Inorg. Chem. **2007**, *46*, 720–733

Inorganic Chemistry
Article

Synthesis, Structure, Photophysics, Electrochemistry, and Ion-Binding Studies of Ruthenium(II) 1,10-Phenanthroline Complexes Containing Thia-, Selena-, and Aza-Crown Pendants

Mei-Jin Li, Ben Wai-Kin Chu, Nianyong Zhu, and Vivian Wing-Wah Yam*

Open Laboratory of Chemical Biology of the Institute of Molecular Technology for Drug Discovery and Synthesis,† and Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong SAR, People's Republic of China

Received August 10, 2006

A series of ruthenium(II) diimine complexes containing thia-, selena- and aza-crowns 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, luminescence, and ^{1}H NMR spectroscopy. The crystal structures of $[Ru(bpy)_2(\mathbf{L1})](PF_6)_2$, $[Ru(bpy)_2(\mathbf{L2})](ClO_4)_2$, $[Ru(bpy)_2(\mathbf{L3})](ClO_4)_2$, and $[Ru(bpy)_2(\mathbf{L4})](ClO_4)_2$ have been determined. The luminescence properties of $[Ru(bpy)_2(\mathbf{L1})](ClO_4)_2$ were found to be sensitive and selective toward the presence of Hg^{2+} ions in an acetonitrile solution. The addition of alkaline-earth metal ions, Zn^{2+}, Cd^{2+}, and Hg^{2+} ions, to the solution of $[Ru(bpy)_2(\mathbf{L6})](ClO_4)_2$ in acetonitrile gave rise to large changes in the UV–vis and emission spectra. The binding of metal ions to $[Ru(bpy)_2(\mathbf{L6})](ClO_4)_2$ was found to cause a strong enhancement in the emission intensities of the complex, with high specificity toward Hg^{2+} ions.

Introduction

Supramolecular host−guest interaction and molecular recognition have attracted much attention in the past several decades.[1] The design of highly selective and sensitive receptors for metal ions is of great importance in the area of ion transport, chemosensing, biomedical, and environmental applications.[2] There have been quite a number of reports on the utilization of transition-metal complexes containing a macrocylic binding site for the sensing of alkali and alkaline-earth metal ions with increasing awareness of the interesting photochemical and photophysical properties associated with the metal-to-ligand charge-transfer (MLCT) excited state.[3] In the past years, increasing attention has been paid to the variation of the donor atoms to S, Se, or N in order to tune the crown ether cation-binding ability.[4] Despite considerable work carried out on the development of ruthenium(II) polypyridyl-containing crown ether complexes as spectro-

* To whom correspondence should be addressed. E-mail: wwyam@hku.hk.

† Area of Excellence Scheme, University Grants Committee (Hong Kong).

(1) (a) Pedersen, C. J. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1021. (b) Cram, D. J. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1009. (c) Lehn, J. M. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 89. (d) Cram, D. J.; Kaneda, T.; Lein, G. M.; Helgeson, R. C. *J. Chem. Soc., Chem. Commun.* **1979**, *21*, 948. (e) Fabbrizzi, L.; Poggi, A. *Chem. Soc. Rev.* **1995**, *24*, 197. (f) Desvergne, J. P., Czarnik, A. W., Eds. *Chemosensors of Ion and Molecule Recognition*; NATO Advanced Study Institute Series; Kluwer: Dordrecht, The Netherlands, 1997. (g) De Silva, A. P.; Gunaratne, H. Q. N.; Gunnlaugsson, T.; Huxley, A. J. M.; McCoy, C. P.; Rademacher, J. T.; Rice, T. E. *Chem. Rev.* **1997**, *97*, 1515. (h) Valeur, B.; Leray, I. *Coord. Chem. Rev.* **2000**, *205*, 3. (i) Beer, P. D.; Bayly, S. R. *Top. Curr. Chem.* **2005**, *255*, 125.

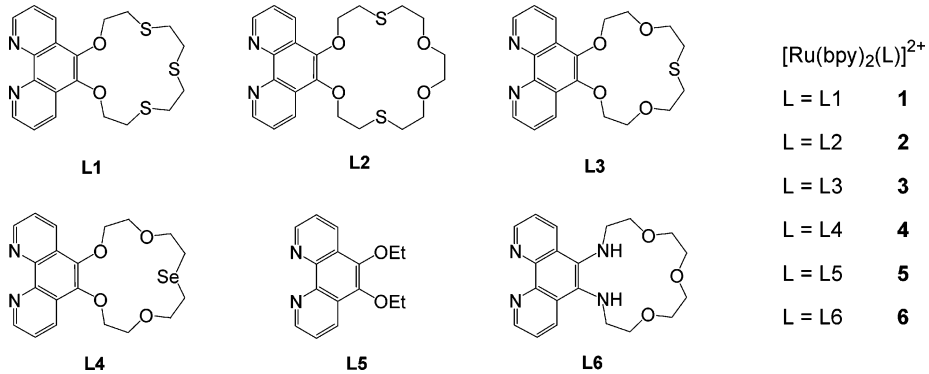
(2) Prodi, L.; Bolletta, F.; Montalti, M.; Zaccheroni, N. *Coord. Chem. Rev.* **2000**, *205*, 59.

(3) (a) Pedersen, C. J. *J. Am. Chem. Soc.* **1967**, *89*, 7017. (b) Lamb, J. D.; Izatt, R. M.; Swain, C. S.; Christensen, J. J. *J. Am. Chem. Soc.* **1980**, *102*, 475. (c) Izatt, R. M.; Bradshaw, J. S.; Nielsen, S. A.; Lamb, J. D.; Christensen, J. J.; Sen, D. *Chem. Rev.* **1985**, *85*, 271. (d) Simon, J.; Engel, M. K.; Soulie, C. *New J. Chem.* **1992**, *16*, 287. (e) Beer, P. D.; Kocian, O.; Mortimer, R. J.; Ridgway, C. *J. Chem. Soc., Dalton Trans.* **1993**, 2629. (f) Yam, V. W.-W.; Lee, V. W. M. *J. Chem. Soc., Dalton Trans.* **1997**, 3005. (g) Yam, V. W.-W.; Tang, R. P. L.; Wong, K. M. C.; Lu, X. X.; Cheung, K. K.; Zhu, N. Y. *Chem.—Eur. J.* **2002**, *8*, 4066. (h) Yam, V. W.-W.; Lu, X. X.; Ko, C. C. *Angew. Chem., Int. Ed.* **2003**, *42*, 3385. (i) Lazarides, T.; Miller, T. A.; Jeffer, J. C.; Ronson, T. K.; Adams, H.; Ward, M. D. *J. Chem. Soc., Dalton Trans.* **2005**, 528.

(4) (a) Frensdorff, H. K. *J. Am. Chem. Soc.* **1971**, *93*, 600. (b) Christensen, J. J.; Eatough, D. J.; Izatt, R. M. *Chem. Rev.* **1974**, *74*, 351. (c) Oue, M.; Akama, K.; Kimura, K.; Tanaka, M.; Shono, T. *J. Chem. Soc., Perkin Trans. 1* **1989**, 1675. (d) Sato, S. D.; Habata, Y.; Sato, M.; Akabori, S. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 3963. (e) Blake, A. J.; Reid, G.; Schroder, M. *J. Chem. Soc., Chem. Commun.* **1992**, 1074. (f) Wu, G.; Jiang, W.; Lamb, J. D.; Bradshaw, J. S.; Izatt, R. M. *J. Am. Chem. Soc.* **1991**, *113*, 6538. (g) Sibert, J. W.; Lange, S. J.; Stern, C. L.; Barrett, A. G. M.; Hoffman, B. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2020. (h) Gawley, R. E.; Pinet, S.; Cardona, C. M.; Datta, P. K.; Ren, T.; Guida, W. C.; Nydick, J.; Leblanc, R. M. *J. Am. Chem. Soc.* **2002**, *124*, 13448. (i) Kondo, S. I.; Kinjo, T.; Yano, Y. *Tetrahedron Lett.* **2005**, *46*, 3183.

10.1021/ic061507z CCC: $37.00 © 2007 American Chemical Society
Published on Web 01/10/2007

Chart 1



chemical and luminescence sensors[3f,5] and some reports on complexes containing azaoxa and polyaza macrocycles sensing heavy-transition-metal ions,[6] the selectivity of these complexes toward metal ion binding was often poor. Sensing receptors for toxic heavy-metal ions are of interest in areas such as environmental chemistry, where the development of highly selective analytical tools is of great importance. However, there are only a few studies on the utilization of transition-metal complexes for the sensing of the highly toxic Hg^{2+} and other heavy-metal ions. Although $[Ru(bpy)_2(phen\text{-}15\text{-}crown)]^{2+}$ was synthesized and characterized by Ward and co-workers, no significant changes of optical spectroscopic properties were found upon the addition of alkaline-earth metal ions.[7] As an extension of our previous work on luminescent metal complexes containing thia- and selena-crown pendants,[8] herein we report the synthesis, structure, photophysics, electrochemistry, and ion-binding studies of a series of ruthenium(II) diimine complexes with appended crown ether ligands derived from 1,10-phenanthroline with either one or more of the O donor atoms replaced by other softer donor atoms such as S, Se, and N (Chart 1). The crown ether moiety covalently bonded to 1,10-phenanthroline, which is a relatively conjugated ligand, is expected to give rise to rich photophysical behaviors upon sensing of various cations. Complexes containing thia- and selena-crown pendants were found to show specific binding toward Hg^{2+} ions in acetonitrile, and the luminescent properties of the complexes were found to show high sensitivity and specificity toward Hg^{2+} ions in an acetonitrile solution, rendering them ideal candidates for the selective optical sensing of Hg^{2+} ions. The ion-binding properties of the complex containing aza-crown pendants with various metal ions such as Mg^{2+}, Ca^{2+}, Ba^{2+}, Zn^{2+}, Cd^{2+}, and Hg^{2+} in acetonitrile have also been studied by UV−vis and luminescence spectroscopy, and the complex was found to be highly sensitive and selective toward Hg^{2+} ions. The differences in the cation-binding ability among the complexes were investigated.

Experimental Section

Materials and Reagents. Chloroethanol, 2-(2-chloroethoxy)-ethanol, sodium formaldehydesulfoxylate, 2-mercaptoethyl sulfide, 3,6-dioxa-1,8-octanedithiol, dithiooxamide, tetra(ethylene glycol), thionyl chloride, silver(I) trifluoromethanesulfonate, ruthenium(III) chloride hydrate, lithium perchlorate, and ammonium hexafluorophosphate were purchased from Aldrich Chemical Co. 2,2′-Bipyridine, sodium sulfide nonahydrate, selenium powder, iodoethane, anhydrous 1,10-phenathroline, sodium hydride (60% dispersion in mineral oil), and *p*-toluenesulfonyl chloride were all of analytical grade and were purchased from Lancaster Synthesis Ltd. Tetra-*n*-butylammonium perchlorate, mercury(II) perchlorate hydrate, silver(I) perchlorate, magnesium(II) perchlorate, calcium(II) perchlorate tetrahydrate, barium(II) perchlorate, cadmium(II) perchlorate hydratem, and zinc(II) nitrate hydrate were purchased from Aldrich Chemical Co. with purity of over 99.0%. Sodium iodide, sodium carbonate, and other salts and solvents are all of analytical grade. *cis*-$Ru(bpy)_2Cl_2 \cdot xH_2O$,[9] 5,6-dihydroxyphenanthroline,[10] 2-iodoethanol,[11] 3,9-dioxa-6-thiaundecane-1,11-diol,[12] 3,9-dioxa-6-thiaundecane-1,11-ditosylate,[13] 3,9-dioxa-6-selenaundecane-1,11-diol,[14] 3,9-dioxa-6-selenaundecane-1,11-ditosylate,[13] 1,11-diiodo-3,6,9-trioxaundecane,[11] and $[Ru(bpy)_2(5,6\text{-diamino-}1,10\text{-phenanthroline})]^{2+}$ [15] were prepared according to the literature procedures.

Safety Note. ***Caution!*** *Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of these materials should be prepared, and they should be handled with great caution.*

Synthesis. 5,6-Bis(2-hydroxyethoxy)-1,10-phenanthroline was synthesized by modification of a literature procedure for phen-15-

(5) (a) Beer, P. D.; Kocian, O.; Mortimer, R. J.; Ridgway, C. *J. Chem. Soc., Chem. Commun.* **1991**, 1460. (b) Ward, M. D.; Barigelletti, F. *Coord. Chem. Rev.* **2001**, *216*, 127. (c) Charbonniere, L. J.; Ziessel, R. F.; Sams, C. A.; Harriman, A. *Inorg. Chem.* **2003**, *42*, 3466. (d) Li, M. J.; Chu, B. W. K.; Yam, V. W.-W. *Chem.—Eur. J.* **2006**, *12*, 3528. (e) Davidson, G. J. E.; Loeb, S. J.; Passaniti, P.; Silvi, S.; Credi, A. *Chem.—Eur. J.* **2006**, *12*, 3233.

