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# Functionalized Rhenium(I) Complexes with Crown Ether Pendants Derived from 1,10-Phenanthroline: Selective Sensing for Metal Ions

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A series of rhenium(I) tricarbonyl diimine complexes with crown ether pendants has been synthesized and characterized. The complexes showed selective and specific binding properties for various metal ions of different sizes and degrees of hardness and softness by variation of the cavity size and donor atoms of the crown ether. Upon binding of metal ions, obvious spectral changes were observed in the UV−vis spectra of the complexes and the emission intensity was found to be strongly enhanced. The X-ray crystal structure of one of the complexes has also been determined.

## Introduction

Since the pioneering works of Wrighton in the mid-1970s,[1] the rhenium(I) tricarbonyl diimine system has attracted much research interest because of its versatile photophysical and photochemical properties such as low-lying metal-to-ligand charge transfer (MLCT) excited states, relatively long radiative lifetimes, intense luminescence in the visible region of the spectrum, and thermal, chemical, and photochemical stabilities. Recently, there has been increasing attention on the design of luminescent chemosensors based on various transition metal complexes that show MLCT excited-state properties, including those of ruthenium(II),[2] rhenium(I),[3] iridium(III),[4] copper(I),[5] platinum(II),[6] and others, as they could provide an easy spectrochemical and luminescence handle for the selective and specific monitoring of substrates binding. Despite considerable work carried out on the development of transition metal complexes as chemosensors, most of the works have been focused on the design of selective receptors for either alkali or alkaline earth cations, with relatively less attention on the incorporation of soft donor atoms such as S and Se into the crown units to tune their complexation ability for the transition-metal ions.

Our previous works in the utilization of transition-metal complexes containing crown ether pendants with the oxygen atoms in the crown ether ligands replaced by softer atoms such as nitrogen, sulfur, or selenium to serve as chemosensors, which showed specific binding to transition metal ions such as $Ag^+$ or $Hg^{2+}$ ions,[5a,7] have prompted us to design and explore other related complexes for the specific sensing of other transition-metal ions such as $Pb^{2+}$ ions. Herein we report the synthesis, structure, photophysics, electrochemistry, and ion-binding studies of a series of Re(I) diimine complexes with appended crown ether ligands derived from 1,10-phenanthroline with either one or more of the oxygen donor atoms replaced by softer donor atoms such as sulfur and selenium (Chart 1). Variation of the cavity size of the crown ethers has also been performed to achieve different complexation ability. Selective sensing of $Hg^{2+}$ ions and $Pb^{2+}$ ions have been demonstrated in some of the complexes, in which the luminescence of the complexes was found to be strongly enhanced upon metal ion-binding, and their binding constants were determined by both UV−vis and luminescence spectroscopy.

## Experimental

Rhenium(I) pentacarbonyl chloride (Strem), silver trifluoromethanesulfonate (99%, Aldrich) and ammonium hexafluoro-

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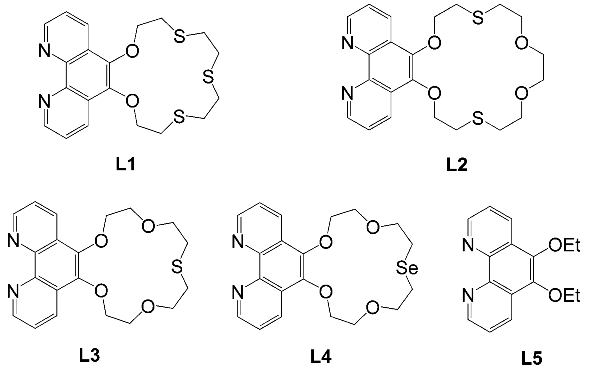
**Chart 1**



$[Re(CO)_3(L)(py)]^+$

L = L1 **1**
L = L2 **2**
L = L3 **3**
L = L4 **4**
L = L5 **5**

phospate (Strem) for synthesis were used without purification. Tetra-*n*-butylammonium perchlorate, mercury(II) perchlorate hydrate, silver(I) perchlorate, and lead(II) perchlorate hydrate were purchased from Aldrich Chemical Co. with purity over 99.0%. The ligands **L1**−**L5** were prepared according to the procedures reported previously.[7b] $Re(CO)_5(OTf)$ was prepared according to the literature procedures.[8] $[Re(CO)_5(py)]OTf$ was synthesized by modification of the literature method.[9]

Safety Note. Caution! Metal perchlorate salts are potentially explosive. Only small amounts of these materials should be handled and with great caution.

**Synthesis.** Rhenium(I) 1,10-phenanthroline complexes containing crown ether pendants were prepared by modification of a literature procedure.[9] The ligand (0.27 mmol) was dissolved in dry THF (5 mL) under $N_2$, and the solution was heated to reflux. To the solution was added dropwise a solution of $[Re(CO)_5(py)]OTf$ (100 mg, 0.18 mmol) in dry THF (10 mL) over 1 h. The mixture was heated to reflux for an additional 3 h, cooled to room temperature, and evaporated to dryness. The mixture was purified by column chromatography on alumina (neutral) using $CH_3CN$−toluene (1:2 v/v) as eluent to give the desired product as the second band. After column chromatography on alumina and subsequent removal of solvent, the residue was dissolved in a minimum amount of water, and metathesis reaction afforded the desired complex as the $PF_6^-$ salt upon addition of a saturated aqueous solution of $NH_4PF_6$. The complex was collected by filtration. Subsequent recrystallization by vapor diffusion of diethyl ether into an acetonitrile solution of the complex afforded the desired complex as yellow crystals.

**$[Re(CO)_3(py)(L1)]PF_6$ (1).** Yield: 49 mg, 30%. $^1H$ NMR ($d_6$-acetone): $\delta$ 9.71 (dd, $J$ = 5.0, 1.3 Hz, 2H, phen), 9.13 (dd, $J$ = 8.5, 1.3 Hz, 2H, phen), 8.49 (d, $J$ = 6.5 Hz, 2H, py), 8.20 (dd, $J$ = 8.5, 5.1 Hz, 2H, phen), 7.79 (t, $J$ = 7.7 Hz, 1H, py), 7.26 (t, $J$ = 6.5 Hz, 2H, py), 4.41 (m, 4H, $CH_2O$), 3.05 (t, $J$ = 7.0 Hz, 4H, $CH_2S$), 2.85 (m, 4H, $CH_2S$), 2.74 (m, 4H, $CH_2S$). Positive FAB-MS: $m/z$ 768 ($[M - PF_6]^+$). Anal. Found (%): C, 36.50; H, 3.14; N, 4.69. Calcd for $C_{28}H_{27}F_6N_3O_5PReS_3{\cdot}0.5H_2O$: C, 36.48; H, 3.06; N, 4.56.

