Synthesis, photophysics, and electrochemistry of dinuclear cadmium(II) diimine complexes with bridging chalcogenolate ligands. X-Ray crystal structures of $[(phen)_2Cd(\mu\text{-}SC_6H_4CH_3\text{-}p)]_2(PF_6)_2$ and $[(phen)_2Cd(\mu\text{-}SeC_6H_5)]_2(PF_6)_2$

Vivian Wing-Wah Yam,* Yung-Lin Pui and Kung-Kai Cheung

Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong, P. R. China. E-mail: wwyam@hku.hk

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A new series of luminescent dinuclear six-coordinate cadmium(II) diimine complexes with bridging chalcogenolate ligands has been synthesized and characterized, and shown to exhibit interesting photophysical and electrochemical properties. The X-ray crystal structures of $[(phen)_2Cd(\mu\text{-}SC_6H_4CH_3\text{-}p)]_2(PF_6)_2$ (**11**) and $[(phen)_2Cd(\mu\text{-}SeC_6H_5)]_2(PF_6)_2$ (**12**) have been determined.

Thiolate ligands are extensively employed in transition metal chemistry and the versatility of sulfur as a ligand in organotransition metal chemistry has been widely established. Recent works by us and others have shown that chalcogenolate complexes of a number of metal centres such as copper(I),[1] silver(I),[1b,h–j,2] gold(I),[3] platinum(II),[4] zinc(II),[5] cadmium(II),[5,6] rhenium(I),[7] zirconium(IV),[8] and hafnium(IV)[9] are capable of displaying luminescence behaviour. As part of our efforts to explore new luminescent d^{10} metal complex systems, a series of novel dinuclear six-coordinate cadmium(II) complexes with bridging chalcogenolate ligands have been synthesized and shown to exhibit interesting photophysical and electrochemical properties. Numerous thiolate[5a–d,6a–e] and selenolate[5a,d,e,6b,c,f] complexes of Cd(II) are known and, most of them possess a tetrahedral coordination geometry; the corresponding six-coordinate cadmium(II) complexes are relatively less explored.[10] In this report, the X-ray crystal structures of two such complexes, $[(phen)_2Cd(\mu\text{-}SC_6H_4CH_3\text{-}p)]_2(PF_6)_2$ (**11**) and $[(phen)_2Cd(\mu\text{-}SeC_6H_5)]_2(PF_6)_2$ (**12**), have been determined.

Experimental

Reagents and materials

Thiophenol was obtained from Aldrich Chemical Co. Cadmium acetate, *p*-thiocresol, 4-methoxythiophenol, 4-chlorothiophenol, bis(4-chlorophenylselenide), 2,2′-bipyridine and 1,10-phenanthroline were obtained from Lancaster Synthesis Ltd. Diphenyldiselenide and ammonium hexafluorophosphate were obtained from Strem Chemicals Inc. 4,4′-Di-*tert*-butyl-2,2′-bipyridine (Bu^t_2bpy) was prepared by a modification of the literature procedure.[11a,b] 4′-Mercaptomonobenzo-15-crown-5 (HL) was synthesized according to a published literature procedure.[11c] All other reagents were of analytical grade and were used as received.

Synthesis

$[(bpy)_2Cd(\mu\text{-}SC_6H_5)]_2(PF_6)_2$ (1). To a stirred solution of cadmium acetate dihydrate (40 mg, 0.15 mmol) in methanol (5 mL) was added a solution of 2,2′-bipyridine (47 mg, 0.30 mmol) in methanol (5 mL). The resultant solution was stirred for 10 min. Thiophenol (17 mg, 0.15 mmol), dissolved in methanol (5 mL), was then added to the reaction mixture dropwise with stirring to produce a yellow solution. After the mixture was stirred for 4 h, ammonium hexafluorophosphate was added to isolate the PF_6^- salts as yellow solids, which were then filtered off and washed with methanol and dried. The solid was dissolved in acetonitrile and recrystallized by diffusion of diethyl ether vapour into its concentrated solution to give **1** as pale yellow crystals. Yield: 91 mg (89%). ^{1}H NMR: δ 6.5 (m, 8H, aryl H *ortho* and *meta* to S), 6.75 (t, 2H, aryl H *para* to S), 7.65 (t, 8H, bpy H), 8.15 (t, 8H, bpy H), 8.3 (m, 8H, bpy H), 8.7 (m, 8H, bpy H). Positive ESI-MS: *m/z* 534 $[M]^{2+}$, 379 $[M - 2bpy]^{2+}$. Anal. calcd for $C_{52}H_{42}F_{12}N_8P_2S_2Cd_2$: C, 46.00; H, 3.12; N, 8.25; found: C, 45.80; H, 3.12; N, 8.24.

$[(bpy)_2Cd(\mu\text{-}SC_6H_4CH_3\text{-}p)]_2(PF_6)_2$ (2). The procedure is similar to that described for the preparation of **1**, except *p*-thiocresol was used in place of thiophenol to give yellow crystals of **2**. Yield: 90 mg (87%). ^{1}H NMR: δ 2.15 (s, 6H, CH_3), 6.3 (d, 4H, aryl H *ortho* to S), 6.4 (d, 4H, aryl H *meta* to S), 7.75 (t, 8H, bpy H), 8.25 (t, 8H, bpy H), 8.35 (m, 8H, bpy H), 8.8 (m, 8H, bpy H). Positive ESI-MS: *m/z* 548 $[M]^{2+}$, 393 $[M - 2bpy]^{2+}$. Anal. calcd for $C_{54}H_{46}F_{12}N_8P_2S_2Cd_2$: C, 46.80; H, 3.35; N, 8.09; found: C, 46.67; H, 3.20; N, 8.03.

