

Synthesis, photophysics and electrochemistry of copper(I) diimine complexes containing thia-, seleno- and telluro-crowns. A spectrochemical and luminescence ion probe for soft metal ions

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A series of copper(I) diimine complexes containing benzo-10-thia-15-crown-5, benzo-10-selena-15-crown-5, benzo-10-tellura-15-crown-5 and benzo-7,10,13-trithia-15-crown-5 moieties have been synthesized and characterized and their photophysics and electrochemistry studied. The encapsulation of soft metal ions by the cavity of the complexes has been investigated by electronic absorption and emission spectroscopy. The crystal structures of $[\text{Cu}(\text{PPh}_3)_2(\text{dic-S})]\text{BF}_4$ and $[\text{Cu}(\text{PPh}_3)_2(\text{dic-Se})]\text{BF}_4$ have been determined.

Introduction

The design of highly selective receptors for metal ions is of great importance in the area of ion transport and chemosensing applications. The design and synthesis of such molecules have continued to develop since the pioneering work of Pedersen,¹ Lehn² and Cram³ involving the preparation of cation selective crown ethers, cryptands and spherands. It has now been well established that crown ethers bind strongly to those metal cations in which the ionic radii best match the radius of the cavity formed by the polyether ring. Consequently, crown ethers of varying cavity sizes can selectively bind metal cations of different ionic radii.^{4,5} Over the past three decades increasing attention has been paid to variation of the donor atoms to include sulfur or nitrogen in order to tune the crown ether cation binding.^{4,6}

Although there have been numerous reports on the complexation of alkali and alkaline earth metal ions with crown ethers and macrocycles,⁷ corresponding studies on the complexation of transition or late transition metal cations are less extensive.⁸

As an extension of our previous work on copper(I) diimine complexes containing crown ether pendants,⁹ herein we report the synthesis and ion-binding studies of a series of copper(I) diimine-crown complexes with either one or more of the oxygen atoms replaced by other softer donor atoms such as sulfur, selenium or tellurium.

Experimental

Catechol and selenium powder were obtained from Lancaster Synthesis Ltd. Tellurium powder was obtained from Strem Chemicals Inc. Bis(2-hydroxyethyl) sulfide, bis(2-sulfanylethyl) sulfide and 2-pyridinecarbaldehyde were obtained from Aldrich Chemical Co. *p*-Toluenesulfonyl chloride was obtained from Acros. Nitric acid (65%) and palladium/charcoal were obtained from Merck. Pyridine and hydrazine hydrate were purchased from BDH Chemical Co. $[\text{Cu}(\text{MeCN})_4]\text{BF}_4$ was prepared by the modification of a literature procedure^{10a} and $[\text{Cu}(\text{PPh}_3)_2(\text{MeCN})_2]\text{BF}_4$ was prepared by a published procedure.^{10b} 1,2-Bis(2-hydroxyethoxy)benzene,¹¹ 1,2-bis(2-hydroxyethoxy)-4-nitrobenzene^{11a} and 1,2-bis[2-(*p*-tosyloxy)ethoxy]-4-nitrobenzene¹² were synthesized according to literature procedures. All other reagents were of analytical grade and were used as received.

Syntheses

4'-Nitrobenzo-10-thia-15-crown-5. This was synthesized by modification of a procedure for 4'-nitrobenzo-15-crown-5.^{11a,12,13} Sodium (1.38 g, 60 mmol) was added to *tert*-butyl alcohol (200 mL) and the mixture was heated to reflux until the sodium dissolved. Bis(2-hydroxyethyl) sulfide (3.29 g, 27 mmol) in *tert*-butyl alcohol (20 mL) was then added and the mixture was refluxed for 1 h. A solution of 1,2-bis[2-(*p*-tosyloxy)ethoxy]-4-nitrobenzene (14.96 g, 27 mmol) in THF (100 mL) was then added very slowly. Reflux was continued for 12 h. After cooling, the solid was filtered and extracted with chloroform, and the filtrate together with the chloroform extract was concentrated on a rotary evaporator. The residue was then dissolved in dichloromethane and purified by column chromatography on silica gel, using CH_2Cl_2 - Et_2O (50:1, v/v) as the eluent. Subsequent recrystallization from ethanol gave the desired product as yellow crystals. Yield: 1.60 g (18%); mp 104–105 °C. ¹H NMR (300 MHz, CDCl_3): δ 2.86 (m, 4H, CH_2SCH_2), 3.86 (m, 4H, $\text{C}_6\text{H}_3\text{OCH}_2\text{CH}_2\text{O}$), 3.95 (m, 4H, $\text{OCH}_2\text{CH}_2\text{S}$), 4.20 (m, 4H, $\text{C}_6\text{H}_3\text{OCH}_2$), 6.88 (d, 1H, C_6H_3), 7.73 (d, 1H, C_6H_3), 7.90 (dd, 1H, C_6H_3). EI-MS: m/z 329 (M^+) (Found: C, 50.81; H, 5.78; N, 4.23. Calc. for $\text{C}_{14}\text{H}_{19}\text{NO}_6\text{S}$: C, 51.05; H, 5.81; N, 4.25%).

4'-Aminobenzo-10-thia-15-crown-5. This was synthesized by modification of a procedure for 4'-aminobenzo-15-crown-5.^{11a} To a mixture of 4'-nitrobenzo-10-thia-15-crown-5 (1.65 g, 5 mmol) in ethanol (60 mL) was added 10% Pd/C (0.2 g) and the mixture was heated to reflux under nitrogen. Hydrazine hydrate (8 mL) was added and the mixture was refluxed for 12 h. After cooling, Pd/C was filtered off and extracted with chloroform. The filtrate was diluted with water (20 mL) and extracted with chloroform. The combined chloroform solution was washed with water and dried over anhydrous magnesium sulfate. After the solvent was evaporated, the residue was recrystallized from ethanol to give white plate-like crystals. Yield: 1.27 g (85%); mp 132–134 °C. ¹H NMR (300 MHz, CDCl_3): δ 2.83 (m, 4H, CH_2SCH_2), 3.45 (s, 2H, NH_2), 3.87 (m, 8H, CH_2OCH_2), 4.07 (m, 4H, $\text{C}_6\text{H}_3\text{OCH}_2$), 6.23 (dd, 1H, C_6H_3), 6.29 (d, 1H, C_6H_3), 6.73 (d, 1H, C_6H_3). EI-MS: m/z 299 (M^+) (Found: C, 56.13; H, 7.06; N, 4.51. Calc. for $\text{C}_{14}\text{H}_{21}\text{NO}_4\text{S}$: C, 56.17; H, 7.07; N, 4.68%).

