Studies on the Synthesis and Complexing Behavior of Crown Ethers with External Coordination Center

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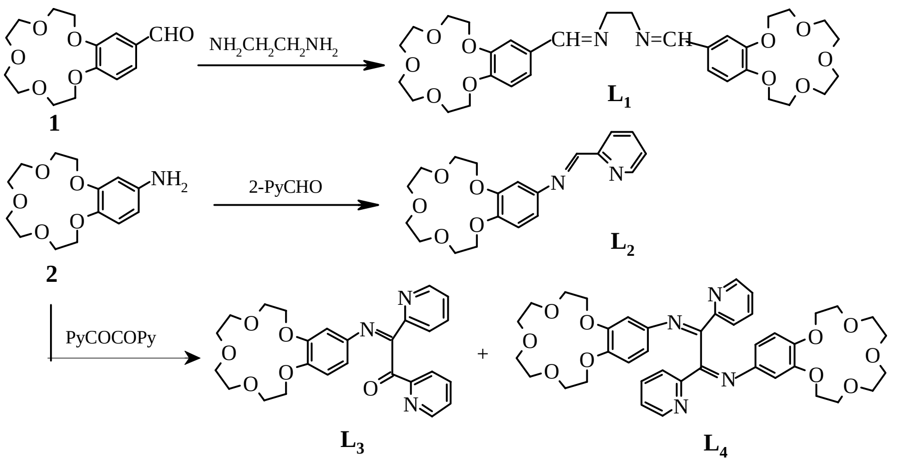
Abstract: The synthesis, characterization of five ditopic or tritopic crown compounds were reported in this paper together with the preparation of the corresponding hetero-dinuclear and hetero-trinuclear complexes with different metal cations.

Keywords: Polytopic crown ether, hetero-polynuclear complex, co-ordination.

Ligands capable of positioning two or more very different metal cations, like transition metal and alkali or alkaline earth metal cations, have been described recently[1-3]. Reinhoudt *et al.* have synthesized a number of ligands with the cavity for transition metal cations as well as the cavity for alkali metal cations and the corresponding comlexes with different kinds of metal ions[4,5]. It was anticipated that co-complexation of a hard cation closing to the complexed transition metal cation would change the redox properties of the complex. Therefore, the ultimate goal is to realize bimetallic catalysis with well-defined complexes.

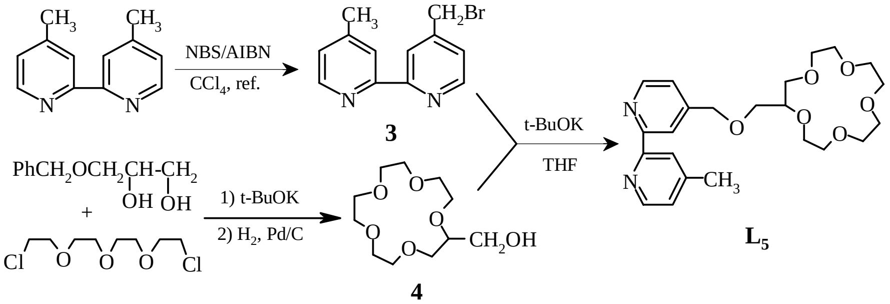
In this paper, five ditopic or tritopic crown compounds were synthesized for being of complexing behavior with their hard and soft coordination centers. The Schiff base type polytopic crown compounds **L_1 ~ L_4** were synthesized as shown in **Scheme 1.**

Scheme 1

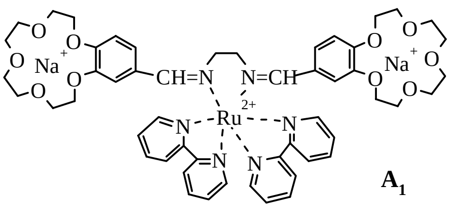


4′-Formylbenzo15-crown-5 **1**[6] and 4′-aminobenzo-15-crown-5 **2**[7] were prepared according to the literature methods. $\mathbf{L_5}$ was obtained as a colorless oil by treating 4-methyl-4′-bromomethyl-2,2′-bipyridine **3** and 2-hydroxymethyl-15-crown-5 **4** in anhy-drous THF in the presence of t-BuOK (**Scheme 2**).

