

# Syntheses and structural characterization of novel luminescent heteronuclear rhenium(III)–zinc(II) and –cadmium(II) chalcogenolate complexes†

Vivian Wing-Wah Yam,\* Yung-Lin Pui, Keith Man-Chung Wong and Kung-Kai Cheung

Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong SAR, People's Republic of China. E-mail: wwyam@hku.hk

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Novel heteronuclear rhenium(III)–zinc(II) and –cadmium(II) complexes with chalcogenolate ligands have been synthesized and shown to exhibit rich luminescence properties; the X-ray crystal structures of  $[(\text{bpy})\text{Re}(\text{CO})_3(\mu\text{-SC}_6\text{H}_4\text{Me-}p)]_2\text{-Zn}(\text{bpy})](\text{PF}_6)_2$  (**2**) and  $[(\text{bpy})\text{Re}(\text{CO})_3(\mu\text{-SC}_6\text{H}_4\text{Me-}p)]_2\text{-Cd}(\text{bpy})_2](\text{PF}_6)_2$  (**4**) have been determined.

There has been a growing interest in luminescence studies of transition metal complexes, particularly with the increasing attention on the design of functional materials with unique properties.<sup>1,2</sup> The most widely studied and well-documented systems are those of the  $d^6$  metal polypyridines<sup>1–3</sup> and very recently, the  $d^8$  and  $d^{10}$  metal complexes.<sup>4,5</sup> Recently, a series of mono- and di-nuclear rhenium(III) diimine complexes with chalcogenolate ligands have been reported by us to show rich luminescence behaviour.<sup>6</sup> It is believed that extension of this work to heterometallic complex formation by using mono-nuclear rhenium(III) chalcogenolates as metalloligands, would give rise to a novel series of luminescent mixed-metal rhenium(III) complexes. In view of the known luminescence properties of zinc(II) and cadmium(II) thiolate systems<sup>7</sup> and our continuing interest in luminescent  $d^{10}$  metal complexes,<sup>5</sup> a series of trinuclear mixed-metal rhenium(III)–zinc(II) and –cadmium(II) chalcogenolate complexes have been synthesized and their luminescence behaviour studied. It is also envisaged that the attachment of zinc and cadmium moieties to the rhenium chalcogenolate would serve as an efficient method to perturb the excited state properties of the complexes. The X-ray crystal structures of  $[(\text{bpy})\text{Re}(\text{CO})_3(\mu\text{-SC}_6\text{H}_4\text{Me-}p)]_2\text{Zn}(\text{bpy})](\text{PF}_6)_2$  and  $[(\text{bpy})\text{Re}(\text{CO})_3(\mu\text{-SC}_6\text{H}_4\text{Me-}p)]_2\text{Cd}(\text{bpy})_2](\text{PF}_6)_2$  have been determined.†

Reaction of  $[(\text{bpy})\text{Re}(\text{CO})_3(\text{SC}_6\text{H}_4\text{R})]^{6b}$  with a mixture of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and 2,2'-bipyridine in a molar ratio of 2:1:1 in methanol under an inert atmosphere of nitrogen, followed by metathesis with  $\text{NH}_4\text{PF}_6$  and subsequent recrystallization from  $\text{MeCN-Et}_2\text{O}$ , afforded  $[(\text{bpy})\text{Re}(\text{CO})_3(\mu\text{-SC}_6\text{H}_4\text{R})]_2\text{Zn}(\text{bpy})](\text{PF}_6)_2$  ( $\text{R} = \text{H}$  **1**,  $\text{Me-}p$  **2**). Similar reactions of  $[(\text{N-N})\text{Re}(\text{CO})_3(\mu\text{-EC}_6\text{H}_4\text{R})]$  with  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  and 2,2'-bipyridine in a molar ratio of 2:1:2 gave  $[(\text{N-N})\text{Re}(\text{CO})_3(\mu\text{-EC}_6\text{H}_4\text{R})]_2\text{Cd}(\text{bpy})_2](\text{PF}_6)_2$  ( $\text{N-N} = \text{bpy}$ ,  $\text{E} = \text{S}$ ,  $\text{R} = \text{H}$  **3**,  $\text{Me-}p$  **4**;  $\text{N-N} = \text{bpy}$ ,  $\text{E} = \text{Se}$ ,  $\text{R} = \text{H}$  **5**;  $\text{N-N} = \text{Bu}_2\text{bpy}$ ,  $\text{E} = \text{S}$ ,  $\text{R} = \text{Me-}p$  **6**). All the complexes have been characterized by  $^1\text{H}$  NMR spectroscopy and positive ESI-MS and gave satisfactory elemental analyses.†