**$[Re(CO)_3(py)(L2)]PF_6$ (2).** Yield: 70 mg, 41%. $^1H$ NMR ($d_6$-acetone): $\delta$ 9.71 (dd, $J$ = 5.1, 1.2 Hz, 2H, phen), 9.08 (dd, $J$ = 8.5, 1.2 Hz, 2H, phen), 8.48 (d, $J$ = 6.5 Hz, 2H, py), 8.19 (dd, $J$ = 8.5, 5.1 Hz, 2H, phen), 7.80 (t, $J$ = 7.6 Hz, 1H, py), 7.26 (t, $J$ = 6.5 Hz, 2H, py), 4.45 (m, 4H, $CH_2O$), 3.62 (t, $J$ = 5.8 Hz, 4H, $CH_2O$), 3.52 (s, 4H, $CH_2O$), 3.11 (t, $J$ = 6.6 Hz, 4H, $CH_2S$), 2.74-(t, $J$ = 5.8 Hz, 4H, $CH_2S$). Positive FAB-MS: $m/z$ 796 ($[M - PF_6]^+$). Anal. Found (%): C, 38.28; H, 3.40; N, 4.94. Calcd for $C_{30}H_{31}F_6N_3O_7PReS_2$: C, 38.30; H, 3.32; N, 4.47.

**$[Re(CO)_3(py)(L3)]PF_6$ (3).** Yield: 64 mg, 40%. $^1H$ NMR ($CDCl_3$): $\delta$ 9.37 (dd, $J$ = 5.1, 1.3 Hz, 2H, phen), 8.97 (dd, $J$= 8.5, 1.3 Hz, 2H, phen), 8.17 (d, $J$ = 6.4 Hz, 2H, py), 8.05 (dd, $J$ = 8.5, 5.1 Hz, 2H, phen), 7.72 (t, $J$ = 7.6 Hz, 1H, py), 7.34 (t, $J$ = 6.4 Hz, 2H, py), 4.52 (m, 4H, $CH_2O$), 3.99 (m, 4H, $CH_2O$), 3.93 (m, 4H, $CH_2O$), 2.91(t, $J$ = 6.2 Hz, 4H, $CH_2S$). Positive FAB-MS: $m/z$ 736 ($[M - PF_6]^+$). Anal. Found (%): C, 38.63; H, 3.19; N, 4.90. Calcd for $C_{28}H_{27}F_6N_3O_7PReS{\cdot}0.25CH_3CN$: C, 38.42; H, 3.14; N, 5.15.

**$[Re(CO)_3(py)(L4)]PF_6$ (4).** Yield: 75 mg, 45%. $^1H$ NMR ($CD_3CN$): $\delta$ 9.52 (dd, $J$ = 5.2, 1.2 Hz, 2H, phen), 8.97 (dd, $J$ = 8.4, 1.2 Hz, 2H, phen), 8.28 (d, $J$ = 6.4 Hz, 2H, py), 8.07 (dd, $J$ = 8.4, 5.2 Hz, 2H, phen), 7.77 (t, $J$ = 8.0 Hz, 1H, py), 7.22 (t, $J$ = 6.4 Hz, 2H, py), 4.39 (m, 4H, $CH_2O$), 3.96 (m, 8H, $CH_2O$), 2.89 (t, $J$ = 6.5 Hz, 4H, $CH_2Se$). Positive FAB-MS: $m/z$ 782 ($[M - PF_6]^+$). Anal. Found (%): C, 36.62; H, 3.10; N, 5.07. Calcd for $C_{28}H_{27}F_6N_3O_7PReSe{\cdot}0.5CH_3CN$: C, 36.73; H, 3.03; N, 5.17.

**$[Re(CO)_3(py)(L5)]PF_6$ (5).** Yield: 60 mg, 44%. $^1H$ NMR ($CDCl_3$): $\delta$ 9.40 (dd, $J$ = 5.1, 1.2 Hz, 2H, phen), 8.96 (dd, $J$ = 8.4, 1.2 Hz, 2H, phen), 8.24 (d, $J$ = 6.5 Hz, 2H, py), 8.07 (dd, $J$ = 8.4, 5.1 Hz, 2H, phen), 7.71 (t, $J$ = 7.6 Hz, 1H, py), 7.34 (t, $J$ = 6.5 Hz, 2H, py), 4.44 (m, 4H, $CH_2O$), 1.52 (m, 6H, $CH_3$). Positive FAB-MS: $m/z$ 619 ($[M - PF_6]^+$). Anal. Found (%): C, 37.51; H, 2.84; N, 5.67. Calcd for $C_{24}H_{21}F_6N_3O_5PRe$: C, 37.80; H, 2.78; N, 5.51.

**Physical Measurments and Instrumentation.** Electronic absorption spectra were recorded on a Hewlett-Packard 8452A diode array spectrophotometer. Steady-state emission and excitation spectra at room temperature and 77 K were recorded on a Spex Fluorolog-2 model F111 fluorescence spectrophotometer. Solid-state photophysical measurements were carried out with solid samples contained in a quartz tube inside a quartz-walled Dewar flask. Measurements of the EtOH−MeOH (4:1 v/v) glass or solid-state samples at 77 K were similarly conducted with liquid nitrogen filled in the optical Dewar flask. Luminescence quantum yield was measured by the optically dilute method reported by Demas and Crosby.[10] A degassed solution of $[Ru(bpy)_3]^{2+}$ in acetonitrile ($\phi_{em}$ = 0.062, excitation wavelength at 436 nm) was used as the reference.[11] Emission lifetime measurements were performed using a conventional nanosecond pulsed laser system. The excitation source used was the 355-nm output (third harmonic, 8 ns) from a Spectra-Physics Quanta-Ray Q-switched GCR-150−10 pulsed Nd:YAG laser (10 Hz). Luminescence decay signals were detected by a Hamamatsu R928 photomultiplier tube and recorded on a Tektronix model TDS-620A (500 MHz, 2 GS/s) digital oscilloscope. All solution samples for luminescence lifetime and quantum yield studies were degassed with no fewer than four successive freeze−pump−thaw cycles.

$^1H$ NMR spectra were recorded on a Bruker DPX-300 or Bruker DPX-400 Fourier Transform NMR spectrometer with chemical shifts reported relative to tetramethylsilane. Positive-ion FAB and

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EI mass spectra were recorded on a Finnigan MAT95 mass spectrometer. Positive ion electrospray ionization (ESI) mass spectra were recorded on a Finnigan LCQ spectrometer. Elemental analysis of the complexes was performed on a Carlo Erba 1106 elemental analyzer at the Institute of Chemistry of the Chinese Academy of Sciences in Beijing.

Cyclic voltammetric measurements were performed by using a CH Instruments, Inc. CHI 620 electrochemical analyzer. A Ag−$AgNO_3$ (0.1 M in $CH_3CN$) reference electrode was used. The working electrode was a 2-mm-diameter glassy carbon (CH Instruments, Inc.) with a platinum wire acting as the counter electrode. The ferrocenium−ferrocene couple was used as the internal reference for the electrochemical measurements in acetonitrile (0.1 M $^n\mathrm{Bu_4NClO_4}$).