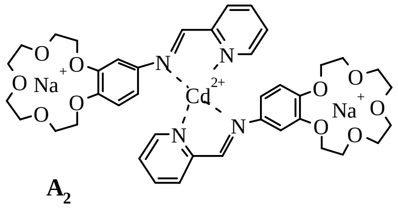
Scheme 2



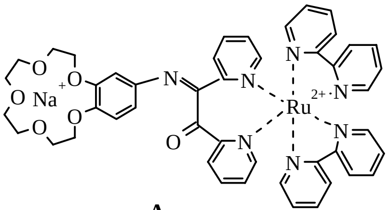
The preparation of the five hetero-dinuclear and hetero-trinuclear complexes $\mathbf{A_1}$~$\mathbf{A_5}$ is schematically depicted as follows:



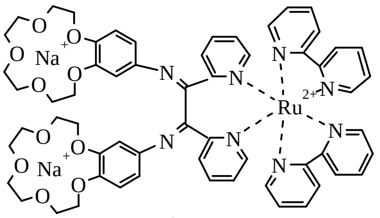
$\mathbf{A_1}$



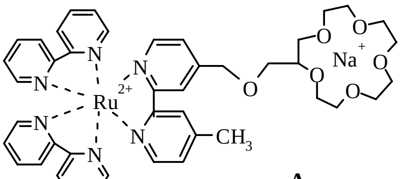
$\mathbf{A_2}$



$\mathbf{A_3}$



$\mathbf{A_4}$



$\mathbf{A_5}$

1) $L_1 + Ru(bpy)_2Cl_2 + 2NaPic \rightarrow L_1{\cdot}Ru(bpy)_2Cl_2{\cdot}2NaPic{\cdot}H_2O$ ($\mathbf{A_1}$)
2) $2L_2 + CdI_2 + 2NaI \rightarrow 2L_2{\cdot}2NaI{\cdot}CdI_2$ ($\mathbf{A_2}$)
3) $L_3 + Ru(bpy)_2Cl_2 + NaPic \rightarrow L_3{\cdot}Ru(bpy)_2Cl_2{\cdot}NaPic$ ($\mathbf{A_3}$)
4) $L_4 + Ru(bpy)_2Cl_2 + 2NaPic \rightarrow L_4{\cdot}Ru(bpy)_2Cl_2{\cdot}2NaPic$ ($\mathbf{A_4}$)
5) $L_5 + Ru(bpy)_2Cl_2 + NaPic \rightarrow L_5{\cdot}Ru(bpy)_2Cl_2{\cdot}NaPic{\cdot}H_2O$ ($\mathbf{A_5}$)

Synthesis of ligands

Bis-crown compound **L_1** was synthesized according to the literature method[8].

4′-[(2-pyridyl) methynylamino] benzo-15-crown-5 L_2

To a refluxing solution of 2.13g (7.55 mmol) 4′-aminobenzo-15-crown-5 in 20 mL of methanol was added dropwise a solution of 0.8g (7.55 mmol) 2-pyridinecarboxaldehyde in 5 mL of methanol under nitrogen atmosphere. The mixture was refluxed with stirring for 8 h and then concentrated under reduced pressure. The residue obtained was purified by chromatography on silica gel (eluent: chloroform/ethanol, 9/1), recrystallized with iso-propanol/petroleum ether (5:1) to give a yellowish crystal, yield 76%, mp 101-103℃. Anal. Calcd. for $C_{20}H_{24}N_2O_5$: C 64.51, H 6.45, N 7.53; found: C 64.66, H 6.32, N 7.64. MS (*m/z*): 372 (M^+). ^1H NMR ($CDCl_3$, δ_{ppm}): 8.70-7.36 (m, 4H, Py-H); 8.63 (s, 1H, N=CH); 6.93 (m, 3H, H-Ph); 3.75-4.18 (m, 16H, CH_2OCH_2). IR (KBr, cm^{-1}) 1625, 1585, 1505, 1380, 1265, 1120, 1040, 985, 935, 860, 810, 755.