Fig. 1 and 2 show perspective drawings of the complex cations of **2** and **4** with atomic numbering, respectively. In **2**, the two Re centres adopt a distorted octahedral geometry with a  $\text{S}(1)\text{-Re}(1)\text{-N}(1)$  angle of  $81.6(2)^\circ$  and a  $\text{S}(2)\text{-Re}(2)\text{-N}(5)$  angle of  $85.7(2)^\circ$ . The zinc centre adopts a distorted tetrahedral geometry with a  $\text{S}(1)\text{-Zn}(1)\text{-S}(2)$  angle of  $110.45(9)^\circ$ . The angles  $\text{Re}(1)\text{-S}(1)\text{-Zn}(1)$  and  $\text{Re}(2)\text{-S}(2)\text{-Zn}(1)$  are  $114.01(10)$  and  $112.17(10)^\circ$ , respectively. The average Re–S and Zn–S bond lengths are  $2.523(2)$  and  $2.285(8)$  Å, respectively, which

are comparable to those observed in other related rhenium(III)<sup>6,8</sup> and zinc(II) thiolate complexes.<sup>7c,9</sup> In **4**, the two Re and the Cd centres adopt a distorted octahedral geometry with a  $\text{S}(1)\text{-Re}(1)\text{-N}(1)$  angle of  $88.0(1)^\circ$ , a  $\text{S}(1)\text{-Cd}(1)\text{-S}(1^*)$  angle of  $100.89(8)^\circ$  and a  $\text{Re}(1)\text{-S}(1)\text{-Cd}(1)$  angle of  $150.49(7)^\circ$ . The average Re–S and Cd–S bond lengths are  $2.523(2)$  and  $2.713(2)$  Å, respectively, which are comparable to those found in related rhenium(III)<sup>6,8</sup> and cadmium(II) thiolate complexes.<sup>7f,9,10</sup>

The electronic absorption spectra of complexes **1–6** show absorption bands at ca. 350–380 nm with absorption shoulders at ca. 450–520 nm in MeCN. The photophysical data of the

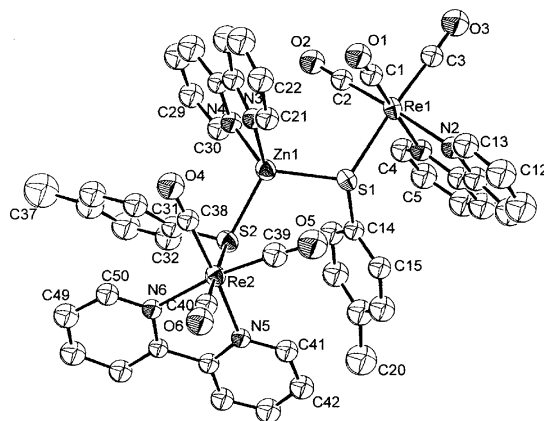


Fig. 1 Perspective drawing of the complex cation of **2** with the atomic numbering scheme. Selected bond distances (Å) and bond angles ( $^\circ$ ):  $\text{Re}(1)\text{-S}(1)$  2.519(2),  $\text{Re}(2)\text{-S}(2)$  2.527(2),  $\text{Zn}(1)\text{-S}(1)$  2.284(2),  $\text{Zn}(1)\text{-S}(2)$  2.287(3),  $\text{S}(1)\text{-Zn}(1)\text{-S}(2)$  110.45(9),  $\text{Re}(1)\text{-S}(1)\text{-Zn}(1)$  114.01(10),  $\text{Re}(2)\text{-S}(2)\text{-Zn}(1)$  112.17(10).

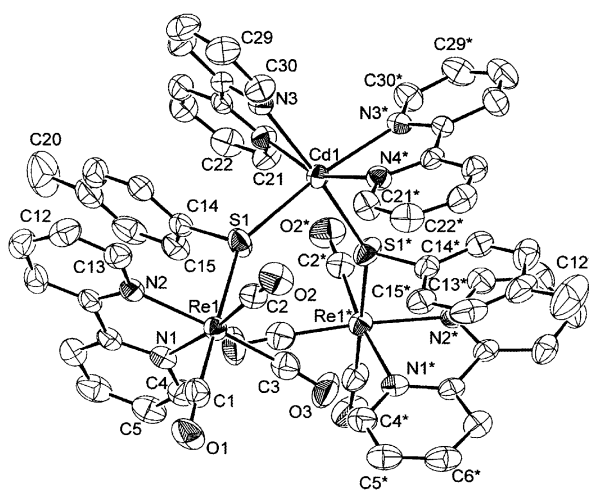


Fig. 2 Perspective drawing of the complex cation of **4** with the atomic numbering scheme. Selected bond distances (Å) and bond angles ( $^\circ$ ):  $\text{Re}(1)\text{-S}(1)$  2.523(2),  $\text{Cd}(1)\text{-S}(1)$  2.713(2),  $\text{S}(1)\text{-Re}(1)\text{-N}(1)$   $88.0(1)^\circ$ ,  $\text{S}(1)\text{-Cd}(1)\text{-S}(1^*)$   $100.89(8)^\circ$ ,  $\text{Re}(1)\text{-S}(1)\text{-Cd}(1)$   $150.49(7)^\circ$ .