(6) (a) Padilla-Tosta, M. E.; Lloris, J. M.; Martinez-Manez, R.; Benito, A.; Soto, J.; Pardo, T.; Miranda, M. A.; Marcos, M. D. *Eur. J. Inorg. Chem.* **2000**, 741. (b) Padilla-Tosta, M. E.; Lloris, J. M.; Martinez-Manez, R.; Marcos, M. D.; Miranda, M. A.; Pardo, T.; Sancenon, F.; Soto, J. *Eur. J. Inorg. Chem.* **2001**, *6*, 1475. (c) Costero, A. M.; Monrabal, E.; Sanjuan, F.; Martinez-Manez, R.; Padilla-Tosta, M. E.; Pardo, T.; Soto, J. *Tetrahedron* **1999**, *55*, 15141.

(7) Rice, C. R.; Guerrero, A.; Bell, Z. R.; Motson, G. R.; Jeffery, J. C.; Ward, M. D. *New J. Chem.* **2001**, *25*, 185.

(8) (a) Yam, V. W.-W.; Pui, Y. L.; Li, W. P.; Lo, K. K. W.; Cheung, K. K. *J. Chem. Soc., Dalton Trans.* **1998**, 3615. (b) Yam, V. W.-W.; Pui, Y. L.; Li, W. P.; Cheung, K. K.; Zhu, N. *New J. Chem.* **2002**, *26*, 536. (c) Wong, K. M. C.; Li, W. P.; Cheung, K. K.; Yam, V. W.-W. *New J. Chem.* **2005**, *29*, 165.

(9) Sullivan, B. P.; Salmon, D. J.; Meyer, T. J. *Inorg. Chem.* **1978**, *17*, 3334.

(10) Paw, W.; Eisenberg, R. *Inorg. Chem.* **1997**, *36*, 2287.

(11) Bennani, Y. L.; Hanessian, S. *Tetrahedron* **1996**, *52*, 13837.

(12) Maas, G. E.; Bradshaw, J. S.; Izatt, R. M.; Christensen, J. J. *J. Org. Chem.* **1977**, *42*, 3937.

(13) Bradshaw, J. S.; Nakatsuji, Y.; Huszthy, P.; Wilson, B. E.; Dalley, N. K.; Izatt, R. M. *J. Heterocycl. Chem.* **1986**, *23*, 353.

(14) Xu, H. S.; Li, W. P.; Liu, X. F. *Chin. Chem. Lett.* **1991**, *2*, 195.

(15) Ishow, E.; Gourdon, A.; Launay, J. P.; Chiorboli, C.; Scandola, F. *Inorg. Chem.* **1999**, *38*, 1504.

crown-5.[7] NaH (0.62 g, 15.5 mmol) was added to a dry *N,N*-dimethylformamide (DMF) solution (80 mL) of 5,6-dihydroxyphenanthroline (1.43 g, 6.7 mmol) under N_2, and the mixture was stirred for 10 min. A solution of 2-iodoethanol (2.44 g, 14.2 mmol) in DMF (40 mL) was added, and the mixture was stirred at 80 °C for 20 h. Distilled water (50 mL) was then added to the reaction mixture, and the product was extracted with CH_2Cl_2. Subsequent drying over anhydrous $MgSO_4$, followed by filtration and evaporation of the solvent under reduced pressure, gave the product as a white solid. Recrystallization of the white solid from ethanol afforded the product as pure white crystals. Yield: 1.08 g, 50%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.15 (dd, $J_1 = 4.2$ Hz, $J_2 = 1.7$ Hz; 2H, phen), 8.56 (dd, $J_1 = 8.2$ Hz, $J_2 = 1.7$ Hz; 2H, phen), 7.67 (dd, $J_1 = 8.2$ Hz, $J_2 = 4.2$ Hz; 2H, phen), 4.39 (m, 4H, CH_2O), 4.03 (m, 4H, CH_2O), 3.11 (b, 2H, OH). Positive EI-MS: *m/z* 300 (M^+).

5,6-Bis(2-chloroethoxy)-1,10-phenanthroline was prepared by modification of a literature procedure for 1,2-bis(2-chloroethoxy)-benzene.[16] A solution of 5,6-bis(2-hydroxyethoxy)-1,10-phenanthroline (1.5 g, 5.0 mmol) and pyridine (1.0 g, 12.7 mmol) in benzene (20 mL) was stirred at 80 °C. Thionyl chloride (1.64 g, 13.8 mmol) in benzene (10 mL) was added to the solution dropwise over 1 h, and the mixture was stirred for 20 h at 80 °C. The mixture was cooled to room temperature, and concentrated HCl (0.7 mL) was added. The resultant organic phase was washed twice with water, then dried over anhydrous Na_2SO_4, and evaporated to dryness. The residue was purified by column chromatography on silica gel using CH_2Cl_2−MeOH (100:1, v/v) as the eluent to afford the product as a white solid. Yield: 1.04 g, 62%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.16 (dd, $J_1 = 4.3$ Hz, $J_2 = 1.7$ Hz; 2H, phen), 8.70 (dd, $J_1 = 8.3$ Hz, $J_2 = 1.7$ Hz; 2H, phen), 7.68 (dd, $J_1 = 8.3$ Hz, $J_2 = 4.3$ Hz; 2H, phen), 4.55 (m, 4H, CH_2), 3.93 (m, 4H, CH_2). Positive EI-MS: *m/z* 337 (M^+).

(a) 1,13-Dioxa-4,7,10-trithiacyclopentadecano[2,3-*f*][1,10]-phenanthroline (L1). L1 was prepared by modification of a literature method for nitrobenzo-15-trithia-crown-5.[17] Sodium hydroxide (0.44 g, 11.0 mmol) was dissolved in absolute ethanol (25 mL) under N_2. To this solution was added 2-mercaptoethyl sulfide (0.51 g, 3.3 mmol) in ethanol (10 mL) in a dropwise manner over 30 min, and the mixture was heated to gentle reflux. 5,6-Bis(2-chloroethoxy)-1,10-phenanthroline (1.01 g, 3.0 mmol) dissolved in ethanol (25 mL) was added cautiously over 1 h with stirring, and the mixture was heated to reflux for 2 h. The solvent was then removed in vacuo, after which water (20 mL) was added, and the mixture was extracted three times with CH_2Cl_2. The combined extracts were dried over anhydrous Na_2SO_4, filtered, and evaporated to dryness. The residue was column chromatographed on silica gel with $CHCl_3$−hexane (40:1, v/v) as the eluent to give ligand **L1** as a white solid. Yield: 0.37 g, 30%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.14 (dd, $J_1 = 4.3$ Hz, $J_2 = 1.8$ Hz; 2H, phen), 8.63 (dd, $J_1 = 8.3$ Hz, $J_2 = 1.8$ Hz; 2H, phen), 7.65 (dd, $J_1 = 8.3$ Hz, $J_2 = 4.3$ Hz; 2H, phen), 4.44 (m, 4H, CH_2O), 3.06 (m, 4H, CH_2S), 2.99 (m, 4H, CH_2S), 2.87 (m, 4H, CH_2S). Positive EI-MS: *m/z* 418 (M^+). Anal. Calcd for $C_{20}H_{22}N_2O_2S_3$: C, 57.39; H, 5.30; N, 6.69. Found: C, 57.23; H, 5.40; N, 6.69.

(b) 1,7,10,16-Tetraoxa-4,13-dithiacyclohexadodecano[2,3-*f*][1,10]phenanthroline (L2). L2 was prepared using a procedure similar to that for **L1** except 1,8-dimercapto-3,6-dioxaoctane (0.60 g, 3.3 mmol) was used instead of 2-mercaptoethyl sulfide to react with 5,6-bis(2-chloroethoxy)-1,10-phenanthroline (1.01 g, 3.0 mmol). Chromatography on silica gel with $CHCl_3$−hexane (50:1, v/v) as the eluent gave **L2** as a white solid. Yield: 0.47 g, 35%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.13 (dd, $J_1 = 4.3$ Hz, $J_2 = 1.7$ Hz; 2H, phen), 8.61 (dd, $J_1 = 8.3$ Hz, $J_2 = 1.7$ Hz; 2H, phen), 7.65 (dd, $J_1 = 8.3$ Hz, $J_2 = 4.3$ Hz; 2H, phen), 4.45 (m, 4H, CH_2O), 3.83 (m, 4H, CH_2O), 3.70 (s, 4H, CH_2O), 3.21 (m, 4H, CH_2S), 2.90 (m, 4H, CH_2S). Positive EI-MS: *m/z* 446 (M^+). Anal. Calcd for $C_{22}H_{26}N_2O_4S_2$: C, 59.17; H, 5.87; N, 6.27. Found: C, 59.26; H, 5.74; N, 6.20.

(c) 1,4,10,13-Tetraoxa-7-thiacyclopentadecano[2,3-*f*][1,10]-phenanthroline (L3). L3 was prepared using a procedure similar to that for 5,6-bis(2-hydroxyethoxy)-1,10-phenanthroline except 3,9-dioxa-6-thiaundecane-1,11-ditosylate (1.35 g, 2.6 mmol) was used instead of 2-iodoethanol to react with 5,6-dihydroxyphenanthroline (0.5 g, 2.4 mmol). Chromatography on silica gel with CH_2Cl_2−methanol (100:1, v/v) as the eluent gave **L3** as a white solid. Yield: 0.28 g, 30%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.14 (dd, $J_1 = 4.3$ Hz, $J_2 = 1.7$ Hz; 2H, phen), 8.56 (dd, $J_1 = 8.3$ Hz, $J_2 = 1.7$ Hz; 2H, phen), 7.65 (dd, $J_1 = 8.3$ Hz, $J_2 = 4.3$ Hz; 2H, phen), 4.37 (m, 4H, CH_2O), 4.02 (m, 4H, CH_2O), 3.99 (m, 4H, CH_2O), 2.95 (m, 4H, CH_2O). Positive EI-MS: *m/z* 386 (M^+). Anal. Calcd for $C_{20}H_{22}N_2O_4S$: C, 61.44; H, 5.80; N, 7.16. Found: C, 61.50; H, 5.82; N, 7.08.

(d) 1,4,10,13-Tetraoxa-7-selenacyclopentadecano[2,3-f][1,10]-phenanthroline (L4). L4 was prepared using a procedure similar to that for 5,6-bis(2-hydroxyethoxy)-1,10-phenanthroline except 3,9-dioxa-6-selenaundecane-1,11-ditosylate (1.93 g, 5.2 mmol) was used instead of 2-iodoethanol to react with 5,6-dihydroxyphenanthroline (1.0 g, 4.8 mmol). Chromatography on silica gel with CH_2Cl_2−methanol (50:1, v/v) as the eluent gave **L4** as a white solid. Yield: 0.43 g, 22%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.13 (dd, $J_1 = 4.3$ Hz, $J_2 = 1.8$ Hz; 2H, phen), 8.56 (dd, $J_1 = 8.4$ Hz, $J_2 = 1.8$ Hz; 2H, phen), 7.65 (dd, $J_1 = 8.4$ Hz, $J_2 = 4.3$ Hz; 2H, phen), 4.42 (m, 4H, CH_2O), 4.08 (m, 4H, CH_2O), 4.02 (m, 4H, CH_2O), 2.97 (m, 4H, CH_2Se). Positive EI-MS: *m/z* 433 (M^+). Anal. Calcd for $C_{20}H_{22}N_2O_4Se$: C, 55.44; H, 5.12; N, 6.46. Found: C, 55.18; H, 5.06; N, 6.42.

(e) 5,6-Diethoxy-1,10-phenanthroline (L5). L5 was prepared using a procedure similar to that for 5,6-bis(2-hydroxyethoxy)-1,10-phenanthroline except iodoethane (0.93 g, 6.0 mmol) was used instead of 2-iodoethanol to react with 5,6-dihydroxyphenanthroline (0.5 g, 2.4 mmol). Chromatography on silica gel with CH_2Cl_2−methanol (50:1, v/v) as the eluent gave **L5** as a pale-yellow solid. Yield: 0.38 g, 60%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.11 (dd, $J_1 = 4.3$ Hz, $J_2 = 1.6$ Hz; 2H, phen), 8.58 (dd, $J_1 = 8.3$ Hz, $J_2 = 1.6$ Hz; 2H, phen), 7.64 (dd, $J_1 = 8.3$ Hz, $J_2 = 4.3$ Hz; 2H, phen), 4.34 (m, 4H, CH_2O), 2.50 (m, 6H, CH_3). Positive EI-MS: *m/z* 268 (M^+). Anal. Calcd for $C_{16}H_{16}N_2O_2$: C, 71.62; H, 6.01; N, 10.44. Found: C, 71.56; H, 6.08; N, 10.31.