4'-(2-Pyridylmethyleneamino)benzo-10-thia-15-crown-5 (dic-S). The synthetic procedure was similar to that used for 4'-(2-pyridylmethyleneamino)benzo-15-crown-5.¹⁴ To a heated solution of 4'-aminobenzo-10-thia-15-crown-5 (1.32 g, 4.4 mmol) in ethanol (10 mL) was added 2-pyridinecarbaldehyde (0.47 g, 4.4 mmol) and the mixture was refluxed for 1 h. After cooling, the yellow crystals were collected and washed with ethanol. Yield: 1.45 g (85%); mp 109–111 °C. ¹H NMR (300 MHz, CDCl₃): δ 2.85 (t, 4H, CH₂SCH₂), 3.90 (m, 8H, CH₂OCH₂), 4.17 (m, 4H, C₆H₃OCH₂), 6.93 (m, 3H, C₆H₃), 7.36 (m, 1H, C₅H₄N), 7.80 (m, 1H, C₅H₄N), 8.17 (d, 1H, C₅H₄N), 8.63 (s, 1H, CH=N), 8.71 (d, 1H, C₅H₄N). EI-MS: *m/z* 388 (M⁺) (Found: C, 60.84; H, 6.01; N, 6.99. Calc. for C₂₀H₂₄N₂O₄S·0.5H₂O: C, 60.43; H, 6.34; N, 7.05%).

4'-Nitrobenzo-10-selena-15-crown-5. The procedure was similar to that of 4'-nitrobenzo-10-thia-15-crown-5 except bis(2-hydroxyethyl) selenide¹⁵ was used instead of bis(2-hydroxyethyl) sulfide. Yield: 1.22 g (12%). ¹H NMR (300 MHz, CDCl₃): δ 2.87 (m, 4H, CH₂SeCH₂), 3.95 (m, 8H, CH₂OCH₂), 4.20 (m, 4H, C₆H₃OCH₂), 6.88 (d, 1H, C₆H₃), 7.74 (d, 1H, C₆H₃), 7.91 (dd, 1H, C₆H₃). EI-MS: *m/z* 377 (M⁺) (Found: C, 44.04; H, 4.96; N, 3.40. Calc. for C₁₄H₁₉NO₆Se·0.5H₂O: C, 43.64; H, 5.23; N, 3.64%).

4'-Aminobenzo-10-selena-15-crown-5. The procedure was similar to that of 4'-aminobenzo-10-thia-15-crown-5 except 4'-nitrobenzo-10-selena-15-crown-5 was used. Yield: 1.32 g (76%). ¹H NMR (300 MHz, CDCl₃): δ 2.84 (m, 4H, CH₂SeCH₂), 3.46 (s, 2H, NH₂), 3.91 (m, 8H, CH₂OCH₂), 4.07 (m, 4H, C₆H₃OCH₂), 6.22 (dd, 1H, C₆H₃), 6.29 (d, 1H, C₆H₃), 6.73 (d, 1H, C₆H₃). EI-MS: *m/z* 347 (M⁺) (Found: C, 48.50; H, 6.11; N, 3.96. Calc. for C₁₄H₂₁NO₄Se: C, 48.56; H, 6.11; N, 4.05%).

4'-(2-Pyridylmethyleneamino)benzo-10-selena-15-crown-5 (dic-Se). The procedure was similar to that of dic-S except 4'-aminobenzo-10-selena-15-crown-5 was used instead of 4'-aminobenzo-10-thia-15-crown-5. Yield: 1.57 g (82%). ¹H NMR (300 MHz, CDCl₃): δ 2.86 (t, 4H, CH₂SeCH₂), 3.97 (m, 8H, CH₂OCH₂), 4.18 (m, 4H, C₆H₃OCH₂), 6.94 (m, 3H, C₆H₃), 7.36 (m, 1H, C₅H₄N), 7.80 (m, 1H, C₅H₄N), 8.17 (d, 1H, C₅H₄N), 8.63 (s, 1H, CH=N), 8.70 (d, 1H, C₅H₄N). EI-MS: *m/z* 436 (M⁺) (Found: C, 55.14; H, 5.44; N, 6.27. Calc. for C₂₀H₂₄N₂O₄Se: C, 55.18; H, 5.56; N, 6.43%).

4'-Nitrobenzo-10-tellura-15-crown-5. Bis(2-hydroxyethyl) telluride was prepared by modification of a literature procedure.¹⁵ The procedure for synthesis of 4'-nitrobenzo-10-thia-15-crown-5 was similar to that of 4'-nitrobenzo-10-thia-15-crown-5 except bis(2-hydroxyethyl) telluride was used instead of bis(2-hydroxyethyl) sulfide. Yield: 0.98 g (9%); mp 117–120 °C. ¹H NMR (300 MHz, CDCl₃): δ 2.90 (m, 4H, CH₂TeCH₂), 3.96 (m, 4H, C₆H₃OCH₂CH₂O), 4.04 (m, 4H, OCH₂CH₂Te), 4.22 (m, 4H, C₆H₃OCH₂), 6.90 (d, 1H, C₆H₃), 7.75 (d, 1H, C₆H₃), 7.91 (dd, 1H, C₆H₃). EI-MS: *m/z* 427 (M⁺) (Found: C, 39.37; H, 4.40; N, 3.14. Calc. for C₁₄H₁₉NO₆Te: C, 39.57; H, 4.51; N, 3.30%).

4'-Aminobenzo-10-tellura-15-crown-5. The procedure was similar to that of 4'-aminobenzo-10-thia-15-crown-5 except 4'-nitrobenzo-10-tellura-15-crown-5 was used instead of 4'-nitrobenzo-10-thia-15-crown-5. Yield: 1.39 g (70%); mp 167–170 °C. ¹H NMR (300 MHz, CDCl₃): δ 2.88 (m, 4H, CH₂TeCH₂), 3.47 (s, 2H, NH₂), 3.89 (m, 4H, C₆H₃OCH₂CH₂O), 4.05 (m, 8H, C₆H₃OCH₂, OCH₂CH₂Te), 6.25 (dd, 1H, C₆H₃), 6.30 (d, 1H, C₆H₃), 6.74 (d, 1H, C₆H₃). EI-MS: *m/z* 397 (M⁺) (Found: C, 41.93; H, 5.25; N, 3.35. Calc. for C₁₄H₂₁NO₄Te·0.5H₂O: C, 41.63; H, 5.49; N, 3.47%).

