, 1.75; N, 4.56%.

$[Hg(\mu\text{-}SeC_6H_5)(bpy)]_n[PF_6]_n$ 5. The procedure was similar to that described for the preparation of complex **1**, except NaSePh (57 mg, 0.32 mmol), prepared from PhSeSePh (50 mg, 0.16 mmol) and an excess of $NaBH_4$ (24 mg, 0.64 mmol), was used to give yellow crystals of **5**. Yield: 80 mg (39%). ^{1}H NMR (300 MHz, CD_3CN, 298 K, relative to Me_4Si): δ 7.28 (m, 3H, aryl H *ortho* and *para* to Se), 7.73 (m, 2H, aryl H *meta* to Se), 7.82 (t, 2H, bpy H), 8.30 (t, 2H, bpy H), 8.40 (d, 2H, bpy H) and 8.55 (d, 2H, bpy H). Positive FAB-MS (*m*/*z*): 513 {M}$^+$. Calc. for $C_{16}H_{13}F_6HgN_2PSe$: C, 29.22; H, 1.99; N, 4.26. Found: C, 28.99; H, 1.80; N, 4.21%.

$[Hg(\mu\text{-}SCr)(bpy)]_n[PF_6]_n$ 6. The procedure was similar to that described for the preparation of complex **1**, except 4′-sulfanylmonobenzo-15-crown-5[17] (100 mg, 0.33 mmol) was used to give yellow crystals of **6**. Yield: 75 mg (30%). ^{1}H NMR (300 MHz, CD_3CN, 298 K, relative to Me_4Si): δ 3.60 (m, 8H, CH_2OCH_2), 3.75 (m, 4H, CH_2OCH_2), 3.98 (m, 2H, $C_6H_3OCH_2$), 4.05 (m, 2H, $C_6H_3OCH_2$), 6.83 (d, 1H, aryl H), 7.16 (m, 2H, aryl H), 7.82 (t, 2H, bpy H), 8.30 (t, 2H, bpy H), 8.40 (d, 2H, bpy H) and 8.55 (d, 2H, bpy H). Positive ESI-MS (*m*/*z*): 657 {M}$^+$. Calc. for $C_{24}H_{27}F_6HgN_2O_5PS$: C, 35.98; H, 3.40; N, 3.50. Found: C, 35.89; H, 3.19; N, 3.26%.

$[Hg(\mu\text{-}SC_6H_4CH_3\text{-}p)(^tBu_2bpy)]_n[PF_6]_n$ 7. The procedure was similar to that described for the preparation of complex **2**, except 4,4′-di-*tert*-butyl-2,2′-bipyridine[16] (86 mg, 0.32 mmol) was used to give white crystals of **7**. Yield: 80 mg (35%). ^{1}H NMR (300 MHz, CD_3CN, 298 K, relative to Me_4Si): δ 1.45 (s, 18H, ^{t}Bu), 2.32 (s, 3H, CH_3), 7.10 (d, 2H, aryl H *ortho* to S), 7.50 (d, 2H, aryl H *meta* to S), 7.82 (d, 2H, bpy H), 8.28 (d, 2H, bpy H) and 8.50 (d, 2H, bpy H). Positive FAB-MS (*m*/*z*): 593. Calc. for $C_{25}H_{31}F_6HgN_2PS$: C, 40.73; H, 4.23; N, 3.80. Found: C, 40.46; H, 4.25; N, 3.84%.

$[Hg(\mu\text{-}SC_6H_4CH_3\text{-}p)(phen)]_n[PF_6]_n$ 8. The procedure was similar to that described for the preparation of complex **2**, except 1,10-phenanthroline (58 mg, 0.32 mmol) was used to give yellow crystals of **8**. Yield: 86 mg (42%). ^{1}H NMR (300 MHz, CD_3CN, 298 K, relative to Me_4Si): δ 2.34 (s, 3H, CH_3), 7.12 (d, 2H, aryl H *ortho* to S), 7.52 (d, 2H, aryl H *meta* to S), 8.12 (q, 2H, bpy H), 8.23 (s, 2H, bpy H), 8.78 (dd, 2H, bpy H) and 8.85 (dd, 4H, bpy H). Positive FAB-MS (*m*/*z*): 505 {M}$^+$. Calc. for $C_{19}H_{15}F_6HgN_2PS$: C, 35.17; H, 2.33; N, 4.32. Found: C, 35.21; H, 2.27; N, 4.30%.