**Stability Constant Determination.** The electronic absorption spectral titration was performed on a Hewlett-Packard 8452A diode array spectrophotometer at room temperature, while the emission titration was performed on a Spex Fluorolog-2 model F111 spectrofluorometer. Supporting electrolyte (0.1 M $^n\mathrm{Bu_4NClO_4}$) was added to maintain a constant ionic strength of the sample solution. Binding constants for 1:1 complexation were obtained by a nonlinear least-squares fit[12] of the absorbance ($A$) or emission intensity versus the concentration of the metal ion added ($c_M$) according to the following equation:

$$A = A_o + \frac{A_{lim} - A_o}{2c_o}[c_o + c_M + 1/K_s - [(c_o + c_M + 1/K_s)^2 - 4c_oc_M]^{1/2}] \quad (1)$$

where $A_o$ and $A$ are the absorbance of the complex at a selected wavelength in the absence and presence of the metal cation, respectively, $c_o$ is the total concentration of the crown ether-containing rhenium(I) complex, $c_M$ is the concentration of the added metal cation, $A_{lim}$ is the limiting value of absorbance at saturation level, and $K_s$ is the stability constant. For emission titration studies, eq 1 can be modified to give eq 2, written as

$$I = I_o + \frac{I_{lim} - I_o}{2c_o}[c_o + c_M + 1/K_s - [(c_o + c_M + 1/K_s)^2 - 4c_oc_M]^{1/2}] \quad (2)$$

where $I_o$ and $I$ are the emission intensity of the complex at a selected wavelength in the absence and presence of the metal cation, respectively, and $I_{lim}$ is the limiting value of emission intensity at saturation level. For systems involving complexation of complex with metal ion in both 1:1 and 2:1 complexation stoichiometry, the binding constants $K_1$ and $K_2$ were determined by the following equations.

$$\mathrm{M} + \mathrm{C} \overset{K_1}{\rightleftharpoons} \mathrm{C(M)}$$

$$\mathrm{C(M)} + \mathrm{C} \overset{K_2}{\rightleftharpoons} \mathrm{C_2(M)}$$

$$K_1 = \frac{[\mathrm{C(M)}]}{[\mathrm{C}][\mathrm{M}]}$$

$$K_2 = \frac{[\mathrm{C_2(M)}]}{[\mathrm{C(M)}][\mathrm{C}]}$$

$$c_o = [\mathrm{C}] + [\mathrm{C(M)}] + 2[\mathrm{C_2(M)}]$$

$$c_M = [\mathrm{M}] + [\mathrm{C(M)}] + [\mathrm{C_2(M)}]$$

$$c_M = [\mathrm{M}] + K_1[\mathrm{C}][\mathrm{M}] + K_1K_2[\mathrm{M}][\mathrm{C}]^2$$

$$[\mathrm{M}] = \frac{c_M}{1 + K_1[\mathrm{C}] + K_1K_2[\mathrm{C}]^2}$$

$$c_o = [\mathrm{C}] + K_1[\mathrm{M}][\mathrm{C}] + 2K_1K_2[\mathrm{M}][\mathrm{C}]^2$$

$$c_o = [\mathrm{C}] + \frac{K_1[\mathrm{C}]c_M}{1 + K_1[\mathrm{C}] + K_1K_2[\mathrm{C}]^2} + \frac{2K_1K_2[\mathrm{C}]^2c_M}{1 + K_1[\mathrm{C}] + K_1K_2[\mathrm{C}]^2}$$

$$K_1K_2[\mathrm{C}]^3 + (2K_1K_2c_M - K_1K_2c_o + K_1)[\mathrm{C}]^2 + (K_1c_M - c_oK_1 + 1)[\mathrm{C}] - c_o = 0$$

$$A = \frac{A_{lim}}{c_o}[\mathrm{C}] + \frac{A_{lim}}{c_o}[\mathrm{C(M)}] + \frac{2A_{lim}}{c_o}[\mathrm{C_2(M)}]$$

(assumption: $\epsilon_{C2(M)} = 2\epsilon_{C(M)}$)

$$A = A_{lim} + (A_o - A_{lim})\frac{[\mathrm{C}]}{c_o} \quad (3)$$

where [C] is the concentration of the complex in the unbound state, [M] is the concentration of metal ion in the unbound state, [C(M)] and [$C_2$(M)] are the concentrations of the 1:1 and 2:1 ion-bound adducts, respectively, and $K_1$ and $K_2$ are the stability constants for 1:1 and 2:1 complexation, assuming that the extinction coefficient of $C_2$(M) is twice that of C(M).

**X-ray Crystallography.** A yellow crystal of complex **1** with dimensions of 0.4 mm × 0.3 mm × 0.15 mm mounted in a glass capillary was used for data collection at −20 °C 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 2° oscillation step of $\varphi$, 7 min exposure time, and scanner distance at 120 mm. A total of 100 images were collected and interpreted, and intensities were integrated using program DENZO.[13] The structure was solved by direct methods employing SHELXS-97 program[14] on a PC. Re and many non-hydrogen atoms were located according to the direct methods. The positions of the other non-hydrogen atoms were found after successful refinement by full-matrix least-squares using program SHELXL-97[15] on PC. The positions of H atoms were calculated on the basis of the riding mode with thermal parameters equal to 1.2 times that of the associated C atoms and participated in the calculation of final $R$-indices. One crystallographic asymmetric unit consisted of two formula units, including two hexafluorophosphate anions, three acetonitrile molecules, and half a molecule of water, with one of the $PF_6^-$ disordered by rotation around the P atom.

Crystal data for **1**: $C_{28}H_{27}F_6N_3O_5PReS_3 \cdot 1.5CH_3CN \cdot 0.25H_2O$, $M_r$ = 978.96, triclinic, space group $P\bar{1}$ (No. 2), $a$ = 13.551(3) Å, $b$ = 15.774(3) Å, $c$ = 20.193(4) Å, α = 94.07(3)°, $\beta$ = 93.67(3)°, $\gamma$ = 114.56(3)°, $V$ = 3895.1(13) Å$^3$, $Z$ = 4, $D_c$ = 1.669 g cm$^{-3}$, $\mu$(Mo Kα) = 3.394 mm$^{-1}$, $F$(000) = 1936, $T$ = 253 K, 17819 reflections measured, 10998 unique ($R_{int}$ = 0.0494) reflections of which 7085