(f) 1,13-Diaza-4,7,10-trioxacyclopentadecano[2,3-*f*][1,10]-phenanthroline (L6). L6 was prepared by modification of a literature method for 1,2-bis[2-(*N*-hexylamino)ethoxy]benzene.[16] To a mixture of 5,6-diamino-1,10-phenanthroline (0.5 g, 2.38 mmol) and anhydrous Na_2CO_3 (0.63 g, 5.94 mmol) in dry CH_3CN (200 mL) was added under N_2 1,11-diiodo-3,6,9-trioxaundecane (1.08 g, 2.61 mmol) in dry CH_3CN (50 mL) in a dropwise manner over 30 min, and the resulting solution was then heated to reflux for 5 days. The solvent was then removed in vacuo, water (100 mL) was added, and the mixture was extracted three times with CH_2Cl_2. The combined extracts were dried over anhydrous Na_2SO_4, filtered, and evaporated under reduced pressure to dryness. The residue was column chromatographed on silica gel using $CHCl_3$−methanol (50:

(16) Topal, G.; Demirel, N.; Togrul, M.; Turgut, Y.; Hosgoren, H. *J. Heterocycl. Chem.* **2001**, *38*, 281.
(17) Oue, M.; Ishigaki, A.; Kimura, K.; Matsui, Y.; Shono, T. *J. Polym. Sci., Part A: Polym. Chem.* **1985**, *23*, 2033.

1, v/v) as the eluent to afford the product as an oil. Subsequent trituration and recrystallizaton from $CHCl_3$−hexane gave **L6** as pale-yellow needlelike crystals. Yield: 53 mg, 6%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.05 (dd, $J_1 = 4.2$ Hz, $J_2 = 1.6$ Hz; 2H, phen), 8.58 (dd, $J_1 = 8.3$ Hz, $J_2 = 1.6$ Hz; 2H, phen), 7.59 (dd, $J_1 = 8.3$ Hz, $J_2 = 4.2$ Hz; 2H, phen), 3.82 (m, 4H, NCH_2), 3.74 (m, 4H, CH_2O), 3.51 (m, 4H, CH_2O), 3.37 (m, 4H, CH_3). Positive EI-MS: *m/z* 368 (M^+). Anal. Calcd for $C_{20}H_{24}N_4O_3{\cdot}0.5H_2O$: C, 63.64; H, 6.68; N, 14.84. Found: C, 63.85; H, 6.42; N, 14.63.

(g) [Ru(bpy)$_2$(L1)](ClO$_4$)$_2$ (1). This compound was prepared by modification of a literature method for $[Ru(bpy)_2(phen)]^{2+}$.[18] To a solution of *cis*-$Ru(bpy)_2Cl_2{\cdot}xH_2O$ (100 mg, 0.19 mmol) in absolute ethanol (50 mL) was added **L1** (88 mg, 21.0 mmol), and the mixture was heated to reflux under N_2 for 5 h, during which the purple-black solution turned red-orange. After removal of the solvent under reduced pressure, the residue in the form of chloride salt was dissolved in a minimum amount of methanol, and metathesis reaction upon the addition of a saturated methanolic solution of $LiClO_4$ afforded the desired complex as a red-orange solid, which was then obtained by filtration, and subsequent recrystallization by vapor diffusion of diethyl ether into acetonitrile solutions of the complexes gave **1** as red crystals. Yield: 98 mg, 50%. X-ray-quality single crystals were obtained for the PF_6^- salt. ^{1}H NMR (400 MHz, CD_3CN): δ 8.80 (dd, $J_1 = 8.4$ Hz, $J_2 = 1.2$ Hz; 2H, phen), 8.50 (m, 4H, bpy), 8.09 (m, 2H, bpy), 7.99 (m, 4H, bpy), 7.83 (dd, $J_1 = 5.2$ Hz, $J_2 = 1.2$ Hz; 2H, phen), 7.71 (d, $J_1 = 8.4$ Hz, $J_2 = 5.2$ Hz; 2H, phen), 7.54 (d, $J = 5.2$ Hz; 2H, bpy), 7.44 (m, 2H, bpy), 7.25 (m, 2H, bpy), 4.50 (m, 4H, CH_2O), 3.10 (m, 4H, CH_2S), 2.96 (m, 4H, CH_2S), 2.84 (m, 4H, CH_2S). Positive FAB-MS: *m/z* 930 ([M − ClO_4]$^+$), 831 ([M − 2ClO_4]$^+$). Anal. Calcd for $C_{40}H_{38}Cl_2N_6O_{10}RuS_3{\cdot}1.5H_2O$: C, 45.40; H, 3.90; N, 7.94. Found: C, 45.50; H, 3.74; N, 8.15.

(h) [Ru(bpy)$_2$(L2)](ClO$_4$)$_2$ (2). The procedure was similar to that for **1** except **L2** (94 mg, 21.0 mmol) was used instead of **L1**. Recrystallization from MeCN−Et_2O gave **2** as red crystals. Yield: 100 mg, 50%. ^{1}H NMR (400 MHz, CD_3CN): δ 8.76 (dd, $J_1 = 8.4$ Hz, $J_2 = 1.2$ Hz; 2H, phen), 8.50 (m, 4H, bpy), 8.09 (m, 2H, bpy), 7.99 (m, 4H, bpy), 7.82 (dd, $J_1 = 5.2$ Hz, $J_2 = 1.7$ Hz; 2H, phen), 7.69 (d, $J_1 = 8.4$ Hz, $J_2 = 5.2$ Hz; 2H, phen), 7.53 (d, $J = 5.2$ Hz; 2H, bpy), 7.44 (m, 2H, bpy), 7.23 (m, 2H, bpy), 4.52 (m, 4H, CH_2O), 3.75 (m, 4H, CH_2O), 3.62 (s, 4H, CH_2O), 3.19 (m, 4H, CH_2S), 2.85 (m, 4H, CH_2S). Positive FAB-MS: *m/z* 959 ([M − ClO_4]$^+$), 860 ([M − 2ClO_4]$^+$). Anal. Calcd for $C_{42}H_{42}Cl_2N_6O_{12}RuS_2{\cdot}H_2O$: C, 46.84; H, 4.12; N, 7.80. Found: C, 46.94; H, 4.14; N, 8.05.

(i) [Ru(bpy)$_2$(L3)](ClO$_4$)$_2$ (3). The procedure was similar to that for **1** except **L3** (81 mg, 21.0 mmol) was used instead of **L1**. Recrystallization from MeCN−Et_2O afforded **3** as red crystals. Yield: 75 mg, 40%. ^{1}H NMR (400 MHz, CD_3CN): δ 8.72 (dd, $J_1 = 8.4$ Hz, $J_2 = 1.7$ Hz; 2H, phen), 8.50 (m, 4H, bpy), 8.09 (m, 2H, bpy), 7.98 (m, 4H, bpy), 7.82 (dd, $J_1 = 5.2$ Hz, $J_2 = 1.7$ Hz; 2H, phen), 7.69 (d, $J_1 = 8.4$ Hz, $J_2 = 5.2$ Hz; 2H, phen), 7.53 (d, $J = 5.2$ Hz; 2H, bpy), 7.44 (m, 2H, bpy), 7.22 (m, 2H, bpy), 4.44 (m, 4H, CH_2O), 3.98 (m, 4H, CH_2O), 3.90 (m, 4H, CH_2O), 2.88 (m, 4H, CH_2S). Positive FAB-MS: *m/z* 899 ([M − ClO_4]$^+$), 799 ([M − 2ClO_4]$^+$). Anal. Calcd for $C_{40}H_{38}Cl_2N_6O_{12}RuS{\cdot}H_2O$: C, 47.25; H, 3.96; N, 8.26. Found: C, 47.43; H, 3.79; N, 8.20.

(j) [Ru(bpy)$_2$(L4)](ClO$_4$)$_2$ (4). The procedure was similar to that for **1** except **L4** (91 mg, 21.0 mmol) was used instead of **L1**. Recrystallization from MeCN−Et_2O gave **4** as red crystals. Yield: 79 mg, 40%. ^{1}H NMR (300 MHz, CD_3CN): δ 8.75 (dd, $J_1 = 8.4$ Hz, $J_2 = 1.2$ Hz; 2H, phen), 8.52 (m, 4H, bpy), 8.11 (m, 2H, bpy), 8.01 (m, 4H, bpy), 7.85 (dd, $J_1 = 5.2$ Hz, $J_2 = 1.2$ Hz; 2H, phen), 7.71 (dd, $J_1 = 8.4$ Hz, $J_2 = 5.2$ Hz; 2H, phen), 7.55 (d, $J = 5.2$ Hz; 2H, bpy), 7.46 (m, 2H, bpy), 7.26 (m, 2H, bpy), 4.47 (m, 4H, CH_2O), 4.00 (m, 8H, CH_2O), 2.93 (m, 4H, CH_2Se). Positive FAB-MS: *m/z* 946 ([M − ClO_4]$^+$), 847 ([M − 2ClO_4]$^+$). Anal. Calcd for $C_{40}H_{38}Cl_2N_6O_{12}RuSe{\cdot}H_2O$: C, 45.17; H, 3.79; N, 7.90. Found: C, 45.33; H, 3.72; N, 7.85.

(k) [Ru(bpy)$_2$(L5)](ClO$_4$)$_2$ (5). The procedure was similar to that for **1** except **L5** (56 mg, 21.0 mmol) was used instead of **L1**. Recrystallization from MeCN−Et_2O afforded **5** as red crystals. Yield: 78 mg, 45%. ^{1}H NMR (400 MHz, CD_3CN): δ 8.73 (dd, $J_1 = 8.4$ Hz, $J_2 = 1.7$ Hz; 2H, phen), 8.50 (m, 4H, bpy), 8.09 (m, 2H, bpy), 7.99 (m, 4H, bpy), 7.83 (dd, $J_1 = 5.2$ Hz, $J_2 = 1.7$ Hz; 2H, phen), 7.68 (dd, $J_1 = 8.4$ Hz, $J_2 = 5.2$ Hz; 2H, phen), 7.54 (d, $J = 5.2$ Hz; 2H, bpy), 7.44 (m, 2H, bpy), 7.24 (m, 2H, bpy), 4.40 (m, 4H, CH_2O), 1.51 (m, 6H, CH_3). Positive FAB-MS: *m/z* 818 ([M − ClO_4]$^+$), 718 ([M − 2ClO_4]$^+$). Anal. Calcd for $C_{36}H_{32}Cl_2N_6O_{10}Ru{\cdot}0.5Et_2O$: C, 49.73; H, 4.06; N, 9.16. Found: C, 49.88; H, 4.25; N, 9.30.

(l) [Ru(bpy)$_2$(L6)](ClO$_4$)$_2$ (6). The procedure was similar to that for **1** except **L6** (77 mg, 21.0 mmol) was used instead of **L1**. Recrystallization from MeCN−Et_2O afforded **6** as red crystals. Yield: 40 mg, 30%. ^{1}H NMR (300 MHz, CD_3CN): δ 8.69 (dd, $J_1 = 8.4$ Hz, $J_2 = 1.2$ Hz; 2H, phen), 8.50 (m, 4H, bpy), 8.08 (m, 2H, bpy), 7.99 (m, 2H, bpy), 7.89 (dd, $J_1 = 5.1$ Hz, $J_2 = 1.2$ Hz; 2H, phen), 7.83 (d, $J = 5.6$ Hz; 2H, bpy), 7.62 (dd, $J_1 = 8.4$ Hz, $J_2 = 5.1$ Hz; 2H, phen), 7.55 (d, $J = 5.6$ Hz; 2H, bpy), 7.43 (m, 2H, bpy), 7.24 (m, 2H, bpy), 5.04 (b, 2H, NH), 3.74 (m, 8H, CH_2O), 3.41 (m, 4H, CH_2N). Positive FAB-MS: *m/z* 881 ([M − ClO_4]$^+$), 781 ([M − 2ClO_4]$^+$). Anal. Calcd for $C_{40}H_{40}Cl_2N_8O_{11}Ru{\cdot}H_2O$: C, 48.06; H, 4.20; N, 11.21. Found: C, 48.18; H, 4.06; N, 11.27.

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 F 111 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 N_2 filled in the optical Dewar flask.