$[(bpy)_2Cd(\mu\text{-}SC_6H_4OCH_3\text{-}p)]_2(PF_6)_2$ (3). The procedure is similar to that described for the preparation of **1**, except 4-methoxythiophenol was used in place of thiophenol to give bright yellow crystals of **3**. Yield: 90 mg (85%). ^{1}H NMR: δ 3.55 (s, 6H, OCH_3), 5.95 (d, 4H, aryl H *ortho* to S), 6.30 (d, 4H, aryl H *meta* to S), 7.50 (t, 8H, bpy H), 8.05 (t, 8H, bpy H), 8.15 (m, 8H, bpy H), 8.5 (m, 8H, bpy H). Positive ESI-MS: *m/z* 1109 $[M - bpy \cdot PF_6]^+$, 959 $[M - 2bpy \cdot PF_6]^+$, 564 $[M]^{2+}$, 409 $[M - 2bpy]^{2+}$. Anal. calcd for $C_{54}H_{46}F_{12}N_8P_2O_2S_2Cd_2$: C, 45.74; H, 3.27; N, 7.90; found: C, 45.75; H, 3.10; N, 7.95.

$[(bpy)_2Cd(\mu\text{-}SC_6H_4Cl\text{-}p)]_2(PF_6)_2$ (4). The procedure is similar to that described for the preparation of **1**, except 4-chlorothiophenol was used in place of thiophenol to give pale yellow crystals of **4**. Yield: 98 mg (92%). ^{1}H NMR: δ 6.35 (d,

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4H, aryl H *ortho* to S), 6.45 (d, 4H, aryl H *meta* to S), 7.55 (t, 8H, bpy H), 8.10 (t, 8H, bpy H), 8.25 (m, 8H, bpy H), 8.55 (m, 8H, bpy H). Positive ESI-MS: *m/z* 1282 $[M \cdot PF_6]^+$, 1124 $[M - bpy \cdot PF_6]^+$, 569 $[M]^{2+}$, 413 $[M - 2bpy]^{2+}$. Anal. calcd for $C_{52}H_{40}Cl_2F_{12}N_8P_2S_2Cd_2$: C, 43.78; H, 2.83; N, 7.85; found: C, 43.98; H, 2.73; N, 7.95.

$[(bpy)_2Cd(\mu\text{-}SeC_6H_5)]_2(PF_6)_2$ (5). The procedure is similar to that described for the preparation of **1**, except diphenyldiselenide and sodium borohydride were used in place of thiophenol to give yellow crystals of **5**. Yield: 86 mg (79%). ^{1}H NMR: δ 6.30 (t, 4H, aryl H *ortho* to Se), 6.60 (m, 6H, aryl H *meta* and *para* to Se), 7.30 (t, 8H, bpy H), 7.85 (t, 8H, bpy H), 8.05 (m, 8H, bpy H), 8.25 (m, 8H, bpy H). Positive ESI-MS: *m/z* 580 $[M]^{2+}$, 425 $[M - 2bpy]^{2+}$. Anal. calcd for $C_{52}H_{42}F_{12}N_8P_2Se_2Cd_2$: C, 43.03; H, 2.92; N, 7.72; found: C, 43.24; H, 2.81; N, 7.73.

$[(bpy)_2Cd(\mu\text{-}SeC_6H_4Cl\text{-}p)]_2(PF_6)_2$ (6). The procedure is similar to that described for the preparation of **1**, except bis(4-chlorophenylselenide) and sodium borohydride were used in place of thiophenol to give yellow crystals of **6**. Yield: 86 mg (75%). ^{1}H NMR: δ 6.50 (d, 4H, aryl H *ortho* to Se), 6.90 (d, 6H, aryl H *meta* to Se), 7.55 (t, 8H, bpy H), 8.10 (t, 8H, bpy H), 8.30 (m, 8H, bpy H), 8.40 (m, 8H, bpy H). Positive ESI-MS: *m/z* 614 $[M]^{2+}$, 459 $[M - 2bpy]^{2+}$. Anal. calcd for $C_{52}H_{40}Cl_2F_{12}N_8P_2Se_2Cd_2$: C, 41.08; H, 2.65; N, 7.37; found: C, 40.95; H, 2.52; N, 7.37.

$[(Bu^t_2bpy)_2Cd(\mu\text{-}SC_6H_5)]_2(PF_6)_2$ (7). The procedure is similar to that described for the preparation of **1**, except 4,4′-di-*tert*-butyl-2,2′-bipyridine[11a,b] was used in place of 2,2′-bipyridine to give pale yellow crystals of **7**. Yield: 125 mg (92%). ^{1}H NMR: δ 1.35 (s, 72H, Bu^t), 6.15 (m, 8H, aryl H *ortho* and *meta* to S), 6.55 (t, 2H, aryl H *para* to S), 7.55 (m, 8H, bpy H), 8.00 (m, 8H, bpy H), 8.55 (m, 8H, bpy H). Positive ESI-MS: *m/z* 1392 $[M - Bu^t_2bpy \cdot PF_6]^+$, 1124 $[M - 2Bu^t_2bpy \cdot PF_6]^+$, 759 $[M]^{2+}$, 489 $[M - 2Bu^t_2bpy]^{2+}$. Anal. calcd for $C_{84}H_{106}F_{12}N_8P_2S_2Cd_2$: C, 55.84; H, 5.91; N, 6.20; found: C, 55.78; H, 5.83; N, 6.07.

