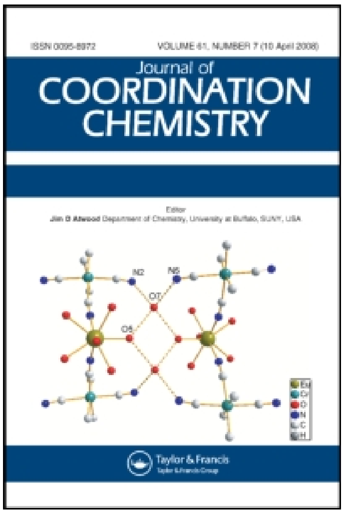

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SYNTHESES, CRYSTAL STRUCTURES AND ELECTRONIC SPECTRA OF MIXED-LIGAND ZINC(II) COMPLEXES WITH DIIMINES AND DITHIOLATES

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SYNTHESES, CRYSTAL STRUCTURES AND ELECTRONIC SPECTRA OF MIXED-LIGAND ZINC(II) COMPLEXES WITH DIIMINES AND DITHIOLATES

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Three zinc(II) complexes, $[Zn(bipy)(dmit)]_2$ (**1**), $[Zn(phen)(dmit)]_2$ (**2**) and Zn(py)(mnt) (**3**), where bipy = 2,2′-bipyridine, phen = 1,10-phenanthroline, py = pyridine, H_2dmit = 4,5-dimercapto-1,3-dithiol-2-thione, mnt = maleonitriledithiolate, have been synthesized and their crystal structures determined. Complex **1** is monoclinic, space group $P2_1/c$, with $a = 11.570(3)$, $b = 9.137(3)$, $c = 15.051(6)$ Å, $\beta = 109.56(2)°$, $Z = 2$ and was refined to $R_1 = 0.039$. Complex **2** is monoclinic, space group $P2_1/n$, with $a = 9.363(2)$, $b = 13.732(3)$, $c = 12.767(3)$, $\beta = 94.06(3)°$, $Z = 2$ and was refined to $R_1 = 0.038$. Complex **3** is orthorhombic, space group $P2_12_12_1$, with $a = 8.621(3)$, $b = 10.546(4)$, $c = 16.848(2)$, $Z = 4$ and was refined to $R_1 = 0.040$. IR and electronic absorption spectra were investigated.

Keywords: Zinc(II); diimine; dithiolate; crystal structure

INTRODUCTION

An interesting class of metal complexes is that containing two different unsaturated chelating ligands in which one is more easily reduced and the other more easily oxidized. An example of this class was described by Matsubayashi *et al.* who synthesized and studied square planar platinum(II) complexes containing a diimine and an unsaturated dithiolate chelating

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* Corresponding author.

ligand.[1] They observed that the complexes exhibited a solvatochromic band in the visible region of their electronic spectra assigned to a ligand-to-ligand $\pi-\pi^*$ charge transfer (LLCT) from the dithiolate to the diimine ligand. Vicente *et al.* have prepared M(dmit)(phen) complexes (M = Pd(II), Pt(II)) and studied their electronic spectra.[4]

Our interest in zinc(II) complexes stems from a desire to understand the origin of the absorption and luminescence properties from molecules with nd^{10} ions coordinated with both electron-withdrawing and electron-donating ligands. In mixed-ligand chelates of closed-shell zinc(II) ions we will be able to demonstrate unequivocally the intramolecular LLCT phenomenon. On the other hand, in mixed-ligand complexes of open-shell metal ions (such as Ni(II), Pd(II) and Pt(II)) there may exist both metal ion transition and LLCT transitions. Some zinc(II) complexes containing diimine and dithiolate ligands, such as $[Zn(bdt)(bpyrm)]_2$, Zn(bdt)(biq) and $[Zn(bdt)(phen)]_2$, have been reported previously.[2,3] Herein we report the syntheses, crystal structures, IR and electronic spectra of three new zinc(II) complexes containing dithiolate (mnt^{2-}, $dmit^{2-}$) and diimine (bipy, phen) ligands.