† Electronic supplementary information (ESI) available: characterization for complexes **1–6** and experimental crystallographic details for **2**. See <http://www.rsc.org/suppdata/cc/b0/b005092j/>

**Table 1** Photophysical data for complexes **1–6**<sup>a</sup>

Complex	Medium (T/K)	$\lambda_{\text{abs}}/\text{nm}$ ( $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ )	$\lambda_{\text{em}}/\text{nm}$ ( $\tau_e/\mu\text{s}$ ) <sup>c</sup>
1	MeCN (298)	247 (76 610), 296 (54 620), 308 (52 840), 354(sh) (9590), 480(sh) (1080)	567 [597]
	Solid (298) Glass (77) <sup>b</sup>		536(0.58) [539] 525(sh), 593 [617]
2	MeCN (298)	247 (75 240), 296 (47 150), 308 (46 080), 368(sh) (8780), 488(sh) (1410)	588 [607]
	Solid (298) Glass (77) <sup>b</sup>		550(0.51) [552] 525(sh), 596 [608]
3	MeCN (298)	246 (97 600), 296 (70 600), 308 (61 510), 355 (9380), 485(sh) (920)	548 [565 (sh)]
	Solid (298) Glass (77) <sup>b</sup>		559(0.69) [560] 548 [570]
4	MeCN (298)	246 (95 480), 295 (64 780), 308 (55 240), 364 (7160), 494(sh) (1300)	553(0.12) [564 (sh)]
	Solid (298) Glass (77) <sup>b</sup>		600(0.53) [600] 560 [565]
5	MeCN (298)	248 (79 010), 297 (57 390), 308 (52 090), 368 (9000), 502(sh) (1320)	557(0.11) [560(sh)]
	Solid (298) Glass (77) <sup>b</sup>		562(0.49) [560] 554 [562]
6	MeCN (298)	246 (89 080), 295 (62 460), 306 (54 500), 356 (8200), 475(sh) (1240)	532(0.16) [590(sh)]
	Solid (298) Glass (77) <sup>b</sup>		555(0.45) [556] 540 [564]

<sup>a</sup> Absorption and emission wavelengths are reported to  $\pm 2$  nm. <sup>b</sup> Ethanol–methanol (4:1 v/v) glass. <sup>c</sup> Excitation wavelength at 355 nm. Values in square brackets are  $\lambda_{\text{em}}$  with excitation wavelength at 450 nm.

complexes are summarized in Table 1. The former is tentatively assigned as  $\pi_{\pi}(\text{SR}^-) \rightarrow \pi^*(\alpha, \alpha'-diimine on  $\text{Re}^{\text{I}}$  or  $\text{Zn}^{\text{II}}$  or  $\text{Cd}^{\text{II}}$ ) LLCT transitions as similar spectral assignments have been suggested in related zinc(II),<sup>7a–c</sup> cadmium(II)<sup>7a,7f</sup> and rhenium(I) systems,<sup>6</sup> while the latter is assigned as a  $d_{\pi}(\text{Re}) \rightarrow \pi^*(\alpha, \alpha'-diimine on Re) MLCT transition. Similar assignments have also been made in related  $\text{Re}(\text{I})$   $\alpha, \alpha'$ -diimine systems.<sup>1–3,6</sup> These have been further supported by the observation of an energy dependence on the nature of the chalcogenolate and the diimine ligands. The lower LLCT absorption energies in **2** compared to **1** and in **4** compared to **3** are in accordance with the presence of the more electron rich 4-methylthiophenolate ligand relative to thiophenolate. In view of the almost identical absorption patterns and energies for the  $\text{Re}^{\text{I}}\text{–Zn}^{\text{II}}\text{–Re}^{\text{I}}$  and  $\text{Re}^{\text{I}}\text{–Cd}^{\text{II}}\text{–Re}^{\text{I}}$  analogues, it is reasonable to assume that the transitions are dominated by the LLCT and MLCT transitions of the rhenium(I) diimine thiolate core, with minor contributions due to the zinc and cadmium moieties.$$