1-[N-(4′-benzo-15-crown-5)imino]-2-oxa-1,2-bis(2′-pyridyl) ethane L_3 and 1,2-bis [N-(4′-benzo-15-crown-5)imino]-1,2-bis (2′-pyridyl) ethane L_4

To a solution of 4′–aminobenzo-15-crown-5 (6.15 mmol, in 50 mL anhydrous ethanol) was added 1.3 g (6.15 mmol) 2,2′-pyridil under nitrogen. The mixture was refluxed with stirring for 4 h and filtered in hot. The dark-red filtrate was evaporated to dryness under reduced pressure. The residue obtained was separated by chromatography on silica gel (eluent: acetone). The second band and the third band were collected to give **L_3** and **L_4**, respectively.

L_3 brilliant yellow crystal, yield 35%, mp 142-144℃. Anal. Calcd. for $C_{26}H_{27}N_3O_6$: C 65.41, H 5.66, N 8.81; found: C 65.41, H 5.72, N 8.70. MS (*m/z*): 477 (M^+). ^1H NMR ($CDCl_3$, δ_{ppm}): 8,56-7.35 (m, 8H, Py-H); 6.50-6.70 (m, 3H, Ar-H); 3.60-4.04 (m, 16H, CH_2OCH_2). IR (KBr, cm^{-1}) 2900, 2850, 1690, 1620, 1580, 1505, 1460, 1360, 1260, 1230, 1130, 1050, 995, 980, 930, 865, 810, 750.

L_4 yellow solid, yield 25%, mp 191-193℃. Anal. Calcd. for $C_{40}H_{46}N_4O_{10}$: C 64.69, H 6.20, N 7.55; found: C 64.62, H 6.33, N 7.67. MS (*m/z*): 742 (M^+). ^1H NMR (DMSO-d_6, δ_{ppm}): 8.52-7.46 (m, 8H, Py-H); 6.74-6.06 (m, 6H, Ar-H); 3.60-3.98 (m, 32H, CH_2OCH_2). IR (KBr, cm^{-1}) 2900, 2850, 1620, 1580, 1505, 1460, 1380, 1255, 1220, 1125, 1050, 990, 940, 830, 745.

4-methyl-4′-[(15-crown-5)-methoxymethyl]-2,2′-bipyridine L_5

To a solution of t-BuOK (0.39 g K in 10 mL t-BuOH), was added a solution of 1.9 g (7.6 mmol) 2-hydroxymethyl-15-crown-5 in 40 mL THF (anhydrous). After refluxing for 30 min., a solution of 4-methyl-4′-bromomethyl-2, 2′-bipyridine in 40 mL anhydrous THF was added dropwise with stirring and then refluxed for 15 h. The solvent was removed under reduced pressure and the dark-red residue obtained was purified by chromatography (eluent: acetone). The product was colorless oil, yield 36%. Anal. Calcd. for $C_{23}H_{32}N_2O_6$: C 63.89, H 7.41, N 6.48; found: C 64.12, H 7.53, N 6.26. ^1H NMR ($CDCl_3$, δ_{ppm}): 8.61-7.43 (m, 6H, Py-H); 4.45 (s, 2H, OCH_2Py); 3.36-3.72 (m, 21H, CH_2OCH_2); 2.54 (s, 3H, CH_3). IR (paraffin oil, cm^{-1}) 1590, 1550,1455, 1370, 1350, 1245, 1100, 985, 935, 820.