EXPERIMENTAL

Physical Measurements

Infrared spectra were recorded on a Nicolet 170-SX FT-IR spectrometer and electronic spectra on a Shimadzu UV-3000 spectrometer with *N*,*N*-dimethylformamide as solvent. Elemental analyses were carried out on a Perkin-Elmer 240C instrument. Na_2mnt was prepared as described in the literature.[4b]

$[Zn(bipy)(dmit)]_2$ (1)

$(NBu_4)_2Zn(dmit)_2$ (0.5 g, 0.5 mmol) was dissolved in dichloromethane (15 cm^3) and mixed with a solution of $Zn(NO_3)_2 \cdot 6H_2O$ (0.15 g, 0.5 mmol) in methanol (10 cm^3). With stirring, 2,2′-bipyridine (0.156 g, 1 mmol) in methanol (10 cm^3) was added dropwise to the mixture, affording a red precipitate, which was then filtered off and dried. The product was redissolved in *N*,*N*-dimethylformamide and single crystals were obtained after slow diffusion of ether into the solution. Yield 0.26 g, 62%. *Anal.* Calcd. for $C_{26}H_{16}N_4S_{10}Zn_2$ (%): C, 37.33; H, 1.91; N, 6.70. Found: C, 36.89; H, 2.10; N, 6.54. Medium-IR (KBr pellet, cm^{-1}): 1593s, 1471s, 1441s, 1429vs, 1315m, 1157m, 1061s, 1030vs, 1018vs, 891m, 766s; Far-IR (CsI pellet, cm^{-1}): 467s, 351w, 326m, 287s, 235s.

$[Zn(phen)(dmit)]_2$ (2)

Complex **2** was prepared in a manner similar to the procedure described above except for using 1,10-phenanthroline instead of 2,2′-bipyridine. Yield 0.33 g, 72%. *Anal.* Calcd. for $C_{30}H_{16}N_4S_{10}Zn_2$ (%): C, 40.73; H, 1.81; N, 6.34. Found: C, 40.29; H, 1.65; N, 6.42. Medium-IR (KBr pellet, cm^{-1}): 1585m, 1518s, 1435sh, 1427vs, 1051vs, 1034vs, 889m, 839s, 723s. Far-IR (CsI pellet, cm^{-1}): 465m, 351w, 328m, 291s, 243m.

[Zn(py)(mnt) (3)

$Zn(NO_3)_2 \cdot 6H_2O$ (0.15 g, 0.5 mmol) was dissolved in methanol (10 cm^3) and added dropwise to a solution of Na_2mnt (0.09 g, 0.5 mmol) in methanol (5 cm^3) with stirring. The resulting light yellow solution was treated with two drops of pyridine and stirred for a further 2 h, then filtered. Crystals of **3** were produced when the solvent was reduced. *Anal.* Calcd. for $C_{14}H_{10}N_4S_2Zn$ (%): C, 46.2; H, 2.7; N, 15.4. Found: C, 45.6; H, 2.9; N, 15.7. Medium-IR (KBr pellet, cm^{-1}): 2199vs, 1606s, 1487m, 1448vs, 1217s, 1151s, 1120s, 1068s, 1041s, 756s, 696vs; Far-IR (CsI pellet, cm^{-1}): 515s, 341m, 309w, 282m, 233s.

X-ray Crystallography

Diffraction data for complex **1** were collected on a Siemens Smart/CCD area-detector diffractometer with graphite-monochromated Mo*Kα* ($\lambda = 0.71073$ Å) radiation using an ω scan mode in the range $1.87° < \theta < 25°$. Data reduction and cell refinement were performed with Smart-CCD software.[5a] An absorption correction using the SADABS method[5a] was applied. Diffraction data for complexes **2** and **3** were collected on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo*Kα* radiation ($\lambda = 0.71073$ Å) using an $\omega/2\theta$ scan mode in the range $2.18° < \theta < 26°$ for **2** and $2.30° < \theta < 27°$ for **3**, respectively. Intensities were corrected for *L*p factors and empirical absorption based on the ψ scan technique.[6a] Crystal data and details of data collection are given in Table I. The crystal structures were solved by direct methods and successive Fourier syntheses, and refined by full-matrix least-squares procedures with anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms were generated geometrically. The calculations for compound **1** and **2** were performed on a PC