4'-(2-Pyridylmethyleneamino)benzo-10-tellura-15-crown-5 (dic-Te). The procedure was similar to that of dic-S except 4'-aminobenzo-10-tellura-15-crown-5 was used instead of 4'-aminobenzo-10-thia-15-crown-5. Yield: 1.99 g (93%). ¹H NMR (300 MHz, CDCl₃): δ 2.92 (t, 4H, CH₂TeCH₂), 3.98 (m, 4H, C₆H₃OCH₂CH₂O), 4.08 (t, 4H, OCH₂CH₂Te), 4.20 (m, 4H, C₆H₃OCH₂), 6.96 (m, 3H, C₆H₃), 7.38 (m, 1H, C₅H₄N), 7.83 (m, 1H, C₅H₄N), 8.20 (d, 1H, C₅H₄N), 8.65 (s, 1H, CH=N), 8.72 (d, 1H, C₅H₄N). EI-MS: *m/z* 486 (M⁺).

4'-Nitrobenzo-7,10,13-trithia-15-crown-5. The procedure was similar to that of 4'-nitrobenzo-10-thia-15-crown-5 except bis(2-sulfanylethyl) sulfide was used instead of bis(2-hydroxyethyl) sulfide. Yield: 4.19 g (43%). ¹H NMR (300 MHz, CDCl₃): δ 2.91 (m, 4H, CH₂SCH₂), 3.09 (m, 8H, CH₂SCH₂), 4.36 (m, 4H, C₆H₃OCH₂), 6.90 (d, 1H, C₆H₃), 7.75 (d, 1H, C₆H₃), 7.92 (dd, 1H, C₆H₃). EI-MS: *m/z* 361 (M⁺) (Found: C, 46.56; H, 5.29; N, 3.77. Calc. for C₁₄H₁₉NO₄S₃: C, 46.52; H, 5.30; N, 3.88%).

4'-Aminobenzo-7,10,13-trithia-15-crown-5. The procedure was similar to that of 4'-aminobenzo-10-thia-15-crown-5 except 4'-nitrobenzo-7,10,13-trithia-15-crown-5 was used instead of 4'-nitrobenzo-10-thia-15-crown-5. Yield: 1.42 g (86%). ¹H NMR (300 MHz, CDCl₃): δ 2.86 (m, 4H, CH₂SCH₂), 3.01 (m, 8H, CH₂SCH₂), 3.54 (s, 2H, NH₂), 4.20 (m, 4H, C₆H₃OCH₂), 6.25 (dd, 1H, C₆H₃), 6.30 (d, 1H, C₆H₃), 6.72 (d, 1H, C₆H₃). EI-MS: *m/z* 331 (M⁺) (Found: C, 50.60; H, 6.36; N, 4.10. Calc. for C₁₄H₂₁NO₂S₃: C, 50.72; H, 6.39; N, 4.23%).

4'-(2-Pyridylmethyleneamino)benzo-7,10,13-trithia-15-crown-5 (dic-3S). The procedure was similar to that of dic-S except 4'-aminobenzo-7,10,13-trithia-15-crown-5 was used instead of 4'-aminobenzo-10-thia-15-crown-5. Yield: 1.70 g (92%). ¹H NMR (300 MHz, CDCl₃): δ 2.90 (m, 4H, CH₂SCH₂), 3.07 (m, 8H, CH₂SCH₂), 4.32 (m, 4H, C₆H₃OCH₂), 6.93 (m, 3H, C₆H₃), 7.37 (m, 1H, C₅H₄N), 7.82 (m, 1H, C₅H₄N), 8.18 (d, 1H, C₅H₄N), 8.65 (s, 1H, CH=N), 8.71 (d, 1H, C₅H₄N). EI-MS: *m/z* 420 (M⁺) (Found: C, 57.06; H, 5.70; N, 6.58. Calc. for C₂₀H₂₄N₂O₂S₃: C, 57.11; H, 5.75; N, 6.66%).

[Cu(PPh₃)₂(dic-S)]BF₄ 1. This was prepared according to a modified method.⁹ To a solution of dic-S (39 mg, 0.1 mmol) in dichloromethane (4 mL) was added a solution of [Cu(PPh₃)₂(MeCN)₂]BF₄ (76 mg, 0.1 mmol) in dichloromethane (4 mL) and the mixture was stirred at room temperature for 1 h during which the solution changed from colourless to orange. After evaporation of the solvent, the residue was dissolved in dichloromethane and diffusion of diethyl ether vapour into its concentrated solution gave **1** as orange crystals. Yield: 80 mg (75%). ¹H NMR (300 MHz, CDCl₃): δ 2.85 (m, 4H, CH₂SCH₂), 3.82 (m, 8H, CH₂OCH₂), 3.90 (t, 2H, C₆H₃OCH₂), 4.10 (t, 2H, C₆H₃OCH₂), 6.56 (d, 1H, C₆H₃), 6.83 (dd, 1H, C₆H₃), 7.02 (d, 13H, phenyl H *ortho* to P, C₆H₃), 7.20 (t, 12H, phenyl H *meta* to P), 7.27 (d, 1H, C₅H₄N), 7.37 (t, 6H, phenyl H *para* to P), 8.00 (m, 2H, C₅H₄N), 8.42 (d, 1H, C₅H₄N), 9.14 (s, 1H, CH=N). Positive FAB-MS: *m/z* 975 (M⁺), 713 (M - PPh₃)⁺, 451 (M - 2PPh₃)⁺ (Found: C, 61.58; H, 4.91; N, 2.27. Calc. for C₅₆H₅₄BF₄N₂O₄P₂SCu·0.5CH₂Cl₂: C, 61.91; H, 5.01; N, 2.53%).

[Cu(PPh₃)₂(dic-Se)]BF₄ 2. This was prepared by a procedure similar to that for **1** except dic-Se was used in place of dic-S to give orange crystals of **2**. Yield: 80 mg (72%). ¹H NMR (300 MHz, CDCl₃): δ 2.80–2.89 (m, 4H, CH₂SeCH₂), 3.78 (m, 4H, C₆H₃OCH₂OCH₂), 3.92 (m, 6H, C₆H₃OCH₂, OCH₂CH₂Se), 4.10 (t, 2H, C₆H₃OCH₂), 6.57 (d, 1H, C₆H₃), 6.83 (dd, 1H, C₆H₃), 7.02 (d, 13H, phenyl H *ortho* to P, C₆H₃), 7.20 (t, 12H, phenyl H *meta* to P), 7.27 (d, 1H, C₅H₄N), 7.37 (t, 6H, phenyl H *para* to P), 8.00 (m, 2H, C₅H₄N), 8.42 (d, 1H, C₅H₄N), 9.14 (s, 1H, CH=N). Positive FAB-MS: *m/z* 1023 (M⁺), 761

(M - PPh₃)⁺, 499 (M - 2PPh₃)⁺ (Found: C, 60.50; H, 4.72; N, 2.47. Calc. for C₅₆H₅₄BF₄N₂O₄P₂SeCu: C, 60.58; H, 4.90; N, 2.52%).