$[(Bu^t_2bpy)_2Cd(\mu SC_6H_4Cl\text{-}p)]_2(PF_6)_2$ (8). The procedure is similar to that described for the preparation of **4**, except 4,4′-di-*tert*-butyl-2,2′-bipyridine was used in place of 2,2′-bipyridine to give pale yellow crystals of **8**. Yield: 125 mg (89%). ^{1}H NMR: δ 1.25 (s, 72H, Bu^t), 5.95 (d, 4H, aryl H *ortho* to S), 6.05 (d, 4H, aryl H *meta* to S), 7.45 (m, 8H, bpy H), 7.95 (m, 8H, bpy H), 8.45 (m, 8H, bpy H). Positive ESI-MS: *m/z* 1730 $[M \cdot PF_6]^+$, 1460 $[M - Bu^t_2bpy \cdot PF_6]^+$, 792 $[M]^{2+}$, 525 $[M - 2Bu^t_2bpy]^{2+}$. Anal. calcd for $C_{84}H_{104}Cl_2F_{12}N_8P_2S_2Cd_2$: C, 53.79; H, 5.59; N, 5.97; found: C, 53.83; H, 5.41; N, 5.79.

$[(Bu^t_2bpy)_2Cd(\mu\text{-}SeC_6H_5)]_2(PF_6)_2$ (9). The procedure is similar to that described for the preparation of **5**, except 4,4′-di-*tert*-butyl-2,2′-bipyridine was used in place of 2,2′-bipyridine to give yellow crystals of **9**. Yield: 110 mg (77%). ^{1}H NMR: δ 1.35 (s, 72H, Bu^t), 6.35 (m, 4H, aryl H *ortho* to Se), 6.60 (m, 4H, aryl H *meta* to Se), 6.75 (t, 2H, aryl H *para* to Se), 7.50 (m, 8H, bpy H), 8.15 (m, 8H, bpy H), 8.35 (m, 8H, bpy H). Positive ESI-MS: *m/z* 805 $[M]^{2+}$, 537 $[M - 2Bu^t_2bpy]^{2+}$. Anal. calcd for $C_{84}H_{106}F_{12}N_8P_2Se_2Cd_2$: C, 53.09; H, 5.62; N, 5.90; found: C, 53.08; H, 5.49; N, 5.66.

$[(phen)_2Cd(\mu\text{-}SC_6H_5)]_2(PF_6)_2$ (10). The procedure is similar to that described for the preparation of **1**, except 1,10-phenanthroline was used in place of 2,2′-bipyridine to give yellow crystals of **10**. Yield: 100 mg (92%). ^{1}H NMR: δ 5.85 (m, 4H, aryl H *ortho* to S), 6.20 (m, 6H, aryl H *meta* and *para* to S), 8.10 (dd, 8H, phen H), 8.20 (s, 8H, phen H), 8.80 (dd, 8H, phen H), 9.30 (dd, 8H, phen H). Positive ESI-MS: *m/z* 582 $[M]^{2+}$, 401 $[M - 2phen]^{2+}$. Anal. calcd for $C_{60}H_{42}F_{12}N_8P_2S_2Cd_2$: C, 49.57; H, 2.91; N, 7.71; found: C, 49.41; H, 2.85; N, 7.72.

$[(phen)_2Cd(\mu\text{-}SC_6H_4CH_3\text{-}p)]_2(PF_6)_2$ (11). The procedure is similar to that described for the preparation of **2**, except 1,10-phenanthroline was used in place of 2,2′-bipyridine to give yellow crystals of **11**. Yield: 110 mg (99%) ^{1}H NMR: δ 2.10 (s, 6H, CH_3), 5.30 (d, 4H, aryl H *ortho* to S), 5.70 (d, 6H, aryl H *meta* to S), 7.85 (dd, 8H, phen H), 7.95 (s, 8H, phen H), 8.55 (dd, 8H, phen H), 9.10 (dd, 8H, phen H). Positive ESI-MS: *m/z* 1157 $[M - phen \cdot PF_6]^+$, 596 $[M]^{2+}$, 417 $[M - 2phen]^{2+}$. Anal. calcd for $C_{62}H_{46}F_{12}N_8P_2S_2Cd_2$: C, 50.25; H, 3.13; N, 7.56; found: C, 50.19; H, 3.01; N, 7.57.

$[(phen)_2Cd(\mu\text{-}SeC_6H_5)]_2(PF_6)_2$ (12). The procedure is similar to that described for the preparation of **5**, except 1,10-phenanthroline was used in place of 2,2′-bipyridine to give bright yellow crystals of **12**. Yield: 100 mg (86%). ^{1}H NMR: δ 5.95 (m, 4H, aryl H *ortho* to Se), 6.30 (t, 6H, aryl H *para* to Se), 6.50 (m, 6H, aryl H *meta* to Se), 7.85 (dd, 8H, phen H), 8.05 (s, 8H, phen H), 8.60 (dd, 8H, phen H), 8.90 (dd, 8H, phen H). Positive ESI-MS: *m/z* 628 $[M]^{2+}$, 449 $[M - 2phen]^{2+}$. Anal. calcd for $C_{60}H_{42}F_{12}N_8P_2Se_2Cd_2 \cdot H_2O$: C, 46.03; H, 2.83; N, 7.16; found: C, 45.99; H, 2.55; N, 7.16.

$[(phen)_2Cd(\mu\text{-}L)]_2(PF_6)_2$ (13). The procedure is similar to that described for the preparation of **10**, except 4′-mercaptomonobenzo-15-crown-5 (HL)[11c] was used in place of thiophenol to give yellow crystals of **13**. Yield: 98 mg (71%). ^{1}H NMR: δ 3.40 (m, 4H, CH_2OCH_2), 3.65 (m, 20H, CH_2OCH_2), 3.75 (m, 4H, $C_6H_3OCH_2$), 3.90 (t, 4H, CH_2OCH_2), 5.55 (m, 6H, aryl H), 7.85 (dd, 8H, bpy H), 8.05 (s, 8H, bpy H), 8.60 (dd, 8H, bpy H), 8.95 (dd, 8H, bpy H). Positive ESI-MS: *m/z* 772 $[M]^{2+}$. Anal. calcd for $C_{76}H_{70}F_{12}N_8O_{10}P_2S_2Cd_2 \cdot CH_2Cl_2$: C, 48.19; H, 3.78; N, 5.84; found: C, 48.56; H, 3.82; N, 6.05.