TABLE I Summary of crystallographic data for complexes **1–3**

	1	**2**	**3**
Formula	$C_{26}H_{16}N_4S_{10}Zn_2$	$C_{30}H_{16}N_4S_{10}Zn_2$	$C_{14}H_{10}N_4S_2Zn$
M	835.76	883.8	363.76
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$P2_1/n$	$P2_12_12_1$
a (Å)	11.570(3)	9.363(2)	8.621(3)
b (Å)	9.137(3)	13.732(3)	10.546(4)
c (Å)	15.051(6)	12.767(3)	16.848(2)
α, β, γ (°)	$\beta = 109.56(2)$	$\beta = 94.06(3)$	$\alpha = \beta = \gamma = 90$
V (Å^3)	1499.3(9)	1637.4(6)	1531.7(71)
Z	2	2	4
F(000)	840	888	736
D_{calc} (g cm^{-3})	1.851	1.793	1.58
Crystal size (mm)	0.40 × 0.25 × 0.10	0.25 × 0.20 × 0.12	0.80 × 0.20 × 0.20
Radiation Mo*Kα* (Å)	0.71073	0.71073	0.71073
Temperature (K)	293	293	293
Scan mode	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
Range of *h*, *k*, *l*	$-13 \sim 13, -10 \sim 10, -17 \sim 13$	$-11 \sim 11, 0 \sim 16, 0 \sim 15$	$0 \sim 11, 0 \sim 13, 0 \sim 21$
θ_{max} (°)	25	26	27
Reflections measured	7130	3345	1939
Independent reflections	2628	3206	1939
Observed reflections	1927	2525	1511
Criterion of observing	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
Parameters refined	190	209	191
Absp. Coeff. (mm^{-1})	2.325	2.134	1.90
T_{min} and T_{max}	0.57, 1.00	0.74, 1.00	0.867, 0.999
Goodness of fit	0.967	1.007	1.00
R_1[a]	0.039	0.038	0.040
wR_2	0.090[b]	0.087[b]	0.046[c]
Largest residual (eÅ^3)	0.708, −0.463	0.542, −0.331	0.63, −0.16

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

[b] $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (0.044P)^2)]$ for **1** and $w = 1/[\sigma^2(F_o^2) + (0.052P)^2]$ for **2**, $P = (F_o^2 + 2F_c^2)/3$.

[c] $wR_2 = [\sum[w(F_o - F_c)^2]/\sum[w(F_o)^2]]^{1/2}$ where $w = 1/[\sigma^2(F)]$.

586 computer using the *SHELXTL-PC* program package[5b,5c] with scattering factors taken from *International Tables for Crystallography* (*Vol. C*), and for **3** using the *MolEN* program package.[6b]

RESULTS AND DISCUSSION

Description of Structures

Selected bond lengths and angles for complexes **1–3** are listed in Tables II–IV, respectively. Complex **1** consists of discrete dinuclear molecules (Figure 1) having a crystallographic inversion centre. There are no unusual intermolecular interactions. It is evident that one of the S atoms

TABLE II Selected bond distances (Å) and angles (°) for complex **1**

Zn-N1	2.114(3)	S4-C13	1.720(4)
Zn-N2	2.174(3)	S4-C12	1.752(4)
Zn-S2	2.3396(13)	S5-C13	1.661(4)
Zn-S1*	2.4861(13)	N1-C1	1.325(5)
Zn-S1	2.5023(13)	N1-C5	1.351(5)
S1-C11	1.750(4)	N2-C10	1.326(5)
S2-C12	1.740(4)	N2-C6	1.348(5)
S3-C13	1.710(4)	C1-C2	1.376(6)
C11-C12	1.340(5)	S3-C11	1.746(4)
N1-Zn-N2	76.16(13)	S2-Zn-S1*	106.97(5)
N1-Zn-S2	154.65(9)	N1-Zn-S1	94.01(10)
N2-Zn-S2	93.60(9)	N2-Zn-S1	166.00(10)
N1-Zn-S1*	97.20(9)	S2-Zn-S1	91.29(4)
N2-Zn-S1	95.73(9)	S1*-Zn-S1	95.38(4)

Symmetry code *: $-x+1, -y, -z$.

