Synthesis and Co-ordination Chemistry of New Schiff-base Bis(crown ether) Ligands containing Recognition Sites for Alkali- and Transition-metal Guest Cations. Crystal Structure of a Copper(I)–Potassium Complex‡

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New Schiff-base bis(crown ether) ligands L^1–L^5 containing recognition sites for alkali- and transition-metal guest cations have been prepared by the condensation of two equivalents of 15-formyl-2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecine with diamines H_2NXNH_2 ($X = [CH_2]_2S[CH_2]_2$, $[CH_2]_2S[CH_2]_2S[CH_2]_2$, $[CH_2]_2S[CH_2]_3S[CH_2]_2$, $[CH_2]_3S[CH_2]_2S[CH_2]_3$ or $[CH_2]_2NH[CH_2]_2$). The sodium cation forms 2:1 Na^+ : L complexes, whereas the larger potassium cation produces 1:1 intramolecular sandwich complexes with these ligands. Homometallic copper(I) complexes and heteropolymetallic copper(I)–sodium and –potassium complexes have also been isolated. A single-crystal X-ray structure of one copper–potassium complex has been determined. Heteropolymetallic silver(I)–sodium and –potassium ligand complexes have also been prepared. Carbon-13 NMR titration studies suggest that the stoichiometry of the Schiff-base bis(crown ether) ligand to potassium guest cations is dependent upon the stereochemical requirements of the co-bound silver(I) guest cation.

The design and synthesis of multisite macrocyclic ligands containing recognition sites for binding several guest species such as 'hard' and 'soft' metal cations is of considerable current interest.[1–6] Such receptors may exhibit novel allosteric, co-operative and catalytic properties by binding sequentially two or more guest metal cations in close proximity to one another. For example, Rebek *et al.*[7] and more recently our own group[8] have incorporated the 3,3′-disubstituted 2,2′-bipyridine unit into crown ether structural frameworks and shown these systems to display allosteric behaviour. The resulting homo- or hetero-nuclear complexes may also serve as models of relevance to bioinorganic chemistry such as metalloproteins and metalloenzymes.[9]

We report here the synthesis and co-ordination chemistry of a number of new Schiff-base bis(crown ether) ligands containing recognition sites for alkali- and transition-metal guest cations and also the single-crystal X-ray structure of a copper(I)–potassium heterobimetallic complex. A preliminary report of this work has recently appeared.[5]

Experimental

Solvent and Reagent Pretreatment.—Where necessary solvents were purified by distillation prior to use. The following drying agents and conditions were used before distillation: acetonitrile was distilled from CaH_2, dichloromethane from P_2O_5, hexane and diethyl ether from sodium, toluene and tetrahydrofuran (thf) from sodium using benzophenone as the indicator, dimethylformamide (dmf) under reduced pressure from $MgSO_4$, and thionyl chloride from triphenyl phosphite.

Unless otherwise stated, commercial grade chemicals were used without further purification.

Methods.—Melting points were recorded on a Gallenkamp apparatus in open capillaries and are uncorrected. Literature values for known compounds are cited in parentheses. Infrared spectra were obtained on a Perkin-Elmer 297 instrument (4000–600 cm^{-1}) as KBr discs, NMR spectra on JEOL FX-90Q, GX-270 and Bruker WH400 instruments using tetramethylsilane as internal standard ($\delta = 0$). Mass spectra and fast atom bombardment (FAB) mass spectra were recorded on a Kratos MS80 RF mass spectrometer with an argon primary beam and 3-nitrobenzyl alcohol as the matrix. The UV/VIS spectra were recorded on a Shimadzu UV-240 spectrophotometer. All elemental analyses were performed at the University of Birmingham.

The following compounds were prepared according to literature procedures: H_2NXNH_2 ($X = [CH_2]_2S[CH_2]_2$,[10] $[CH_2]_2S[CH_2]_2S[CH_2]_2$,[11] $[CH_2]_2S[CH_2]_3S[CH_2]_2$[11] or $[CH_2]_3S[CH_2]_2S[CH_2]_3$[12]), 15-formyl-2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecine **2**,[13] 1,8-bis(2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecin-15-ylmethyleneamino)-3,6-dithiaoctane(L^2)(ref. 5*b*) and $[Cu(CH_3CN)_4]PF_6$.[14]

Syntheses.—1,5-Bis(2,3,5,6,8,9,11,12-*octahydro*-1,4,7,10,13-*benzopentaoxacyclopentadecin*-15-*ylmethyleneamino*)-3-*azapentane* (L^5). 15-Formyl-2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecine **2** (2.5 g, 8.44 mmol) was heated to 120 °C and diethylenetriamine (0.43 g, 4.22 mmol) was added with stirring. The temperature was maintained at 120 °C for 30 min. The resulting liquid was allowed to cool and triturated with diethyl ether to give L^5 as a pale yellow solid. Yield 2.19 g (79%), m.p. 92–94 °C. IR: 1646 cm^{-1} (C=N stretch). Electron impact (EI) mass spectrum: *m*/*z* 658. ^1H NMR ($CDCl_3$, 270 MHz): δ 2.98 (4 H, br s, $NHCH_2$), 3.76 (20 H, m, $C=NCH_2$ and OCH_2CH_2O), 3.91 (8 H, m, aryl-OCH_2CH_2O), 4.13 (8 H, m, aryl–OCH_2), 6.81 (2 H, d, ^3J = 8.2 Hz, aryl H), 7.07 (2 H, br s, aryl H), 7.28 (2 H, s, aryl H), and 8.15 (2 H, s, N=CH) (Found: C, 59.8; H, 7.6; N, 6.2. Calc. for $C_{34}H_{49}N_3O_{10}$: C, 61.9; H, 7.5; N, 6.4%).

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1,5-*Bis*(2,3,5,6,8,9,11,12-*octahydro*-1,4,7,10,13-*benzopentaoxacyclopentadecin*-15-*ylmethyleneamino*)-3-*thiapentane* (L^1). This was prepared in an analogous method to L^5 by replacing diethylenetriamine with 3-thiapentane-1,5-diamine **1a**. Yield of pale yellow powder 90%, m.p. 83.5–85.5 °C. IR 1646 cm^{-1} (C=N stretch). FAB mass spectrum: *m/z* 677, $[M + H]^+$. NMR ($CDCl_3$): ^1H (270 MHz); δ 2.89 (4 H, t, ^3J = 6.9, SCH_2), 3.76 (20 H, m, NCH_2 and OCH_2CH_2O), 3.91 (8 H, m, aryl–$OCH_2C\mathit{H}_2O$), 4.16 (8 H, m, aryl–OCH_2), 6.85 (2 H, d, ^3J = 8.1, aryl H), 7.13 (2 H, d, ^3J = 8.1 Hz, aryl H), 7.28 (2 H, s, aryl H) and 8.16 (2 H, s, N=CH); ^{13}C (22.6 MHz), δ 33.42 (SCH_2), 61.55 (NCH_2), 68.83, 69.45, 70.46 and 71.21 (OCH_2), 111.46, 112.76, 123.36, 129.57, 149.31, and 151.55 (aryl C), and 161.63 (N=C) (Found: C, 60.4; H. 7.0; N, 4.4. Calc. for $C_{34}H_{48}N_2O_{10}S$: C, 60.3; H, 7.2; N, 4.1%).

1,9-*Bis*(2,3,5,6,8,9,11,12-*octahydro*-1,4,7,10,13-*benzopentaoxacyclopentadecin*-15-*ylmethyleneamino*)-3,7-*dithianonane* (L^3). This compound was prepared using an analogous method to the synthesis of L^5, by replacing diethylenetriamine with 3,7-dithianonane-1,9-diamine **1c**. Yield of pale yellow powder 55%, m.p. 86–88 °C. IR 1646 cm^{-1} (C=N stretch). FAB mass spectrum: *m/z* 751, $[M + H]^+$. ^1H NMR ($CDCl_3$, 270 MHz): δ 1.88 (2 H, qnt, ^3J = 7.1, $SCH_2C\mathit{H}_2CH_2S$), 2.65 (4 H, t, ^3J = 7.1 Hz, $SC\mathit{H}_2CH_2C\mathit{H}_2S$), 2.82 (4 H, t, ^3J = 7.0, $SC\mathit{H}_2CH_2N$), 3.41 (8 H, m, aryl–$OCH_2C\mathit{H}_2O$), 3.76 (20 H, m, NCH_2 and OCH_2CH_2O), 4.17 (8 H, m, aryl–OCH_2), 6.85 (2 H, d, ^3J = 8.1, aryl H), 7.16 (2 H, d, ^3J = 8.1 Hz, aryl H), 7.36 (2 H, s, aryl H) and 8.18 (2 H, s, N=CH) (Found: C, 59.5; H, 7.0; N, 4.0. Calc. for $C_{37}H_{54}N_2O_{10}S_2$: C, 59.2; H, 7.2; N, 3.7%).