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 spectrofluorometer. ^{1}H NMR spectra were recorded on a Bruker DPX-300 FT-NMR spectrometer (300 MHz) in $CDCl_3$ at 298 K and chemical shifts are reported relative to Me_4Si. Positive ESI mass spectra were recorded on a Finnigan LCQ 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 performed by using a CH Instruments, Inc. CHI 620 electrochemical analyser 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} $Bu^n_4NPF_6$).[12a] 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.[12b]

Crystal structure determination

Single crystals of **11** and **12** were obtained by vapour diffusion of diethyl ether into concentrated acetonitrile solutions of the respective complexes.

Crystal data for 11. $[(C_{62}H_{46}N_8S_2Cd_2)^{2+}2PF_6^- \cdot 2CH_3CN]$; $M = 1564.07$, triclinic, space group $P\bar{1}$ (No. 2), $a = 9.266(2)$, $b = 13.309(2)$, $c = 14.782(3)$ Å, $\alpha = 64.28(2)$, $\beta = 82.88(2)$, $\gamma = 86.51(2)°$, $U = 1629.6(6)$ Å^3, $Z = 2$, μ(Mo-Kα) = 8.51 cm^{-1}, $T = 301$ K. Data were collected on a MAR diffractometer with a 300 mm image plate detector using graphite monochromatized Mo-Kα radiation ($\lambda = 0.71073$ Å). Data collection was made with 3° oscillation (70 images) at 120 mm distance and 310 s exposure. The images were interpreted and intensities integrated using the program DENZO.[13a] A total of 16241 measured reflections were obtained, of which 5620 were unique ($R_{int} = 0.031$). Of these 4959 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 successful refinement of the structure solved by direct methods (SIR92[13b]) and expanded by Fourier method and refined by full-matrix least-squares using the software package TeXsan[13c] on a Silicon Graphics Indy computer. One crystallographic asymmetric unit consists of half of one formula unit. Convergence for 415 variable parameters by least-squares refinement on F with $w = 4F_o^2/\sigma^2(F_o^2)$, where $\sigma^2(F_o^2) = [\sigma^2(I) + (0.041\ F_o^2)^2]$ was reached at $R = 0.057$ and $wR = 0.086$.

Crystal data for 12. $[(C_{60}H_{42}N_8Se_2Cd_2)^{2+}2PF_6^- \cdot 2CH_3CN]$; $M = 1629.82$, triclinic, space group $P\bar{1}$ (No. 2), $a = 9.3987(9)$, $b = 13.184(1)$, $c = 15.983(2)$ Å, $\alpha = 66.133(8)$, $\beta = 83.369(8)$, $\gamma = 85.087(1)°$, $U = 1580.9(3)$ Å^3, $Z = 2$, μ(Mo-Kα) = 19.61 cm^{-1}, $T = 301$ K. Data were collected on a Rigaku AFC7R diffractometer with graphite monochromatized Mo-Kα radiation ($\lambda = 0.71073$ Å). Unit cell dimensions were determined based on the setting angles of 25 reflections in the 2θ range of 34.5 to 40.3°. Intensity data were corrected for decay and for Lorentz and polarization effects and empirical absorption corrections based on the ψ-scan of five strong reflections (minimum and maximum transmission factors 0.786 and 1.000). A total of 5838 reflections were measured, of which 5570 were unique and $R_{int} = 0.029$. Of these 4095 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 direct methods (SIR92[13b]) and expanded by Fourier method and refined by full-matrix least-squares using the software package TeXsan[13c] on a Silicon Graphics Indy computer. One crystallographic asymmetric unit consists of half of one formula unit. Convergence for 413 variable parameters by least-squares refinement on F with $w = 4F_o^2/\sigma^2(F_o^2)$, where $\sigma^2(F_o^2) = [\sigma^2(I) + (0.038\ F_o^2)^2]$ was reached at $R = 0.035$ and $wR = 0.050$.
CCDC reference number 440/147. See http://www.rsc.org/suppdata/nj/1999/1163/ for crystallographic files in .cif format.

Results and discussion

Unlike the reaction of cadmium(II) acetate with the same molar ratio of diimine and two equivalents of thiol, which gave the mononuclear $[Cd(N–N)(SR)_2]$,[14a] reaction of $Cd(OAc)_2 \cdot 2H_2O$ with diimine and chalcogenol in a molar ratio of 1 : 2 : 1 afforded a series of dinuclear six-coordinate cadmium(II) diimine chalcogenolate complexes, $[(N–N)_2Cd(\mu\text{-}ER)]_2^{2+}$, isolated as the hexafluorophosphate salt. All of them gave satisfactory elemental analyses and were characterized by ESI-mass spectrometry and ^{1}H NMR spectroscopy.