Physical measurements and instrumentation

UV/vis spectra were obtained on a Hewlett-Packard 8452A diode array spectrophotometer, and steady-state excitation and emission spectra on a Spex Fluorolog 111 spectrofluorimeter. ^{1}H NMR spectra were recorded on a Bruker DPX-300 FT-NMR spectrometer in CD_3CN at 298 K and chemical shifts are reported relative to Me_4Si. Positive ion FAB mass spectra were recorded on a Finnigan MAT95 mass spectrometer. Elemental analyses of the new complexes were performed on a Carlo Erba 1106 elemental analyzer at the Institute of Chemistry, Chinese Academy of Sciences. Cyclic voltammetric measurements were made by using a CH Instruments, Inc. CHI 620 electrochemical analyzer interfaced to an IBM-compatible PC. The electrolytic cell used was a conventional two-compartment cell. The salt bridge of the reference electrode was separated from the working electrode compartment by a Vycor glass bridge. A Ag–$AgNO_3$ (0.1 mol dm^{-3} in CH_3CN) reference electrode was used. The ferrocenium–ferrocene couple ($FeCp_2^{+/0}$) was used as the internal reference in the electrochemical measurements in acetonitrile (0.1 mol dm^{-3} $^nBu_4NPF_6$).[18a] The working electrode was a glassy carbon (Atomergic Chemetals V25) electrode with a platinum foil acting as the counter electrode. Treatment of the electrode surfaces was as reported previously.[18b]

Crystal structure determination

Crystal data for complex 3. $[(C_{17}H_{15}HgN_2OS)^+PF_6^-]$, $M_r = 640.93$, monoclinic, space group $C2/c$ (no. 15), $a = 28.454(2)$, $b = 6.991(2)$, $c = 20.473(2)$ Å, $\beta = 106.756(6)°$, $V = 3899.9(9)$ Å^3, $Z = 8$, $D_c = 2.183$ g cm^{-3}, μ(Mo-Kα) = 81.70 cm^{-1}, $T = 301$ K. Unit-cell dimensions were determined based on the setting angles of 25 reflections in the 2θ range of 23.3 to 29.1°. 3841 Reflections were measured, of which 3755 were unique and $R_{int} = 0.023$. 2168 Reflections with $I > 3\sigma(I)$ were considered observed and used in the structural analysis. The space group was determined based on a statistical analysis of intensity distribution and the successful refinement of the structure solved by Patterson methods and expanded by Fourier methods (PATTY[19a]) and refined by full-matrix least-squares using the software package TEXSAN[19b] on a Silicon Graphics Indy computer. One crystallographic asymmetric unit consists of one formula unit. The structure is polymeric with Hg(1) bonded to S(1*) of the starred monomeric cation ($C_{17}H_{15}HgN_2OS$) at $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$ and S(1) bonded to the doubly starred monomeric cation ($C_{17}H_{15}HgN_2OS$) at $\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$. In the least-squares refinement, all 29 non-H atoms were refined anisotropically and 15 H atoms at calculated positions with thermal parameters equal to 1.3 times that of the attached C atoms were not refined. Convergence for 262 variable parameters by least-squares refinement on F was reached at $R = 0.028$ and $wR = 0.035$. The final difference Fourier map was featureless, with maximum positive and negative peaks of 0.73 and 0.50 e Å^{-3} respectively.