1,10-*Bis*(2,3,5,6,8,9,11,12-*octahydro*-1,4,7,10,13-*benzopentaoxacyclopentadecin*-15-*ylmethyleneamino*)-4,7-*dithiadecane* (L^4). This was prepared by the same procedure as for L^5 by replacing diethylenetriamine with 4,7-dithiadecane-1,10-diamine **1d** followed by recrystallisation from propan-2-ol. Yield of white powder 16%, m.p. 72–74 °C. IR 1646 cm^{-1} (C=N stretch). FAB mass spectrum: *m/z* 765, $[M + H]^+$. NMR ($CDCl_3$): ^1H (270 MHz), δ 1.97 (4 H, qnt, ^3J = 6.9, $SCH_2CH_2C\mathit{H}_2N$), 2.62 (4 H, t, ^3J = 6.9, $SC\mathit{H}_2CH_2CH_2N$), 2.74 (4 H, s, SCH_2CH_2S), 3.65 (4 H, t, ^3J = 6.9, $SCH_2CH_2C\mathit{H}_2N$), 3.76 and 3.77 (16 H, m, OCH_2CH_2O), 3.91 (8 H, m, aryl–$OCH_2C\mathit{H}_2O$), 4.17 (8 H, m, aryl–OCH_2), 6.85 (2 H, d, ^3J = 8.3, aryl H), 7.13 (2 H, dd, ^3J = 8.3, ^4J = 1.8, aryl H), 7.36 (2 H, d, ^4J = 1.8 Hz, aryl H) and 8.18 (2 H, s, N=CH); ^{13}C (22.6 MHz), δ 29.83 ($SCH_2\mathit{C}H_2CH_2N$), 30.66 (SCH_2CH_2S), 32.13 ($S\mathit{C}H_2CH_2CH_2N$), 59.76 (NCH_2), 68.77, 68.87, 69.39, 70.36 and 71.11 (OCH_2), 111.37, 112.73, 123.17, 129.70, 149.25 and 151.39 (aryl C), and 160.68 (N=C) (Found: C, 59.8; H, 7.0; N, 3.5. Calc. for $C_{38}H_{56}N_2O_{10}S_2$: C, 59.7; H, 7.4; N, 3.7%).

1,5-*Bis*(3,4-*dimethoxybenzoylideneamino*)-3-*azapentane* (L^7). This was prepared using an analogous method to that for L^5 by replacing compound **2** with 3,4-dimethoxybenzaldehyde **4**. Yield of yellow solid 86%, m.p. 75–76 °C. IR 1646 cm^{-1} (C=N stretch). FAB mass spectrum: *m/z* 400, $[M + H]^+$. ^1H NMR ($CDCl_3$, 270 MHz): δ 1.88 (1 H, br s, NH), 3.01 (4 H, br s, $HNC\mathit{H}_2$), 3.74 (4 H, br s, $HNCH_2C\mathit{H}_2N$), 3.86 and 3.89 (12 H, 2 s, OCH_3), 6.81 (2 H, d, ^3J = 8.2, aryl H), 7.02 (2 H, d, ^3J = 8.2 Hz, aryl H), 7.33 (2 H, s, aryl H) and 8.2 (2 H, s, N=CH) (Found: C, 66.2; H, 7.3; N, 10.5. Calc. for $C_{22}H_{29}N_3O_4$: C, 66.1; H, 7.3; N, 10.5%).

Alkali-metal salts. $[KL^1]$ PF_6. The bis(imine) L^1 (0.21 g, 0.32 mmol) and potassium hexafluorophosphate (0.3 g, 3.2 mmol) were dissolved in dry acetonitrile (40 cm^3) and refluxed for 1 h under nitrogen. The solvent was removed *in vacuo* and the yellow solid redissolved in dichloromethane (10 cm^3) and left to crystallise. Yield of yellow solid 50%, m.p. 108–110 °C. IR 1644 (C=N stretch) and 840 cm^{-1} (PF_6). FAB mass spectrum: *m/z* 715, $[M - PF_6]^+$. ^1H NMR ($CDCl_3$, 270 MHz): δ 2.94 (4 H, ^3J = 6.0 Hz, SCH_2), 3.60–3.95 (28 H, m, NCH_2, OCH_2CH_2O and aryl–$OCH_2C\mathit{H}_2O$), 4.05 (8 H, s, aryl–OCH_2), 6.76 (4 H, br s, aryl H), 7.20 (2 H, d, ^3J = 8.2 Hz, aryl H) and 8.09 (2 H, s, N=CH) (Found: C, 46.4; H, 5.7; N, 3.1. Calc. for $C_{34}H_{50}F_6KN_2O_{11}PS$; C, 46.5; H, 5.7; N, 3.2%).

$[KL^2]PF_6$. This was prepared as above replacing ligand L^1 by L^2. Yield of yellow solid 62%, m.p. 123–125 °C. IR 1644 cm^{-1} (C=N stretch). FAB mass spectrum: *m/z* 776, $[M - PF_6]^+$. ^1H NMR ($CDCl_3$, 270 MHz): δ 2.91 (8 H, s, SCH_2), 3.65–3.90 (36 H, m, NCH_2, OCH_2CH_2O and aryl–OCH_2CH_2O), 5.54 (2 H, d, ^3J = 8.3, aryl H), 6.88 (2 H, s, aryl H), 7.23 (2 H, d, ^3J = 8.3 Hz, aryl H) and 8.20 (2 H, s, N=CH).

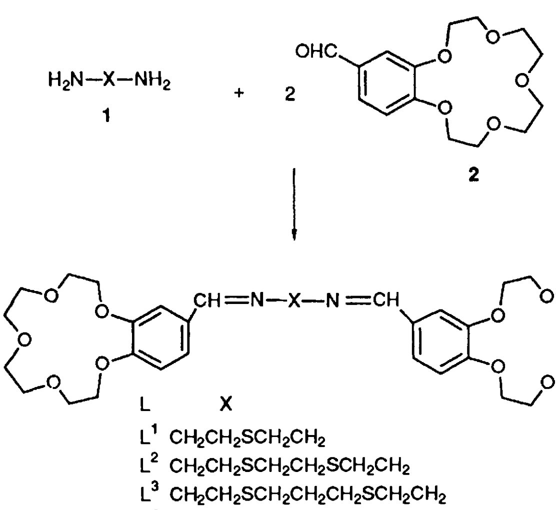
$[Na_2L^2][PF_6]_2$. The ligand L^2 (0.1 g, 0.14 mmol) and sodium hexafluorophosphate (4.6 mg, 0.26 mmol) were dissolved in dry acetonitrile (30 cm^3) and stirred at room temperature for 2 h. The solvent was removed *in vacuo* and the residue washed with dry hexane (10 cm) before recrystallisation from tetrahydrofuran–hexane. Yield of yellow solid 70 mg (48%), m.p. 89–91 °C. IR 1644 (C=N stretch) and 840 cm^{-1} (PF_6). FAB mass spectrum: *m/z* 927 $[M - PF_6]^+$; and 759 $[M - Na - 2PF_6]^+$. NMR $[(CD_3)_2SO]$: ^1H (270 MHz), δ 2.75 (4 H, s, SCH_2CH_2S), 2.81 (4 H, t, ^3J = 6.5, $SC\mathit{H}_2CH_2N$), 3.62 (16 H, s, OCH_2CH_2O), 3.71 (4 H, t, ^3J = 6.5, NCH_2), 3.78 (8 H, s, aryl–$OCH_2C\mathit{H}_2O$), 4.09 (8 H, aryl–OCH_2), 7.01 (2 H, d, ^3J = 8.2, aryl H), 7.24 (2 H, d, ^3J = 8.2 Hz, aryl H), 7.36 (2 H, s, aryl H) and 8.23 (2 H, s, N=CH); ^{13}C (67.8 MHz), δ 32.26 (SCH_2CH_2S), 32.72 ($S\mathit{C}H_2CH_2N$), 61.17 (NCH_2), 68.55, 68.91, 69.78 and 70.53 (OCH_2), 111.53, 113.29, 123.33, 129.77, 148.86 and 151.07 (aryl C) and 161.64 (N=C) (Found: C, 40.0; H, 4.9; N, 2.9. Calc. for $C_{34}H_{52}F_{12}N_2Na_2O_{10}P_2S_2$: C, 40.3; H, 4.9; N, 2.6%).