X-Ray crystal structure determination

The crystal structures of the complex cations of **11** and **12** with atomic numbering are depicted in Fig. 1 and 2, respectively. Selected bond distances and angles for **11** and **12** are summarized in Table 1. The Cd centre adopts a distorted octahedral geometry with S1–Cd1–S1* and N1–Cd1–N2 angles of 88.25(4)° and 70.0(2)° for **11**, and Se1–Cd1–Se1* and N1–Cd1–N2 angles of 90.94(2)° and 69.4(1)° for **12**. The average Cd–S and Cd–Se bond distances are 2.666(1) and 2.772(6) Å for **11** and **12** respectively, which are comparable to other related systems.[5b,c,15]

Electronic absorption and photophysical properties

The electronic absorption spectra of the complexes show low energy absorption bands at *ca.* 340–370 nm and higher energy absorptions at *ca.* 200–300 nm (Table 2). The latter are assigned as intraligand (IL) transitions of the diimines and chalcogenolates since the free ligands also absorb at similar energy. The low energy absorption band is found to show a slight dependence on the nature of the chalcogenolate ligands. The energy of this band for the $[(bpy)_2Cd(SR)]_2(PF_6)_2$ series is found to follow the order: **3** < **2** < **1** < **4**, which is in line with the electron-donating ability of the ligand, where SC_6H_4OMe-*p* > SC_6H_4Me-*p* > SC_6H_5 > SC_6H_4Cl-*p*. A slight energy dependence is also observed for the low energy absorption band of the $[(bpy)_2Cd(ER)]_2(PF_6)_2$ series in which **5** is found to absorb at lower energy than **1** and **6**. This is also consistent with the σ-donating ability of SeC_6H_5 > SeC_6H_4Cl-*p* ≈ SC_6H_5. Similar findings were observed in the

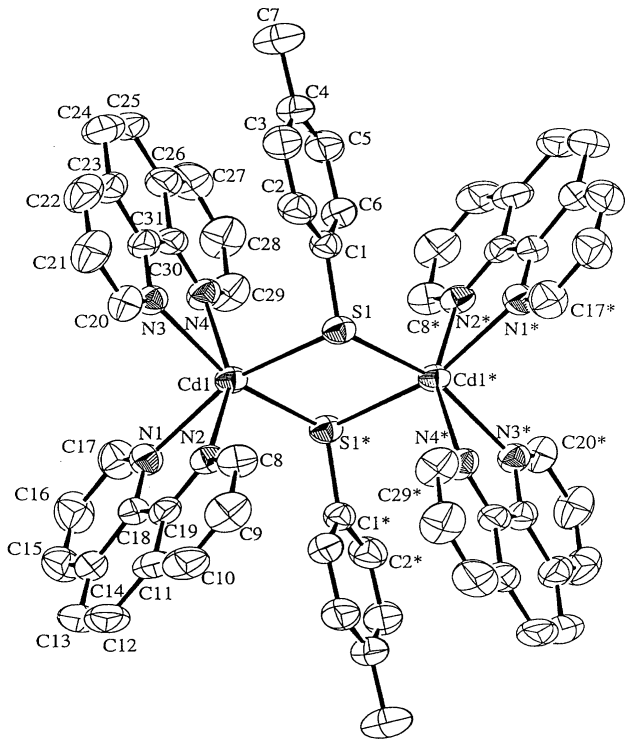

Fig. 1 Perspective drawing of the complex cation of $[(phen)_2Cd(\mu\text{-}SC_6H_4Me\text{-}p)]_2(PF_6)_2$ (**11**) with the atomic numbering scheme. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are shown at the 40% probability level. Asterisked atoms have coordinates at $1 - x, -y, -z$.

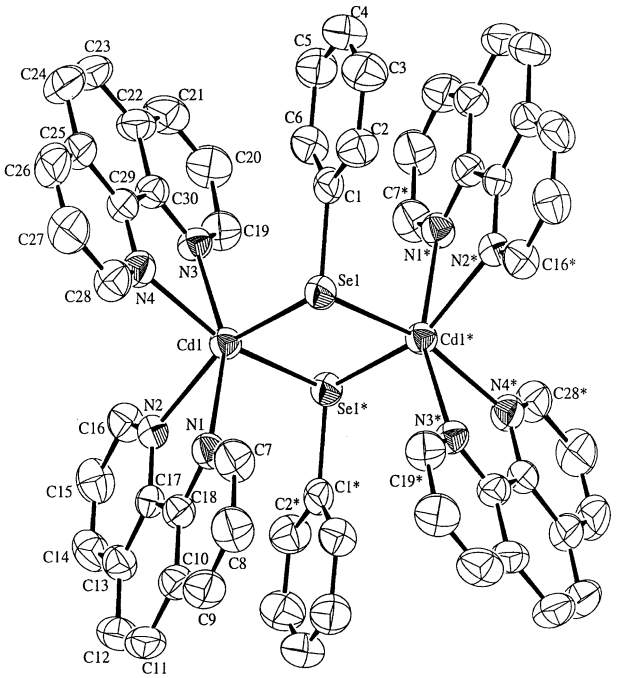

Fig. 2 Perspective drawing of the complex cation of $[(phen)_2Cd(\mu\text{-}SeC_6H_5)]_2(PF_6)_2$ (**12**) with the atomic numbering scheme. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are shown at the 40% probability level. Asterisked atoms have coordinates at $1-x, -y, 1-z$.

$[(Bu^t_2bpy)_2Cd(ER)]_2(PF_6)_2$ and $[(phen)_2Cd(ER)]_2(PF_6)_2$ series in which the absorption energy for the low energy band follows the order: **9** < **7** ≈ **8**; **13** < **11** < **10** and **12** < **10**. Comparison of the absorption energies in $[(N\text{–}N)_2Cd(ER)]_2(PF_6)_2$ for the same ER ligand shows that the nature of the diimine ligand also plays a role in governing the low energy absorption band energies. For example, for the series $[(N\text{–}N)_2Cd(SC_6H_5)]_2(PF_6)_2$ the low energy absorption energies follow the order phen < bpy < Bu^t_2bpy, which is the same as that of the π*(N–N) orbital energies. Thus, it would appear that the low energy absorption band at *ca.* 340–370 nm is likely to be derived from a ligand-to-ligand charge transfer [LLCT, $p_\pi(ER^-) \rightarrow \pi^*(N\text{–}N)$] transition, similar to the spectral assignment suggested for the related $[Cd(N\text{–}N)(SR)_2]$ monomer.[14a] However, in view of the fairly small shift of absorption energies on changing the chalcogenolate ligands and the fact that intraligand π–π* transitions of the diimine ligands also occur at similar energies, an assignment of the low energy absorption band as a mixed LLCT/IL transition is favoured and appears to best describe the nature of the transition.