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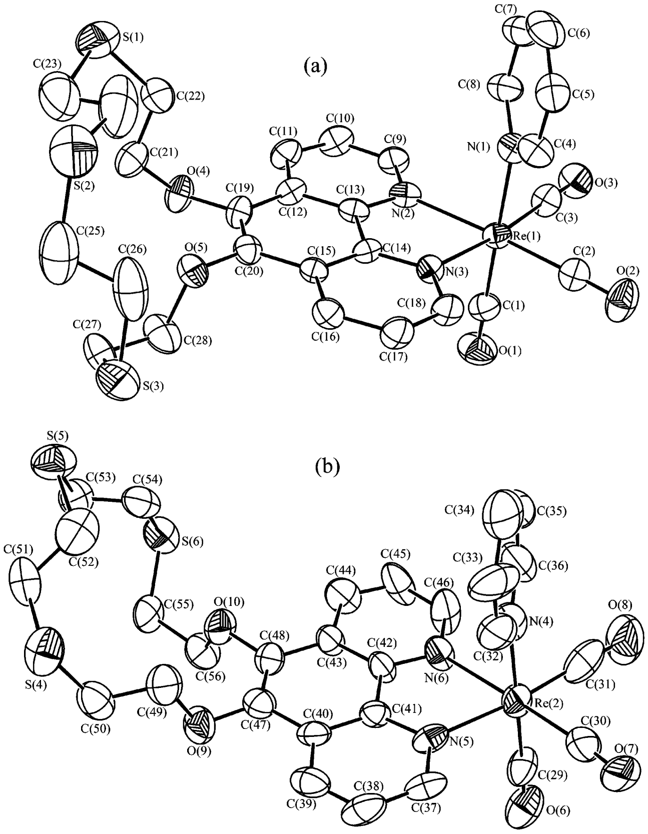

**Figure 1.** Perspective drawings of the two independent complex cations of **1** with atomic numbering. Hydrogen atoms and solvent molecules have been omitted for clarity. Thermal ellipsoids are shown at 30% probability level.

$[I > 2\sigma(I)]$ reflections were used for refinement with $R_1 = 0.0606$ and $wR_2 = 0.1595$ with a goodness-of-fit of 0.963.

## Results and Discussion

**Crystal Structure Determination.** Single crystals of **1** were obtained by vapor diffusion of diethyl ether into a concentrated acetonitrile solution of the complex. A perspective drawing of **1** is depicted in Figure 1 and the selected bond distances and angles are listed in Table 1. There are two independent formula units for complex **1** in one crystallographic asymmetric unit, which are different in configuration. The structure of **1** shows a distorted octahedral geometry with three carbonyl ligands in a facial arrangement, which is commonly observed in other related rhenium(I) tricarbonyl diimine complexes.[3g,16] The bond distances of Re−C and Re−N were 1.896−1.957 Å and 2.160−2.202 Å, which were typical of that found in rhenium(I) tricarbonyl diimine complexes.[16] Angles subtended by the nitrogen atoms of ligand **L1** at the rhenium center, N(3)−Re(1)−N(2) and N(5)−Re(2)−N(6), were 75.1° and 75.4°, respectively, for the two independent formula units, which are smaller than the ideal angle of 90° adopted in octahedral geometry, as required by the steric requirement of the chelating phenanthroline ligand.[3g,16]

**Photophysical Properties.** The electronic absorption spectra of complexes **1**−**5** in acetonitrile showed similar patterns with very intense absorption bands, with molar extinction coefficients in the order of $10^4$ dm$^3$ mol$^{-1}$ cm$^{-1}$ at ca. 250 and 290 nm, which are tentatively assigned as intraligand (IL) $\pi \rightarrow \pi^*$ transitions of the 1,10-phenanthroline derivative moieties. The absorption bands with molar extinction coefficients in the order of $10^3$ dm$^3$ mol$^{-1}$ cm$^{-1}$ at ca. 390 nm are ascribed to the metal-to-ligand charge transfer (MLCT) [d$\pi$(Re) $\rightarrow$ $\pi^*$(L)] transition, typical of rhenium(I) tricarbonyl diimine systems.[17] The electronic absorption data of rhenium(I) tricarbonyl complexes were collected in Table 2.

The rhenium(I) complexes are strongly emissive at room temperature in solution and at 77 K in EtOH−MeOH (4:1 v/v) glass. The room-temperature emission spectra of the complexes all showed broad structureless bands, which are characteristic of MLCT emissions of the Re(I) diimine complexes, and are tentatively assigned as $^3$MLCT [d$\pi$(Re) $\rightarrow$ $\pi^*$(L)] emissions, typical of this type of complexes.[1,18] This is further supported by the radiative lifetimes of the complexes (Table 2). These values in the submicrosecond range are comparable to those observed for MLCT emissions of other related Re(I), Os(II), and Ru(II) complexes and are much too short for a ligand-localized phosphorescence. The emission energy maxima of the complexes in acetonitrile at room temperature were similar (ca. 555 nm), which demonstrated that the effects of the substituents on the remote polyether crown pendants on the phenanthroline unit were small. However, the presence of crown ether substituents on the phenanthroline ligands in these complexes resulted in an emission energy shift to higher energy in acetonitrile solution when compared to the unsubstituted $[\mathrm{Re(CO)_3(phen)(py)}]^+$ ($\lambda_{\mathrm{em}} = 567$ nm)[19] owing to the electron-donating ability of the crown ether moiety. The low-temperature spectra of the solid samples showed vibronic structures at about 550 nm with progressional spacings ($\nu_{\mathrm{M}}$) of ca. 1300 cm$^{-1}$, which are typical of aromatic C=C and C=N vibrational modes and are commonly observed in rhenium(I) polypyridyl complexes at low temperature.[18b,19] Compared to the spectra recorded at room temperature, the emission maxima were shifted slightly to higher energy and the lifetimes in the solid state were increased by ca. 4- to 5-fold at low temperature. The emission spectra of the complexes in EtOH−MeOH (4:1 v/v) mixture at room temperature showed broad and structureless bands with emission maximum at ca. 550 nm, originated from the $^3$MLCT state. In the emission spectra of the complexes at 77 K in frozen glass (EtOH−MeOH, 4:1 v/v), the vibronic structures were well resolved, and the emission maxima were shifted to ca. 490 nm with vibrational progressional spacings ($\nu_{\mathrm{M}}$) of ca. 1300 cm$^{-1}$. The lifetimes of the complexes were also increased tremendously, with values of 0.59, 0.51, 0.36, 0.38, and 0.54 ms for **1**−**5**, respectively, which were too long for a pure $^3$MLCT emission and were attributed largely to that of a $\pi-\pi^*$

