

Electronic Supplementary Information

Lead(II) tetrafluoroborate and hexafluorophosphate complexes with crown ethers, mixed O/S- and O/Se-donor macrocycles and unusual [BF₄]⁻ and [PF₆]⁻ coordination

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Modified preparations for the mixed donor oxa-thia/selena macrocycles, based on the original methods reported.^{S1,S2} (literature yields are given in parentheses)

1,11-dichloro-3,6,9-trioxaundecane

To benzene (80 mL) was added pyridine (48.0 mL, 0.6 mol) and tetraethylene glycol (51.5 g, 0.265 mol). The mixture was heated to 80°C and allowed to cool. As the mixture cooled, thionyl chloride (43.6 mL, 0.6 mol) in benzene (50 mL) was added dropwise over 1.5 h. The reaction was stirred at reflux for 20 h. A yellow-brown solution and precipitate formed which was hydrolysed *via* addition of HCl (10.0 mL, 11.6 mol dm⁻³) in water (100 mL) over 1.5 h., dissolving the precipitate. The benzene layer was separated, and the aqueous layer extracted with benzene (3 x 50 mL), The combined organics were dried over MgSO₄. Filtration followed by removal of the benzene left a light brown oil which was used without further purification. Yield: 46.9 g, 0.20 mol, 76%. ¹H NMR (CDCl₃): δ = 3.55 (t, [4H], CH₂Cl), 3.59 (s, [8H], OCH₂), 3.67 (t, [4H], OCH₂CH₂Cl); ¹³C{¹H} NMR (CDCl₃): δ = 42.5 (ClCH₂), 70.3 (OCH₂CH₂O), 71.0 (CH₂O).

1,8-dibromo-3,6-dioxaoctane

To benzene (50 mL) was added pyridine (36.4 mL, 0.45 mol) and triethylene glycol (30.0 g, 0.20 mol). To the stirring mixture was added thionyl bromide (34.8 mL, 0.45 mol) in benzene (50 mL) over 1 h. The reaction was stirred at 65°C for 16 h. Two phases formed, the heavier one being much darker with a minimal amount of precipitate. This was hydrolysed using HCl (10.0 mL, 11.6 mol dm⁻³) in water (100 mL) over 1 h. The benzene layer was separated and the aqueous layer was extracted with benzene (3 x 50 mL), and the combined organics were dried over MgSO₄. After filtering and removal of the volatiles, a red-brown oil and a yellow

precipitate remained. The latter was removed by further filtration, affording the product. Yield: 33.1 g, 0.11 mol, 60%. ^1H NMR (CDCl_3): $\delta = 3.38$ (t, [4H], CH_2Br), 3.57 (s, [4H], CH_2O), 3.72 (t, [4H], $\text{OCH}_2\text{CH}_2\text{Br}$); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = 30.2$ (BrCH_2), 70.0 ($\text{O}(\text{CH}_2\text{CH}_2\text{O})$), 70.7 (CH_2O).

1,4,7-dioxathiacyclononane ([9]aneO₂S) and 1,4,10,13-tetraoxa-7,16-dithiacyclooctadecane ([18]aneO₄S₂)

In two separate graduated addition funnels, ethanolic solutions (2x300mL) of 11,8-dibromo-3,6-dioxaoctane (33.1g, 0.12 mol) and ground $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ (28.8g, 0.12 mol) were placed. They were added dropwise to a stirring reservoir of NaOH (2.0g, 0.055mol in ethanol (700mL) over 24hrs. The yellow/orange mixture was neutralised using HCl in water (100mL). The ethanol was boiled off. The organic components were extracted using diethyl ether (2 x 200mL) and dried over MgSO_4 . The ether was removed on a rotary evaporator leaving behind a white solid (4.0g, 0.0135 mol, yield: 22.5 % (lit: 12.5%) and an off-colour oil. The oil and solid were separated *via* Buchner filtration and subsequent washings of cold hexane. The oil was distilled under vacuum (80°C/0.05mmHg) giving the smaller ring (2.6g, 0.018 mol, yield: 14.6 % (lit: 5%). ^1H NMR [CDCl_3]: δ 2.80 (t, [4H], $\text{SCH}_2\text{CH}_2\text{O}$), δ 3.60 (s, [4H], CH_2OCH_2), δ 3.89 (t, [4H], $\text{SCH}_2\text{CH}_2\text{O}$); $^{13}\text{C}\{^1\text{H}\}$ NMR [CDCl_3]: δ 31.8 (SCH_2), 71.3 ($\text{O}(\text{CH}_2\text{CH}_2\text{O})$), 74.9 (CH_2O).