^{1}H NMR spectra were recorded on a Bruker DPX-300 or Bruker AV400 FT NMR spectrometer with chemical shifts reported relative to tetramethylsilane. Positive-ion fast atom bombardment (FAB) and electron impact (EI) mass spectra were recorded on a Finnigan MAT95 mass spectrometer, and positive-ion electrospray ionization (ESI) mass spectra were recorded on a Finnigan LCQ spectrometer. Elemental analysis of the new ligands and complexes were 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 $^nBu_4NClO_4$).

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 111 spectrofluorometer. Supporting electrolyte (0.1 M

(18) Crosby, G. A.; Elfring, W. H. *J. Phys. Chem.* **1976**, *80*, 2206.

Table 1. Crystal and Structure Determination Data for Complexes **1**−**4**

	1	**2**	**3**	**4**
formula	$C_{44}H_{47}F_{12}N_{6.50}O_3P_2RuS_3$	$C_{44}H_{49}Cl_2N_7O_{14}RuS_2$	$C_{44}H_{44}Cl_2N_8O_{12}RuS$	$C_{44}H_{44}Cl_2N_8O_{12}RuSe$
fw	1202.07	1135.99	1080.90	1127.80
T/K	301(2)	301(2)	253(2)	253(2)
λ/Å	0.71073	0.71073	0.71073	0.71073
cryst syst	triclinic	triclinic	tetragonal	tetragonal
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P4_32_12$	$P4_32_12$
a/Å	9.257(2)	12.101(2)	11.9425(17)	11.977(2)
b/Å	13.092(3)	12.517(2)	11.9425(17)	11.977(2)
c/Å	22.265(5)	18.818(4)	33.669(7)	33.623(7)
α/deg	90.74(3)	91.05(3)	90	90
β/deg	98.33(3)	103.92(3)	90	90
γ/deg	101.94(3)	114.18(3)	90	90
V/Å^3	2609.6(10)	2501.8(8)	4802.0(14)	4823.2(14)
Z	2	2	4	4
D/g cm^{-3}	1.530	1.508	1.495	1.553
μ/mm^{-1}	0.570	0.575	0.550	1.259
F(000)	1221	1168	2216	2288
V/mm^3	0.5 × 0.2 × 0.15	0.4 × 0.25 × 0.15	0.4 × 0.25 × 0.15	0.4 × 0.3 × 0.15
reflns collcd	8261	8719	21790	11417
unique reflns	5272	786	3626	2544
final R1, wR2[a]	0.0605, 0.1540	0.0721, 0.1920	0.0731, 0.2003	0.0645, 0.1669

[a] $R1 = \sum||F_o| - |F_c||/|F_o|$; $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/[w(F_o^2)^2]\}^{1/2}$ $[I > \sigma 2(I)]$.

^{n}Bu$_4$NClO$_4$) 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[19] of the absorbance (A) vs the concentration of the metal ion added (c_M) according to the following equation:

$$A = A_0 + \frac{A_{lim} - A_0}{2c_0}[c_0 + c_M + 1/K_s - [(c_0 + c_M + 1/K_s)^2 - 4c_0c_M]^{1/2}] \quad (1)$$

where A_0 and A are the absorbance of the complex at a selected wavelength in the absence and presence of the metal cation, respectively, c_0 is the total concentration of the crown ether-containing Ru(II) complex, c_M is the concentration of the metal cation, A_{lim} is the limiting value of the absorbance in the presence of a large excess of metal ion, and K_s is the stability constant.

For emission titration studies, eq 1 can be modified to give eq 2, written as

$$I = I_0 + \frac{I_{lim} - I_0}{2c_0}[c_0 + c_M + 1/K_s - [(c_0 + c_M + 1/K_s)^2 - 4c_0c_M]^{1/2}] \quad (2)$$

where I_0 and I are the emission intensities 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 the emission intensity in the presence of excess metal ion.

Crystal Structure Determination. Single crystals of complexes **1**−**4** suitable for X-ray diffraction studies were obtained by slow diffusion of diethyl ether vapor into a concentrated acetonitrile solution of the respective complexes. A red crystal of the respective complex mounted in a glass capillary was used for data collection at +28 °C for complexes **1** and **2** and at −20 °C for complexes **3** and **4** on an MAR diffractometer with a 300-mm image plate detector using graphite-monochromatized Mo Kα radiation (λ = 0.710 73 Å). Data collections were made with 2° oscillation of φ, 600-s exposure time for complexes **1** and **2** and 10-min exposure time for complexes **3** and **4**, and a scanner distance at 120 mm. A total of 100 images were collected and interpreted, and intensities were integrated using the program *DENZO*.[20] The structures of complexes **1** and **2** were solved by direct methods employing the *SIR-97* program[21] on a PC, and Ru, S, and many non-H atoms were located according to the direct methods. The structures of complexes **3** and **4** were solved by direct methods employing the *SHELXS-97* program[22] on a PC, and Ru and S atoms were located according to the direct methods. The positions of the other non-H atoms were found after successful refinement by full-matrix least squares using the program *SHELXL-97*[23] on a PC. The positions of the H atoms were calculated based on 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. Crystallographic and structural refinement data are given in Table 1.

Results and Discussion

Synthesis and Characterization. The synthetic routes for the crown ether-containing 1,10-phenanthroline ligands are summarized in Scheme 1. 2-Iodoethanol and 1,11-diiodo-3,6,9-trioxaundecane were synthesized from the corresponding chloro-substituted alcohol by reaction with sodium iodide in acetone according to the literature method.[11] 5,6-Bis(2-hydroxyethoxy)-1,10-phenanthroline was prepared by reaction of 5,6-dihydroxy-1,10-phenanthroline with 2-iodoethanol in anhydrous DMF under N_2 using sodium hydride as the base. Conversion of 5,6-bis(2-hydroxyethoxy)-1,10-phenanthroline to 5,6-bis(2-chloroethoxy)-1,10-phenanthroline was achieved via heating to reflux in thionyl chloride. This was followed by reaction with 2-mercaptoethyl sulfide or

(19) Bourson, J.; Pouget, J.; Valeur, B. *J. Phys. Chem.* **1993**, *97*, 4552.

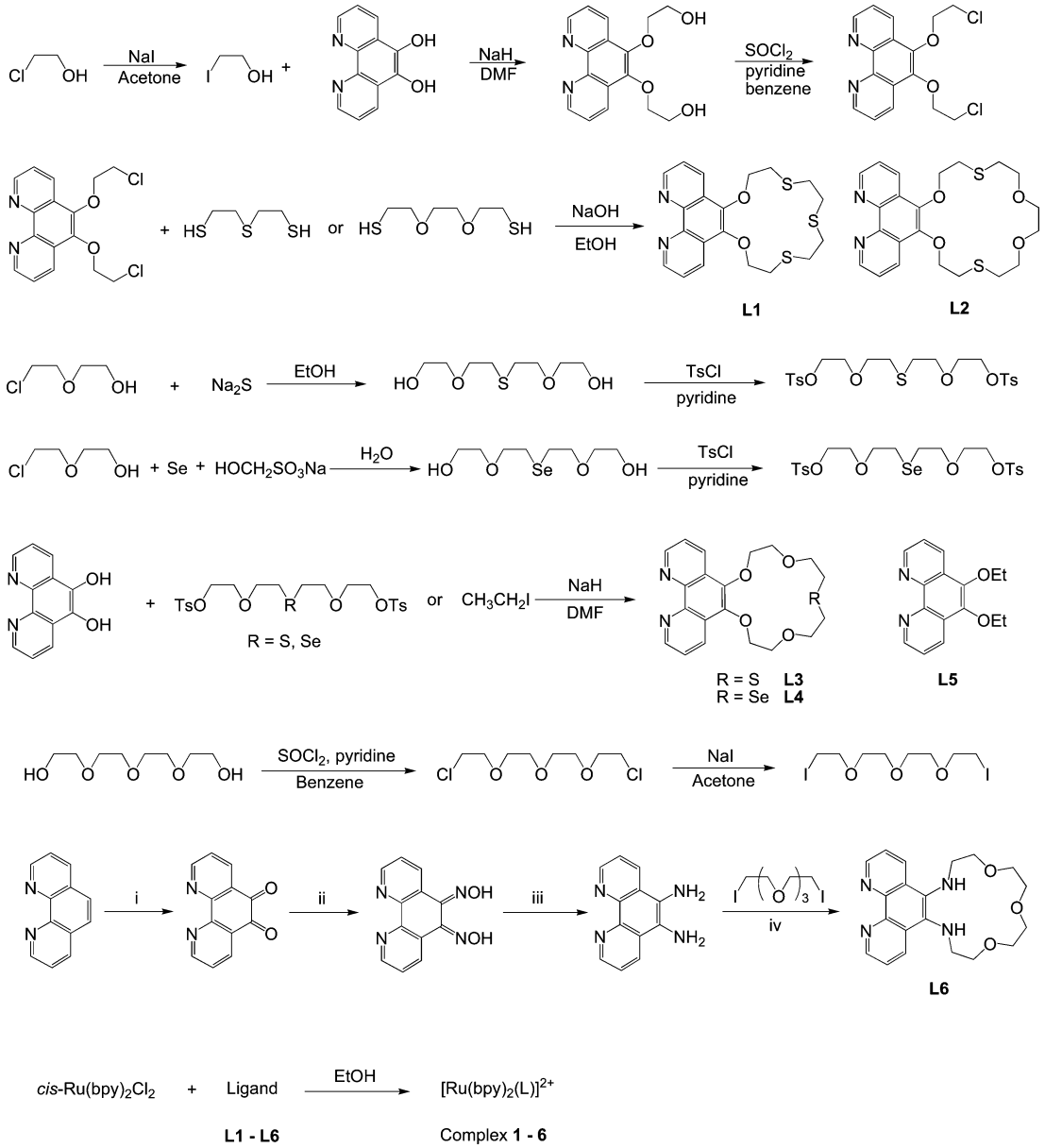
(20) Otwinowski, Z.; Minor, W. Processing of X-ray Diffraction Data Collected in Oscillation Mode. In *Methods in Enzymology*; Carter, C. W., Sweet, R. M., Jr., Eds.; Academic Press: New York, 1997; Vol. 276, pp 307−326.

(21) SIR97: Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagn, R. *J. Appl. Crystallogr.* **1999**, *32*, 115.

(22) SHELXS97: Sheldrick, G. M. *SHELX97, Programs for Crystal Structure Analysis*, release 97-2; University of Goettingen: Goettingen, Germany, 1997.

(23) SHELXL97: Sheldrick, G. M. *SHELX97, Programs for Crystal Structure Analysis*, release 97-2; University of Goettingen: Goettingen, Germany, 1997.

Scheme 1. Synthetic Routes for the Target Ligands and Complexes **1**−**6**[a]



[a] Experimental conditions: (i) H_2SO_4, HNO_3; (ii) $NH_2OH{\cdot}HCl$; (iii) Pd/C, $NH_2NH_2{\cdot}xH_2O$, EtOH; (iv) Na_2CO_3, CH_3CN.

1,8-dimercapto-3,6-dioxaoctane in the presence of a base in ethanol to afford **L1** and **L2**, respectively. 3,9-Dioxa-6-thiaundecane-1,11-diol[12] and 3,9-dioxa-6-selenaundecane-1,-11-diol[14] were reacted with *p*-toluenesulfonyl chloride to produce the corresponding ditosylate.[13] The reaction of the ditosylate or 2-iodoethanol with 5,6-dihydroxy-1,10-phenanthroline in the presence of sodium hydride in dry DMF at 80 °C gave **L3**−**L5**. The reaction of 5,6-diamino-1,10-phenanthroline[24] with 1,11-diiodo-3,6,9-trioxaundecane produced **L6**. The Ru(II) complexes were synthesized by reacting the ligands with *cis*-$Ru(bpy)_2Cl_2{\cdot}xH_2O$ in absolute ethanol under reflux overnight under N_2. Subsequent metathesis to perchlorate salts was accomplished by the addition of a saturated methanolic solution of $LiClO_4$ to afford the Ru(II) complexes **1**−**6**, which were isolated as red crystals by recrystallization from CH_3CN-Et_2O.

The identities of the ligands **L1**−**L6** and complexes **1**−**6** were confirmed by satisfactory elemental analyses, ^{1}H NMR spectroscopy, and EI or FAB mass spectrometry. Complexes **2**−**4** have also been characterized by X-ray crystallography. While crystals of the perchlorate salt of complex **1** were too small in size for structural determination, conversion to the corresponding PF_6^- salt and subsequent recrystallization from CH_3CN-Et_2O afforded red crystals that were suitable for crystallographic characterization.