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**Table 1. Selected Bond Distances (Å) and Angles (deg) with Estimated Standard Deviations (esds) in Parentheses for Complex 1**

| | | | | | |
|---|---|---|---|---|---|
| Re(1)−C(2) | 1.896(12) | Re(1)−C(1) | 1.902(13) | S(1)−C(22) | 1.810(14) |
| Re(1)−C(3) | 1.947(12) | Re(1)−N(3) | 2.170(8) | S(2)−C(25) | 1.908(19) |
| Re(1)−N(2) | 2.188(8) | Re(1)−N(1) | 2.202(8) | S(3)−C(27) | 1.788(15) |
| O(1)−C(1) | 1.159(13) | O(2)−C(2) | 1.143(12) | S(1)−C(23) | 2.14(3) |
| O(3)−C(3) | 1.127(12) | O(4)−C(19) | 1.398(11) | S(2)−C(24) | 2.03(3) |
| O(4)−C(21) | 1.452(13) | O(5)−C(20) | 1.399(12) | S(3)−C(26) | 1.844(18) |
| O(5)−C(28) | 1.441(12) | C(3)−Re(1)−N(3) | 174.0(4) | C(25)−S(2)−C(24) | 101.4(7) |
| C(2)−Re(1)−N(2) | 171.3(4) | N(3)−Re(1)−N(2) | 75.1(3) | C(22)−S(1)−C(23) | 106.3(7) |
| C(19)−O(4)−C(21) | 119.0(8) | C(1)−Re(1)−N(1) | 179.5(4) | C(27)−S(3)−C(26) | 102.5(6) |
| C(20)−O(5)−C(28) | 114.7(8) | | | | |
| Re(2)−C(31) | 1.91(3) | Re(2)−C(29) | 1.913(17) | S(4)−C(50) | 1.781(16) |
| Re(2)−C(30) | 1.957(16) | Re(2)−N(5) | 2.160(10) | S(5)−C(53) | 1.825(14) |
| Re(2)−N(4) | 2.177(17) | Re(2)−N(6) | 2.197(9) | S(6)−C(55) | 1.819(15) |
| S(4)−C(51) | 1.833(18) | O(6)−C(29) | 1.154(16) | O(7)−C(30) | 1.124(16) |
| S(5)−C(52) | 1.892(18) | O(8)−C(31) | 1.16(2) | O(9)−C(47) | 1.367(14) |
| S(6)−C(54) | 1.830(16) | O(9)−C(49) | 1.494(17) | O(10)−C(48) | 1.384(14) |
| O(10)−C(56) | 1.445(14) | C(31)−Re(2)−N(5) | 173.3(5) | C(53)−S(5)−C(52) | 100.0(7) |
| C(30)−Re(2)−N(6) | 173.0(6) | C(29)−Re(2)−N(4) | 178.7(6) | C(50)−S(4)−C(51) | 101.3(7) |
| C(47)−O(9)−C(49) | 112.9(10) | N(5)−Re(2)−N(6) | 75.4(3) | C(55)−S(6)−C(54) | 102.6(7) |
| C(48)−O(10)−C(56) | 112.0(11) | | | | |

**Table 2. Photophysical Data for Complexes 1−5**

| complex | absorption $\lambda_{max}$/nm[a] ($\epsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$) | medium ($T$/K) | emission $\lambda_{em}$/nm ($\tau_o$/$\mu$s) | $\phi_{em}$ |
|---|---|---|---|---|
| 1 | | CH$_3$CN (298) | 553 (9.2) | 0.127 |
| | 248 (41220), | solid (298) | 568 (1.6) | |
| | 290 (29990), | solid (77) | 519 (8.4), 556 sh | |
| | 332 (8100), | glass (77)[b] | 496 (593.5), 531 sh | |
| | 383 (3320) | EtOH−MeOH (4:1 v/v, 298) | 550 (10.3) | |
| 2 | | CH$_3$CN (298) | 551(13.8) | 0.121 |
| | 250 (42160), | solid (298) | 550 (6.6) | |
| | 290 (29980), | solid (77) | 517 (18.5), 550 sh | |
| | 330 (8770), | glass (77)[b] | 493 (513.0), 530 sh | |
| | 385 (3490) | EtOH−MeOH (4:1 v/v, 298) | 548 (20.5) | |
| 3 | | CH$_3$CN (298) | 555 (16.4) | 0.072 |
| | 248 (40070), | solid (298) | 566 (2.2) | |
| | 290 (31760), | solid (77) | 517 (10.0), 553 sh | |
| | 332 (8190), | glass (77)[b] | 490 (360.8), 523 sh | |
| | 381 (3600) | EtOH−MeOH (4:1 v/v, 298) | 547 (18.5) | |
| 4 | | CH$_3$CN (298) | 555 (5.8) | 0.043 |
| | 248 (37820), | solid (298) | 560 (1.9) | |
| | 290 (29900), | solid (77) | 519 (8.0), 556 sh | |
| | 330 (7840), | glass (77)[b] | 491(380.6), 524 sh | |
| | 383 (3300) | EtOH−MeOH (4:1 v/v, 298) | 548 (3.4) | |
| 5 | | CH$_3$CN (298) | 547 (37.2) | 0.159 |
| | 249 (36310), | solid (298) | 560 (28.5) | |
| | 290 (29790), | solid (77) | 510 (40.2), 545 sh | |
| | 332 (8210), | glass (77)[b] | 493 (542), 530 sh | |
| | 384 (3220) | EtOH−MeOH (4:1 v/v, 298) | 545 (26.2) | |

[a] In CH$_3$CN solvent. [b] EtOH−MeOH (4:1 v/v).

**Table 3. Electrochemical Data for Complexes 1−5 in Acetonitrile Solution (0.1 M $^n$Bu$_4$NClO$_4$) at 298 K[a]**

| complex | oxidation $E_{pa}$/V vs SCE[b] | reduction $E_{1/2}$/V vs SCE[c] ($\Delta E_p$/mV)[d] |
|---|---|---|
| 1 | +1.78 | −1.15 (65), −1.48 (62), −1.70 (101) |
| 2 | +1.84 | −1.11 (88), −1.41 (59), −1.70 (117) |
| 3 | +1.80 | −1.16 (67), −1.42 (59), −1.77 (134) |
| 4 | +1.74 | −1.17 (67), −1.49 (58), −1.72 (91) |
| 5 | +1.82 | −1.19 (65), −1.50 (60), −1.76 (108) |

[a] Working electrode, glassy carbon; scan rate, 100 mV s$^{-1}$. [b] $E_{pa}$ was anodic peak potential. [c] $E_{1/2}$ was ($E_{pa}$ + $E_{pc}$)/2, $E_{pa}$ and $E_{pc}$ were anodic and cathodic peak potentials, respectively. [d] $\Delta E_p$ is $|E_{pa} - E_{pc}|$.

intraligand phosphorescence, as was observed in other related rhenium(I) tricarbonyl complexes containing substituted phenanthroline ligands.[18b,19] While room-temperature emissions of the complexes were $^3$MLCT in character, their 77 K emissions were predominantly ligand-localized $\pi-\pi^*$ intraligand phosphorescence instead. It is likely that at room-temperature the $^3$MLCT states lie below the $\pi-\pi^*$ $^3$IL state, leading to $^3$MLCT phosphorescence. However, the unrelaxed $^3$MLCT state was shifted to sufficiently high-energy such that it lies at similar or even higher energy than the $\pi-\pi^*$ $^3$IL state at 77 K. This could be explained by the fact that at room temperature the solvent molecules could readily reorient themselves in response to the charge redistribution in a fluid medium, so that the lowest $^3$MLCT emitting state could be equilibrated with its immediate solvent environment. However, when the medium was frozen, the $^3$MLCT excited-state was not fully equilibrated, since the solvent cage still remained in the ideal ground-state situation. Thus the lowest $^3$MLCT state lies at higher energy in the rigid matrix and in some cases could be higher than the $^3$IL state. The luminescence was then mainly derived from the lowest $^3$IL state, as observed in the complexes.