The larger ring, the white solid ^1H NMR [CDCl_3]: δ 2.84 (t, [8H], $\text{SCH}_2\text{CH}_2\text{O}$), δ 3.63 (s, [8H], CH_2OCH_2), δ 3.72 (t, [8H], $\text{SCH}_2\text{CH}_2\text{O}$); $^{13}\text{C}\{^1\text{H}\}$ NMR [CDCl_3]: δ 31.5 (SCH_2), 70.5 ($\text{O}(\text{CH}_2\text{CH}_2\text{O})$), 72.1 (CH_2O).

1,4,7-oxadithiacyclononane ([9]aneOS₂) and 1,10-dioxa-4,7,13,16-tetrathiacyclooctadecane ([18]aneO₂S₄)

In two separate graduated addition funnels, were placed ethanolic solutions (2 x 300mL) of bis(2-bromoethyl)ether (22.3g, 0.096 mol) and 1,2-ethanedithiol (8.0 mL, 0.096 mol). Dropwise they were added to a stirring reservoir of ethanol (350mL) and NaOH (10g, 0.25 mol). This was done over 24hrs, the reservoir became cloudy after 4hr. It was left to stir for an extra day, a lot of white solid deposited. HCl(aq) solution was used to neutralise any remaining base and the solid was filtered off. The ethanol was removed under vacuum leaving behind a clear oil that was taken up in diethyl ether (2x100mL). The solid retained from the filtration was suspended in CH_2Cl_2 and then filtered and pumped to dryness leaving behind a

large amount of white powder recrystallised from chloroform:hexane at 5°C giving pure large macrocycle (2.0g, 0.006 mol, Yield: 12.7%(lit: 4%). ¹H NMR [CDCl₃]: δ 2.76 (t, [8H], SCH₂CH₂O), δ 2.88 (s, [8H], SCH₂), δ 3.69 (t, [8H], OCH₂); ¹³C {¹H} NMR [CDCl₃]: δ 31.2(SCH₂), 32.5(S(CH₂)₂S), 72.0(CH₂O).

The ether fractions were dried over MgSO₄ and filtered. After removing the ether the remaining oil was distilled using a Kugelrohr at 70°C/0.05 mmHg over 3 days, the light oil collected was the small ring (6.4g, 0.039 mol, Yield 41% (lit:6%), ¹H NMR [CDCl₃]: δ 2.64 (t, [4H], SCH₂CH₂O), δ 2.90 (s, [4H], SCH₂), δ 3.78 (t, [4H], SCH₂CH₂O); ¹³C {¹H} NMR [CDCl₃]: δ 32.7 (SCH₂), 34.6 (S(CH₂)₂S), 73.6 (CH₂O).

1,4,7-trioxa-10,13,16-trithiacyclooctadecane ([18]aneO₃S₃)

NaOH (49.2g, 1.23mol) was dissolved in a reservoir of dry EtOH (600mL), to this 1,11-dichloro-3,6,9-trioxaundecane (24.65g, 0.1mol) along with 3-thia-pentane-1,5-dithiol (13.8mL, 0.106mol) in EtOH (2 x 300mL) were added dropwise simultaneously. The initial reaction mixture began to opalesce. After 24h the solution was neutralised using HCl and the reaction filtered. The ethanol was distilled off leaving a yellow precipitate, this was extracted using diethyl ether (3 x 200 mL), and the ethereal fractions combined and dried over MgSO₄. Removal of the volatiles afforded pale yellow oil. The oil was distilled under vacuum (160°C/0.05mmHg). Only a small amount of oil was extracted, the rest remained in the starting flask. Upon cooling the oil in the bulb solidified, this solid was removed using diethyl ether (40 mL) and hexane (5 mL). The suspension was filtered and the white solid washed with cold hexane and dried *in vacuo*. Yield: 9.81g, Yield 29.4% (lit: 11%). ¹H NMR [CDCl₃]: δ 2.76 (t), 2.77 (s), 3.65 (s) 3.67 (t). ¹³C {¹H} NMR [CDCl₃]: δ 70.39, 70.63, 71.11, 76.8, 77.00, 77.42.

1,4,10, 13-tetraoxa-7,16-diselenacyclooctadecane ([18]aneO₄Se₂)

Sodium (2.5 g, 0.054 mol+ plus a slight excess) was dissolved in liquid NH₃ (400 mL) and selenium powder (4.29g, 0.054 mol) added. The suspension was allowed to stir and warm up to room temperature. Upon warming a white solid immediately began to form, the blue colour of the solution persisted. The ammonia was allowed to evaporate off over 18 hr., the reaction was maintained under N₂ at all times. The white solid was then taken up in previously dried ethanol (300 mL) and transferred to a graduated dropping funnel. In a separate graduated dropping funnel an ethanolic solution (300 mL) of 1,8-dibromo-3,6-dioxaoctane (15g, 0.054 mol) was made up. Both solutions were allowed to add simultaneously to a stirring reservoir of ethanol (700 mL) and NaOH (4.2g, 0.10 mol) over 3 days. Colour changes were observed ranging from yellow to orange as the addition rates for the two solutions were equilibrated,