[Cu(PPh₃)₂(dic-Te)]BF₄ 3. This was prepared by a procedure similar to that for **1** except dic-Te was used in place of dic-S to give **3** as an orange-yellow solid. Yield: 100 mg (86%). ¹H NMR (300 MHz, CDCl₃): δ 2.85 (m, 4H, CH₂TeCH₂), 3.78 (d, 4H, C₆H₃OCH₂CH₂O), 3.90 (d, 2H, C₆H₃OCH₂), 3.95 (m, 4H, OCH₂CH₂Te), 4.10 (t, 2H, C₆H₃OCH₂), 6.58 (d, 1H, C₆H₃), 6.85 (dd, 1H, C₆H₃), 7.06 (s, 13H, phenyl H *ortho* to P, C₆H₃), 7.22 (t, 12H, phenyl H *meta* to P), 7.27 (d, 1H, C₅H₄N), 7.38 (t, 6H, phenyl H *para* to P), 7.97 (s, 2H, C₅H₄N), 8.40 (d, 1H, C₅H₄N), 9.14 (s, 1H, CH=N). Positive FAB-MS: *m/z* 1072 (M⁺), 811 (M - PPh₃)⁺, 549 (M - 2PPh₃)⁺ (Found: C, 55.11; H, 4.39; N, 1.99. Calc. for C₅₆H₅₄BF₄N₂O₄P₂TeCu·CH₂Cl₂: C, 55.04; H, 4.54; N, 2.25%).

[Cu(PPh₃)₂(dic-3S)]BF₄ 4. This was prepared by a procedure similar to that for **1** except dic-3S was used in place of dic-S to give **4** as orange crystals. Yield: 91 mg (83%). ¹H NMR (300 MHz, CDCl₃): δ 2.88 (m, 6H, CH₂SCH₂), 3.05 (m, 6H, CH₂SCH₂), 3.88 (s, 2H, C₆H₃OCH₂), 4.23 (t, 2H, C₆H₃OCH₂), 6.60 (d, 1H, C₆H₃), 6.87 (dd, 1H, C₆H₃), 6.98 (d, 1H, C₆H₃), 7.04 (d, 12H, phenyl H *ortho* to P), 7.23 (t, 12H, phenyl H *meta* to P), 7.27 (d, 1H, C₅H₄N), 7.37 (t, 6H, phenyl H *para* to P), 7.96 (t, 2H, C₅H₄N), 8.40 (d, 1H, C₅H₄N), 9.15 (s, 1H, CH=N). Positive FAB-MS: *m/z* 1007 (M⁺), 745 (M - PPh₃)⁺, 483 (M - 2PPh₃)⁺ (Found: C, 58.73; H, 4.65; N, 2.16. Calc. for C₅₆H₅₄BF₄N₂O₂P₂S₃Cu·CH₂Cl₂: C, 59.01; H, 4.78; N, 2.37%).

Physical measurements and instrumentation

UV/VIS spectra were obtained on a Hewlett-Packard 8452A diode array spectrophotometer, and steady-state excitation and emission spectra on a Spex Fluorolog 111 spectrofluorimeter. ¹H NMR spectra were recorded on a Bruker DPX-300 FT-NMR spectrometer in CDCl₃ at 298 K and chemical shifts are reported relative to Me₄Si. Positive ion FAB mass spectra were recorded on a Finnigan MAT95 mass spectrometer. Elemental analyses of the new complexes were performed on a Carlo Erba 1106 elemental analyzer at the Institute of Chemistry, Chinese Academy of Sciences.

The electronic absorption spectral titration for binding constant determination was performed with a Hewlett-Packard 8452A diode array spectrophotometer at 25 °C which was controlled by a Lauda RM6 compact low-temperature thermostat. Supporting electrolyte (0.1 mol dm⁻³ NⁿBu₄PF₆) was added to maintain a constant ionic strength of the sample solution during the titration in order to avoid any changes arising from a change in the ionic strength of the medium. This is especially important for complexes showing a MLCT transition since their absorption characteristics are usually rather sensitive to the nature of the solution medium.

Cyclic voltammetric measurements were performed by using a CH Instruments, Inc. CHI 620 electrochemical analyzer interfaced to an IBM-compatible PC. The electrolytic cell used was a conventional two-compartment cell. The salt bridge of the reference electrode was separated from the working electrode compartment by a Vycor glass bridge. A Ag-AgNO₃ (0.1 mol dm⁻³ in CH₃CN) reference electrode was used. The ferrocenium-ferrocene couple (FcP₂⁺⁰) was used as the internal reference in the electrochemical measurements in dichloromethane (0.1 mol dm⁻³ NⁿBu₄PF₆).^{16a} The working electrode was a glassy carbon (Atomergic Chemetals V25) electrode with a platinum foil acting as the counter electrode. Treatment of the electrode surfaces was as reported previously.^{16b}

Crystal structure determination

Single crystals of **1** and **2** were obtained by vapour diffusion of

diethyl ether into concentrated dichloromethane solutions of the respective complexes.

Crystal data for 1. C₅₆H₅₄N₂O₄P₂SCuBF₄, *M* = 1063.41, triclinic, space group *P* $\bar{1}$ (no. 2), *a* = 14.219(3), *b* = 15.053(4), *c* = 13.124(3) Å, *a* = 99.23(2), *β* = 98.50(2), *γ* = 77.67(4)°, *U* = 2689(1) Å³, *Z* = 2, *D*_c = 1.313 g cm⁻³, μ(Mo-Kα) = 5.64 cm⁻¹, *F*(000) = 1104, *T* = 301 K. 7397 reflections were measured, of which 7059 were unique and *R*_{int} = 0.015. 5357 reflections with *I* > 3σ(*I*) were considered observed and used in the structural analysis. One crystallographic asymmetric unit consists of one formula unit with the F atoms of the anion disordered. In the least-squares refinement, all 66 non-H atoms of the complex cation were refined anisotropically, the 5 F atoms having occupancy numbers 1.0, 1.0, 0.67, 0.67 and 0.66 respectively and the B atom were refined isotropically, and 54 H atoms at calculated positions with thermal parameters equal to 1.3 times that of the attached C atoms were not refined. Convergence for 619 variable parameters by least-squares refinement on *F* with *w* = 4*F*_o²/σ²(*F*_o²), where σ²(*F*_o²) = [σ²(*I*) + (0.011 *F*_o²)²] for 5357 reflections with *I* > 3σ(*I*) was reached at *R* = 0.065 and *wR* = 0.073 with a goodness-of-fit of 2.87.