Copper(I) *complexes.* $[CuL^2]PF_6$. A solution of L^2 (0.3 g, 0.41 mmol) and $[Cu(CH_3CN)_4]PF_6$ (0.15 g, 0.41 mmol) in dry acetonitrile (40 cm^3) was refluxed for 2 h under nitrogen. Removal of the solvent *in vacuo* gave a bright yellow solid which was recrystallised from acetonitrile. Yield 235 mg (87%), m.p. 90–94 °C. IR 1634 (C=N stretch) and 840 cm^{-1} (PF_6). FAB mass spectrum: *m/z* 800, $[M - PF_6]^+$. NMR ($CDCl_3$): ^1H (270 MHz), δ 2.46 (8 H, s, SCH_2CH_2S and $SC\mathit{H}_2CH_2N$), 3.70–4.10 (40 H, m, NCH_2, OCH_2), 6.76 (2 H, d, ^3J = 8.0 Hz, aryl H), 7.49 (4 H, br s, aryl H) and 8.47 (2 H, s, N=CH); ^{13}C (22.6 MHz), δ 32.09 (SCH_2CH_2S), 33.39 ($S\mathit{C}H_2CH_2N$), 60.15 (NCH_2), 68.50, 69.16, 70.30 and 70.88 (OCH_2), 112.54, 113.84, 124.18, 126.10, 148.63 and 153.15 (aryl C) and 165.80 (N=C) (Found: C, 45.4; H, 5.5; N, 3.1. Calc. for $C_{36}H_{52}CuF_6N_2O_{10}PS_2$: C, 45.7; H, 5.5; N, 3.0%).

$[CuL^3]PF_6$. This was prepared by the same method as above, replacing L^2 with L^3. Yield of bright yellow solid (81%), m.p. 86–88 °C. IR 1635 (C=N stretch) and 840 cm^{-1} (PF_6). FAB mass spectrum: *m/z* 814, $[M - PF_6]^+$. ^1H NMR ($CDCl_3$, 270 MHz): δ 1.99 (2 H, br s, $SCH_2C\mathit{H}_2CH_2S$), 2.78 (4 H, br s, $SC\mathit{H}_2CH_2C\mathit{H}_2S$), 2.45 (4 H, br s, $SC\mathit{H}_2CH_2N$), 3.70–4.15 (36 H, m, NCH_2 and OCH_2), 6.80 (2 H, d, ^3J = 8.1 Hz, aryl H), 7.21 (2 H, s, aryl H), 7.38 (2 H, d, ^3J = 8.1 Hz, aryl H) and 8.47 (2 H, s, N=CH) (Found: C, 46.0; H, 5.9; N, 2.9. Calc. for $C_{37}H_{54}CuF_6N_2O_{10}PS_2$: C, 46.3; H, 5.7; N, 2.9%).

$[CuL^4]PF_6$. This was prepared by the same method as above replacing L^3 with L^4. Yield of yellow solid (96%), m.p. 72–74 °C. IR 1634 (C=N stretch) and 840 cm^{-1} (PF_6). FAB mass spectrum: *m/z* 827, $[M - PF_6]^+$. NMR ($CDCl_3$): ^1H (270 MHz), δ 2.00 (4 H, s, $SCH_2C\mathit{H}_2CH_2N$), 2.76 (4 H, s, $SC\mathit{H}_2CH_2CH_2N$), 2.95 (4 H, s, SCH_2CH_2S), 3.70–4.15 (36 H, m, NCH_2 and OCH_2), 6.80 (2 H, d, ^3J = 8.1, aryl H), 7.20 (2 H, s, aryl H), 7.35 (2 H, d, ^3J = 8.1 Hz, aryl H) and 8.47 (2 H, s, N=CH); ^{13}C (67.8 MHz), δ 24.71 ($SCH_2\mathit{C}H_2CH_2N$), 31.86 ($S\mathit{C}H_2CH_2CH_2N$), 34.7 (SCH_2CH_2S), 58.76 (NCH_2), 68.38, 69.04, 69.43, 69.71, 70.09, 70.39, 70.77 and 70.97 (OCH_2), 112.42, 115.60, 123.24, 126.34, 148.40 and 153.16 (aryl C) and 165.88 (N=C) (Found: C, 46.6; H, 5.9; N, 2.7. Calc. for $C_{38}H_{56}CuF_6N_2O_{10}PS_2$: C, 46.9; H, 5.8; N, 2.9%).

$[(CuL^1)_2][PF_6]_2$. This was prepared by the same method as above, replacing L^4 with L^1. Yield of yellow solid (74%), m.p. 91–93 °C. IR 1635 (C=N stretch) and 840 cm^{-1} (PF_6). FAB mass spectrum: *m/z* 1625, $[M - PF_6]^+$; and 739, $[M - 2PF_6]^{2+}$. NMR ($CDCl_3$): ^1H (270 MHz), δ 2.38 (8 H, br s, SCH_2), 3.57 (8



Scheme 1

H, br s, NCH$_2$), 3.74–4.19 (64 H, m, OCH$_2$), 6.95 (4 H, s, aryl H), 7.27 (4 H, aryl H), 7.56 (4 H, s, aryl H) and 8.42 (4 H, s, N=CH); ^{13}C (67.8 MHz), δ 33.45 (SCH$_2$), 58.03 (NCH$_2$), 68.97, 69.17, 69.95, 70.15 and 70.82 (OCH$_2$), 112.91, 115.68, 120.97, 127.29, 149.07 and 153.20 (aryl C) and 168.62 (N=C) (Found: C, 46.2; H, 5.7; N, 3.2. Calc. for $C_{68}H_{96}Cu_2F_{24}N_4O_{20}P_2S_2$: C, 46.1; H, 5.5; N, 3.2%).

Heterometallic complexes. [CuNa$_2$L^2][PF$_6$]$_3$. The complex [CuL^2]PF$_6$ (0.1 g, 0.11 mmol) and sodium hexafluorophosphate (36 mg, 0.22 mmol) were dissolved in dry acetonitrile (30 cm^3) under nitrogen. The resulting solution was stirred at room temperature for 2 h and the solvent removed *in vacuo*. The residue was washed with dry ethanol (2 × 10 cm^3) and dry heptane (10 cm^3) to give a lemon-yellow solid. Yield 96 mg (71%), m.p. 188–190 °C. IR 1630 (C=N stretch) and 840 cm^{-1} (PF$_6$). FAB mass spectrum: *m/z* 1135, [*M* − PF$_6$]$^+$. NMR [(CD$_3$)$_2$SO]: ^{1}H (270 MHz), δ 2.88 (4 H, s, SCH$_2$CH$_2$S), 3.14 (4 H, s, SC*H*$_2$CH$_2$N), 3.57–4.06 (36 H, m, NCH$_2$ and OCH$_2$), 7.00 (2 H, d, ^3J = 8.0, aryl H), 7.55 (2 H, d, ^3J = 8.0 Hz, aryl H), 7.77 (2 H, s, aryl H) and 8.70 (2 H, s, N=CH); ^{13}C (67.8 MHz), δ 31.18 (SCH$_2$CH$_2$S), 31.91 (SCH$_2$CH$_2$N), 60.36 (NCH$_2$), 67.78, 68.10, 68.21, 69.11, 69.24, 70.04 and 70.07 (OCH$_2$), 111.29, 112.48, 125.23, 125.88, 147.93 and 152.12 (aryl C) and 165.19 (N=C) (Found: C, 34.4; H, 4.6; N, 3.0. Calc. for $C_{36}H_{52}CuF_8N_2Na_2O_{10}P_3S_2$: C, 33.7; H, 4.1; N, 2.2%).