Crystal data for complex 5. $[(C_{16}H_{13}HgN_2Se)^+PF_6^-]$, $M_r = 657.81$, monoclinic, space group $P2_1/c$ (no. 14), $a = 12.786(1)$, $b = 7.134(4)$, $c = 20.342(2)$ Å, $\beta = 95.977(8)°$, $V = 1845(1)$ Å^3, $Z = 4$, $D_c = 2.368$ g cm^{-3}, μ(Mo-Kα) = 104.83 cm^{-1}, $T = 301$ K. Unit-cell dimensions were determined based on the setting angles of 25 reflections in the 2θ range of 36.9 to 42.6°. 3651 Reflections were measured, of which 3495 were unique and $R_{int} = 0.024$. 2187 Reflections with $I > 3\sigma(I)$ were considered observed and used in the structural analysis. The space group was determined as for **3**. One crystallographic asymmetric unit consists of one formula unit. The structure is polymeric with Hg(1) bonded to Se(1*) of the starred monomeric cation ($C_{16}H_{13}HgN_2Se$) at $-x, \frac{1}{2} + y, \frac{1}{2} - z$ and Se(1) bonded to the doubly starred monomeric cation ($C_{16}H_{13}HgN_2Se$) at $-x, -\frac{1}{2} + y, \frac{1}{2} - z$. In the least-squares refinement, all 27 non-H atoms were refined anisotropically and 13 H atoms at calculated positions with thermal parameters equal to 1.3 times that of the attached C atoms were not refined. Convergence for 146 variable parameters by least-squares refinement on F was reached at $R = 0.029$ and $wR = 0.036$. The final difference Fourier map was featureless, with maximum positive and negative peaks of 1.09 and 1.09 e Å^{-3} respectively.

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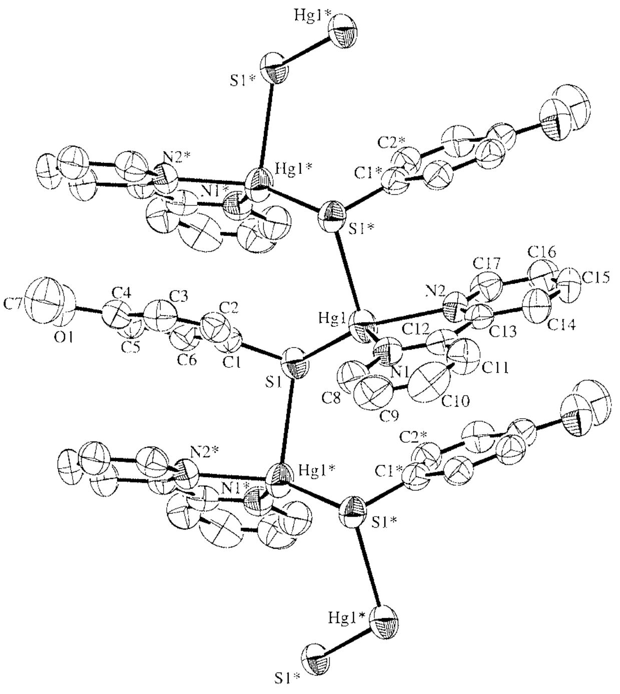

Fig. 1 Perspective drawing of three units of the complex cation of $[Hg(\mu\text{-}SC_6H_4OCH_3\text{-}p)(bpy)]_n[PF_6]_n$ **3** with the atomic numbering scheme. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are shown at the 40% probability level. The coordinates of the S atom at the top are x, $1 + y$, z and of the Hg(1) atom at the bottom are x, $-1 + y$, z.

See http://www.rsc.org/suppdata/dt/b0/b005085g/ for crystallographic files in .cif format.

Results and discussion

Polynuclear mercury(II) chalcogenolate complexes were synthesized by treating a methanolic solution of the diimine ligand with a mixture of $Hg(OAc)_2$ and chalcogenol in methanol, followed by metathesis with ammonium hexafluorophosphate, to give the complexes as the hexafluorophosphate salts. All the newly synthesized complexes have been characterized by positive ion FAB-mass spectrometry and ^1H NMR spectroscopy, and gave satisfactory elemental analyses.