Crystal data for 2. C₅₆H₅₄N₂O₄P₂SeCuBF₄, *M* = 1110.31, triclinic, space group *P* $\bar{1}$ (no. 2), *a* = 14.236(5), *b* = 15.092(8), *c* = 13.186(7) Å, *a* = 99.54(4), *β* = 99.19(3), *γ* = 77.15(4)°, *U* = 2701(2) Å³, *Z* = 2, *D*_c = 1.365 g cm⁻³, μ(Mo-Kα) = 11.97 cm⁻¹, *F*(000) = 1140, *T* = 301 K. 6510 reflections were measured, of which 6197 were unique and *R*_{int} = 0.027. 3811 reflections with *I* > 3σ(*I*) were considered observed and used in the structural analysis. One crystallographic asymmetric unit consists of one formula unit with the F atoms of the anion disordered. In the least-squares refinement, all 66 non-H atoms of the complex cation were refined anisotropically, the 7 F atoms having occupancy numbers 1.0, 0.7, 0.5, 0.5, 0.5, 0.4 and 0.4 respectively and the B atom were refined isotropically, and 54 H atoms at calculated positions with thermal parameters equal to 1.3 times that of the attached C atoms were not refined. Convergence for 627 variable parameters by least-squares refinement on *F* with *w* = 4*F*_o²/σ²(*F*_o²), where σ²(*F*_o²) = [σ²(*I*) + (0.022 *F*_o²)²] for 3811 reflections with *I* > 3σ(*I*) was reached at *R* = 0.058 and *wR* = 0.069 with a goodness-of-fit of 2.42.

The space groups for both **1** and **2** were determined based on a statistical analysis of intensity distribution and the successful refinement of the structure solved by Patterson methods and expanded by Fourier methods (PATTY^{17a}) and refinement by full-matrix least squares using the software package TeXsan^{17b} on a Silicon Graphics Indy computer.

CCDC reference number 186/1144.

Results and discussion

The ligands dic-S, dic-Se, dic-Te and dic-3S were synthesized by the reaction of the corresponding 4'-aminobenz-15-crown-5 with 2-pyridinecarbaldehyde in ethanol, modified from the procedure reported for (2-pyridylmethyleneamino)benzo-15-crown-5 (dic).¹⁴ All the newly synthesized complexes have been characterized by positive ion FAB-MS and ¹H NMR spectroscopy and gave satisfactory elemental analyses. The crystal structures of [Cu(PPh₃)₂(dic-S)](BF₄) **1** and [Cu(PPh₃)₂(dic-Se)](BF₄) **2** have also been determined.

Crystal structure determination

The crystal structures of the complex cation of **1** and **2** with their atomic numbering are depicted in Figs. 1 and 2, respectively. Selected bond distances and angles for **1** and **2** are summarized in Table 1. The Cu(I) center adopts a distorted tetrahedral geometry with the N(1)-Cu-N(2) angles, 79.8(2)° for **1** and 80.1(3)° for **2**, being much smaller than that expected for a

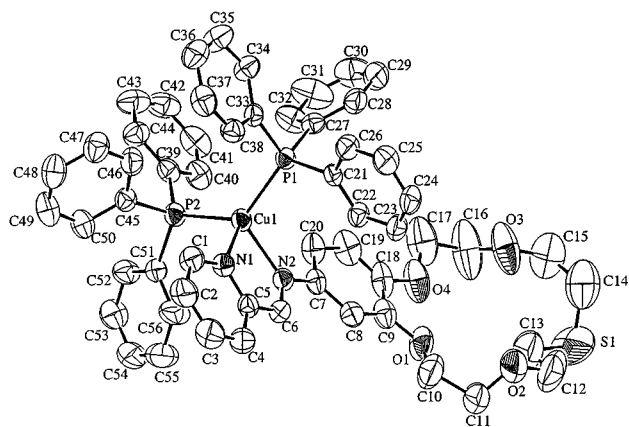


Fig. 1 Perspective view of the cation of complex **1** with atomic numbering scheme. Thermal ellipsoids are drawn at the 40% probability level.

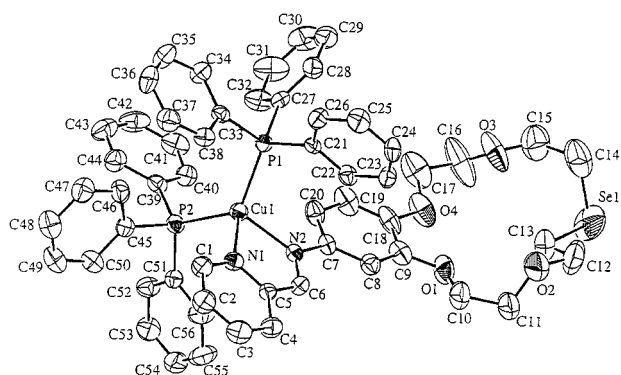
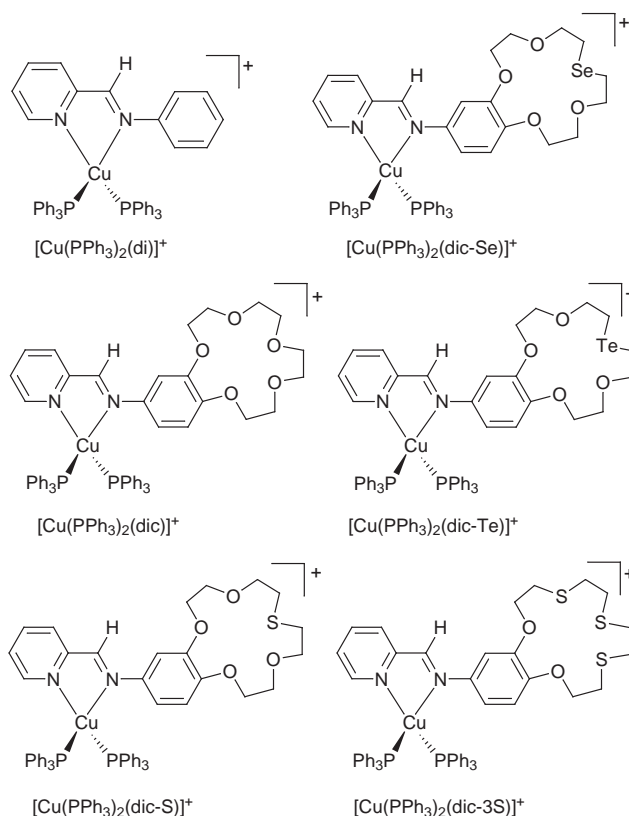