[CuKL^2][PF$_6$]$_2$. This was prepared by the same method as above replacing NaPF$_6$ by KPF$_6$. It was recrystallised from dry acetonitrile layered with dry ethanol. Yield of yellow crystals (63%), m.p. (decomp.) > 245 °C. IR 1632 (C=N stretch) and 840 cm^{-1} (PF$_6$). FAB mass spectrum: *m/z* 984, [*M* − PF$_6$]$^+$. NMR [(CD$_3$)$_2$SO]: ^{1}H (270 MHz), δ 2.41 (4 H, s, SCH$_2$CH$_2$S), 3.12 (4 H, s, SC*H*$_2$CH$_2$N), 3.60–4.00 (36 H, m, NCH$_2$ and OCH$_2$), 6.84 (2 H, d, ^3J = 8.4, aryl H), 7.54 (2 H, d, ^3J = 8.4 Hz, aryl H), 7.59 (2 H, s, aryl H) and 8.69 (2 H, s, N=CH); ^{13}C (67.8 MHz), δ 31.56 (SCH$_2$CH$_2$S), 32.35 (SCH$_2$CH$_2$N), 60.22 (NCH$_2$), 67.70, 67.75, 68.05, 68.14, 68.70, 69.03 and 69.73 (OCH$_2$), 112.56, 124.55, 126.27, 147.60 and 151.85 (aryl C) and 165.33 (N=C) (Found: C, 39.0; H, 4.5; N, 2.6. Calc. for $C_{36}H_{52}CuF_{12}KN_2O_{10}P_2S_2$: C, 38.3; H, 4.6; N, 2.5%).

[AgNa$_2$L^2][PF$_6$]$_3$. Ligand L^2 (0.07 g, 0.1 mmol) was dissolved in acetone (75%)–chloroform (23%) and silver nitrate (0.02 g, 0.12 mmol) was added all at once. After stirring at room temperature for 5 min an aqueous solution of sodium nitrate (1 mmol) was added. Subsequent addition of ammonium hexafluorophosphate (0.2 g) precipitated a white solid which was recrystallised from ethanol to give the product in 62% yield. IR 1630 cm^{-1} (C=N stretch) (Found: C, 32.8; H, 4.2; N, 2.4. Calc. for $C_{36}H_{52}AgF_8N_2Na_2O_{10}P_3S_2$: C, 32.6; H, 3.9; N, 2.1%).

[AgK$_2$L^2][PF$_6$]$_3$. This was prepared by same method as above using potassium nitrate instead of sodium nitrate. It was recrystallised from ethanol to give a pale yellow solid in 60% yield. IR 1632 cm^{-1} (C=N stretch) (Found: C, 32.8; H, 4.6; N, 2.4. Calc. for $C_{36}H_{52}AgF_8K_2N_2O_{10}P_3S_2$: C, 31.9; H, 3.9; N, 2.1%).

[AgKL^3][PF$_6$]$_2$. This was prepared by the same method described above with L^3 instead of L^2. It was recrystallised from ethanol to give an off-white solid in 52% yield. IR 1634 cm^{-1} (C=N stretch) (Found: C, 37.0; H, 4.6; N, 2.5. Calc. for $C_{37}H_{54}AgF_{12}KN_2O_{10}P_2S_2$: C, 37.3; H, 4.5; N, 2.4%).

^{13}C *NMR Titration Experiments.*[15]—The experimental procedure consisted of measuring Δδ as a function of the concentration of the alkali-metal salt while the concentration of the appropriate ligand or transition-metal-complexed ligand was kept constant. In a typical experiment the ligand (0.08 mmol) was dissolved in a deuteriated solvent (3 cm^3) and the resulting solution transferred to a ^{13}C NMR tube (10 cm^3). The ^{13}C NMR chemical shifts were measured *versus* tetramethylsilane as internal standard after sequential additions of alkali-metal salt in D$_2$O or CD$_3$CN. Titration curves were obtained by plotting Δδ of the most downfield crown ether carbon *versus* [alkali-metal salt]/[ligand or complex].

Crystal Structure Determination of [CuKL^2][PF$_6$]$_2$.—*Crystal data.* $C_{36}H_{52}CuF_{12}KN_2O_{10}P_2S_2$, M = 1105.1, triclinic, space group $P\bar{1}$, a = 9.515(13), b = 13.737(14), c = 18.171(22) Å, α = 90.2(1), β = 87.1(2), γ = 79.0(2)°, U = 2328.4 Å^3, $F(000)$ = 1175, D_m = 1.57, Z = 2, D_c = 1.58 g cm^{-3}, Mo-Kα radiation (λ = 0.7107 Å), μ(Mo-Kα) = 9.11 cm^{-1}.

A crystal of approximate size 0.3 × 0.3 × 0.3 mm was set up to rotate about the axis on a Stoe Stadi2 diffractometer and data were collected *via* variable-width ω scans. Background counts were for 20 s and a scan rate of 0.0333° s^{-1} was applied to a width of (1.5 sin μ/tan θ). 6195 Independent reflections were measured with a maximum 2θ of 50° of which 2941 with $I > 2\sigma(I)$ were used in subsequent refinement.

The structure was determined by the heavy-atom method. There were three independent PF$_6^-$ anions of which two had crystallographically imposed centres of symmetry. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in calculated positions. Calculations were performed using full-matrix least-squares methods with a weighting scheme $w = 1/[\sigma^2(F) + 0.003F^2]$. Calculations were performed using SHELX 76[16] and some of our programs on the Amdahl 5870 Computer at the University of Reading, but the final refinement cycles were carried out on the CRAY X-MP at the University of London computer centre. In the final cycle of refinement no shift/error ratio was greater than 0.2:1. There were no significant peaks in the final Fourier difference map (maximum electron density 0.48 e Å^{-3}, minimum −0.62 e Å^{-3}). The final R factor was 0.065 (R' = 0.072). Positional coordinates are given in Table 1 and the molecular dimensions in the metal co-ordination spheres are given in Tables 2 and 3.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters, and remaining bond lengths and angles.

Results and Discussion

Syntheses.—The condensation of the appropriate diamine **1** with two moles of the crown ether **2**[13] gave the respective Schiff-base bis(crown ether) ligand (L) in generally very good yields (Scheme 1). Melt reactions were typically used in which **2** was heated to approximately 110 °C and the diamine added dropwise to the stirred melt. After 10 min, in which time the water liberated in the condensation evaporates, the reaction was allowed to cool and the desired product solidified on addition of diethyl ether. However, attempts to prepare ligand L^2 by this melt reaction failed and a simple alternative procedure of dissolving the reactants in dry ethanol at room temperature

Table 1 Atomic coordinates (× 10^4) with estimated standard deviations in parentheses for $[CuKL^2][PF_6]_2$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Cu	4 842(2)	2 165(1)	3 669(1)	O(18)	5 515(13)	4 699(8)	8 997(6)
K	5 458(4)	3 052(2)	8 086(2)	C(19)	4 219(22)	5 456(12)	9 052(9)
P(1)	0	0	5 000	C(20)	2 963(22)	5 014(13)	8 937(8)
F(11)	497(11)	528(7)	4 279(5)	O(21)	2 919(12)	4 640(8)	8 208(6)
F(12)	−1 596(10)	166(8)	4 752(6)	C(22)	2 589(19)	5 362(12)	7 671(9)
F(13)	−357(11)	1 019(7)	5 423(6)	C(23)	2 877(15)	4 886(11)	6 927(8)
P(2)	0	5 000	5 000	O(24)	4 455(11)	4 522(8)	6 895(5)
F(21)	1 548(8)	4 769(6)	4 563(4)	S(2)	3 901(5)	3 185(3)	2 683(2)
F(22)	−576(11)	4 284(9)	4 471(6)	C(00)	5 517(18)	1 538(13)	1 981(8)
F(23)	507(11)	4 118(8)	5 511(6)	C(01)	4 051(18)	2 237(13)	1 972(9)
P(3)	10 043(5)	2 080(4)	1 090(3)	C(51)	1 998(17)	3 287(11)	3 049(9)
F(31)	8 436(13)	2 611(10)	1 255(10)	C(52)	1 876(16)	2 398(11)	3 556(8)
F(32)	11 647(12)	1 508(10)	981(7)	N(53)	2 838(13)	2 199(8)	4 072(7)
F(33)	10 559(18)	3 060(11)	1 177(11)	C(54)	2 359(15)	2 091(9)	4 715(8)
F(34)	10 250(17)	1 912(14)	1 929(7)	C(55)	3 241(15)	1 803(9)	5 359(8)
F(35)	9 407(16)	1 110(9)	1 108(10)	C(56)	2 707(17)	2 114(10)	6 065(9)
F(36)	9 885(17)	2 195(16)	294(8)	C(57)	3 570(17)	1 953(10)	6 634(8)
S(1)	5 732(4)	837(3)	2 816(2)	C(58)	5 008(17)	1 427(10)	6 510(9)
C(2)	7 625(16)	854(12)	3 008(8)	C(59)	5 508(17)	1 067(10)	5 837(8)
C(3)	7 909(16)	1 821(12)	3 255(8)	C(60)	4 617(15)	1 255(9)	5 276(8)
N(4)	6 893(11)	2 254(8)	3 826(6)	O(61)	5 795(11)	1 307(7)	7 124(6)
C(5)	7 322(17)	2 611(10)	4 384(10)	C(62)	7 242(17)	708(11)	7 056(9)
C(6)	6 565(18)	3 157(10)	5 032(8)	C(63)	7 737(19)	498(12)	7 800(9)
C(7)	7 247(15)	3 197(11)	5 680(8)	O(64)	7 912(12)	1 411(8)	8 110(7)
C(8)	6 514(16)	3 651(10)	6 280(9)	C(65)	8 353(21)	1 296(13)	8 828(11)
C(9)	5 048(16)	4 109(10)	6 249(8)	C(66)	7 283(24)	1 108(14)	9 378(10)
C(10)	4 411(18)	4 065(11)	5 607(9)	O(67)	6 090(16)	1 933(11)	9 397(8)
C(11)	5 115(16)	3 608(10)	4 985(8)	C(68)	4 884(28)	1 774(20)	9 830(11)
O(12)	7 059(11)	3 752(9)	6 945(6)	C(69)	3 718(25)	1 613(19)	9 399(13)
C(13)	8 629(16)	3 539(12)	7 024(8)	O(70)	3 328(15)	2 253(12)	8 875(7)
C(14)	8 821(19)	4 076(13)	7 703(9)	C(71)	2 056(22)	2 227(17)	8 515(10)
O(15)	8 193(12)	3 645(8)	8 306(5)	C(72)	2 302(21)	1 803(15)	7 799(10)
C(16)	8 073(22)	4 265(14)	8 948(9)	O(73)	3 134(12)	2 350(7)	7 318(5)
C(17)	6 775(23)	5 113(12)	8 992(10)				