TABLE III Selected bond distances (Å) and angles (°) for complex **2**

Zn-N1	2.127(3)	S3-C13	1.745(3)
Zn-N2	2.169(3)	S4-C15	1.709(4)
Zn-S2	2.3357(11)	S4-C14	1.747(3)
Zn-S1*	2.4555(11)	S5-C15	1.651(4)
Zn-S1	2.5375(10)	N1-C1	1.321(4)
S1-C13	1.750(3)	N1-C12	1.354(4)
S2-C14	1.729(3)	N2-C10	1.319(4)
S3-C15	1.730(4)	N2-C11	1.350(4)
C13-C14	1.345(5)	C11-C12	1.427(5)
N1-Zn-N2	77.24(10)	S2-Zn-S1*	108.03(5)
N1-Zn-S2	151.38(8)	N1-Zn-S1	93.06(8)
N2-Zn-S2	92.20(8)	N2-Zn-S1	162.26(8)
N1-Zn-S1*	100.08(8)	S2-Zn-S1	89.44(3)
N2-Zn-S1*	100.50(8)	S1*-Zn-S1	95.76(3)

Symmetry code *: $-x, -y+1, -z$.

TABLE IV Selected bond distances (Å) and angles (°) for complex **3**

Zn-S1	2.315(2)	C4-N2	1.149(8)
Zn-S2	2.280(2)	N4-C21	1.333(8)
Zn-N3	2.031(4)	N4-C25	1.335(8)
Zn-N4	2.056(5)	C1-C2	1.357(8)
S1-C1	1.742(6)	C12-C11	1.381(8)
S2-C2	1.734(6)	C14-C13	1.37(1)
N3-C11	1.340(7)	C14-C15	1.370(8)
N3-C15	1.328(7)	C3-N1	1.128(8)
C1-C3	1.438(8)	C4-C2	1.426(8)
S1-Zn-S2	95.76(6)	N3-Zn-N4	96.6(2)
S1-Zn-N3	108.9(1)	Zn-S1-C1	95.5(2)
S1-Zn-N4	108.8(1)	Zn-S2-C2	96.4(2)
S2-Zn-N3	128.7(1)	S1-C1-C2	126.1(4)
S2-Zn-N4	117.3(1)	C1-C3-N1	178.2(6)
C2-C4-N2	179.1(6)		

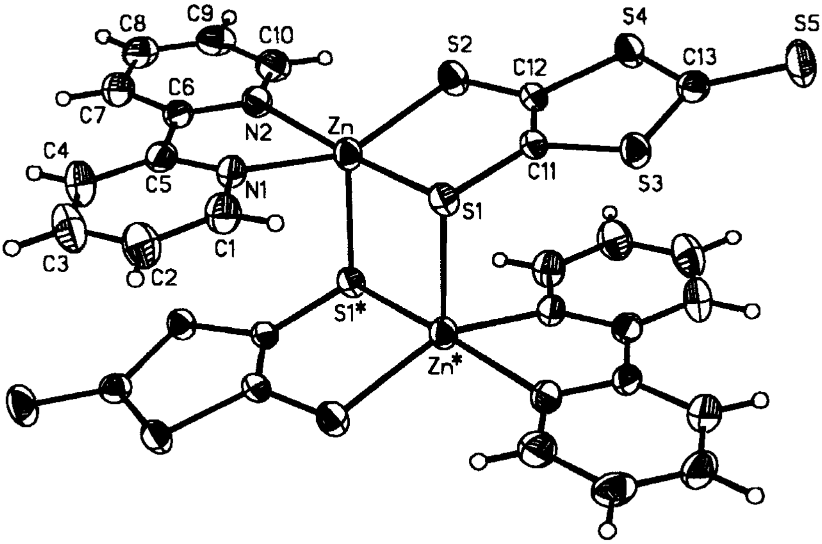

FIGURE 1 Molecular structure and atom labelling scheme for complex **1**. Displacement ellipsoids are shown at 50% probability levels.

of the dmit ligand (S1) functions as a bridge between the two Zn atoms. The zinc atoms adopt a distorted square pyramidal geometry. The central Zn_2S_2 moiety is strictly coplanar as required by the symmetry and comprises two different Zn–S distances, with one bond within the chelate ring (Zn–S1 2.502(2) Å) being longer than the other (Zn*–S1 2.486(2) Å). This feature has been noted in other dinuclear Zn(II) complexes containing bridging dithiolate ligands.[2] The Zn–S2 bond distance (2.340(2) Å) is shorter than the Zn–S distances involving bridging S atoms (Zn–S1, Zn–S1*) and is close to the mean Zn–S bond distance of 2.338(2) Å observed in $(NBu_4)_2Zn(dmit)_2$.[7] Zinc–nitrogen bond lengths are 2.114(3) and 2.174(3) Å for Zn–N1 and Zn–N2, respectively. The Zn···Zn* separation is 3.357(3) Å indicating there is no metal–metal interaction. The 2,2′-bipyridine ligand is slightly distorted with a dihedral angle of 6.7° between the two pyridyl rings.