Fig. 2 Perspective view of the cation of complex **2** with atomic numbering scheme. Thermal ellipsoids are drawn at the 40% probability level.



tetrahedral molecule. Similar findings have been reported in other related systems,¹⁸ attributable to the steric demand of the bidentate diimine ligand. The average bond distances of Cu–P

Table 1 Selected bond lengths (Å) and angles (°) for complexes **1** and **2**

| | 1 | 2 | |
|------------------|----------|-------------------|----------|
| Cu–N(1) | 2.110(5) | Cu–N(1) | 2.118(6) |
| Cu–N(2) | 2.106(5) | Cu–N(2) | 2.095(7) |
| Cu–P(1) | 2.266(2) | Cu–P(1) | 2.263(2) |
| Cu–P(2) | 2.259(2) | Cu–P(2) | 2.260(2) |
| S(1)–C(13) | 1.840(2) | Se(1)–C(13) | 1.970(3) |
| S(1)–C(14) | 1.750(2) | Se(1)–C(14) | 1.910(2) |
| | | | |
| N(1)–Cu–N(2) | 79.8(2) | N(1)–Cu–N(2) | 80.1(3) |
| P(1)–Cu–P(2) | 126.3(7) | P(1)–Cu–P(2) | 126.4(9) |
| P(1)–Cu–N(1) | 110.9(1) | P(1)–Cu–N(1) | 110.9(2) |
| P(1)–Cu–N(2) | 109.0(1) | P(1)–Cu–N(2) | 109.0(2) |
| P(2)–Cu–N(1) | 104.6(1) | P(2)–Cu–N(1) | 104.4(2) |
| P(2)–Cu–N(2) | 116.1(1) | P(2)–Cu–N(2) | 115.9(2) |
| C(13)–S(1)–C(14) | 101.3(6) | C(13)–Se(1)–C(14) | 98.7(6) |
| S(1)–C(13)–C(12) | 105.0(1) | Se(1)–C(13)–C(12) | 102.0(1) |
| S(1)–C(14)–C(15) | 115.0(1) | Se(1)–C(14)–C(15) | 112.0(1) |

Table 2 Photophysical data for complexes **1–4**

| Complexes | Medium (T/K) | $\lambda_{\text{abs}}/\text{nm}$ ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) | Emission (λ/nm) |
|-----------|---------------------------------------|--|----------------------------------|
| 1 | Solid (298) | | 532 |
| | Solid (77) | | 584 |
| | Glass (77) ^a | | 639, 698 (sh) |
| | MeOH (298) | 264 (30,690), 376 (10,180) | 446, 582 (sh) |
| | CH ₂ Cl ₂ (298) | 266 (30,420), 386 (9,330) | 478, 652 (sh) |
| 2 | Solid (298) | | 646 |
| | Solid (77) | | 640, 706 |
| | Glass (77) ^a | | 636, 698 (sh) |
| | MeOH (298) | 264 (37,670), 376 (10,110) | 455, 565 (sh) |
| | CH ₂ Cl ₂ (298) | 264 (31,030), 388 (9,540) | 452, 638 (sh) |
| 3 | Solid (298) | | 544 |
| | Solid (77) | | 597, 650 (sh) |
| | Glass (77) ^a | | 630, 695 (sh) |
| | MeOH (298) | 264 (29,240), 376 (9,690) | 435, 554 (sh) |
| | CH ₂ Cl ₂ (298) | 264 (30,910), 376 (8,910) | 510, 542 (sh) |
| 4 | Solid (298) | | 534, 645 |
| | Solid (77) | | 642, 708 (sh) |
| | Glass (77) ^a | | 638, 695 (sh) |
| | MeOH (298) | 264 (30,360), 376 (9,910) | 433, 588 (sh) |
| | CH ₂ Cl ₂ (298) | 264 (38,980), 376 (9,330) | 501 |

^a In EtOH–MeOH 4:1 (v/v).

(2.2625(2) Å), Cu–N (2.108(5) Å) for **1**, and Cu–P (2.2615(2) Å), Cu–N (2.1065(7) Å) for **2** are found to be typical of other related systems¹⁸ and comparable to those of [Cu(PPh₃)₂(dic)]⁺.⁹

Electronic absorption and photophysical properties

All the complexes show low-energy absorption bands at *ca.* 370–390 nm and a higher energy band at *ca.* 260–270 nm (Table 2). The latter is assigned as intraligand (IL) transitions of PPh₃ since free PPh₃ is found to absorb at similar energy. With reference to previous spectroscopic work on related systems,⁹ the low-energy band is assigned as a mixture of metal-to-ligand charge transfer (MLCT, [dπ(Cu) → π*(L)]) and IL [π(L) → π*(L) or n → π*(L)] transitions, where L = dic-S, dic-Se, dic-Te or dic-3S. The assignment is supported by the fact that the free diimine-crown ligands also absorb at such low energies (for example, dic-S, λ_{abs} (MeOH) = 354 nm, λ_{abs} (CH₂Cl₂) = 352 nm. It is found that the low energy absorption band of [Cu(PPh₃)₂L]BF₄ occurs at higher energy than that of the uncrowned analogue⁹ (λ_{abs} = 395 nm in methanol). This observation is attributable to the destabilization of the π* orbital of L by the electron-donating polyether ring in [Cu(PPh₃)₂L]BF₄.