Similar to the related mononuclear $[Cd(N\text{–}N)(SR)_2]$ system,[14a] complexes **1**–**13** are shown to be luminescent with emission maxima at *ca.* 500–610 nm, both in the solid state at 298 and 77 K and in 77 K glasses upon excitation at λ > 350 nm. All complexes show luminescence at room temperature in degassed acetonitrile solutions. The photophysical data are summarized in Table 2. The lifetimes in the microsecond range are suggestive of a triplet parentage. Similar to the electronic absorption data, the emission energies are found to depend on the nature of both the chalcogenolate and the diimine ligand (Figs. 3 and 4). For the $[(bpy)_2Cd(ER)]_2(PF_6)_2$ series, an emission energy trend in the order **3** < **2** < **1** ≤ **4** is observed, again in line with the electron-donating ability of the thiophenolate ligands. The lower emission energy of **5** relative to **1** and **6** is similarly ascribed to the better donating

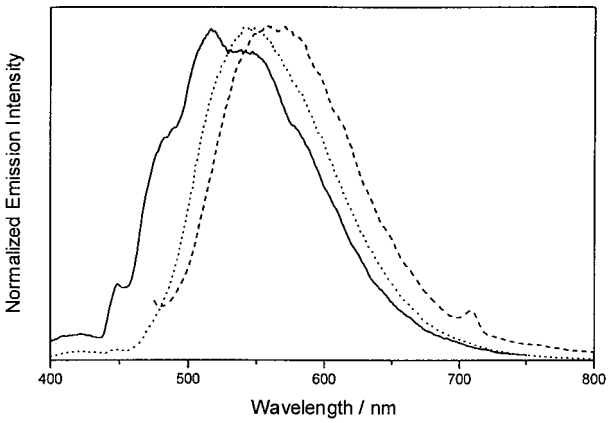

Fig. 3 Emission spectra of Cd(II) complexes in the solid state at 77 K: (——) $[(bpy)_2Cd(\mu\text{-}SC_6H_4Cl\text{-}p)]_2(PF_6)_2$ (**4**), (···) $[(bpy)_2Cd(\mu\text{-}SC_6H_4Me\text{-}p)]_2(PF_6)_2$ (**2**) and (– – –) $[(bpy)_2Cd(\mu\text{-}SC_6H_4OMe\text{-}p)]_2(PF_6)_2$ (**3**).

Table 1 Selected bond lengths (Å) and angles (°) for **11** and **12**

11		**12**	
Cd1–S1	2.650(1)	Cd1–Se1	2.768(4)
Cd1–S1*	2.682(1)	Cd1–Se1*	2.775(8)
Cd1–N1	2.365(4)	Cd1–N1	2.441(4)
Cd1–N2	2.419(4)	Cd1–N2	2.360(4)
Cd1–N3	2.378(4)	Cd1–N3	2.413(4)
Cd1–N4	2.432(5)	Cd1–N4	2.363(4)
S1–C1	1.782(5)	Se1–C1	1.924(5)
S1–Cd1–S1*	88.25(4)	Se1–Cd1–Se1*	90.94(2)
S1–Cd1–N1	158.8(1)	Se1–Cd1–N1	87.72(10)
S1–Cd1–N2	91.1(1)	Se1–Cd1–N2	156.03(10)
S1–Cd1–N3	90.6(1)	Se1–Cd1–N3	109.55(10)
S1–Cd1–N4	103.3(1)	Se1–Cd1–N4	91.5(1)
S1*–Cd1–N1	89.8(1)	Se1–Cd1–N1	103.4(1)
S1*–Cd1–N2	110.8(1)	Se1*–Cd1–N2	87.72(9)
S1*–Cd1–N3	156.4(1)	Se1*–Cd1–N3	90.57(10)
S1*–Cd1–N4	88.1(1)	Se1*–Cd1–N4	160.1(1)
N1–Cd1–N2	70.0(2)	N1–Cd1–N2	69.4(1)
N1–Cd1–N3	99.4(2)	N1–Cd1–N3	157.8(1)
N1–Cd1–N4	97.6(2)	N1–Cd1–N4	96.4(1)
N2–Cd1–N3	92.8(2)	N2–Cd1–N3	94.4(1)
N2–Cd1–N4	156.7(2)	N2–Cd1–N4	97.8(1)
N3–Cd1–N4	69.3(2)	N3–Cd1–N4	70.1(1)
Cd1–S1–Cd1*	91.75(4)	Cd1–Se1–Cd1*	89.06(2)
Cd1–S1–C1	102.6(2)	Cd1–Se1–C1	110.9(1)