Table 2 Dimensions (distances in Å, angles in °) in the copper co-ordination sphere

Cu–S(1)	2.389(4)
Cu–N(4)	2.013(11)
Cu–S(2)	2.384(4)
Cu–N(53)	2.000(11)
S(1)–Cu–N(4)	87.8(3)
S(1)–Cu–S(2)	90.1(1)
N(4)–Cu–S(2)	111.7(3)
S(1)–Cu–N(53)	114.5(4)
N(4)–Cu–N(53)	150.1(5)
S(2)–Cu–N(53)	89.0(4)

Table 3 Dimensions (distances in Å, angles in °) in the potassium co-ordination sphere

K–O(12)	2.792(12)	K–O(15)	2.917(13)
K–O(18)	2.809(12)	K–O(21)	2.929(10)
K–O(24)	3.029(10)	K–O(61)	2.920(10)
K–O(64)	2.923(11)	K–O(67)	2.867(15)
K–O(70)	2.816(16)	K–O(73)	2.980(12)
O(12)–K–O(15)	57.3(3)	O(18)–K–O(73)	133.3(3)
O(12)–K–O(18)	92.7(4)	O(21)–K–O(24)	54.3(3)
O(12)–K–O(21)	101.1(3)	O(21)–K–O(61)	125.1(4)
O(12)–K–O(24)	50.8(3)	O(21)–K–O(64)	174.4(4)
O(12)–K–O(61)	83.0(3)	O(21)–K–O(67)	115.6(4)
O(12)–K–O(64)	84.3(3)	O(21)–K–O(70)	74.0(4)
O(12)–K–O(67)	135.8(4)	O(21)–K–O(73)	72.6(3)
O(12)–K–O(70)	162.4(4)	O(24)–K–O(61)	94.9(4)
O(12)–K–O(73)	103.7(3)	O(24)–K–O(64)	131.3(4)
O(15)–K–O(18)	60.9(4)	O(24)–K–O(67)	169.2(4)
O(15)–K–O(21)	115.9(3)	O(24)–K–O(70)	116.7(4)
O(15)–K–O(24)	97.5(3)	O(24)–K–O(73)	71.8(3)
O(15)–K–O(61)	111.9(3)	O(61)–K–O(64)	57.0(4)
O(15)–K–O(64)	65.3(3)	O(61)–K–O(67)	94.5(4)
O(15)–K–O(67)	83.7(4)	O(61)–K–O(70)	86.2(4)
O(15)–K–O(70)	140.2(4)	O(61)–K–O(73)	53.7(3)
O(15)–K–O(73)	159.5(3)	O(64)–K–O(67)	58.8(4)
O(18)–K–O(21)	61.4(3)	O(64)–K–O(70)	101.5(4)
O(18)–K–O(24)	86.9(3)	O(64)–K–O(73)	108.1(3)
O(18)–K–O(61)	172.7(4)	O(67)–K–O(70)	58.9(4)
O(18)–K–O(64)	116.9(4)	O(67)–K–O(73)	110.2(3)
O(18)–K–O(67)	84.4(4)	O(70)–K–O(73)	58.7(3)
O(18)–K–O(70)	99.3(4)		

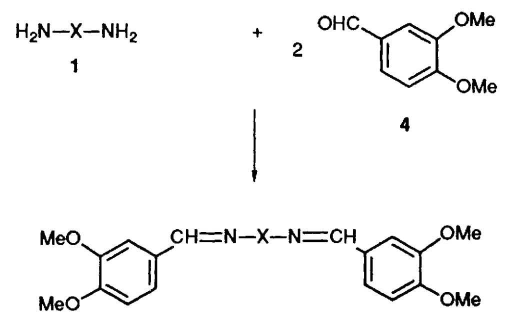
precipitated L^2 in yields of up to 90%.[5b] The structures of all these multisite receptors were characterised by elemental analysis, FAB mass spectrometry, infrared and ^1H and ^{13}C NMR spectroscopy (see Experimental section).

Two other bis(imine) ligands L^6 and L^7 were also prepared using 3,4-dimethoxybenzaldehyde **4** in place of **2** and the appropriate diamine (Scheme 2). These compounds were synthesised in an effort to show subsequently that the binding of alkali-metal ions to the Schiff-base bis(crown ether) compounds L^1–L^5 was a result of the crown ether recognition sites and not due to any other co-ordinating sites within the molecules.

Co-ordination Chemistry.—Alkali-metal complexation. Alkali-metal complexes were prepared by adding sodium or potassium hexafluorophosphate salts to acetonitrile solutions of the respective Schiff-base bis(crown ether) and characterised by elemental analysis, FAB mass spectrometry and infrared spectroscopy. In all cases with the sodium cation a 2:1 Na^+ : L stoichiometry was observed in which the respective two benzo-15-crown-5 moieties of these receptors are acting independently of one another, each complexing one sodium cation (Fig. 1). With the larger potassium cation, 1:1 intramolecular sandwich

Table 4 Imine bond-stretching frequencies of L^2 and its complexes

	$\nu(C{=}N)/cm^{-1}$
L^2	1646
$[Na_2L^2][PF_6]_2$	1644
$[CuL^2]PF_6$	1634
$[CuNa_2L^2][PF_6]_3$	1630
$[CuKL^2][PF_6]_2$	1632



L^6 X = $CH_2CH_2SCH_2CH_2$
L^7 X = $CH_2CH_2NHCH_2CH_2$

Scheme 2

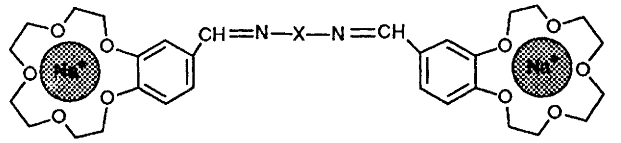


Fig. 1 The 1:2 L:Na^+ complex

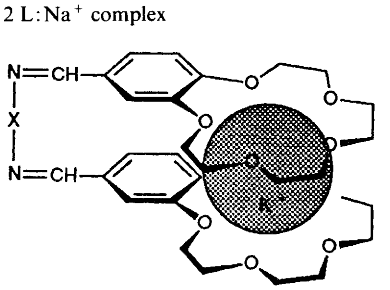


Fig. 2 The 1:1 L:K^+ intramolecular complex

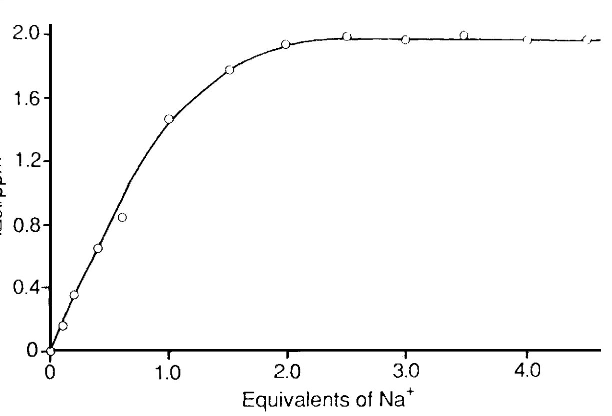


Fig. 3 The ^{13}C NMR titration curve of L^5 with sodium ions in CD_3CN

complexes were isolated, a consequence of the bis crown effect[17] (Fig. 2). A slight shift in the imine stretching frequency of the respective Schiff-base ligand was typically observed on alkali-metal complexation. For example, comparing the free ligand L^3 with the disodium complex $[Na_2L^3][PF_6]_2$, Fourier-transform IR investigations reveal the imine stretch shifts from 1646 to 1642 cm^{-1}. The presence of the sodium ions withdraws electronic charge from the imine bonds; this lessens the bond order and the vibrational frequency decreases.