**Electrochemical Properties.** The electrochemical properties of the Re(I) diimine complexes were studied by cyclic voltammetry which showed very similar electrochemical behavior. Both reduction and oxidation couples were observed in the cyclic voltammograms upon reductive and oxidative scan, respectively, similar to other related rhenium(I) diimine complexes.[20] The electrochemical data were summarized in Table 3. All the complexes displayed a quasi-reversible/irreversible rhenium(I/II) oxidation wave at ca. +1.7 to +1.8 V versus SCE. Three reduction couples between −1.1 and −1.8 V versus SCE were observed. With reference to previous electrochemical studies of related rhenium(I) diimine systems,[20] the first and third reduction waves of all the rhenium(I) complexes are tentatively assigned as the reduction of the diimine ligands. The second wave observed at ca. −1.5 V is tentatively assigned as the metal-centered reduction of rhenium(I) to rhenium(0). Similar reduction couples were reported in other related systems.[1c,16b,18a,21]

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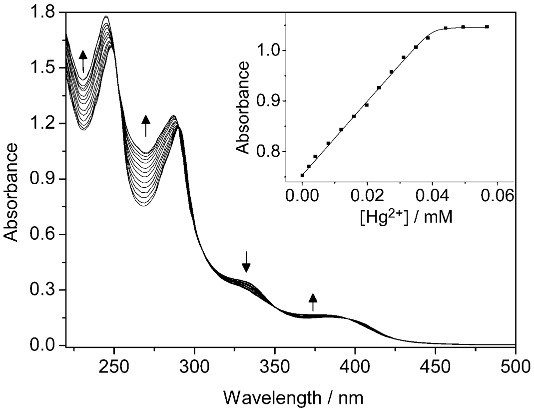

**Figure 2.** UV−vis spectral changes of complex **1** ($4.0 \times 10^{-5}$ M) in $CH_3CN$ (0.1 M $^nBu_4NClO_4$) upon treatment with $Hg(ClO_4)_2$. Inset shows the absorbance at 268 nm as a function of the $Hg^{2+}$ concentration and its theoretical fit (—) for the 1:1 binding of complex **1** with $Hg^{2+}$.

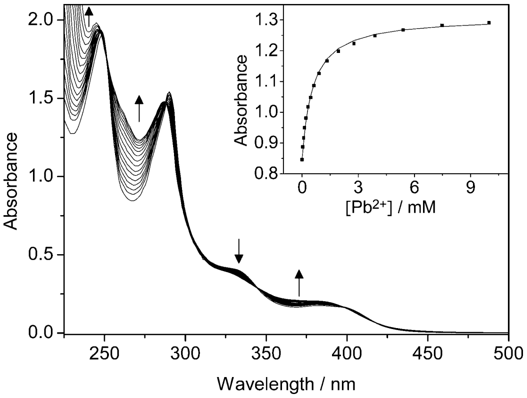

**Figure 3.** UV−vis spectral changes of complex **3** ($5.0 \times 10^{-5}$ M) in $CH_3CN$ (0.1 M $^nBu_4NClO_4$) upon treatment with $Pb(ClO_4)_2$. Inset shows the absorbance at 268 nm as a function of the $Pb^{2+}$ concentration and its theoretical fit (—) for the 1:1 binding of complex **3** with $Pb^{2+}$.

**Cation-Binding Studies.** The cation-binding ability of the rhenium(I) complexes was studied by electronic absorption spectrophotometry. Upon addition of $Hg^{2+}$ to a solution of **1** in acetonitrile containing tetra-*n*-butylammonium perchlorate (0.1 M) as supporting electrolyte, the intraligand absorption bands of the complex were found to show obvious changes and exhibited a slight blue shift in absorption energy in the electronic absorption spectra, while the MLCT band showed only a minor spectral change. The electronic absorption spectral traces upon addition of $Hg^{2+}$ ions to a solution of complex **1** in acetonitrile (0.1 M $^nBu_4NClO_4$) are shown in Figure 2, in which well-defined isosbestic points was observed. The presence of isosbestic points was an indication of a clean reaction. A large binding constant of **1** toward $Hg^{2+}$ ion was attained by a nonlinear least-squares fit[12] of the absorbance versus the concentration of added $Hg^{2+}$ ion, with the titration data fitted nicely to a 1:1 binding model. There were no obvious UV−vis spectral changes of complex **1** upon addition of other metal ions such as $Pb^{2+}$, $Cd^{2+}$, $Zn^{2+}$, $Ag^+$, $Na^+$, and $Mg^{2+}$, which indicated that complex **1** showed a high selectivity toward $Hg^{2+}$ ions. The UV−vis spectrum of complex **2** was also found to show obvious spectral changes upon addition of $Hg^{2+}$, $Pb^{2+}$, and $Ag^+$ ions in acetonitrile solution. The 1:1 binding model was also found between complex **2** and $Hg^{2+}$, $Pb^{2+}$, and $Ag^+$ ions, and the binding constant of complex **2** toward $Hg^{2+}$ ions was found to be smaller than that of **1**, which indicated that complex **2** displayed a lower binding affinity and a poorer selectivity toward $Hg^{2+}$ ions with larger size of crown cavity and smaller number of soft atoms in the crown moiety compared to complex **1**. The UV−vis spectrum of complex **4** was found to show minor spectral changes upon addition of $Hg^{2+}$ ions while obvious spectral changes were observed upon addition of $Pb^{2+}$ ions in acetonitrile solution. The titration data of complex **4** with $Hg^{2+}$ were fitted to a 2:1 binding model according to eq 3, and the log $K_1$ and log $K_2$ were 5.93 ± 0.15 and 5.33 ± 0.05, respectively, which showed a mixture of 1:1 and 2:1 binding for $Hg^{2+}$ ions. The $Hg^{2+}$ ion was probably coordinated by two selenium atoms from two complexes instead of encapsulated inside the crown cavity, owing to the weak binding effect between the oxygen atoms and the $Hg^{2+}$ ion. Addition of $Hg^{2+}$ ions to complex **4** in acetonitrile resulted in the broadening and a downfield shift ($\Delta\delta$) of ca. 0.75 ppm of the signal at $\delta$ 2.87 ppm, corresponding to the $-CH_2Se-$ protons. The methylene protons adjacent to the oxygen atoms ($-CH_2O-$) were shifted to a lesser extent, suggesting the complexation of $Hg^{2+}$ to the Se atoms with a weaker complexation of $Hg^{2+}$ to the O atoms. Similar findings have been reported in the literature,[22] in which crystal structures of $Hg^{2+}$-bound organic oxaselena-crown compounds showed the complexation of two selenium atoms to $Hg^{2+}$ ion and the absence of oxygen atoms involvement in the complexation of oxaselena-crown with $Hg^{2+}$ ion. The identity of the 2:1 ion-bound adduct has further been supported by positive-ion ESI-MS experiments. Both the 1:1 ion-bound adduct, $\{[Re(CO)_3(\mathbf{L4}\text{-}Hg)(py)](ClO_4)_2\}^+$, and the 2:1 ion-bound adduct, $\{[Re(CO)_3(\mathbf{L4})(py)]_2Hg(ClO_4)(PF_6)\}^{2+}$, were observed as ion clusters at *m*/*z* 1182 and 1005, respectively, in the positive-ion ESI-mass spectrum of an acetonitrile solution of complex **4** and $Hg(ClO_4)_2$. The 2:1 binding mode of organic ligands containing one S or Se atom for $Hg^{2+}$ ion has also been demonstrated previously.[23] Alternatively, a 1:1 binding model was found between complex **4** and $Pb^{2+}$ ions. On the contrary, the spectral changes in the UV−visible spectra of complex **3** upon addition of $Hg^{2+}$ ions were too small for an accurate determination of the binding constant. However, upon addition of $Pb^{2+}$ to a solution of **3** in acetonitrile, obvious spectral changes were observed in the UV−vis spectra. The electronic absorption spectral traces upon addition of $Pb^{2+}$ ions to a solution of **3** in acetonitrile (0.1 M $^nBu_4NClO_4$) are shown in Figure 3. The titration data were fitted nicely to a 1:1 binding model between complex **3** and $Pb^{2+}$ ions. There were also no obvious spectral changes of complex **3** upon the addition of other metal ions such as $Cd^{2+}$, $Zn^{2+}$, $Ag^+$, $Na^+$, and $Mg^{2+}$, which showed that complex **3** displayed a strong specificity toward $Pb^{2+}$ ions. The binding constants of the complexes toward different metal ions obtained from UV−vis spectrophotometric method are listed in Table 4. The results demonstrated that the ion-binding ability for soft $Hg^{2+}$ ion was in the order of **1** > **2**, **4** > **3**. The results were in line with the decreasing softness of the crown moieties from **L1** ($O_2S_3$) to **L2** ($O_4S_2$), **L4** ($O_4Se$) to **L3** ($O_4S$). Similar trends have also been reported in other related complexes.[24] The ion-binding ability and selectivity of the complexes for $Pb^{2+}$ ions were found to increase with a decrease in the number of soft atoms in the studied