Crystal structure

Single crystals of complexes **3** and **5** were obtained by vapour diffusion of diethyl ether into concentrated acetonitrile solutions of the respective complexes. The perspective drawings of the complex cations of **3** and **5** with atomic numbering are depicted in Figs. 1 and 2, respectively. Selected bond distances and angles are summarized in Tables 1 and 2, respectively. The Hg adopts a distorted tetrahedral geometry with S(1)–Hg–S(1*) angles of 110.80(5)° and N(1)–Hg(1)–N(2) angles of 73.2(2)° for **3** and Se(1)–Hg–Se(1*) angles of 112.45(2)° and N(1)–Hg(1)–N(2) angles of 73.0(2)° for **5**. The average bond distances of Hg–S and Hg–Se are 2.348(2) Å for **3** and 2.4571(8) Å for **5**, respectively, which are comparable to those of other related systems.[20]

Electronic absorption and emission properties

The electronic absorption spectra of complexes **1**–**8** show low energy absorption shoulders at *ca.* 340–380 nm and higher energy absorptions at *ca.* 240–320 nm. The electronic absorption spectral data are summarized in Table 3. The appearance of the low energy absorptions as broad absorption shoulders makes it difficult for one to determine the exact absorption maxima for the complexes for comparative studies. However, in general, the absorption energies follow the orders **4** > **1** > **2** > **3** > **6**; **1** > **5**; and **7** > **2** > **8**, which are in line with the electron-donating ability of the chalcogenolates as well as the π-accepting ability of the diimine ligands. Thus the low energy absorptions are tentatively ascribed to ligand-to-ligand charge transfer LLCT $[p_\pi(ER^-)\rightarrow\pi^*(N\text{–}N)]$ transitions. The high

Table 1 Selected geometric data (bond lengths in Å, angles in °) for complex **3**

Hg(1)–S(1)	2.348(2)	Hg(1)–S(1*)	2.839(2)
Hg(1)–N(1)	2.325(6)	Hg(1)–N(2)	2.223(6)
S(1)–C(11)	1.782(7)	N(1)–C(8)	1.349(9)
N(1)–C(12)	1.336(9)	N(2)–C(13)	1.342(9)
N(2)–C(17)	1.338(9)		
S(1)–Hg(1)–S(1*)	110.80(5)	S(1)–Hg(1)–N(1)	131.6(2)
S(1)–Hg(1)–N(2)	143.5(1)	S(1*)–Hg(1)–N(1)	91.0(2)
S(1*)–Hg(1)–N(2)	92.0(2)	N(1)–Hg(1)–N(2)	73.2(2)
Hg(1)–S(1)–Hg(1*)	107.47(7)	Hg(1)–S(1)–C(1)	106.7(2)
Hg(1*)–N(1)–C(1)	97.1(2)	Hg(1)–N(1)–C(8)	126.1(5)
Hg(1)–N(1)–C(12)	115.1(5)	Hg(1)–N(2)–C(13)	118.1(4)
Hg(1)–N(2)–C(17)	121.8(5)	S(1)–C(1)–C(6)	116.6(6)
S(1)–C(1)–C(2)	124.3(6)		

Table 2 Selected geometric data (bond lengths in Å, angles in °) for complex **5**

Hg(1)–Se(1)	2.4571(8)	Hg(1)–Se(1*)	2.8695(8)
Hg(1)–N(1)	2.360(6)	Hg(1)–N(2)	2.223(5)
Se(1)–C(11)	1.938(7)	N(1)–C(1)	1.323(9)
N(1)–C(5)	1.343(9)	N(2)–C(6)	1.368(9)
N(2)–C(10)	1.337(9)		
Se(1)–Hg(1)–Se(1*)	112.45(2)	Se(1)–Hg(1)–N(1)	126.7(1)
Se(1)–Hg(1)–N(2)	147.2(1)	Se(1*)–Hg(1)–N(1)	91.7(1)
Se(1*)–Hg(1)–N(2)	90.3(1)	N(1)–Hg(1)–N(2)	73.0(2)
Hg(1)–Se(1)–Hg(1*)	106.94(3)	Hg(1)–Se(1)–C(11)	102.1(2)
Hg(1*)–Se(1)–C(11)	97.1(2)	Hg(1)–N(1)–C(1)	126.5(5)
Hg(1)–N(1)–C(5)	114.2(4)	Hg(1)–N(2)–C(6)	117.5(5)
Hg(1)–N(2)–C(10)	121.3(5)	Se(1)–C(11)–C(12)	115.3(6)
Se(1)–C(11)–C(16)	122.5(6)		