Crystal Structure Determination. Single crystals of **1**−**4** were obtained by vapor diffusion of diethyl ether into concentrated acetonitrile solutions of the respective complexes. Perspective drawings of the complex cations are depicted in Figure 1, respectively. The structure determina-

(24) Bodige, S.; MacDonnell, F. M. *Tetrahedron Lett.* **1997**, *38*, 8159.

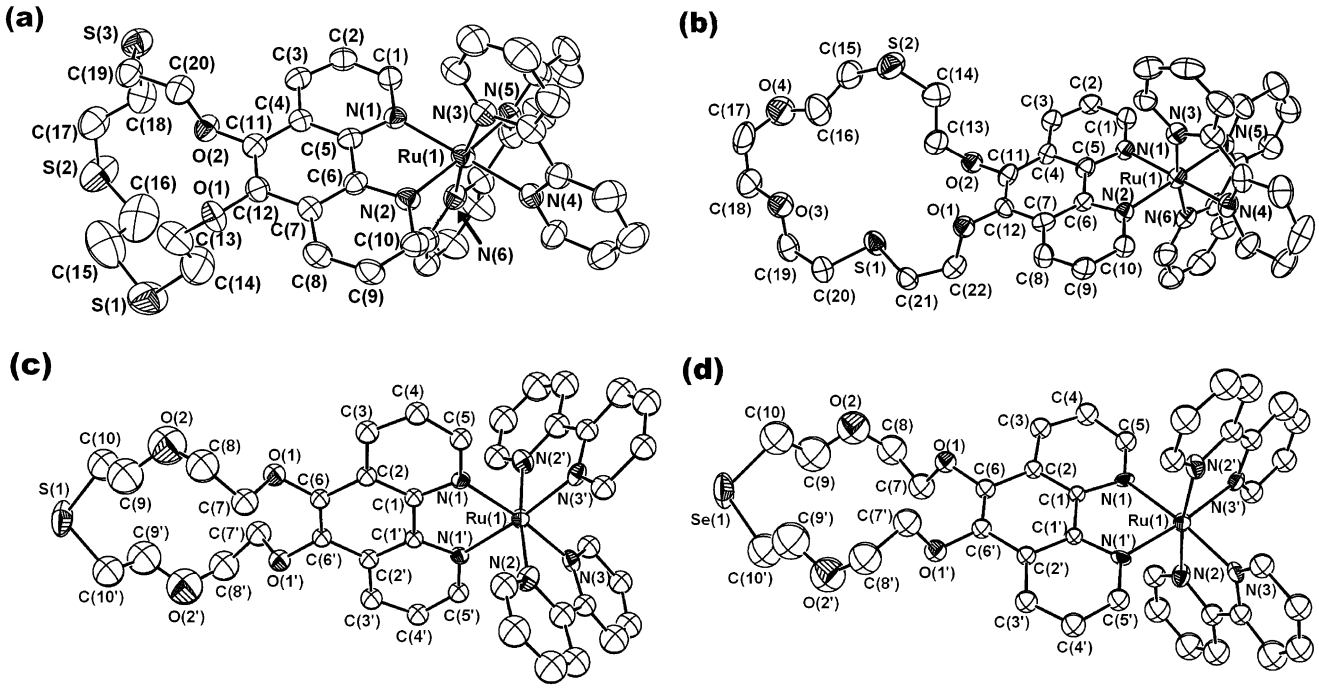


Figure 1. Perspective drawings of the complex cations of **1** (a), **2** (b), **3** (c), and **4** (d) with atomic numbering. H atoms have been omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) with Estimated Standard Deviations (esd's) in Parentheses for Complexes **1**−**4**

1	Ru(1)−N(2)	2.057(6)	O(1)−C(12)	1.354(9)	S(1)−C(15)	1.98(2)
	Ru(1)−N(4)	2.061(7)	O(2)−C(11)	1.379(9)	S(2)−C(16)	1.87(2)
	Ru(1)−N(3)	2.064(7)	Ru(1)−N(6)	2.059(7)	S(3)−C(18)	1.788(11)
	S(1)−C(14)	1.879(12)	Ru(1)−N(5)	2.064(7)	O(1)−C(13)	1.431(12)
	S(2)−C(17)	1.803(11)	Ru(1)−N(1)	2.072(6)	O(2)−C(20)	1.448(9)
	S(3)−C(19)	1.782(10)	N(2)−Ru(1)−N(1)	79.1(3)	N(4)−Ru(1)−N(3)	78.9(3)
	N(6)−Ru(1)−N(5)	78.6(3)	C(14)−S(1)−C(15)	107.3(7)	C(17)−S(2)−C(16)	101.8(6)
	C(19)−S(3)−C(18)	101.7(5)	C(12)−O(1)−C(13)	120.6(7)	C(11)−O(2)−C(20)	113.5(6)
2	Ru(1)−N(3)	2.040(9)	Ru(1)−N(6)	2.044(9)	Ru(1)−N(1)	2.069(7)
	Ru(1)−N(2)	2.052(8)	Ru(1)−N(5)	2.065(9)	Ru(1)−N(4)	2.075(8)
	S(1)−C(21)	1.797(10)	S(1)−C(20)	1.801(12)	S(2)−C(15)	1.804(14)
	S(2)−C(14)	1.792(13)	O(1)−C(22)	1.437(13)	O(3)−C(18)	1.398(14)
	O(1)−C(12)	1.373(11)	O(2)−C(13)	1.455(12)	O(4)−C(17)	1.446(17)
	O(2)−C(11)	1.379(11)	O(3)−C(19)	1.413(14)	O(4)−C(16)	1.469(15)
	N(2)−Ru(1)−N(1)	79.1(3)	N(3)−Ru(1)−N(4)	79.2(4)	N(6)−Ru(1)−N(5)	78.8(4)
	C(21)−S(1)−C(20)	97.7(5)	C(14)−S(2)−C(15)	100.9(7)	C(12)−O(1)−C(22)	115.8(8)
	C(18)−O(3)−C(19)	111.4(11)	C(11)−O(2)−C(13)	117.0(8)	C(17)−O(4)−C(16)	115.4(12)
3	Ru(1)−N(2)	2.035(8)	Ru(1)−N(2′)	2.035(8)	Ru(1)−N(1)	2.064(7)
	Ru(1)−N(3)	2.053(8)	Ru(1)−N(3′)	2.053(8)	Ru(1)−N(1′)	2.064(7)
	S(1)−C(10)	1.851(15)	S(1)−C(10′)	1.851(15)	O(1)−C(7)	1.469(12)
	O(1)−C(6)	1.377(10)	O(1′)−C(7′)	1.469(12)	O(2)−C(9)	1.344(18)
	O(1′)−C(6′)	1.377(10)	O(2)−C(8)	1.383(18)	O(2′)−C(8′)	1.383(18)
	O(2′)−C(9′)	1.344(18)	N(1)−Ru(1)−N(1′)	79.2(4)	N(2)−Ru(1)−N(3)	81.1(3)
	N(2′)−Ru(1)−N(3′)	81.1(3)	C(10)−S(1)−C(10′)	102.8(10)	C(9)−O(4)−C(8)	114.0(15)
	C(9′)−O(3)−C(8′)	114.0(15)	C(6)−O(1)−C(7)	113.1(8)	C(6)−O(2)−C(7′)	113.1(8)
4	Ru(1)−N(2)	2.038(10)	Ru(1)−N(2′)	2.038(10)	Ru(1)−N(1)	2.065(9)
	Ru(1)−N(3)	2.047(10)	Ru(1)−N(3′)	2.047(10)	Ru(1)−N(1′)	2.065(9)
	Se(1)−C(10)	1.973(18)	Se(1)−C(10′)	1.973(18)	O(1)−C(7)	1.489(15)
	O(1)−C(6)	1.377(12)	O(1′)−C(7′)	1.489(15)	O(2)−C(9)	1.309(19)
	O(1′)−C(6′)	1.377(12)	O(2)−C(8)	1.408(18)	O(2′)−C(8′)	1.408(18)
	O(2′)−C(9′)	1.309(19)	N(1)−Ru(1)−N(1′)	80.7(5)	N(2)−Ru(1)−N(3)	79.0(4)
	N(2′)−Ru(1)−N(3′)	79.0(4)	C(10)−Se(1)−C(10′)	101.9(11)	C(6)−O(2)−C(7)	112.8(9)
	C(6′)−O(1)−C(7′)	112.8(9)	C(8)−O(4)−C(9)	115.2(16)	C(8′)-O(3)−C(9′)	115.2(16)

tion data are collected in Table 1, and the selected bond distances and angles are listed in Table 2. Because of the low observed reflections over variables ratio (1842 observed reflections; 163 variables) for the structure refinement, in which the ratio should normally be larger than 7, C atoms were refined isotropically for complexes **3** and **4**. The Ru atom adopted a distorted-octahedral geometry, with the angles subtended by the N atoms of the phenanthroline ligand at the Ru center of 79.1(3), 79.1(3), 79.2(4), and 80.7(5)° for complexes **1**−**4**, respectively, which are much smaller than the ideal angle of 90° adopted in the octahedral geometry. The deviation from the ideal angle is ascribed to the steric requirement of the chelating ligands, which is commonly observed in other related complex systems.[25] In the macrocycle unit, the O−C bonds of O to C(11) and

Table 3. Photophysical Data for Complexes **1**−**6**

complex	absorption λ_{abs}/nm ($\epsilon \times 10^{-4}$/dm^3 mol^{-1} cm^{-1})	medium (T/K)	emission λ_{em}/nm (τ_0/μs)	ϕ_{em}[a]
1	244 (4.55), 285 (6.84),	CH_3CN (298)	617 (0.95)	0.058
	422 (1.35), 451 (1.67)	solid (298)	623 (0.41)	
		solid (77)	597 (2.27), 645 sh	
		glass (77)	578 (6.65), 623 sh	
2	246 (4.29), 286 (6.70),	CH_3CN (298)	607 (0.96)	0.060
	424 (1.36), 452 (1.65)	solid (298)	614 (0.30)	
		solid (77)	604 (1.92), 653 sh	
		glass (77)	575 (6.81), 625 sh	
3	244 (4.48), 285 (6.82),	CH_3CN (298)	616 (0.90)	0.060
	422 (1.21), 451 (1.67)	solid (298)	627 (0.32)	
		solid (77)	612 (2.18), 658 sh	
		glass (77)	576 (6.40), 625 sh	
4	245 (4.76), 285 (6.62),	CH_3CN (298)	607 (0.93)	0.063
	423 (1.29), 451 (1.56)	solid (298)	631 (0.89)	
		solid (77)	616 (3.65), 658 sh	
		glass (77)	578 (7.12), 624 sh	
5	246 (4.32), 286 (6.92),	CH_3CN (298)	605 (0.94)	0.064
	422 (1.37), 452 (1.71)	solid (298)	638 (1.06)	
		solid (77)	610 (3.84), 655 sh	
		glass (77)	578 (7.70), 623 sh	
6	242 (3.86), 287 (7.75),	CH_3CN (298)	610 (1.20)	0.014
	377 (1.14), 424 (1.57)	solid (298)	618 (0.20)	
	456 (1.36)	solid (77)	602 (2.01), 652 sh	
		glass (77)	580 (5.82), 627 sh	

[a] The luminescence quantum yield, measured at room temperature using $[Ru(bpy)_3]^{2+}$ as the standard.[28]

C(12), which were directly attached to the phenanthroline unit, were considerably shorter than that of O to C(13) or C(20) [C(22) for complex **2**], probably because of the strong electron-withdrawing effect of the phenanthroline ring, as well as the conjugation of the heteroatom with the phenanthroline ring. The crown ether pendants were more or less preorganized for metal ion binding as that in $[Ru(bpy)_2(phen\text{-}15\text{-}crown)]^{2+}$.[7]

Electronic Absorption and Emission Properties. All of the complexes showed an intense band at ca. 270−290 nm and low-energy absorption bands at ca. 420−460 nm in acetonitrile. The photophysical data for all of the complexes are collected in Table 3. With reference to previous studies on the related ruthenium(II) polypyridine systems,[26] the higher energy absorption was assigned as an intraligand transition, while the low-energy bands were assigned to the MLCT transitions [dπ(Ru) → π*(bpy)], which were absent in the electronic absorption spectra of the free ligands. Compared to complexes **1**−**5** and $[Ru(bpy)_2(phen\text{-}15\text{-}crown\text{-}5)]^{2+}$,[7] complex **6** showed an additional band at ca. 377 nm. With reference to the UV−vis absorption spectrum of the free ligand **L6**, which shows an absorption band at 335 nm typical of the intramolecular charge-transfer transition from the aza N to the phenanthroline unit, the band at 377 nm in complex **6** is assigned as a metal-perturbed intramolecular charge-transfer transition from the aza N of the crown ligand to the phenanthroline unit coordinated to the Ru(II). Similar transitions were not observed at such low energies in the related oxa-crown analogues. The relatively small changes in the electronic absorption spectra among the series of complexes **1**−**5** compared with that of complex **6** revealed that the electronic effects exerted by the substituents on the remote polyether crown pendants on the phenanthroline ring were small.