Preparation of complexes

All the five complexes ($\mathbf{A}_1$~$\mathbf{A}_5$) were prepared by using suitable proportions of the ligands and different metal salts and were characterized by elemental analysis, IR and ^{1}H NMR spectra[9].

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9. Selected data for $\mathbf{A}_1$~$\mathbf{A}_5$. $\mathbf{A}_1$: Anal. Calcd. for $C_{64}H_{66}N_{12}O_{25}Cl_2Na_2Ru$: C 47.41, H 4.07, N 10.37. Found: C 47.83, H 4.25, N 10.78; ^{1}H NMR (DMSO-$d_{6,}$ δ_{ppm}): 8.78 (s, 4H, Picrate-H), 8.75-7.60 (m, 16H, Py-H), 8.42 (s, 2H, CH=N), 6.91-7.66 (m, 6H, Ar-H), 3.78-4.30 (m, 36H, NCH_2 CH_2N, CH_2OCH_2); IR (KBr, cm^{-1}) 2900, 2850, 1630, 1598, 1580, 1508, 1440, 1340, 1265, 1240, 1125, 1140, 930, 850. $\mathbf{A}_2$: Calcd. for $C_{40}H_{48}N_4O_{10}CdI_4Na_2$: C 34.04, H 3.40, N 3.97. Found: C 34.25, H 3.54, N 4.21; ^{1}H NMR (DMSO-$d_{6,,}$ δ_{ppm}): 8.83 (s, 2H, CH=N), 7.75-8.90 (m, 8H, Py-H), 6.99-7.21 (m, 6H, Ar-H), 4.08-3.63 (m, 32H, CH_2OCH_2); IR (KBr, cm^{-1}) 1625, 1605, 1550, 1500, 1360, 1330, 1260, 1220, 1040, 1165, 1120, 930, 900, 850, 740. $\mathbf{A}_3$: Calcd. for $C_{52}H_{45}N_{10}O_{13}Cl_2NaRu$: C 51.49, H 3.71, N 11.55. Found: C 51.30, H 3.63, N 11.69; ^{1}H NMR (DMSO-$d_{6,}$ δ_{ppm}): 8.77 (s, 2H, Pic-H), 8.72-7.30 (m, 24H, Py-H), 6.89-7.02 (m, 3H, Ar-H), 3.61-4.22 (m, 16H, CH_2OCH_2); IR (KBr, cm^{-1}) 2900, 2850, 1725, 1620, 1600, 1555, 1475, 1450, 1335, 1260, 1220, 1080, 1125, 940, 850, 760, 730. $\mathbf{A}_4$: Calcd. for $C_{72}H_{66}N_{14}$ $O_{24}Cl_2Na_2Ru$: C 50.00, H 3.82, N 11.34. Found: C 49.79, H 3.66, N 11.48; ^{1}H NMR (DMSO-$d_{6,}$ δ_{ppm}): 8.82 (s, 4H, Pic-H), 8.53-6.93 (m, 24H, Py-H), 6.80-6.02 (m, 6H, Ar-H), 4.20-3.59 (m, 32H, CH_2OCH_2); IR (KBr, cm^{-1}) 2900, 2850, 1630, 1580, 1510, 1502, 1450, 1340, 1265, 1220, 1050, 1125, 940, 850, 760, 730. $\mathbf{A}_5$: Calcd. for $C_{49}H_{52}N_9O_{14}Cl_2NaRu$: C 49.62, H 4.39, N 10.63. Found: C 49.28, H 4.44, N 10.26; ^{1}H NMR (DMSO-$d_{6,}$ δ_{ppm}): 8.79 (s, 2H, Pic-H), 8.84-7.36 (m, 22H, Py-H), 4.47 (br, 2H, OCH_2Py), 3.77-3.47 (m, 21H, CH_2 OCH_2), 2.55 (s, 3H, CH_3); IR (KBr, cm^{-1}) 1625, 1605, 1540, 1360, 1260, 1100, 1070, 930, 770.

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