To elucidate the solution alkali-metal co-ordination properties of L^1–L^6, ^{13}C NMR titration studies[15,18] were undertaken. In a standard titration experiment, for example with ligand L^5, the stepwise addition of a concentrated sodium salt (hexafluorophosphate, nitrate or perchlorate) in deuteriated acetonitrile or D_2O to a dilute deuteriated acetonitrile solution of L^5 led to considerable upfield shifts of the resonances of the OCH_2CH_2O carbons of the receptor. Negligible shifts were observed with compound L^7 under identical experimental conditions, suggesting the sodium cations exclusively bind at the crown ether recognition sites. Plotting $\Delta\delta$ of the most downfield crown ether carbon *versus* $[Na^+]/[L^5]$ (Fig. 3) gave the $Na^+:L^5$ stoichiometry of 2:1. The results of analogous titration experiments with L^1–L^4 and L^6 suggested solution stoichiometries the same as those found in the isolated complexes.

Copper(I) *complexes*. The reactions of $[Cu(CH_3CN)_4]PF_6$[14] with the ligands L^1–L^4 all gave bright yellow diamagnetic solids characterised as $[CuL]PF_6$, with the copper(I) presumably in a tetrahedral co-ordination geometry. Interestingly, the product isolated from the reaction of L^1 and $[Cu(CH_3CN)_4]PF_6$ proved to be bimetallic. A monometallic complex was predicted with a co-ordinated molecule of acetonitrile completing the transition-metal's co-ordination sphere. The ^1H and ^{13}C NMR spectra, however, showed only ligand peaks and the elemental analysis was correct for the empirical formulation $[CuL^1]PF_6$. Evidence for the presence of a dimeric product came from FAB mass spectrometry which displayed an isotopic envelope of peaks at 1623–1626 mass units corresponding to the ion fragment $[Cu_2L^1{}_2]PF_6{}^+$. Unfortunately repeated attempts to isolate X-ray-quality crystals for structure determination failed and so the stereochemical co-ordination sphere of each copper ion remains speculative.

The copper(I) complexes of L^1–L^4 were found to be relatively stable in the solid state but prone to rapid oxidation in solution in the presence of oxygen. A copper(I) complex of L^5 could not be isolated. This difference in complex stability may be attributed to consideration of the hard acid–soft base principle.[19] The presence of the relatively hard nitrogen donor atom of L^5 favours the copper(II) oxidation state, whereas the soft copper(I) ion prefers soft donor atoms such as sulphur present in ligands L^1–L^4.

In acetonitrile solution the co-ordination of the copper(I) ion had a marked effect on the ^1H and ^{13}C NMR spectra of the ligands. Typically in the respective ^{13}C NMR spectra large shifts of up to 4 ppm were observed for the NCH_2, SCH_2 and imine carbons whereas only small shifts (< 0.3 ppm) were found for the crown ether carbons, suggesting exclusive tetrahedral co-ordination of the copper(I) cation at the respective Schiff base thia recognition sites. Also large imine vibrational frequency shifts, for example, with the ligand L^4 from 1646 to 1634 cm^{-1}, were also observed on copper(I) complexation.

Copper(I)*–alkali metal heteropolymetallic complexes*. The copper(I)–disodium complexes $[CuNa_2L][PF_6]_3$ and the copper(I)–potassium complexes $[CuKL][PF_6]_2$ of ligands L^1–L^4 were isolated from the reaction of the respective copper(I) complexes and either sodium or potassium hexafluorophosphate in acetonitrile. All these heteropolymetallic complexes were characterised by elemental analysis, FAB mass spectrometry and ^1H NMR spectroscopy. In particular the imine bond stretching frequencies of L^2 and of its various copper(I), sodium and potassium complexes are noteworthy (Table 4).

The copper(I) ion co-ordinates directly to the imine nitrogens withdrawing electronic charge, decreasing the imine bond order and consequently lowering the stretching frequency by 12 cm^{-1} (Table 4). Because of the greater distance of the crown ether binding site from the imine bond, the effect of alkali-metal complexation is much less. Sodium-ion complexation to the

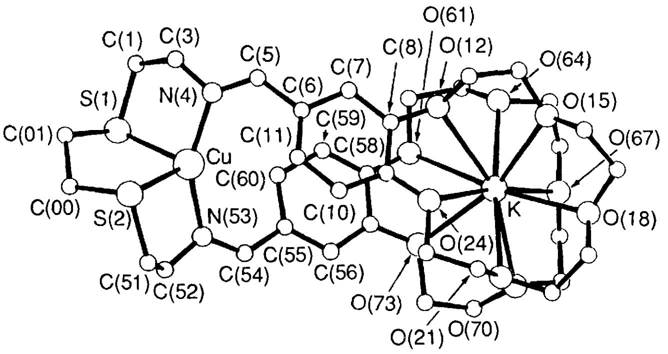


Fig. 4 The structure of $[CuKL^2][PF_6]_2$

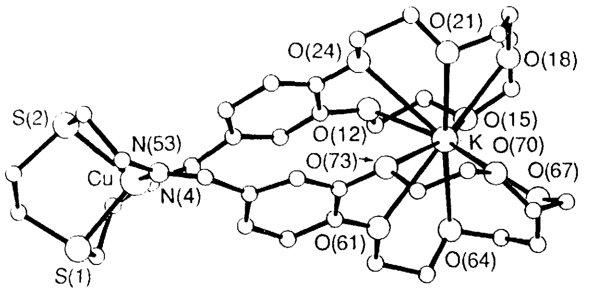


Fig. 5 Another view of the structure of $[CuKL^2][PF_6]_2$

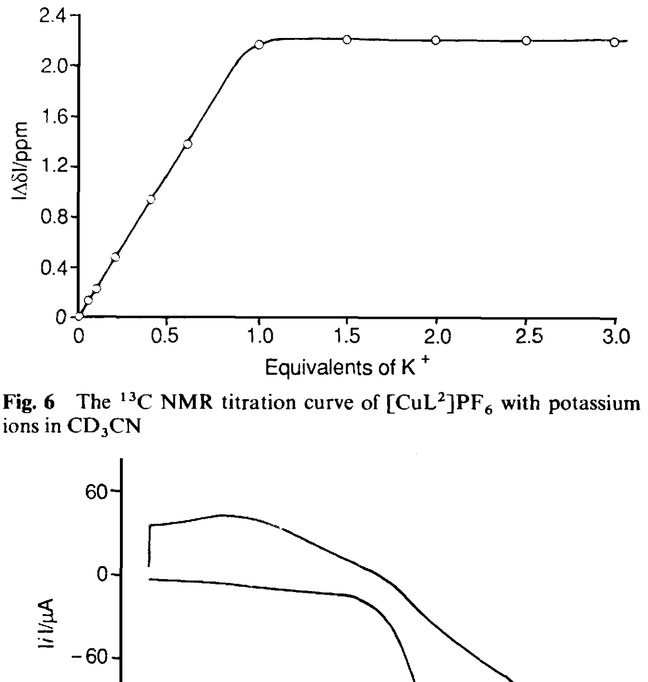


Fig. 6 The ^{13}C NMR titration curve of $[CuL^2]PF_6$ with potassium ions in CD_3CN

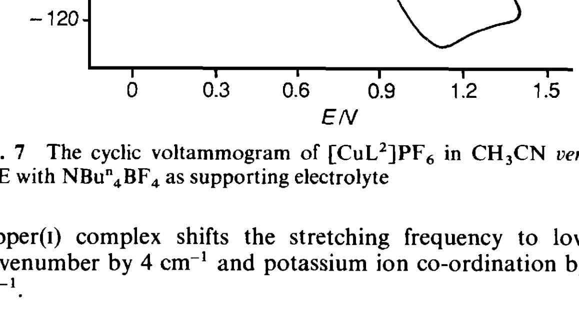


Fig. 7 The cyclic voltammogram of $[CuL^2]PF_6$ in CH_3CN *versus* SCE with $NBu^n{}_4BF_4$ as supporting electrolyte

copper(I) complex shifts the stretching frequency to lower wavenumber by 4 cm^{-1} and potassium ion co-ordination by 2 cm^{-1}.