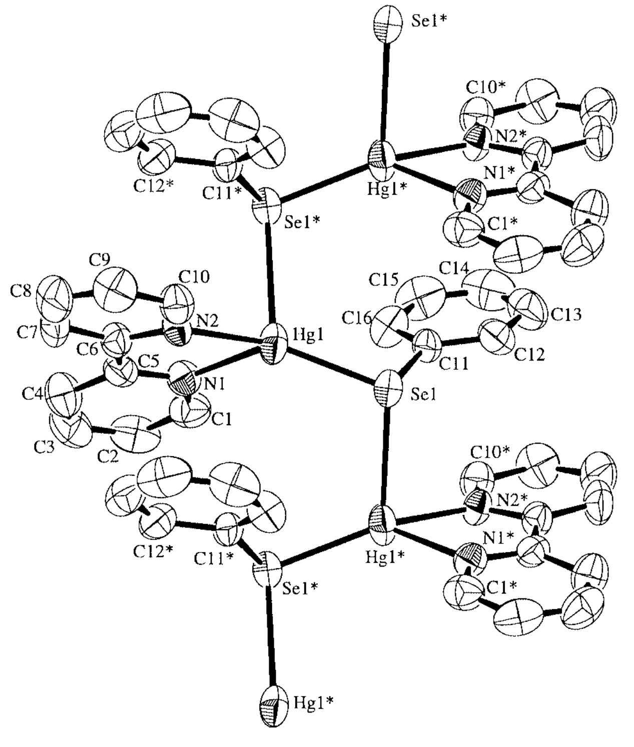

Fig. 2 Perspective drawing of three units of the complex cation of $[Hg(\mu\text{-}SeC_6H_5)(bpy)]_n[PF_6]_n$ **5**. The coordinates of the Se atom at the top are x, $1 + y$, z and of the Hg(1) atom at the bottom are x, $-1 + y$, z. Other details as in Fig. 1.

Table 3 Photophysical data for complexes **1**–**8**[a]

Complex	Medium (T/K)	λ_{abs}/nm (ε/dm^3 mol^{-1} cm^{-1})	Emission (λ_{em}/nm)[b]
1	MeCN (298)	246 (23 260), 300 (14 390), 312 (12 130), 348sh (460)	530sh
	Solid (77)		462, 488, 522[d]
	Glass (77)[c]		461, 490, 525[d]
2	MeCN (298)	247 (22 070), 302 (15 530), 312 (13 100), 352sh (640)	560sh
	Solid (77)		463, 494, 530[d]
	Glass (77)[c]		515
3	MeCN (298)	246 (20 650), 302 (18 310), 312 (14 910), 365sh (510)	570sh
	Solid (77)		536
	Glass (77)[c]		535
4	MeCN (298)	246 (23 620), 302 (14 480), 313 (18 510), 325sh (630)	—
	Solid (77)		457, 492, 527[d]
	Glass (77)[c]		463, 489, 524[d]
5	MeCN (298)	246 (23 730), 302 (14 840), 313 (12 300), 356sh (630)	552sh
	Solid (77)		455, 490, 527, 570,[d] 590sh[e]
	Glass (77)[c]		576sh
6	MeCN (298)	246 (22 850), 302 (19 070), 313 (14 750), 370sh (890)	570sh
	Solid (77)		552
	Glass (77)[c]		536
7	MeCN (298)	248 (24 950), 295 (22 380), 305 (16 050), 346sh (580)	—
	Solid (77)		441, 469, 502[d]
	Glass (77)[c]		453, 484, 512[d]
8	MeCN (298)	233 (35 660), 274 (34 560), 298 (10 290), 372sh (240)	—
	Solid (77)		558
	Glass (77)[c]		550

[a] Absorption and emission wavelengths are reported to ±2 nm. [b] Excitation wavelength 350 nm. [c] EtOH : MeOH : MeCN = 4 : 1 : 1 v/v. [d] Vibronic structures of diimine ligands. [e] Excitation wavelength 450 nm.