Upon excitation of complexes **1–6** at 350–450 nm, emission bands at ca. 520–630 nm were observed in the solid state, in 77 K glasses and in fluid solutions (Table 1). The close resemblance of the emission energies to those reported for the related dinuclear  $[(\text{N–N})\text{Re}(\text{CO})_3]_2(\mu\text{–SR})^+$  complexes<sup>6a</sup> is suggestive of a similar <sup>3</sup>MLCT [ $d_{\pi}(\text{Re}) \rightarrow \pi^*(\alpha, \alpha'-diimine)] emissive origin. Upon monitoring the emission at ca. 560–625 nm, bands at ca. 450–500 nm were observed in the excitation spectra, in regions close to the MLCT absorption. However, the broadness of the band as well as the dependence of the emission energy on the excitation wavelength may be suggestive of a dual luminescence. It is likely that the higher energy emission shoulder is derived from an <sup>3</sup>IL(diimine)/<sup>3</sup>LLCT origin while the low-energy emission is dominated by a <sup>3</sup>MLCT origin. Similar to the trend observed in electronic absorption studies, the lower emission energy of **2** compared to **1** and **4** compared to **3** in the solid state, is in line with the electron donating ability$

of the substituents on the thiophenolate ligand, giving rise to higher  $d_{\pi}(\text{Re})$  and/or  $\pi_{\pi}(\text{SR}^-)$  orbital energies. The higher emission energy of **6** relative to that of **4** is also in line with a <sup>3</sup>MLCT origin, probably with some mixing of <sup>3</sup>LLCT [ $\pi_{\pi}(\text{ER}^-) \rightarrow \pi^*(\alpha, \alpha'-diimine)] character, since the presence of electron rich *tert*-butyl substituents on  $\text{Bu}^t_2\text{bpy}$  would raise the  $\pi^*(\alpha, \alpha'-diimine) orbital energy relative to that of bpy.$$

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## Notes and references

† Crystal data: for **2**:  $[(\text{C}_{50}\text{H}_{38}\text{N}_6\text{O}_6\text{S}_2\text{ZnRe}_2)^+ 2\text{PF}_6^-]$ ;  $M_r = 1610.73$ , triclinic, space group  $P\bar{1}$  (no. 2),  $a = 12.107(5)$ ,  $b = 12.348(5)$ ,  $c = 20.271(4)$  Å,  $\alpha = 74.30(2)$ ,  $\beta = 85.20(2)$ ,  $\gamma = 79.10(2)^\circ$ ,  $U = 2863(3)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 1.868$  g cm<sup>-3</sup>,  $\mu(\text{Mo–K}\alpha) = 48.55$  cm<sup>-1</sup>,  $F(000) = 1556$ ,  $T = 301$  K. 10397 reflections were measured, 9885 were unique ( $R_{\text{int}} = 0.054$ ). 6087 reflections were considered observed and used in the structural analysis.  $w = 4F_o^2/\sigma^2(F_o^2)$ , where  $\sigma^2(F_o^2) = [\sigma^2(I) + (0.030F_o^2)^2]$  for 6087 reflections was reached at  $R = 0.035$  and  $wR = 0.043$  with a goodness-of-fit of 1.34. For **4**:  $[(\text{C}_{60}\text{H}_{46}\text{N}_8\text{O}_6\text{S}_2\text{CdRe}_2)^+ 2\text{PF}_6^-]$ ;  $M_r = 1813.95$ , monoclinic, space group  $P2_1/n$  (no. 13),  $a = 13.691(2)$ ,  $b = 15.663(3)$ ,  $c = 15.551(3)$  Å,  $\beta = 106.34(2)^\circ$ ,  $U = 3200(1)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 1.882$  g cm<sup>-3</sup>,  $\mu(\text{Mo–K}\alpha) = 43.12$  cm<sup>-1</sup>,  $F(000) = 1756$ ,  $T = 301$  K. 6102 unique reflections were obtained from a total of 27436 measured reflections ( $R_{\text{int}} = 0.080$ ). 4914 reflections were considered observed and used in the structural analysis.  $w = 4F_o^2/\sigma^2(F_o^2)$ , where  $\sigma^2(F_o^2) = [\sigma^2(I) + (0.036F_o^2)^2]$  for 4914 reflections was reached at  $R = 0.038$  and  $wR = 0.056$  with a goodness-of-fit of 1.27.

CCDC 182/1738. See <http://www.rsc.org/suppdata/cc/b0/b005092j/> for crystallographic files in .cif format/

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