Table 2 Photophysical data for complexes **1**–**13**

	Medium (T/K)	λ_{abs}/nm ($\varepsilon \times 10^{-4}$/dm^3 mol^{-1} cm^{-1})	λ_{em}/nm (τ_0/μs)
1	Solid (298)		550
	Solid (77)		535
	Glass (77)[a]		496
	MeCN (298)	245(6.60), 295(6.30), 350(0.12)	421, 582sh
2	Solid (298)		558(0.12)
	Solid (77)		546
	Glass (77)[a]		553
	Glass (77)[b]		544
	Glass (77)[c]		537
	MeCN (298)	245(5.90), 287(5.10), 354(0.12)	420, 608sh
3	Solid (298)		570
	Solid (77)		568
	Glass (77)[a]		557
	MeCN (298)	245(6.20), 290(5.20), 362(0.10)	442, 612sh
4	Solid (298)		536(1.26)
	Solid (77)		518
	Glass (77)[a]		490
	MeCN (298)	247(5.10), 286(6.30), 346(0.12)	418, 590sh
5	Solid (298)		562(0.16)
	Solid (77)		578
	Glass (77)[a]		545
	MeCN (298)	242(7.50), 286(6.70), 356(0.11)	420, 598sh(v br)
6	Solid (298)		545
	Solid (77)		555
	Glass (77)[a]		528
	MeCN (298)	245(7.10), 290(8.00), 350(0.14)	424, 594sh(v br)
7	Solid (298)		530
	Solid (77)		540
	Glass (77)[a]		483
	MeCN (298)	250(6.30), 290(6.40), 340(0.17)	416, 580sh
8	Solid (298)		523
	Solid (77)		496
	Glass (77)[a]		470
	MeCN (298)	255(5.10), 290(6.30), 340(0.15)	428, 565sh
9	Solid (298)		540
	Solid (77)		550
	Glass (77)[a]		490
	MeCN (298)	250(8.00), 293(9.00), 350(0.16)	415, 580sh
10	Solid (298)		565
	Solid (77)		564
	Glass (77)[a]		526
	MeCN (298)	230(16.40), 268(14.20), 360(0.15)	420, 582sh(v br)
11	Solid (298)		575
	Solid (77)		608
	Glass (77)[a]		530
	MeCN (298)	230(17.20), 268(14.50), 370(0.13)	434, 585sh
12	Solid (298)		580
	Solid (77)		598
	Glass (77)[a]		530
	MeCN (298)	230(17.20), 268(14.50), 370(0.13)	435, 606sh(v br)
13	Solid (298)		590
	Solid (77)		592
	Glass (77)[a]		570
	MeCN (298)	230(17.30), 268(14.10), 375(0.13)	408

[a] EtOH–MeOH = 4 : 1. [b] EtOH–$CHCl_3$ = 9 : 1. [c] EtOH–$CHCl_3$ = 19 : 1.

ability of the phenylselenolate compared to its thiophenolate analogue or its chloro-substituted derivative. Similar trends were observed in the phenanthroline and the di-*tert*-butylbipyridine series. For the same chalcogenolate ligand, the emission energies are highest for $[(Bu^t_2bpy)_2Cd(ER)]_2^{2+}$ and lowest for $[(phen)_2Cd(ER)]_2^{2+}$, in accordance with the assignment of an LLCT emission, probably mixed with some IL π–π* character.

It is interesting to note that in a related mononuclear $[Zn(phen)X_2]$ system,[14b,c] the high energy π–π* emission of phenanthroline dominates the emission spectrum of $[Zn(phen)Cl_2]$,[14b,c] while replacing the chlorides in $[Zn(phen)Cl_2]$ by 4-chloro- or 4-methoxythiophenolate produces $[Zn(phen)(SR)_2]$, in which a new lower energy emission band ascribed to an LLCT origin dominates the emission spectrum.[14] In the case of $[Zn(phen)(SC_6H_4Cl\text{-}p)_2]$, the phenanthroline π–π* phosphorescence is not entirely quenched in the 77 K glass state.[14]

In our systems, it is interesting to note that the low energy LLCT emission dominates in the 77 K glass state when the thiophenolate in $[(N–N)_2Cd(ER)]_2^{2+}$ is 4-methoxythiophenolate (Fig. 5), while the structured diimine phosphorescence predominates in the spectrum of $[(N–N)_2Cd(SC_6H_4Cl\text{-}p)]_2^{2+}$, with the low energy LLCT band appearing only as a shoulder on the red end of the structured band. The domination of the LLCT phosphorescence over the π–π* emission at higher temperature is reminiscent of the mononuclear $[Zn(N–N)(SR)_2]$[14c,d] and $[Cd(N–N)(SR)_2]$[14c,d] systems. In addition, the LLCT emission of the $[(N–N)_2Cd(ER)]_2^{2+}$ complexes is found to occur at higher

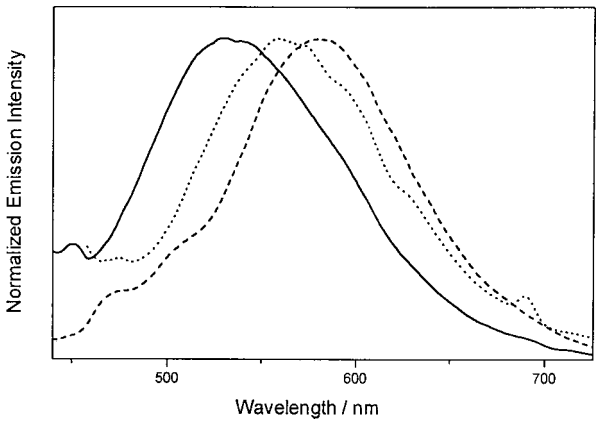

Fig. 4 Emission spectra of Cd(II) complexes in the solid state at 77 K: (——) $[(Bu^t_2bpy)_2Cd(\mu\text{-}SeC_6H_5)]_2(PF_6)_2$ (**9**), (···) $[(bpy)_2Cd(\mu\text{-}SeC_6H_5)]_2(PF_6)_2$ (**5**) and (– – –) $[(phen)_2Cd(\mu\text{-}SeC_6H_5)]_2(PF_6)_2$ (**12**).

energy than that of the mononuclear analogue.[14a,b] This observation is attributable to the stabilization of the p_π orbital of the thiolate ligands in the dinuclear cadmium species in which lone-pair electrons on the thiolate S atom become less available in the μ-bridging mode.