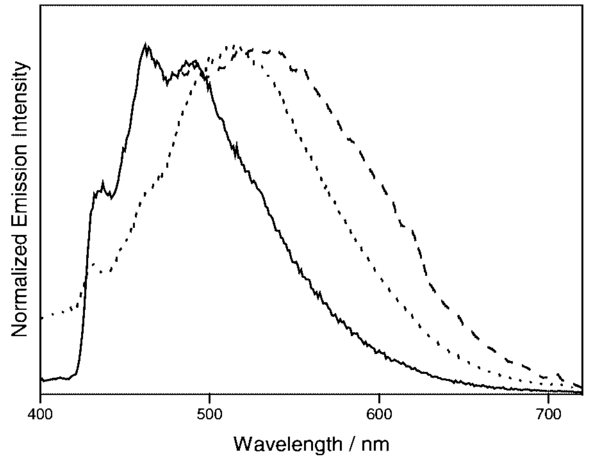

Fig. 3 Normalized emission spectra of mercury(II) complexes in glass state at 77 K: [Hg(μ-$SC_6H_4CH_3$-*p*)(bpy)]$_n$[PF_6]$_n$ (**2**) (- - -), [Hg(μ-$SC_6H_4OCH_3$-*p*)(bpy)]$_n$[PF_6]$_n$ **3** (– – –), and [Hg(μ-SC_6H_4Cl-*p*)(bpy)]$_n$[PF_6]$_n$ **4** (——).

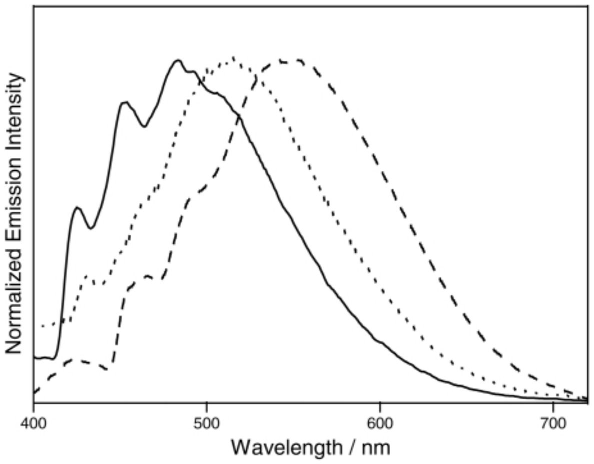

Fig. 4 Normalized emission spectra of mercury(II) complexes in glass state at 77 K: [Hg(μ-$SC_6H_4CH_3$-*p*)(bpy)]$_n$[PF_6]$_n$ **2** (- - -), [Hg(μ-$SC_6H_4CH_3$-*p*)(^{t}Bu$_2$bpy)]$_n$[PF_6]$_n$ **7** (——), and [Hg(μ-$SC_6H_4CH_3$-*p*)(phen)]$_n$[PF_6]$_n$ **8** (– – –).

energy absorptions are ascribed to intraligand IL transitions since similar bands occur for the corresponding "free" ligands.