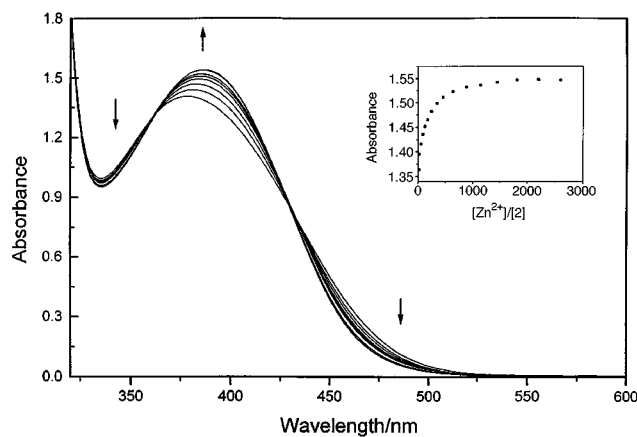


Fig. 3 Electronic absorption spectral traces of **2** in methanol ($0.1 \text{ mol dm}^{-3} \text{ N}^{\text{n}}\text{Bu}_4\text{PF}_6$) upon addition of Zn^{2+} ions at 298 K. The inset shows the UV/VIS spectrophotometric titration curve monitored at 392 nm.

Similar to $[\text{Cu}(\text{PPh}_3)_2(\text{dic})]\text{BF}_4$, complexes **1–4** were found to be luminescent with emission maxima at *ca.* 630–700 nm at 77 K in EtOH–MeOH glass upon excitation at $\lambda > 350 \text{ nm}$. The photophysical data are summarized in Table 2. The emissions are most probably associated with the lowest energy MLCT triplet excited state, and perhaps with some mixing of IL character, which has been reported for other luminescent copper(I) diimine complexes.¹⁹ The high energy emission bands at *ca.* 420–500 nm are assigned as an IL (PPh_3) transition, as reported for other copper(I) phosphine complexes.²⁰

Similarly, the MLCT/IL emission of $[\text{Cu}(\text{PPh}_3)_2\text{L}]\text{BF}_4$ in MeOH and CH_2Cl_2 has been found to occur at higher energy than that of the uncrowned analog $[\text{Cu}(\text{PPh}_3)_2(\text{di})]\text{BF}_4$ (*di* = (2-pyridylmethyleneamino)benzene), which absorbs at 675 nm in MeOH and 682 nm in CH_2Cl_2 .⁹ This shift is in accord with the electronic absorption data and is attributable to the higher π^* orbital energy of the crown ligand owing to the electron-donating effect of the crown.

Cation-binding studies

Unlike $[\text{Cu}(\text{PPh}_3)_2(\text{dic})]\text{BF}_4$ which preferentially binds alkali and alkaline earth metal ions,⁹ addition of alkali or alkaline earth metal ions such as Na^+ , K^+ and Ba^{2+} ions, with respective diameters of 1.94, 2.66 and 2.68 Å,^{1b,21} to complexes **1–4** did not give any observable UV/VIS spectral changes. However, upon addition of transition metal ions such as Zn^{2+} and Cd^{2+} , with respective diameters of 1.48 and 1.94 Å,^{1b,21b} to a methanolic solution of **1–4**, spectral changes occurred with the absorption at *ca.* 370–390 nm exhibiting a slight red-shift. These shifts were ascribed to binding of the cations in the polyether cavity as similar shifts were absent for the uncrowned complex. The observed decrease in MLCT absorption energy upon addition of metal ions is attributed to the stabilization of the ligand π^* orbitals upon complexation of cations to the polyether cavity. It is interesting to note that complexes **1–4** preferentially bind Cd^{2+} ions and not Na^+ ions although they have the same ionic diameter. In view of the high affinity of benzo-15-crown-5 which has a hole diameter of 1.7–2.2 Å^{1b} for Na^+ , it is not unreasonable to ascribe the observed differences in the ion binding property of **1–4** and $[\text{Cu}(\text{PPh}_3)_2(\text{dic})]\text{BF}_4$ to the introduction of soft donor atoms such as S, Se and Te in **1–4**, which would give them a higher affinity for softer metal ions. Thus in the present system, the hard–soft acid–base factor appears to be dominant rather than size-match selectivity in governing the ion binding properties.

Fig. 3 shows the spectral changes and a summary of the titration curve obtained by monitoring the changes in absorbance of a methanolic solution ($0.1 \text{ mol dm}^{-3} \text{ N}^{\text{n}}\text{Bu}_4\text{PF}_6$) of

Table 3 Binding constants of complexes **1–4** for Cd^{2+} and Zn^{2+} cations in MeOH ($0.1 \text{ mol dm}^{-3} \text{ N}^{\text{n}}\text{Bu}_4\text{PF}_6$) at 298 K

| Complex | $\log K_s^a$ | |
|----------|------------------|------------------|
| | Cd^{2+} | Zn^{2+} |
| 1 | 1.61 (1.42) | 1.73 (1.64) |
| 2 | 1.85 (1.70) | 2.00 (1.98) |
| 3 | 1.10 (1.27) | 1.68 (1.73) |
| 4 | 1.86 (1.96) | 1.77 (1.91) |

^a From UV/VIS spectrophotometric method. Data in parentheses from emission studies.

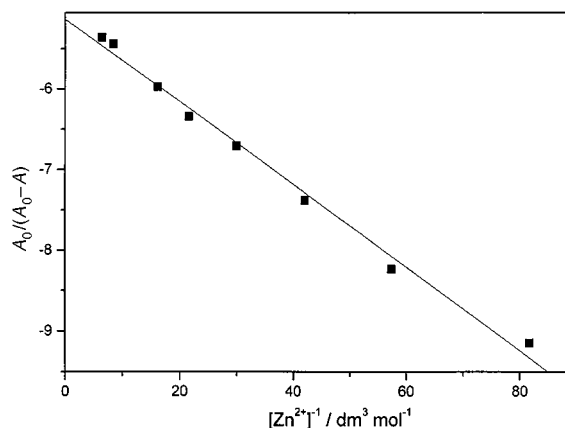


Fig. 4 Plot of $A_0/(A_0 - A)$ vs. $[\text{Zn}^{2+}]^{-1}$ for **2** in MeOH ($0.1 \text{ mol dm}^{-3} \text{ N}^{\text{n}}\text{Bu}_4\text{PF}_6$) monitored at 392 nm.