The complexes were found to emit strongly with emission maxima at ca. 605−617 nm at room temperature upon excitation at λ > 400 nm in a degassed CH_3CN solution, assigned as derived from a ^{3}MLCT state, similar to that observed in other related ruthenium(II) diimine systems,[26] such as $[Ru(bpy)_2(phen\text{-}15\text{-}crown\text{-}5)]^{2+}$.[7] All of the complexes showed very similar emission properties, which indicated that alteration of the heteroatoms on the crown unit did not have a great influence on the excited-state energies of the complexes. The emission spectra of the complexes in the solid state showed a broad and structureless band at room temperature with emission maxima at ca. 618−638 nm and vibronic structures at low temperature (77 K) with vibrational progressional spacings (ν_M) of ca. 1200−1500 cm^{-1}, which were also derived from the lowest-energy ^{3}MLCT state. The complexes also displayed intense vibronic-structured emission bands with emission maxima at ca. 570−580 nm and a shoulder at ca. 625 nm in EtOH−MeOH glass upon excitation at λ > 400 nm at 77 K, which could be assigned as ^{3}MLCT phosphorescence. The vibrational progressions showed progressional spacings typical of aromatic C⋯C vibrational modes and were commonly observed in ruthenium(II) polypyridyl complexes at low temperature.[27] The complexes in degassed acetonitrile showed luminescence quantum yields that were comparable to that of $[Ru(bpy)_3]^{2+}$,[28] with complex **6** showing a relatively lower luminescence quantum yield, probably due to the electron-donating ability of the diaza group on the crown that was directly coordinated to the phenanthroline unit, which would

(25) (a) Ye, B. H.; Chen, X. M.; Zeng, T. X.; Ji, L. N. *Inorg. Chim. Acta* **1995**, *240*, 5. (b) Rillema, D. P.; Jones, D. S.; Woods, C.; Levy, H. A. *Inorg. Chem.* **1992**, *31*, 2935. (c) Biner, M.; Burgi, H. B.; Ludi, A.; Rohr, C. *J. Am. Chem. Soc.* **1992**, *114*, 197.
(26) Juris, A.; Balzani, V.; Barigelletti, F.; Campagna, S.; Belser, P.; von Zelewsky, A. *Coord. Chem. Rev.* **1988**, *84*, 85.

Table 4. Electrochemical Data for Complexes **1**−**6** in an Acetonitrile Solution (0.1 M $^{n}Bu_4NClO_4$) at 298 K[a]

complex	oxidation: $E_{1/2}$/V vs SCE (ΔE_p/mV)	reduction: $E_{1/2}$/V vs SCE (ΔE_p/mV)
1	+1.27 (102)	−1.35 (61), −1.52 (65), −1.75 (65)
2	+1.26 (88)	−1.35 (59), −1.53 (62), −1.76 (64)
3	+1.25 (60)	−1.36 (60), −1.54 (65), −1.77 (71)
4	+1.24 (59)	−1.36 (61), −1.53 (62), −1.77 (70)
5	+1.24 (66)	−1.37 (62), −1.54 (65), −1.77 (64)
6	+1.32 (112)	−1.38 (60), −1.56 (71), −1.79 (95)

[a] Conditions: working electrode, glassy carbon; scan rate, 100 mV s^{-1}. $E_{1/2} = (E_{pa} + E_{pc})/2$; $\Delta E_p = E_{pa} - E_{pc}$.

lead to quenching of the emissive ^{3}MLCT state by photoinduced electron transfer.

Electrochemical Properties. Cyclic voltammetric measurements were conducted in acetonitrile solutions containing $^{n}Bu_4NClO_4$ (0.1 M) as the supporting electrolyte. All of the complexes showed rich electrochemical behavior with redox couples in the cyclic voltammograms, and the electrochemical data of the complexes are listed in Table 4. The complexes showed typical redox properties of ruthenium(II) polypyridine derivatives. In the cyclic voltammograms, a quasi-reversible to reversible oxidation couple with similar $E_{1/2}$ values in the range of +1.24 to +1.32 V (vs SCE) was observed. Complexes **3**−**5** showed a reversible one-electron-oxidation couple with ΔE_p values of ca. 60 mV, while complexes **1**, **2**, and **6** showed a quasi-reversible oxidation couple with ΔE_p values in the range of 88−102 mV at a scan rate of 100 mV s^{-1}. The oxidation couples were typical of those observed in other ruthenium(II) polypyridine complexes and were assigned as the $Ru^{3+/2+}$ couples.[27] The $E_{1/2}$ values were found to vary only slightly, indicating that the stability of the Ru(II) state has not been significantly altered by the replacement of a different substituted 1,10-phenanthroline crown ether ligand. Three one-electron-reduction couples at −1.3 to −1.8 V (vs SCE) in the reductive scan were observed and were tentatively assigned as ligand-centered reduction. The cyclic voltammograms of complexes **1**−**5** exhibited three reversible one-electron-reduction couples with ΔE_p values between 59 and 71 mV irrespective of the scan rate, while complex **6** showed two reversible and one quasi-reversible reduction couples at −1.38, −1.56, and −1.79 V, respectively. With reference to previous studies on related ruthenium(II) polypyridine complexes,[29] the first two reductions were assigned as one-electron reductions on separate bpy ligands, while the third reduction was assigned as a one-electron reduction on the phenanthroline derivative ligand.

Cation-Binding Studies. (a) Electronic Absorption Studies. The cation-binding ability of the complexes was studied by an electronic absorption spectrophotometric method. Upon the addition of metal ions, such as Hg^{2+}, to a solution of the complexes in CH_3CN (0.1 M $^{n}Bu_4NClO_4$), a very small spectral change was observed for complexes **1** and **2**, and no significant changes were observed for complexes **3**−**5** at the ^{1}MLCT absorption maximum at about 450 nm in the UV−vis spectra. The lack of significant absorption changes in complexes **1**−**5** might be due to the fact that the transition-metal ions, which are soft acids, did not bind strongly to the hard O atoms of the crown cavity that were directly attached to the phenanthroline unit, although they did bind to the softer S and Se atoms strongly. However, the binding to the S and Se atoms would not result in significant changes in the UV−vis absorptions because they were quite remote from the phenanthroline unit and would have little influence on the π^* orbital energy of the phenanthroline ligands. On the other hand, the addition of the alkaline-earth metal ions and transition-metal ions such as Mg^{2+}, Ca^{2+}, Ba^{2+}, Zn^{2+}, Cd^{2+}, and Hg^{2+} ions to the CH_3CN (0.1 M $^{n}Bu_4NClO_4$) solution of complex **6** induced large spectral changes in the UV−vis spectra. The MLCT absorption band at about 450 nm increased in the intensity and underwent a small blue shift, while the band at about 377 nm decreased significantly in the intensity and disappeared completely upon the addition of a substantial amount of metal ions, with a well-defined isosbestic point at 408 nm. The disappearance of the metal-perturbed intramolecular charge-transfer band at 377 nm could probably be explained by the fact that the lone-pair electrons on the aza N atoms of the crown ligand in complex **6** would no longer be available after complexation with metal ions, causing the removal of such an intramolecular charge-transfer transition from the aza N to the phenanthroline unit. The spectral changes were ascribed to the binding of the cations to the polyether cavity because similar shifts were observed in the binding studies of other transition-metal crown-containing complexes.[3g,30] Figure 2 shows the UV−vis spectral changes obtained by monitoring the electronic absorption spectra of complex **6** in an acetonitrile solution (0.1 M $^{n}Bu_4NClO_4$) upon the

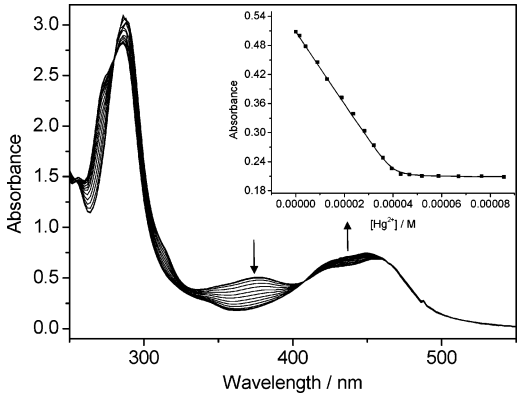


Figure 2. UV−vis spectral changes of complex **6** (4.0×10^{-5} M) in CH_3CN (0.1 M $^{n}Bu_4NClO_4$) upon treatment with $Hg(ClO_4)_2$. Inset: absorbance at 377 nm as a function of the Hg^{2+} concentration and its theoretical fit (−) for the 1:1 binding of complex **6** with Hg^{2+}.

(27) (a) Crosby, G. A. *Acc. Chem. Res.* **1975**, *8*, 231. (b) Bradley, P. G.; Kress, N.; Hornberger, B. A.; Dallinger, R. F.; Woodruff, W. H. *J. Am. Chem. Soc.* **1981**, *103*, 7441. (c) Kober, E. M.; Sullivan, B. P.; Dressick, W. J.; Caspar, J. V.; Meyer, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 7383. (d) Caspar, J. V.; Kober, E. M.; Sullivan, B. P.; Meyer, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 630. (e) Caspar, J. V.; Meyer, T. J. *Inorg. Chem.* **1983**, *17*, 2444.

(28) Caspar, J. V.; Meyer, T. J. *J. Am. Chem. Soc.* **1983**, *105*, 5583.

(29) Braterman, P. S.; Song, J. I.; Peacock, R. D. *Spectrochim. Acta A* **1992**, *48*, 899.

(30) Yam, V. W.-W.; Lo, K. K. W.; Cheung, K. K. *Inorg. Chem.* **1995**, *34*, 4013.

Table 5. Binding Constant (log K_s) of Selected Ru(II) Complexes for Metal Ions in Acetonitrile (0.1 M $^nBu_4NClO_4$)

		log K_s		
complex	metal ion	^{1}H NMR titration	emission	UV−vis absorption
1	Hg^{2+}	4.81 ± 0.02	4.52 ± 0.02	*a*
	Ag^+	3.10 ± 0.02	*a*	*a*
2	Hg^{2+}	4.00 ± 0.01	*a*	*a*
	Ag^+	3.01 ± 0.04	*a*	*a*
3	Hg^{2+}	log K_{11} = 3.24 ± 0.06, log K_{21} = 3.15 ± 0.07	*a*	*a*
	Ag^+	1.23 ± 0.02	*a*	*a*
4	Hg^{2+}	log K_{11}= 3.11 ± 0.05, log K_{21} = 3.60 ± 0.06	*a*	*a*
	Ag^+	1.89 ± 0.03	*a*	*a*
6	Hg^{2+}	*b*	7.76 ± 0.03	7.84 ± 0.06
	Cd^{2+}	*b*	4.61 ± 0.02	4.54 ± 0.01
	Zn^{2+}	4.40 ± 0.04	4.38 ± 0.03	4.34 ± 0.03
	Ba^{2+}	3.42 ± 0.05	3.94 ± 0.01	3.85 ± 0.03
	Ca^{2+}	3.83 ± 0.03	3.60 ± 0.02	3.52 ± 0.02
	Mg^{2+}	*b*	3.76 ± 0.03	3.66 ± 0.04

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

addition of Hg^{2+} ions. The inset shows the changes of the UV−vis absorbance at 377 nm as a function of the added Hg^{2+} concentration. The absorbance at 377 nm dropped in intensity and reached saturation at about 4.5×10^{-5} M Hg^{2+} ions (molar ratio of metal ion to complex was ∼1.1). With such information, the binding constant could be obtained by a nonlinear least-squares fit[19] of the absorbance versus the concentration of the added metal ions (c_M) according to eq 1, and the titration data showed a nice fit to a 1:1 binding model. Similar results were obtained for the other metal ions such as Mg^{2+}, Ca^{2+}, Ba^{2+}, Zn^{2+}, and Cd^{2+}. Very small UV−vis spectral changes were observed for complex **6** upon the addition of Ag^+ ions, and no significant UV−vis spectral changes were observed for complex **6** upon the addition of alkali metal ions. The binding constants for different metal ions are summarized in Table 5. The results showed that complex **6** exhibited a higher binding affinity toward transition-metal ions than alkaline-earth metal ions, especially for the Hg^{2+} ion. On the basis of the hard−soft acid−base principle, the softer N donor atom in the aza-crown ether moiety of complex **6** would enhance the affinity of complex **6** for the softer Hg^{2+} ions, demonstrating the important role of the N atom in the aza-crown ether moiety for the binding of the softer Hg^{2+} ions. According to the literature, no significant UV−vis spectral changes were observed for $[Ru(bpy)_2(phen\text{-}15\text{-}crown\text{-}5)]^{2+}$ upon the addition of alkali and alkaline-earth metal ions.[7] These were suggested to result from the poor electron-donating ability of the two O atoms, originating from the phenanthroline unit, which were directly attached to the strongly electron-withdrawing $[Ru(bpy)_2(phen)]^{2+}$ unit. All of these results showed that the substitution of O atoms, which were directly attached to the phenanthroline unit by softer and more electron-rich atoms such as N, was important to increase the complexation ability of the complex.