Complexes **1**–**8** were found to exhibit luminescence properties with emission maxima at *ca.* 500–580 nm both in the solid state at 77 K and in 77 K glasses upon excitation at $\lambda > 350$ nm. However, all the complexes are not emissive in the solid state at 298 K and only weakly emissive in degassed acetonitrile solutions. The photophysical data are in Table 3. The emission energy was found to change upon variation of both the chalcogenolates and the diimine ligands. The emission energy of the complexes in 77 K glass follows the order **5** < **6** ≈ **3** ≤ **2** < **1** ≤ **4**, which is in accord with the electron richness of the chalcogenolate ligands in which the electron-donating ability of ER$^-$ is: SeC_6H_5 > SCr > $SC_6H_4OCH_3$-*p* ≈ $SC_6H_4CH_3$-*p* > SC_6H_5 > SC_6H_4Cl-*p*. For complexes with the same chalcogenolate ligands the emission energies change with the nature of the diimine ligands. For example, the emission energy in 77 K glass follows the order **7** > **2** > **8**, in line with the π-accepting ability of ^{t}Bu$_2$bpy < bpy < phen. It is likely that the origin of the emission is derived from triplet states of a LLCT origin, probably mixed with some IL character as reflected by the observation of vibronic structured diimine emissions in some cases. The normalized emission spectra for **2**, **3** and **4**, and those of **2**, **7** and **8** in 77 K glass, are displayed in Figs. 3 and 4, respectively.

Electrochemistry

The electrochemical data for complexes **1**–**8** in acetonitrile (0.1 mol dm^{-3} ^{n}Bu$_4$NPF$_6$) are summarized in Table 4. The cyclic voltammograms of these polynuclear mercury(II) complexes showed one irreversible oxidation wave (+1.29 to +1.67 V *vs.* SCE) and two quasi-reversible reduction couples (−0.24 to −1.00 V *vs.* SCE). The oxidation wave is suggested to arise from chalcogenolate ligand-centred oxidation since the potentials of **2**, **7** and **8** with the same benzenethiolate ligand are found to have similar values. The oxidation potential is most anodic for complex **4** with the least electron rich SC_6H_4Cl-*p* ligand and less positive for the more electron rich 4-methoxybenzenethiolate, phenylselenolate and 4′-sulfanylmonobenzo-15-crown-5 complexes, indicating the greater ease of oxidation of the electron

Table 4 Electrochemical data for complexes **1**–**8** in acetonitrile (0.1 mol dm^{-3} ^{n}Bu$_4$NPF$_6$)

Complex	Oxidation ^{a} E_{pa}/V *vs.* SCE	Reduction ^{b} $E_{1/2}$ (E_{pc})^c/V *vs.* SCE
1	+1.58	−0.88, −0.38 (−0.26)
2	+1.54	−0.90, −0.40 (−0.26)
3	+1.39	−0.86, −0.46 (−0.28)
4	+1.67	−0.80, −0.38 (−0.25)
5	+1.37	−0.93, −0.34 (−0.24)
6	+1.29	−0.87, −0.55 (−0.33)
7	+1.52	−1.00, −0.49 (−0.44)
8	+1.53	−0.65, −0.35 (−0.25)

[a] E_{pa} refers to the anodic peak potential of the irreversible oxidation wave. [b] $E_{1/2} = (E_{pa} + E_{pc})/2$ where E_{pa} and E_{pc} are the anodic and cathodic peak potentials of the quasi-reversible reduction couple, respectively. [c] E_{pc} refers to the cathodic peak potential of the irreversible reduction wave.

rich chalcogenolate ligands. For example, the occurrence of the oxidation wave at less positive potential for **3** (+1.39), **5** (+1.37) and **6** (+1.29 V), relative to that of **4** (+1.67 V), is observed. On the other hand, the quasi-reversible reduction couples are tentatively assigned as the successive reduction of the α,α′-diimine ligand in the polymeric mercury(II) complexes. The reduced ease of reduction for **7** (−1.00 V) than **2** (−0.90 V) and **8** (−0.65 V) is in line with the π-accepting ability of the diimine ligands which follows the order: ^{t}Bu$_2$bpy < bpy < phen. Thus the electrochemical behaviour of these polynuclear mercury(II) chalcogenolate complexes further supports the spectral assignment of the lowest energy transition as a $p_\pi(\text{ER}^-)\rightarrow\pi^*(\text{N–N})$ LLCT transition, in which the HOMO has substantial chalcogenolate character while the LUMO is mainly that of diimine π* character.

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