complex **2** at 392 nm upon addition of zinc acetate. The curves show a gradual increase in the absorbance at 392 nm upon increasing the cation concentration, reaching saturation at higher cation concentrations. With such absorption information, the binding constants could be determined by eqn. (1)

$$\frac{A_0}{A_0 - A} = \frac{\epsilon_0}{\epsilon_0 - \epsilon} \left(1 + \frac{1}{K_s[\text{M}]} \right) \quad (1)$$

where A_0 and A are the absorbance of the complex at a selected wavelength λ in the absence and presence of metal cation $[\text{M}]$, respectively, ϵ_0 and ϵ are the respective molar absorption coefficients for the free and cation-bound copper(I) complex at wavelength λ , and K_s is the binding constant. Therefore, from the plot of $A_0/(A_0 - A)$ vs. $[\text{M}]^{-1}$, the stability constant for the cation-bound copper(I) complex can be determined by the ratio of y -intercept/slope.²² The almost perfect linearity of the fit ($R = 0.997$) is supportive of a stoichiometry of 1:1 at high metal cation concentration. The plot of $A_0/(A_0 - A)$ vs. $[\text{M}]^{-1}$ for Zn^{2+} ions in **2** is shown in Fig. 4. The stability constants for the complexes are summarized in Table 3, revealing that the binding constants of Zn^{2+} in methanol for **1–4** are of fairly similar values. The binding constants of Cd^{2+} for **1, 2** and **4** are also similar. However, it is observed that the binding constant of Cd^{2+} for **3** is smaller than that of the others which suggests that the crown cavity of *dic*-Te in **3** may provide a poorer fit for Cd^{2+} . It is likely that Cd^{2+} ions, being larger in size than Zn^{2+} ions, would have a poorer size match with *dic*-Te as a smaller hole diameter would be expected for *dic*-Te than *dic*-Se, *dic*-S and *dic*.

Complexes **1–4** in low temperature glasses show an emission with a maximum at *ca.* 630–700 nm upon excitation at $\lambda > 350 \text{ nm}$. The emission is probably derived from the lowest triplet MLCT state as commonly observed in other copper(I) diimine systems.¹⁹ However, these complexes are only very weakly emissive in MeOH and CH_2Cl_2 solution. Addition of Zn^{2+} or Cd^{2+}

Table 4 Electrochemical data for complexes **1–4** in CH₂Cl₂ (0.1 mol dm⁻³ NⁿBu₄PF₆)

| Complex | Oxidation E_{pa}/V vs. SCE ^a | Reduction E_i/V vs. SCE ^b |
|----------|--|---|
| 1 | +1.32 | -1.23 |
| 2 | +1.30 | -1.24 |
| 3 | +1.27 | -1.31 |
| 4 | +1.28 | -1.25 |

^a E_{pa} refers to the anodic peak potential of the irreversible oxidation wave. ^b $E_i = (E_{pa} + E_{pc})/2$ where E_{pa} and E_{pc} are the anodic and cathodic peak potentials of the quasi-reversible reduction couple, respectively.

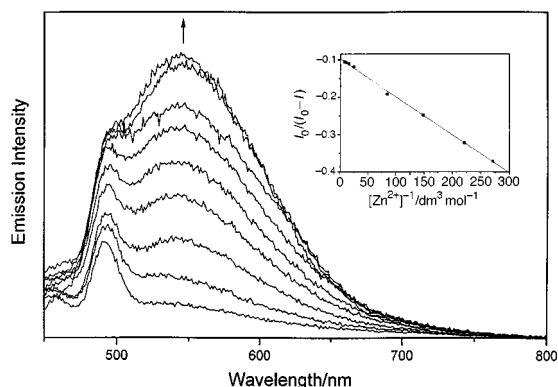


Fig. 5 Emission spectral changes of **2** in methanol (0.1 mol dm⁻³ NⁿBu₄PF₆) upon addition of Zn²⁺ ions at 298 K. Excitation wavelength was selected at the isosbestic wavelength which is at 430 nm. Inset shows the plot of $I_0/(I_0 - I)$ vs. $[Zn^{2+}]^{-1}$ monitored at 545 nm.

ions to the degassed MeOH solution of this class of compounds gave rise to an enhancement of the emission intensities upon excitation at the isosbestic wavelength. Such enhancement in the emission intensity is likely to be a result of the blocking of the intramolecular reductive electron-transfer quenching mechanism since the unbound thia-, seleno- and telluro-crowns could act as good electron donors. Upon cation binding, their donor properties are destroyed and the photoinduced electron transfer no longer represents a substantial quenching pathway. Fig. 5 shows the emission spectral changes of **2** and a plot of $I_0/(I_0 - I)$ vs. $[M]^{-1}$ for Zn²⁺ ions in **2** monitored at 545 nm upon increasing the cation concentration. With such emission information, the binding constants could similarly be determined by eqn. (2)²² where I_0 and I are the emission intensity of the

$$\frac{I_0}{I_0 - I} = \frac{\epsilon_0 \Phi_0}{\epsilon_0 - \epsilon \Phi} \left(1 + \frac{1}{K_s [M]} \right) \quad (2)$$

complex at a selected wavelength λ in the absence and presence of metal cation $[M]$, respectively, ϵ_0 and ϵ are the respective molar absorption coefficients for the free and cation-bound copper(i) complex at wavelength λ , Φ_0 and Φ are the respective quantum yields of the free and cation-bound copper(i) complex at wavelength λ , and K_s is the binding constant. Therefore, from the plot of $I_0/(I_0 - I)$ vs. $[M]^{-1}$, the stability constant for the cation-bound copper(i) complex can be determined by the ratio of y -intercept/slope.²² The stability constants of **1–4** are summarized in Table 3. The stability constants obtained are comparable to those determined using the UV/VIS spectrophotometric method.

Electrochemical properties

The electrochemical data for **1–4** in dichloromethane are summarized in Table 4. Cyclic voltammetric studies of all four complexes in CH₂Cl₂ (0.1 mol dm⁻³ NⁿBu₄PF₆) show similar cyclic voltammograms with an irreversible metal-centered oxidation wave and a quasi-reversible ligand-centered reduction

couple. The more negative value for the reduction of **3** (-1.31 V vs. SCE) as compared to that of the uncrowned analog [Cu(PPh₃)₂(di)]BF₄ (-1.26 V vs. SCE)⁹ indicates the reduced ease of dic-Te reduction compared to that of the uncrowned diimine, which is in accord with the higher π^* energy of dic-Te due to the electron-donating atoms in the crown unit. Similarly, the metal-based oxidation potential of complex **3** (+1.27 V vs. SCE) is less positive than that of the uncrowned analog (+1.34 V vs. SCE),⁹ although the trend for the complexes themselves is not so obvious. The greater ease of oxidation of complexes **1–4** than the uncrowned complex is attributable to the more electron rich metal center in the presence of electron-donating polyether substituents, resulting in the greater ease of oxidation of the metal center.

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