X-Ray Structural Investigation of $[CuKL^2][PF_6]_2$.—Yellow crystals of $[CuKL^2][PF_6]_2$ suitable for X-ray structural investigation were grown by diffusion of dry ethanol into a dilute dry acetonitrile solution of the complex under a nitrogen atmosphere. The structure consists of discrete cations (Figs. 4 and 5) together with PF_6^- anions. The cations have approximate C_2 symmetry. In the cation the copper is four-co-ordinate, bonded to two sulphur [2.389(4), 2.384(4) Å] and two nitrogen atoms [2.013(11), 2.000(11) Å]. The potassium atom is found in a sandwich between two benzo-15-crown-5 moieties and is ten-co-ordinate.

As is apparent from Fig. 4, the copper(I) ion has a very distorted geometry intermediate between square planar and tetrahedral but similar to neither. The N(4)–Cu(1)–N(53) angle is 150.1(5)° while all the other angles are within 22° of the tetrahedral angle. This distortion is caused by the steric constraints of the ligand. The co-ordination sphere could also be considered as octahedral with the two sites *trans* to the sulphur atoms vacant. These sites are effectively blocked by the benzene rings of the benzo-15-crown-5 moieties. Atoms C(60),H(60) and C(11),H(11) are respectively 3.19, 2.54 and 3.15, 2.40 Å from the metal atom. It may be that these Cu ··· H distances represent some weak interaction. A similar interaction between benzene ring hydrogen atoms and metals was previously noted in a binuclear silver complex.[20]

There are several precedents for the bis(benzo-15-crown-5)-potassium sandwich observed in the present structure. A search of the Cambridge Data Centre files came up with six structures: bis(benzo-15-crown-5)potassium iodide,[21] bis(benzo-15-crown-5)potassium 3,5-dinitrobenzoate bis(3,5-dinitrobenzoic acid),[22] bis(benzo-15-crown-5)potassium nitrate monohydrate,[23] bis(benzo-15-crown-5)potassium tetrabromoindate,[24] bis(benzo-15-crown-5)potassium tetraiodoindate(III)[25] and bis[bis(benzo-15-crown-5)potassium] di-μ-chloro-bis(trichlorocuprate).[26]

In these structures the potassium is bonded to all ten oxygen atoms of the two ligands with distance ranges of 2.92–3.11, 2.81–3.02, 2.76–2.86, 2.76–2.96 and 2.88–3.00 Å respectively. In the present structure the K–O distances range from 2.792(12)–3.029(10) Å. Least-squares-plane calculations are shown in Table 5. These show that the benzene rings are twisted out of the plane of the Cu,N,N axis by 28.8 and 31.2°, that the benzene rings are nearly parallel (angle of intersection 6.7°), that the two sets of O_5 donor atoms are considerably distorted from planarity (maximum deviations of 0.32 and 0.33 Å in the two rings) and that the two planes of O_5 donor atoms are themselves parallel (angle of intersection 1°).

In $[CuKL^2][PF_6]_2$ as in all the other structures, in a projection perpendicular to the O_5 planes, the two benzene rings are on the same side of the molecule and overlap to some extent.

Torsion angles are shown in Table 6. As indicated by the least-squares planes for the two O_5 planes, there are significant differences in the conformations of the two benzo-15-crown-5 rings. As is apparent from the torsion angles, these are similar for the eight angles (placed adjacently in Table 6) but the remainder differ significantly. However the conformations permit the sandwich structure of the bis(benzo-15-crown-5)-potassium moiety.

In solution stoichiometric complexation studies the ^{13}C NMR titration experiment of the addition of potassium thiocyanate or hexafluorophosphate to the $[CuL^2]PF_6$ complex in deuteriated acetonitrile (Fig. 6) the solution stoichiometry was found to be $K^+:Cu^I$ 1:1. This result suggests that in solution, as the solid state, the intramolecular sandwich complex with potassium ions is formed.

Electrochemical Studies.—The electrochemical behaviour of $[CuL^2]PF_6$ was investigated using cyclic voltammetry (CV) in acetonitrile, dichloromethane and dimethylformamide and the results are shown in Table 7.

In each solvent an irreversible oxidation was observed (Fig. 7), suggesting the copper(II) complex is unstable under these experimental conditions. Attempts at obtaining reversibility by cooling the electrochemical cells and/or by increasing the scan rate of the CV experiment failed. No reduction

Table 5 Least-squares planes for $[CuKL^2][PF_6]_2$ with deviations (Å) of contributing atoms from the plane

1 Plane	Cu, S(1), S(2)
2 Plane	Cu, N(4), N(53)
3 Plane	C(55) 0.03, C(56) −0.02, C(57) −0.00, C(58) 0.02, C(59) −0.01, C(60) −0.01
4 Plane	C(6) − 0.01, C(7) 0.01, C(8) − 0.00, C(9) 0.00, C(10) − 0.00, C(11) 0.00
5 Plane	O(12) −0.05, O(15) −0.18, O(18) 0.32, O(21) −0.33, O(24) 0.25
6 Plane	O(61) −0.31, O(64) 0.17, O(67) 0.03, O(70) −0.18, O(73) 0.29

Angles (°) between planes
1 and 2, 72.1; 2 and 3, 28.9; 2 and 4, 31.2; 3 and 4, 6.6; 3 and 5, 12.1; 4 and 6, 12.0; 5 and 6, 1.0.

Table 6 Torsion angles (°) in $[CuKL^2][PF_6]_2$

N(4)–C(5)–C(6)–C(11)	−19.0	N(53)–C(54)–C(55)–C(60)	−26.4
O(12)–C(8)–C(9)–O(24)	−2.7	O(73)–C(57)–C(58)–O(61)	4.8
C(8)–C(9)–O(24)–C(23)	−171.6	C(57)–C(58)–O(61)–C(62)	175.2
C(9)–O(24)–C(23)–C(22)	−175.5	C(58)–O(61)–C(62)–C(63)	−167.2
O(24)–C(23)–C(22)–O(21)	−64.4	O(61)–C(62)–C(63)–O(64)	−67.7
C(23)–C(22)–O(21)–C(20)	168.3	C(62)–C(63)–O(64)–C(65)	178.7
C(22)–O(21)–C(20)–C(19)	−72.8	C(63)–O(64)–C(65)–C(66)	−71.8
O(21)–C(20)–C(19)–O(18)	−66.7	O(64)–C(65)–C(66)–O(67)	−60.3
C(20)–C(19)–O(18)–C(17)	171.0	C(65)–C(66)–O(67)–C(68)	170.9
C(19)–O(18)–C(17)–C(16)	178.9	C(66)–O(67)–C(68)–C(69)	−106.7
O(18)–C(17)–C(16)–O(15)	60.6	O(67)–C(68)–C(69)–O(70)	−49.5
C(17)–C(16)–O(15)–C(14)	81.9	C(68)–C(69)–O(70)–C(71)	−170.0
C(16)–O(15)–C(14)–C(13)	−167.3	C(69)–O(70)–C(71)–C(72)	−104.5
O(15)–C(14)–C(13)–O(12)	65.9	O(70)–C(71)–C(72)–O(73)	−60.2
C(14)–C(13)–O(12)–C(8)	159.1	C(71)–C(72)–O(73)–C(57)	173.7
C(13)–O(12)–C(8)–C(9)	−165.2	C(72)–O(73)–C(57)–C(58)	−100.3

Table 7 Electrochemical data for $[CuL^2]PF_6$

Solvent	E_{pa}*/V
CH_3CN	1.15
CH_2Cl_2	0.97
dmf	0.87

* Oxidation peak potential *versus* the saturated calomel electrode as reference with scan rate of 0.2 V s^{-1}; temperature 21 °C; solutions contained 0.2 mol dm^{-3} $NBu^n{}_4BF_4$ as supporting electrolyte.