The crystal structure of **2** (Figure 2) is very similar to that of **1** except for 2,2′-bipyridine being replaced by 1,10-phenanthroline. The dihedral angle between the coordinated phenanthroline and dmit ligand is 15.4°. The Zn···Zn* separation of 3.349(5) Å is slightly shorter than that observed in **1**.

The crystal structure of **3** is shown in Figure 3. The zinc atom is chelated by two sulfur atoms from the mnt^{2-} ligand and two pyridine nitrogen atoms. The coordination environment around the zinc atom can be described as a distorted tetrahedron. The dihedral angle between the planes defined by atoms N3–Zn–N4 and by S1–Zn–S2 is 86.7°. The Zn–S1 and

Zn–S2 bond distances are 2.315(2) and 2.280(2) Å, respectively, nearing the mean values (2.33 Å) observed in $(AsPh_4)_2Zn(mnt)_2$.[8] The bond lengths Zn–N3 and Zn–N4 are 2.031(4) and 2.056(5) Å, respectively, a little shorter than in complexes **1** and **2**. The dihedral angle between the two coordinated

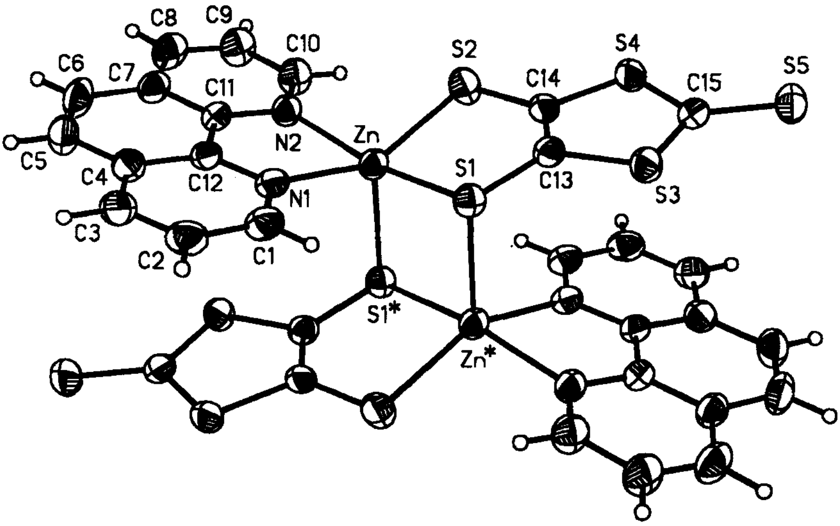

FIGURE 2 Molecular structure and atom labelling scheme for complex **2**. Displacement ellipsoids are shown at 50% probability levels.

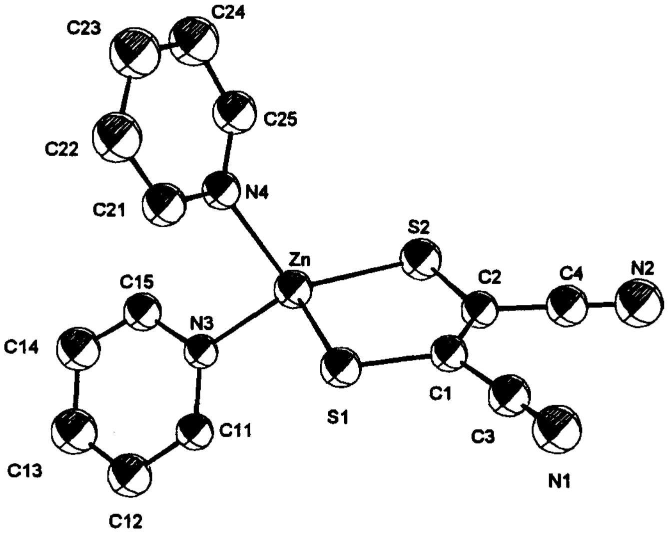

FIGURE 3 Molecular structure and atom labelling scheme for complex **3**. Displacement ellipsoids are shown at 50% probability levels. Hydrogen atoms have been omitted for clarity.

pyridine ligands is 79.1°. The bond angle S1–Zn–S2 in **3** is 95.76(6)°, being larger than those of 91.29(4)° in **1** and 89.44(3)° in **2**.