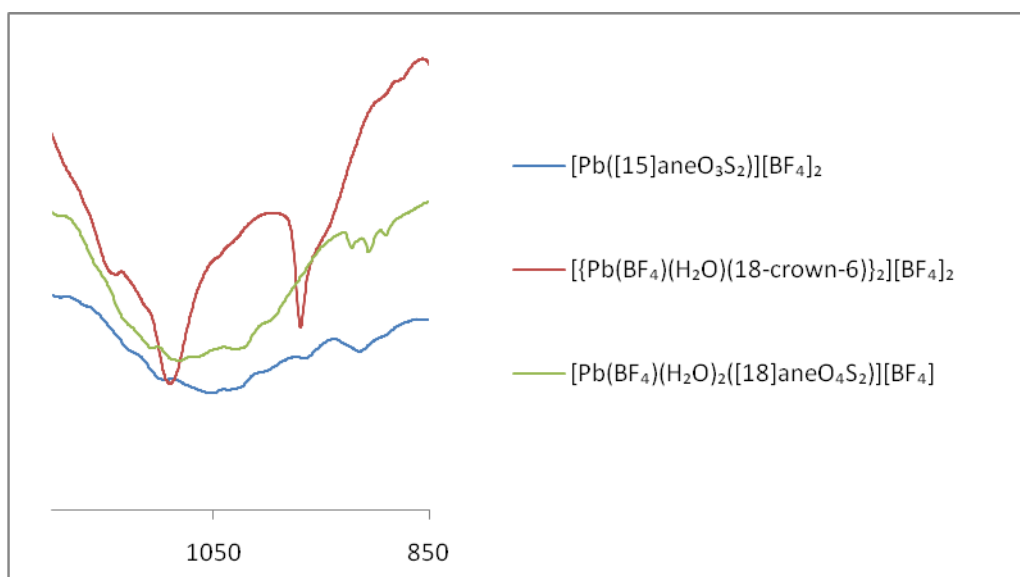
the solution going more orange as the Na₂Se solution became more concentrated in the final reaction mixture. After complete addition the reaction was left to stir for a further 2 days. Some precipitate had formed and the solution lightened to a light yellow. The mixture was hydrolysed using HCl (9.02 mL, 11.6M) in water (200 mL) and then filtered. The EtOH was taken off leaving behind a yellow oil. Analysis *via* ⁷⁷Se{¹H} NMR of the yellow oil showed the presence of three species attributed to the large ring (major component) and polymers (minor). The oil was extracted using CH₂Cl₂ (2x200 mL) and dried over MgSO₄. The volatiles were removed *in vacuo* and the yellow oil dissolved in the minimum CH₂Cl₂ and layered with hexane. At room temperature a fine white solid formed up agitation of the two layers, the crystallisation mixture was left at 5°C and large colourless single crystals formed. These were filtered off. Subsequent recrystallisations using the minimum amount of CH₂Cl₂ and placement at 5°C yielded further crops of the pure large ring. (2.77g, Yield: 26% (lit: 18%).^{S3} ¹H NMR [CDCl₃]: δ 2.86 (t, [8H], SeCH₂CH₂O), δ 3.63 (s, [8H], CH₂OCH₂), δ 3.79 (t, [8H], SeCH₂CH₂O); ¹³C {¹H} NMR [CDCl₃]: δ 22.8 (SeCH₂), 70.4 (O(CH₂)₂O), 72.5 (CH₂O).

X-ray crystallographic data for [Pb(15-crown-5)₂][H₃O][BF₄]₃

Formula	C ₂₀ H ₄₅ B ₃ F ₁₂ O ₁₂ Pb
<i>M</i>	945.18
Crystal system	Monoclinic
Space group (no.)	P2 ₁ /n (14)
<i>a</i> /Å	14.084(3)
<i>b</i> /Å	15.232(3)
<i>c</i> /Å	16.172(6)
<i>α</i> /°	90
<i>β</i> /°	90.693(18)
<i>γ</i> /°	90
<i>U</i> /Å ³	3469.1(14)
<i>Z</i>	4
<i>μ</i> (Mo-K _α) /mm ⁻¹	4.979
<i>F</i> (000)	1864
Total number reflns	23930

R_{int}	0.038
Unique reflns	7901
No. of parameters, restraints	433, 0
$R_1, wR_2 [I > 2\sigma(I)]^b$	0.053, 0.131
R_1, wR_2 (all data)	0.061, 0.137

The IR spectra of the fluoroborate complexes in the BF stretching region



References

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- S2. J. S. Bradshaw, Y. Chan, J. Y. Hui, B. L. Haymore, J.J. Christensen and R. M. Izatt, *J. Heterocycl. Chem.*, 1974, **11**, 45.
- S3. M. J. Hesford, W. Levason, M. L. Matthews and G. Reid, *Dalton Trans.*, 2003, 2852.