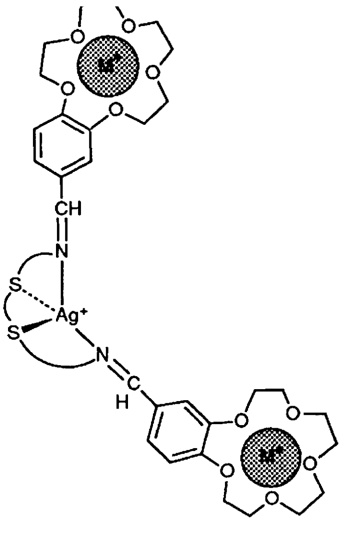


Fig. 8 Heteronuclear silver–disodium and –dipotassium complexes of L^2

waves were observed within the respective solvent redox limits.

Silver(I)-*Alkali-metal Heterometallic Complexes.*—The reaction of L^2 with 1 molar equivalent of silver nitrate followed by an excess of either sodium or potassium nitrate and subsequently ammonium hexafluorophosphate in acetone–chloroform–water solvent mixtures led to the isolation of respective heterometallic complexes $[AgNa_2L^2][PF_6]_3$ and $[AgK_2L^2][PF_6]_3$ (Fig. 8). The latter complex is of particular note since in the presence of the copper(I) ion and in the absence of any transition metal the ligand's benzo crown ether moieties form a 1:1 intramolecular sandwich with the potassium cation. The binding properties of crown ethers are known to be sensitive to changes in the conformations or the effective 'size' of the crown cavity,[19] and these 'solid state' stoichiometric results suggest that the effect of chelation of the Ag^+ at the Schiff base dithia recognition site of L^2 alters the conformation of the respective benzo crown ethers in such a way as to disfavour intramolecular potassium sandwich complex formation. Both silver(I) and copper(I) ions are known to prefer tetrahedral co-ordination geometry, however the ionic radii of Ag^+ and Cu^+ are 1.13 and 0.95 Å respectively.[27] The increase in size on going from copper(I) to silver(I) may account for this observed difference in stoichiometry of potassium ion complexation. That is, the tetrahedrally bound silver(I) ion is of sufficient size and stereochemical requirement as to prevent the benzo crown ethers of the ligand L^2 from acting co-operatively. Subsequent solution ^{13}C NMR titration experiments with L^2, Ag^+ and alkali-metal nitrate or hexafluorophosphate salts in acetone–chloroform–water solvent mixtures gave solution stoichiometries in agreement with those found in the isolated heterometallic complexes.

Interestingly the silver(I) complexes of ligands L^3 and L^4 containing respectively one and two extra methylene units in the transition-metal recognition site form solution silver–potassium heterometallic complexes of 1:1 stoichiometry $[AgKL]PF_6$ suggesting these more flexible ligands enable the benzo crown ether moieties to co-operate in the formation of a potassium sandwich complex.

Conclusion

The synthesis of a series of new multisite receptor molecules containing both alkali-metal and transition-metal co-ordination sites has been achieved and a variety of copper(I), silver(I), sodium and potassium homo- and hetero-metallic complexes have been isolated. Focusing on the bis crown ether ligand L^2, *two types* of alkali-metal ion complex are possible in the absence and presence of a transition metal bound at the Schiff-base dithia recognition site, a 1:1 intramolecular sandwich complex in which the benzo crown ethers act in a co-operative fashion and a 2:1 complex in which one alkali metal is bound in each benzo crown ether moiety. The nature of the alkali-metal complex has been found to be dependent on the ratio of the alkali-metal cation size to the crown ether ring size (*i.e.* the bis crown effect) and the absence or presence of a co-bound silver(I) transition-metal ion.

With ligand L^2, in the absence of a transition metal, a 1:1 intramolecular sandwich bis(benzo crown ether) complex with K^+ results and the smaller Na^+ ion forms a 2:1 $Na^+:L^2$ complex. The prior co-ordination of the copper(I) ion makes no difference to these alkali-metal stoichiometries, suggesting that the stabilisation effect of the bis crown on the K^+ ion outweighs the energy required to distort the idealised tetrahedral co-ordination geometry of the copper(I) ion, which may have favoured the subsequent formation of the 2:1 complex.

With the larger silver(I) ion a 2:1 potassium–silver(I) complex is produced indicating that the combination of size and tetrahedral stereochemical requirement of this co-bound transition-metal cation dictates the potassium cation stoichiometry with L^2.

The co-ordination chemistry of these and related ligands with, in particular alkaline-earth metals and transition metals of catalytic interest, is now being studied.

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References

1 A. Gül and Ö. Bekâroglu, *J. Chem. Soc., Dalton Trans.*, 1983, 2537.

2 S. Can and Ö. Bekâroglu, *J. Chem. Soc., Dalton Trans.*, 1988, 2831.

3 T. M. Handyside, J. C. Lockhart, M. S. McDonnell and P. V. S. Rao, *J. Chem. Soc., Dalton Trans.*, 1982, 2331.

4 A. Carroy and J. M. Lehn, *J. Chem. Soc., Chem. Commun.*, 1986, 1232.

5 (*a*) P. D. Beer, *J. Chem. Soc., Chem. Commun.*, 1986, 1678; (*b*) P. D. Beer and C. G. Crane, *Polyhedron*, 1988, **7**, 2649.

6 F. C. J. M. van Veggel, S. Harkema and D. N. Reinhoudt, *J. Am. Chem. Soc.*, 1988, **110**, 4994; F. C. J. M. van Veggel, M. Bos, S. Harkema, H. van de Bovenkamp, W. Verboom, J. Reedijk and D. N. Reinhoudt, *J. Org. Chem.*, 1991, **56**, 225 and refs. therein.

7 J. Rebek, jun., J. E. Trend, R. V. Wattley and S. Chakravorti, *J. Am. Chem. Soc.*, 1979, **101**, 4333.

8 P. D. Beer and A. S. Rothin, (*a*) *J. Chem. Soc., Chem. Commun.*, 1988, 52; (*b*) *Polyhedron*, 1988, **7**, 137.

9 R. J. P. Williams, *Biochem. Soc. Trans.*, 1990, **18**, 689.

10 A. Lavery, Ph.D. Thesis, Queens University of Belfast, 1983.

11 E. K. Barefield, F. Wagner and K. D. Hodges, *Inorg. Chem.*, 1976, **15**, 1370.

12 P. J. Dwyer and F. Lions, *J. Chem. Soc.*, 1950, 1545.

13 E. M. Hyde, B. L. Shaw and I. Shepherd, *J. Chem. Soc., Dalton Trans.*, 1978, 1696.

14 G. J. Kubas, B. Monzya and A. L. Crumbliss, *Inorg. Synth.*, 1971, **19**, 90.

15 P. D. Beer, E. L. Tite and A. I. Ibbotson, *J. Chem. Soc., Dalton Trans.*, 1990, 2691.

16 G. M. Sheldrick, SHELX 76, Package for Crystal Structure Determination, University of Cambridge, 1976.

17 K. Kimura, H. Sakamoto, Y. Koseki and T. Shono, *Chem. Lett.*, 1985, 1241; K. Kikukawa, G.-X. He, A. Abe, T. Goto, R. Arata, T. Ikada, F. Wada and T. Matsuda, *J. Chem. Soc., Perkin Trans. 2*, 1987, 135.

18 E. Amble and E. Amble, *Polyhedron*, 1983, **2**, 1063.

19 E. Weber and F. Vogtle, *Top. Curr. Chem.*, 1981, **98**, 1.

20 M. G. B. Drew, D. McDowell and J. Nelson, *Polyhedron*, 1988, **7**, 2229.

21 P. R. Mallinson and M. R. Truter, *J. Chem. Soc., Perkin Trans. 2*, 1972, 1818.

22 W. Xu, K. Chinger, M. I. Hackert and N. S. Poonia, *J. Inclusion Phenom.*, 1986, **3**, 163.

23 W. S. Sheldrick and N. S. Poonia, *J. Inclusion Phenom.*, 1986, **4**, 93.

24 Z. Zhixian, Z. Xianxin and H. Jinshun, *J. Inclusion Phenom.*, 1986, **4**, 870.

25 Z. Zhixian, D. Baoshi, Z. Xianxin, L. Shixiong and H. Jinhing, *J. Struct. Chem.*, 1987, **6**, 209.

26 A. Mugnoli, Z. Dauter, E. Luboch, A. Cygan and J. F. Biernat, *J. Inclusion Phenom.*, 1986, **4**, 407.

27 F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 4th edn., Wiley, New York, 1980.

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