Infrared Spectra

IR absorption bands at 1471, 1030(1018), 891 cm^{-1} found in complex **1** can be assigned to $\nu_{C=C}$, $\nu_{C=S}$ and ν_{C-S} of the dmit ligand. The band at 1593 cm^{-1} can be assigned to $\nu_{C=C}$ of the bipyridine ligand. For complex **2**, IR bands at 1435, 1051(1034), 889 cm^{-1} are attributed to $\nu_{C=C}$, $\nu_{C=S}$ and ν_{C-S} of dmit, respectively. The most identifiable IR absorptions for complex **3** are 2199 cm^{-1}, assigned to $\nu_{C\equiv N}$ of mnt, and 1606 cm^{-1}, assigned to $\nu_{C=C}$ of pyridine.

The ν_{Zn-N} bands are usually found in the far-IR region. The identified bands are 351 and 326 cm^{-1} for complex **1**; 351 and 328 cm^{-1} for **2**; 341 and 309 cm^{-1} for **3**. The ν_{Zn-S} bands also appear in the far-IR region and have lower frequencies than ν_{Zn-S} bands. These bands are at 287 and 235 cm^{-1} for **1**; 291 and 243 cm^{-1} for **2**; 283 and 233 cm^{-1} for **3**. Corresponding bands in $Zn_2(i\text{-}mnt)_2(4\text{-}mpy)_4 \cdot CHCl_3$ are reported at 356 and 309 cm^{-1} for ν_{Zn-N} and 277 and 234 cm^{-1} for ν_{Zn-S}.[10]

Electronic Absorption Spectra

The electronic absorption bands measured in *N*,*N*-dimethylformamide solution in the range 200–900 nm are at 282, 305sh and 490 nm for **1**; 290, 310sh and 502 nm for **2**; 272, 350sh, 365sh, and 380 nm for **3**. For complex **1**, the intense band at 282 nm is assigned to the π–π^* transition of the bipyridine ligand. The shoulder at 305 nm and the band at 490 nm are assigned to the dmit ligand transition.[1,9] For complex **2** these bands are similar, except for a small red-shift. For complex **3**, the absorption band at 272 nm can be assigned to the π–π^* transition of pyridine, overlapped with the mnt ligand transition. Shoulders at 350, 365 nm and the band at 380 nm are assigned to the mnt ligand.[9]

There are no absorption bands in the range 200–900 nm that could be clearly identified as LLCT transitions for complexes **1**–**3**. The LLCT energy depends on the overall electronic structure of the mixed-ligand chelate. The overall electronic structure is in turn determined by the electronic configuration and oxidation state of the metal ion, the types of ligands, the coordination number, and the molecular structure of the complex. The energies and intensities of the LLCT transitions can be adjusted, with appropriate mixed-ligand, metal ion, and solvent combinations.[11a] The intensities of LLCT transitions are usually much less than the localized π–π^* transitions of the coordinated ligands, especially in cases where the planes of the aromatic π-systems are perpendicular, and the LLCT bands often appear at somewhat longer wavelength than the absorption bands (the one at longer wave length, for example 490 nm in **1**, 502 nm in **2** and 380 nm in **3**) of the dithiolate ligands.[11] For complexes **1–3**, the LLCT transition bands may be very weak and obscured by the much more intense, broad absorption bands of the dithiolate ligands thus could not be separately elucidated.

Acknowledgments

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Supplementary Material

Crystallographic data for the structures **1–3** have been deposited with the Cambridge Crystallographic Data Center (CCDC). The assignments of CCDC codes are CCDC 115996–CCDC 115998 for complexes **1–3**, respectively.

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