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**Table 4. Binding Constants (log $K_s$) of Selected Rhenium(I) Complexes for Metal Ions in Acetonitrile (0.1 M $^n$Bu$_4$NClO$_4$)**

| | | log $K_s$ | |
|---|---|---|---|
| complex | metal ion | UV−visible absorption | emission |
| **1** | Hg$^{2+}$ | 7.20 ± 0.08 | 7.15 ± 0.08 |
| | Ag$^{+}$ | *a* | *a* |
| | Pb$^{2+}$ | *a* | *a* |
| **2** | Hg$^{2+}$ | 5.46 ± 0.06 | 5.68 ± 0.09 |
| | Ag$^{+}$ | 3.49 ± 0.04 | 3.63 ± 0.02 |
| | Pb$^{2+}$ | 3.02 ± 0.02 | 3.18 ± 0.02 |
| **3** | Hg$^{2+}$ | *a* | *a* |
| | Ag$^{+}$ | *a* | *a* |
| | Pb$^{2+}$ | 3.26 ± 0.01 | 3.27 ± 0.01 |
| **4** | Hg$^{2+}$ | log$K_1$=5.93 ± 0.15,<br>log$K_2$=5.33 ± 0.05 | *b* |
| | Ag$^{+}$ | *a* | *a* |
| | Pb$^{2+}$ | 3.83 ± 0.01 | 3.29 ± 0.01 |

[a] The spectral changes are too small for an accurate determination. [b] Not determined.

complexes, probably because Pb$^{2+}$ ions are slightly harder than Hg$^{2+}$ and are classified as borderline Lewis acids. Such enhancement of the stabilities for Hg$^{2+}$ complexation and reduction of stabilities for Pb$^{2+}$ complexation upon sulfur substitution of oxamacrocycles have been observed in other related systems.[25] Spectral changes were not observed in a control experiment using the crown-free analogue, complex **5**, indicating that these changes were ascribed to the binding of metal ions to the polyether crown. All these results showed that the complexes with the introduction of the softer S and Se atoms would preferentially bind the softer ions, which are unlike the case with all O atoms in the crown, such as [Re(CO)$_3$(phen-18-crown-6)Cl],[2k] where preferential binding of alkali and alkaline-earth metal ions instead would occur.

The effect of the metal ions on the emission properties of the rhenium(I) complexes was also studied. Enhancement in the $^3$MLCT luminescence intensity was observed upon titration with metal ions to the complexes in acetonitrile solution containing $^n$Bu$_4$NClO$_4$ (0.1 M) as supporting electrolyte, with a small red shift in the emission maxima upon photoexcitation at the isosbestic wavelength. Such an enhancement in the emission intensity could be explained by the blocking of the intramolecular reductive electron-transfer quenching mechanism, since coordination of metal ions into the crown cavity would reduce the ability of the donor atoms on the crown unit to quench the emissive $^3$MLCT state by photoinduced electron transfer. The slight red shift of the emission maxima could be explained by the fact that the binding of the cations to the polyether crown would decrease the $\sigma$-donating ability and stabilize the $\pi^*$ orbital of the phenanthroline ligand and hence decreased the emission energy. The emission intensity of complex **1** was enhanced by about 1-fold upon addition of Hg$^{2+}$ ion. The emission maxima underwent a slight red shift upon photoexcitation at the isosbestic wavelength of 395 nm. The fully complexed state was obtained after about 1 equiv of Hg$^{2+}$ ion was added to complex **1**. The experimental data of complex **1** were in close agreement with the theoretical nonlinear least-squares fit to a 1:1 binding model, supportive of the 1:1 complexation stoichiometry for complex **1** and Hg$^{2+}$. A large binding constant of log $K_s$ = 7.15 ± 0.08 was obtained, which was comparable to that determined using the UV−vis spectrophotometric method. The emission intensity of complex **2** was also found to be increased upon the addition of Hg$^{2+}$, Pb$^{2+}$, and Ag$^{+}$ ions with a small red shift of the emission maxima, and the titration data were also fitted to 1:1 binding model. The emission intensity of complex **2** was enhanced most strongly by about 4.5-fold upon addition of Hg$^{2+}$ ions and by about 3-fold for Pb$^{2+}$ and Ag$^{+}$ ions. Figure 4 illustrates the emission spectral changes of complex **2** upon treatment with Hg$^{2+}$ ions, and the inset shows the changes of the emission intensity as a function of the added ion concentration. Addition of Hg$^{2+}$ or Pb$^{2+}$ ions to complex **4** in acetonitrile solution would also induce the enhancement of the emission intensity of the complex and the emission intensity was enhanced by about 1-fold and 4-fold upon addition of Hg$^{2+}$ and Pb$^{2+}$ ions, respectively. The enhancement of emission intensity of complex **3** was observed only by about 0.2-fold upon addition of Hg$^{2+}$ ions and drastic enhancement of the emission intensity of complex **3** was observed by about 5-fold upon addition of Pb$^{2+}$ ions. The emission spectral changes of complex **3** upon addition of Pb$^{2+}$ and the changes of the emission intensity as a function of the added ion concentration are shown in Figure 5. All the binding constants of the complexes toward metal ions from the emission method are listed in Table 4 and the results are comparable to that determined using the UV−vis spectrophotometric method. All these results were in agreement with the observed trends in the ion-binding studies using the UV−vis spectrophotometric method, in which complex **1** gave the largest binding constant for Hg$^{2+}$ ion and complex **3** showed high selectivity toward Pb$^{2+}$ ions as shown in Figure 6. No changes in the emission spectra were observed in a control experiment using the crown-free analogue, complex **5**, which further demonstrated the