Fig. 6 shows the solvent dependence of the emission spectrum of complex **2**. An increase in the alcohol content, and hence the polarity, of the glass is found to decrease the relative amount of π–π* contribution from diimine and also to shift the low energy band to the red. Similar observations have been reported for the emission properties of the related mononuclear system.[14a]

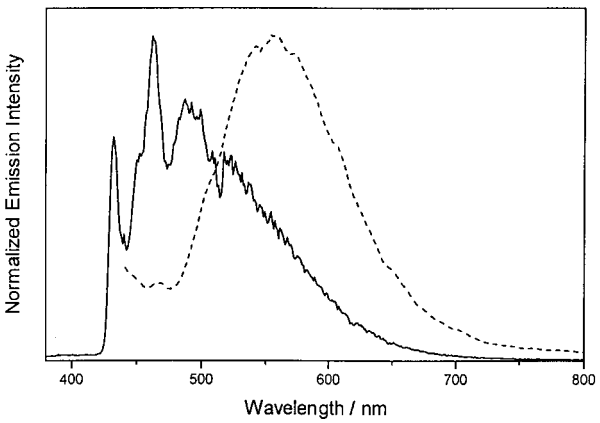

Fig. 5 Emission spectra of Cd(II) complexes in 77 K glass state: (——) $[(bpy)_2Cd(\mu\text{-}SC_6H_4Cl\text{-}p)]_2(PF_6)_2$ (**4**) and (– – –) $[(bpy)_2Cd(\mu\text{-}SC_6H_4OMe\text{-}p)]_2(PF_6)_2$ (**3**).

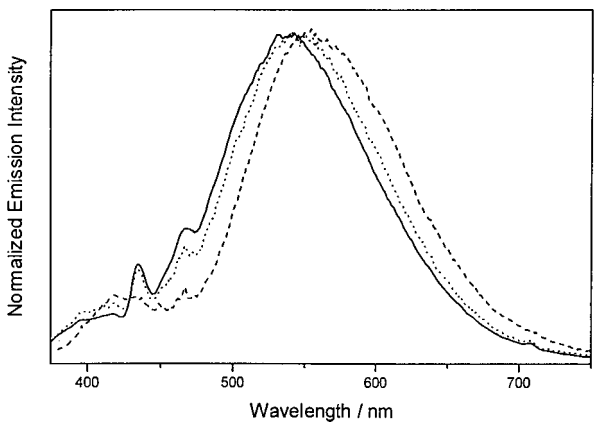

Fig. 6 Solvent dependence of the emission spectra of $[(bpy)_2Cd(\mu\text{-}SC_6H_4Me\text{-}p)]_2(PF_6)_2$ (**2**) in 77 K glass state: (——) $CHCl_3$–EtOH (1 : 9 v/v), (···) $CHCl_3$–EtOH (1 : 19 v/v), and (– – –) MeOH–EtOH (1 : 4 v/v).

Table 3 Electrochemical data for complexes **1**–**13** in MeCN

	Oxidation E_{pa}/V *vs.* SCE[a]	Reduction E_{pc}/V *vs.* SCE[b]
1	+1.62	−1.16, −1.28
2	+1.57	−1.19, −1.30
3	+1.42	−1.20, −1.32
4	+1.74	−1.15, −1.26
5	+1.43	−1.21, −1.36
6	+1.61	−1.19, −1.35
7	+1.62	−1.25, −1.34
8	+1.71	−1.24, −1.32
9	+1.50	−1.23, −1.29
10	+1.63	−1.21, −1.29
11	+1.56	−1.23, −1.30
12	+1.47	−1.25, −1.33
13	+1.28	−1.31, −1.52

[a] E_{pa} refers to the anodic peak potential of the irreversible oxidation wave. [b] E_{pc} refers to the cathodic peak potential of the irreversible reduction wave.

Electrochemical properties

The electrochemical data for **1**–**13** in acetonitrile are summarized in Table 3. Cyclic voltammetric studies of all complexes in acetonitrile (0.1 mol dm^{-3} $Bu^n_4NPF_6$) show similar cyclic voltammograms with one irreversible oxidation wave and two irreversible reduction waves. The two reduction waves are tentatively assigned as the reduction of the α,α′-diimine ligands. The more negative potentials for the reduction of **7** (−1.25 and −1.34 V *vs.* SCE) as compared to those of **1** (−1.16 and −1.28 V *vs.* SCE), are indicative of the reduced ease of reduction of the more electron-rich Bu^t_2bpy ligand relative to the unsubstituted bipyridine. An irreversible oxidation wave observed at +1.28 to +1.74 V *vs.* SCE for all complexes is assigned to the oxidation of the chalcogenolate ligand, in view of the close resemblance of the oxidation potentials of **1**, **7** and **10** with the same thiophenolate ligand. Similarly, complexes with the same chalcogenolate ligand show similar oxidation potentials, irrespective of the identity of the diimine ligands. In general, the oxidation potential is most anodic for the least electron-rich SC_6H_4Cl-*p* ligand and least positive for the more electron-rich 4′-mercaptomonobenzo-15-crown-5 and phenylselenolate complexes, in line with the greater ease of oxidation of the electron-rich chalcogenolate ligands. The electrochemical behaviour is consistent with the assignment of the lowest energy transition as a $p_\pi(ER^-) \rightarrow \pi^*$(N–N) LLCT transition, in which the HOMO has substantial chalcogenolate character while the LUMO is mainly of diimine π* character.

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