(b) Emission Studies. The emission properties of the Ru(II) complexes upon complexation of metal ions were also investigated. Upon the addition of Hg^{2+} ions to an acetonitrile solution (0.1 M $^nBu_4NClO_4$) of complexes **1**−**4**, the characteristic luminescence from the ^{3}MLCT state of the ruthenium(II) diimine complexes was found to decrease in intensity. For complex **1**, the emission intensity was significantly quenched by the addition of Hg^{2+} ions (20 equiv) with a reduction of ca. 40% in the intensity, and the emission maxima underwent a small red shift. The luminescence intensity was quenched by ca. 10% for complexes **2**−**4** upon the addition of 50 equiv of Hg^{2+} ions, which might be ascribed to the weak binding affinity of the O atoms for Hg^{2+} ions. Similar 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 a Hg^{2+} ion to the polyether cavity. All of these results showed that the complexes with the introduction of the softer S and Se atoms would preferentially bind the softer ions, which unlike the case with all O atoms in the crown would preferentially bind alkali and alkaline-earth metal ions instead. As the number of S atoms increased from one to three, a strong binding affinity of the complex for the Hg^{2+} ion would result. Figure 3 illustrates the emission spectral changes and the titration curve obtained by monitoring the emission intensity of complex **1** upon the addition of Hg^{2+} ions to the acetonitrile solution (0.1 M $^nBu_4NClO_4$). The inset shows the changes of the emission intensity as a function of

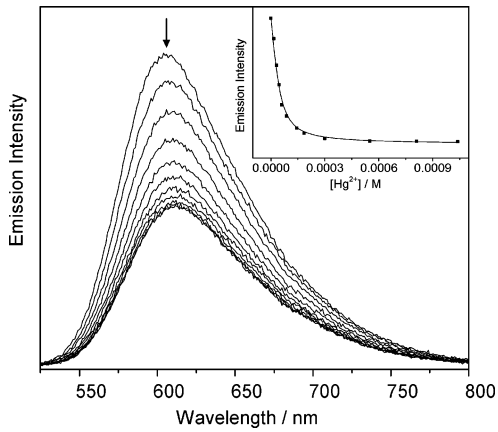


Figure 3. Emission spectral traces of **1** (5.0×10^{-5} M) in CH_3CN (0.1 M $^nBu_4NClO_4$) upon the addition of $Hg(ClO_4)_2$. Excitation wavelength: 450 nm. Inset: emission intensity at 610 nm as a function of the added Hg^{2+} concentration.

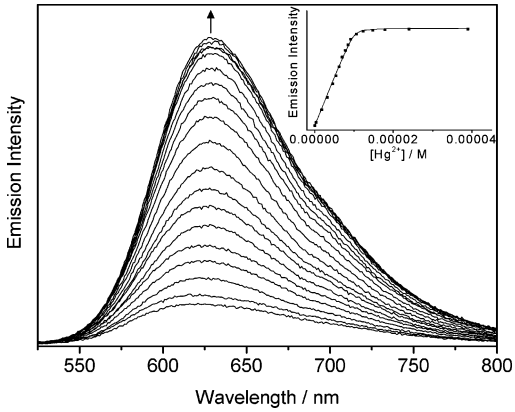


Figure 4. Emission spectral traces of complex **6** (1.0×10^{-5} M) in CH_3CN (0.1 M $^nBu_4NClO_4$) upon the addition of $Hg(ClO_4)_2$. Excitation wavelength at the isosbestic point: 408 nm. Inset: emission intensity at 620 nm as a function of the added Hg^{2+} concentration.

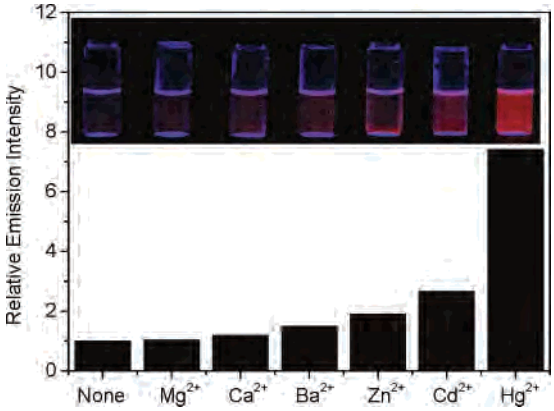


Figure 5. Photograph showing the selectivity of **6** to Hg^{2+} and the relative enhancement of the emission of **6** in the presence of 10 equiv of various metal ions in acetonitrile at 298 K.

the added Hg^{2+} ion concentration. With such information, the binding constant could be obtained by a nonlinear least-squares fit[19] of the emission intensity (I) versus the concentration of the added metal ions (c_M) according to eq 2. A stoichiometry of 1:1 binding was found for complex **1** toward the Hg^{2+} ion. The stability constant, log K_s, for the binding of Hg^{2+} ions was 4.52 ± 0.02. The close agreement of the experimental data with the theoretical fit was supportive of the 1:1 binding stoichiometry. The emission spectral changes were too small for an accurate determination of the binding constants of complexes **2**−**4** toward the Hg^{2+} ion. Interestingly, the addition of $AgClO_4$, $Pb(ClO_4)_2$, $Zn(ClO_4)_2$, and $Cd(ClO_4)_2$ did not induce any change in the emission spectra of complex **1** either, which showed its high selectivity toward the Hg^{2+} ion. On the contrary, an increase in the ^{3}MLCT emission intensity for complex **6** was observed upon the addition of various metal ions. The addition of Mg^{2+}, Ca^{2+}, Ba^{2+}, Zn^{2+}, Cd^{2+}, and Hg^{2+} ions to an acetonitrile solution (0.1 M $^nBu_4NClO_4$) of complex **6** gave rise to a dramatic enhancement of the emission intensities 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 because coordination of the metal ions into the crown cavity would reduce the ability of the donor atoms on the crown unit, especially the N atoms directly attached to the phenanthroline 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 σ-donating ability and stabilize the π^* orbital of the ligand and hence decrease the emission energy. Similar to the UV−vis studies, the emission intensity of complex **6** was only enhanced by about 10% after the addition of 100 equiv of Ag^+ ions; the changes were too small for an accurate determination of the binding constant. Figure 4 shows the emission spectral changes of complex **6** upon treatment with Hg^{2+} ions, and the inset shows the changes of the emission intensity as a function of the added ion concentration. The 1:1 complexation model for metal ion binding was supported by the good agreement of the experimental data with the theoretical fit (shown in the inset). The log K_s values for Hg^{2+}, Cd^{2+}, and Ca^{2+} ions have been found to be 7.76 ± 0.04, 4.61 ± 0.02, and 3.52 ± 0.02, respectively, which were comparable to those determined using the UV−vis spectrophotometric method. The binding constants for other metal ions are also summarized in Table 5. In general, complex **6** exhibited a higher binding affinity toward transition-metal ions than alkaline-earth metal ions, especially for the Hg^{2+} ion, and the emission intensity was enhanced by about 8-fold, as shown in Figure 5, which has also been demonstrated using the UV−vis method described earlier. From the literature, no significant emission spectral changes were observed for $[Ru(bpy)_2(phen\text{-}15\text{-}crown\text{-}5)]^{2+}$ upon the addition of alkali and alkaline-earth metal ions,[7] which further demonstrated that substitution of O atoms, which were directly attached to the phenanthroline unit by the more electron-rich softer atoms such as N, was important to increase the complexation affinity of the complex.

Attempts have been made to further establish the importance of the crown moiety in the binding studies by a comparison study with a control complex, $[Ru(bpy)_2\{phen(NH_2)_2\}]^{2+}$ [$phen(NH_2)_2$ = 5,6-diamino-1,10-phenanthroline]. With the control complex $[Ru(bpy)_2\{phen(NH_2)_2\}]^{2+}$, no obvious spectral changes were observed in both the UV−vis absorption and emission spectra upon the addition of Mg^{2+}, Ca^{2+}, and Ba^{2+} ions to the acetonitrile solution of the complex. Upon the addition of Zn^{2+}, Cd^{2+}, and Hg^{2+} ions to the control complex, small UV−vis absorption spectral changes were observed and the emission intensity of the complex was found to be quenched by 10−20%, indicating the important role of the aza-crown ether in complex **6** for the luminescence enhancement sensing of metal ions.

To further explore the binding properties, the spectroscopic behaviors of complex **6** in an aqueous solution (0.1 M $NaClO_4$) upon complexation of metal ions have also been studied. $NaClO_4$ was selected as the supporting electrolyte because no spectral changes of the complex were observed even after the addition of 1000 equiv of Na^+ ions. No significant spectral changes were observed in both the UV−vis absorption and emission spectra of complex **6** upon the addition of Mg^{2+}, Ca^{2+}, Ba^{2+}, Zn^{2+}, and Cd^{2+} ions. Upon

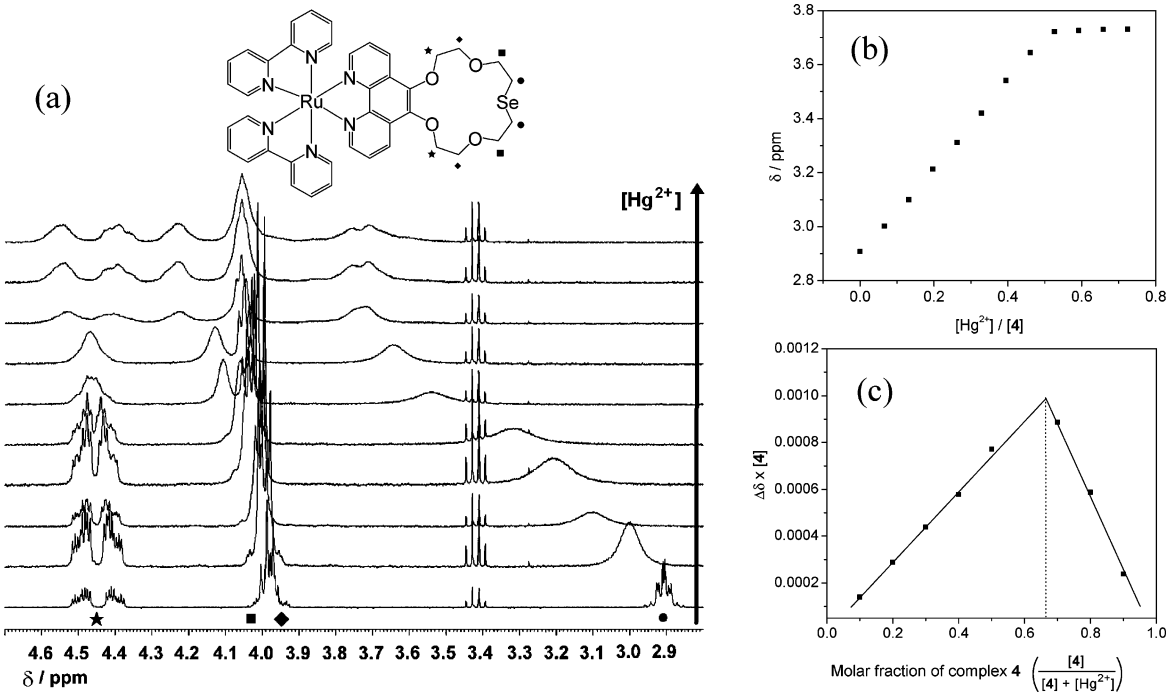


Figure 6. (a) ^{1}H NMR spectral traces of **4** in CD_3CN upon the addition of $Hg(ClO_4)_2$. (b) Plot of proton chemical shifts of $-CH_2Se-$ as a function of the ratio of $[Hg^{2+}]/[\mathbf{4}]$. (c) Job's plot for the binding of complex **4** with Hg^{2+} ions showing a 2:1 stoichiometry.

the addition of Hg^{2+} ions to the complex, some UV−vis absorption spectral changes were observed, and the emission intensity of the complex was enhanced by about 1-fold. These results suggest that the sensitivity of complex **6** to metal ions in an aqueous solution is lower than that found in an acetonitrile solution.