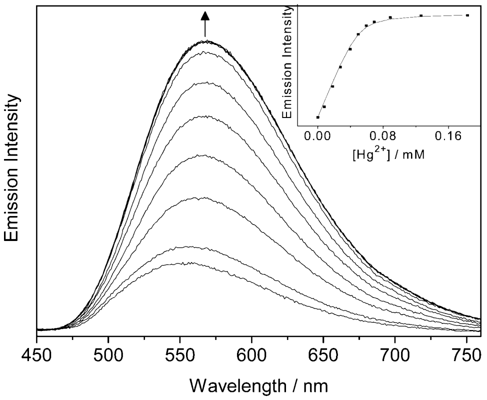

**Figure 4.** Emission spectral traces of complex **2** ($5.0 \times 10^{-5}$ M) in CH$_3$CN (0.1 M $^n$Bu$_4$NClO$_4$) upon additon of Hg(ClO$_4$)$_2$. Excitation at isosbestic point: 394 nm. Inset shows the emission intensity at 553 nm as a function of added Hg$^{2+}$ concentration.

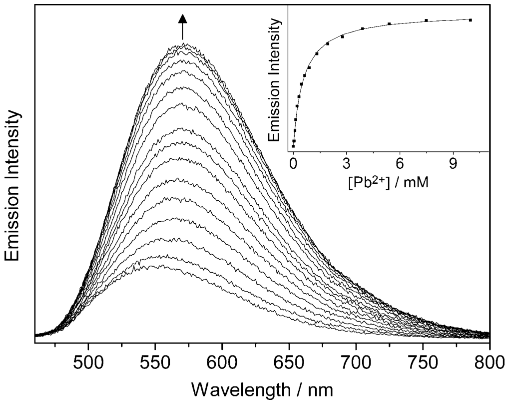

**Figure 5.** Emission spectral traces of complex **3** ($5.0 \times 10^{-5}$ M) in CH$_3$CN (0.1 M $^n$Bu$_4$NClO$_4$) upon additon of Pb(ClO$_4$)$_2$. Excitation at isosbestic point: 397 nm. Inset shows the emission intensity at 555 nm as a function of added Pb$^{2+}$ concentration.

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[25] Izatt, R. M.; Bradshaw, J. S.; Nielsen, S. A.; Lamb, J. D.; Christensen, J. J.; Sen, D. *Chem. Rev.* **1985**, *85*, 271.

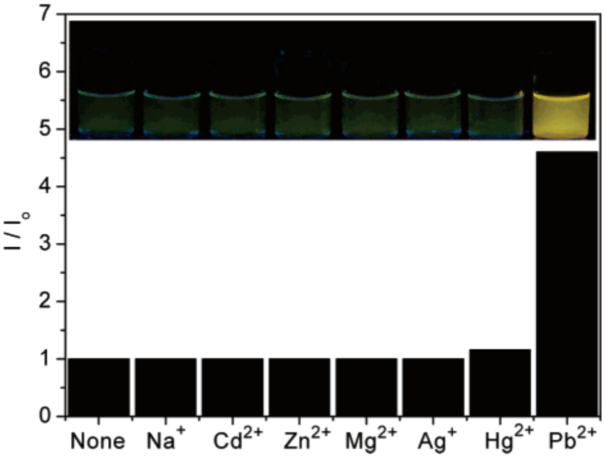

**Figure 6.** Photograph showing the selectivity of **3** to Pb$^{2+}$ and relative enhancement of the emission of **3** in the presence of 100 equiv of various metal ions in acetonitrile (0.1 M $^n$Bu$_4$NClO$_4$) at 298 K.

important role of the crown moiety in the binding studies. Compared to the ruthenium(II) complexes with the same crown ether-containing phenanthroline ligands reported in the previous study,[7b] the larger binding constants of the rhenium(I) complexes (**1** and **2**) observed for Hg$^{2+}$ ions indicated the higher binding affinity of the rhenium(I) complexes toward Hg$^{2+}$ ions, probably because of the smaller charge effect between the Hg$^{2+}$ ions and the monocationic rhenium(I) complexes than the dicationic ruthenium(II) complexes.

## Conclusion

A series of rhenium(I) diimine complexes containing thia-, selena- and azacrowns derived from 1,10-phenanthroline have been synthesized and characterized, and their photophysics, and electrochemistry were studied. Their interaction with metal ions was investigated by UV−vis and emission methods. Moderate spectral changes in the UV−vis spectra and enhancement of emission intensity of the complexes were observed upon addition of metal ions. Complex **1**, with a larger number of sulfur atoms in the oxathiacrown moiety, has been shown to exhibit specific and selective binding toward the softer Hg$^{2+}$ ions. Complex **3** with only one sulfur atom in the oxathiacrown was found to exhibit a high specificity toward Pb$^{2+}$ ions instead. Selective and specific binding properties of the complexes could be readily achieved through a variation of the crown cavity size and donor atoms of the crown ether.

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**Supporting Information Available:** Table of crystal and structure determination data; X-ray crystallographic data in CIF format; derivation of the equation for the determination of binding constants involving a mixture of 1:1 and 2:1 complexation stoichiometry; titration spectra and fitting curves of the complexes upon addition of different metal ions by UV−vis and emission spectroscopic methods; $^1$H NMR spectral changes of complex **4** upon titration with Hg$^{2+}$ ions. This material is available free of charge via the Internet at http://pubs.acs.org.

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