(c) NMR Spectroscopy. The ion-binding experiments have also been carried out using ^{1}H NMR spectroscopy. A shift of proton signals for the protons in the polyether cavity, especially for those methylenes ($-CH_2-$) connected to S or Se atoms has been observed upon metal ion binding, and the stability constants were determined using the *EQNMR*[31] program (Table 5). Upon the addition of the metal ions, the complexation between the metal cations and the complexes would decrease the electron density at the S or Se atom, hence weakening the shielding effect on the neighboring protons and causing a downfield shift of the signal. The addition of $Hg(ClO_4)_2$ to complex **1** in CD_3CN induced significant changes in the chemical shift values of the methylene signals in the ^{1}H NMR spectrum, with the well-resolved resonance signals of the $-CH_2-$ protons becoming broad and downfield-shifted. The experimental data were found to be in good agreement with the theoretical fit obtained from the *EQNMR* program using a 1:1 binding model. The log K_s value of complex **1** for Hg^{2+} was determined to be 4.81 ± 0.02 by using the *EQNMR* program and was close to the result obtained by the emission studies. Similar to complex **1**, the addition of $Hg(ClO_4)_2$ to complex **2** in acetonitrile resulted in a large shift of the $-CH_2S-$ protons with the titration data nicely fitted to a 1:1 binding model, and a binding constant, log K_s, of 4.0 ± 0.01 was obtained, which was smaller than that for complex **1**. Similarly, treatment of complexes **3** and **4** with Hg^{2+} ions gave significant changes in the chemical shift of the methylene signals. The ^{1}H NMR spectral traces of complex **4** upon the addition of Hg^{2+} ions are shown in Figure 6a, in which the well-resolved resonance signals of the polyether chain protons became broad and downfield-shifted. The signal at δ 2.9 ppm that corresponds to the $-CH_2Se-$ protons became very broad at ca. δ 3.6−3.8 ppm, with a downfield shift ($\Delta\delta$) of ca. 0.8 ppm. The protons of $-CH_2O-$ were shifted to a lesser extent by the binding interaction compared to the $-CH_2Se-$ protons. This suggested the weak complexation of Hg^{2+} ions to the O atoms. Figure 6b showed the proton chemical shifts of $-CH_2Se-$ as a function of the ratio of the added Hg^{2+} concentration to [**4**]. The experimental data were found to be nicely fitted to a 2:1 binding model by the *EQNMR* program. The Hg^{2+} ion was believed to be sandwiched between the two S or Se atoms from two complexes, instead of being encapsulated inside the crown, probably as a result of the weaker binding effect of the O atoms to the Hg^{2+} ions, as well as the unfavorable electrostatic effect between the complexes and the Hg^{2+} ion. Job's plot for the complexation of complex **4** for Hg^{2+} also showed 2:1 binding stoichiometry (Figure 6c). For complexes **1**−**4**, a steady downfield shift of the $-CH_2-$ protons was observed upon the addition of Ag^+ ions in acetonitrile. The ^{1}H NMR spectral changes of complex **2** upon the addition of Ag^+ ions and the proton chemical shifts of $-CH_2S-$ as a function of the ratio of added Ag^+ concentration to the complex are shown in Figure 7a,b. Smaller changes in the chemical shift values were observed for the binding of Ag^+ ions than Hg^{2+} ions. The titration data could be fitted nicely using a 1:1 binding model, from which the association constant was determined. The 1:1 binding stoichiometry between the

(31) Hynes, M. J. *J. Chem. Soc., Dalton Trans.* **1993**, 311.

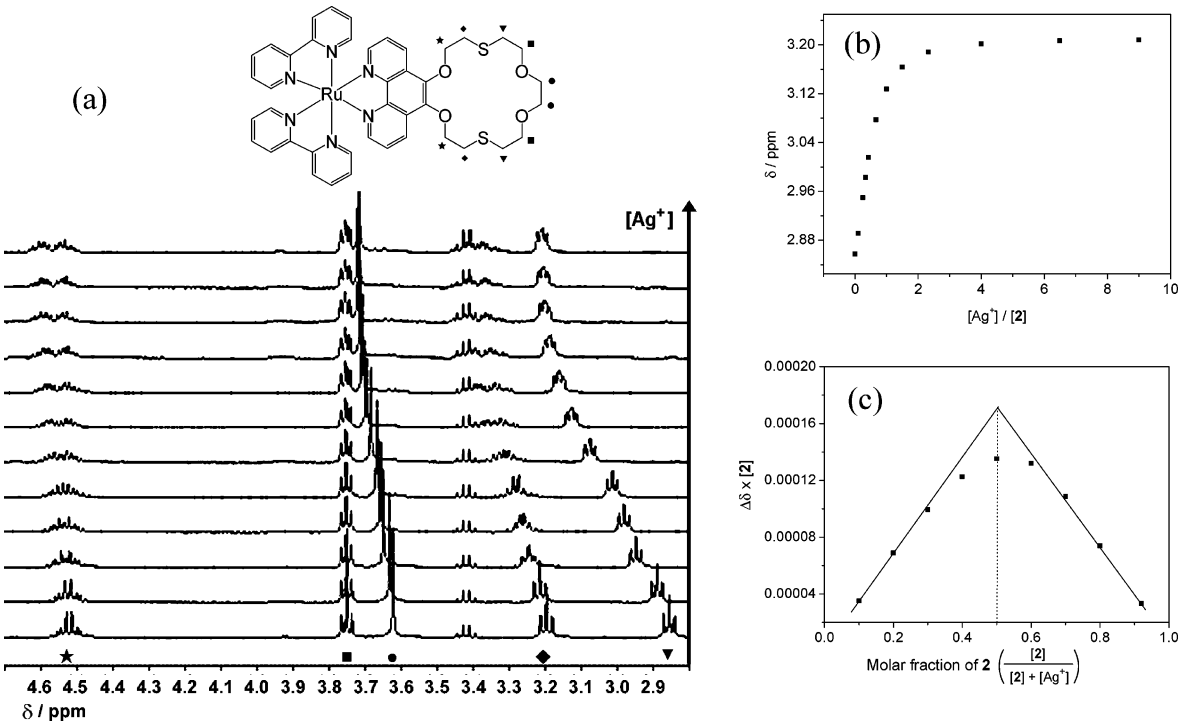


Figure 7. (a) ^{1}H NMR spectral traces of **2** in CD_3CN upon the addition of $AgClO_4$. (b) Plot of proton chemical shifts of $-CH_2S-$ (labeled as ▼) as a function of the ratio of $[Ag^+]/[\mathbf{2}]$. (c) Job's plot for the binding of complex **2** with Ag^+ ions showing a 1:1 stoichiometry.

complex and the Ag^+ ion was also confirmed by Job's plot and is shown in Figure 7c. The Ag^+ ion was believed to be located inside the cavity of the crown probably because of the smaller electrostatic effect between the complexes and the Ag^+ ions. Unlike the crown-containing complexes, no observable changes in the chemical shift were noted for the crown-free complex **5**, when Hg^{2+} or Ag^+ ions were added, suggesting the importance of the S or Se atoms to the cation-binding ability of the complexes. The stability constants for complexes **1**−**4** toward Hg^{2+} and Ag^+ ions are summarized in Table 5. The binding constants of Ag^+ ions in acetonitrile for **1**−**4** were found to be much smaller than that of Hg^{2+}, and the ion-binding ability for the same metal ion was in the order of **1** > **2** > **4** > **3** ≫ **5**. The results were in line with the decreasing electron-richness and softness of the donor atoms on the crown moieties on going from **L1** to **L2** to **L4** to **L3**. The addition of other metal ions such as Na^+, Ba^{2+}, Cd^{2+}, and Zn^{2+} to the complexes in acetonitrile did not induce significant changes in the ^{1}H NMR spectra, confirming the selectivity of the complexes toward Hg^{2+} ions.

The metal ions including Ca^{2+}, Ba^{2+}, and Zn^{2+} were also selected for the study of the binding effect between the cations and complex **6** by ^{1}H NMR spectroscopy. The addition of these metal ions to complex **6** in an acetonitrile solution resulted in significant upfield and downfield shifts of the NH and $-NCH_2-$ proton signals, respectively (Figure S1 in the Supporting Information). The binding constants are also listed in Table 5, all of which were consistent with those determined from the UV−vis and emission studies. A significant upfield shift of the −NH proton resonance signal was also observed upon the addition of Hg^{2+}, and a positive-ion ESI-MS study of an acetonitrile solution of $[Ru(bpy)_2(\mathbf{L6})]^{2+}$ and $Hg(ClO_4)_2$ established the identity of the ion-bound adduct, $\{[Ru(bpy)_2(\mathbf{L6}-Hg)](ClO_4)_3\}^+$ at *m*/*z* 1280, indicating that the −NH protons remain intact and undeprotonated upon binding to the metal ions. Although the crystal structure of the ion-bound adduct of complex **6** was not determined, crystal structures of Hg^{2+}-bound organic aza-crown compounds in the literature[32] commonly show that the −NH protons on the aza-crown remain intact even after complexation to the Hg^{2+} ions, eliminating the possible deprotonation of the aza-crown upon metal ion binding.

Conclusion

A series of ruthenium(II) diimine complexes containing thia-, selena-, and aza-crowns 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, luminescence, and ^{1}H NMR spectroscopy. The absence of spectral changes of complexes **1**−**5** and the large spectral changes observed of complex **6** in the UV−vis spectra upon the addition of metal ions showed the important role of the N atom directly connected to the phenanthroline unit in the aza-crown ether moiety. The luminescence properties of

(32) (a) Aragoni, M. C.; Arca, M.; Bencini, A.; Blake, A. J.; Caltagirone, C.; Decortes, A.; Demartin, F.; Devillanova, F. A; Faggi, E.; Dolci, L. S.; Garau, A.; Isaia, F.; Lippolis, V.; Prodi, L.; Wilson, C.; Valtancoli, B.; Zaccheronie, N. *J. Chem. Soc., Dalton Trans.* **2005**, 2994. (b) Caltagirone, C.; Bencini, A.; Demartin, F.; Devillanova, F. A.; Garau, A.; Isaia, F.; Lippolis, V.; Mariani, P.; Papke, U.; Tei, L.; Verani, G. *J. Chem. Soc., Dalton Trans.* **2003**, 901. (c) Bebout, D. C.; Delanoy, A. E.; Ehmann, D. E.; Kastner, M. E.; Parrish, D. A.; Butcher, R. *Inorg. Chem.* **1998**, *37*, 2952. (d) Park, G.; Ye, N.; Rogers, R. D.; Brechibiel, M. W.; Planalp, R. P. *Polyhedron* **2000**, *19*, 1155. (e) Garcia-Espana, E.; Latorre, J.; Luis, S. V.; Miravet, J. F.; Pozuelo, P. E.; Ramirez, J. A.; Sorinao, C. *Inorg. Chem.* **1996**, *35*, 4591. (f) Panda, S.; Singh, H. B.; Butcher, R. J. *Inorg. Chem.* **2004**, *43*, 8532.

complex **1** were found to be sensitive and selective to the presence of Hg^{2+} ions in an acetonitrile solution. The results demonstrated the important role of the S atom in the oxa-crown ether moiety in complex **1** for the specific binding of the softer Hg^{2+} ions. The results from emission and the ^1H NMR method showed that the complexes would preferentially bind the softer ions after the O atoms, which would preferentially bind alkali and alkaline-earth metal ions, were replaced by the softer S and Se donor atoms. The complexes with a larger number of S atoms would result in a strong binding affinity for the Hg^{2+} ion. Complex **6** was found to exhibit a higher binding affinity toward transition-metal ions than alkaline-earth metal ions, and the binding constant of complex **6** toward Hg^{2+} was much higher than others, confirming its high selectivity and specifity toward the Hg^{2+} ion.

Acknowledgment. V.W.-W.Y. acknowledges support from the University Development Fund of The University of Hong Kong, The University of Hong Kong, and the University Grants Committee of the Hong Kong Special Administrative Region, China (Project AoE/P-10/01). M.-J. L. acknowledges the receipt of a postgraduate studentship, administered by The University of Hong Kong.

Supporting Information Available: X-ray crystallographic data in CIF format and ^1H NMR spectral changes of complex **6** upon titration with Ba^{2+} ions. This material is available free of charge via the Internet at http://pubs.acs.org.

IC061507Z