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Syntheses of the novel thiamacrocycles containing the 1,10-phenanthroline unit

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The syntheses of three new thiamacrocycles **5, 6** and **7** including the 1,10-phenanthroline unit are described and show high selectivity for Pb^{2+} and Ag^{+}.

Keywords: phenanthroline derivatives, macrocycle, synthesis, extraction

Introduction

The 1,10-phenanthroline (phen) nucleus provides an attractive building block for incorporation into hosts. The unit is rigid, and provides two aromatic nitrogen atoms whose unshared electron pairs are beautifully placed to act cooperatively in binding cations.[1] It has been extensively used in both analytical[2] and preparative coordination chemistry.[3, 4] The 2,9-positions are well-spaced and chemically manipulatable to provide sites for incorporation of the unit into interesting cyclic or polycyclic systems of dimensions amenable to cation binding. Thus phen moieties have been incorporated into Schiff-base aza- or thia-macrocycles,[5,6] crown ethers,[7] cryptands[8] and catenands.[9]

We now report the convenient syntheses of three macrocycles **5, 6** and **7** without need of a metal template by condensation of 1,10-phenanthroline-2,9-dicarboxaldehyde with diamines. The complexation behaviour of **5, 6** and **7** has been studied experimentally by liquid-liquid extraction measurements: as designed, the thiamacrocycles **5, 6** and **7** show evidence for Pb^{2+}, Ag^{+} selectivity in extraction. Under the experimental conditions used, the high selectivity for Pb^{2+}, Ag^{+} over Cd^{2+}, Ni^{2+}, Hg^{2+}, Zn^{2+}, Ca^{2+}, K^{+}, Na^{+} is particularly notable.

Experimental

Syntheses

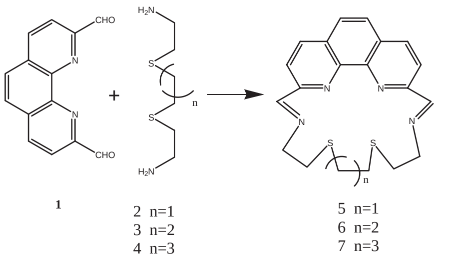
Elemental analyses were performed on a Perkin Elmer 240C elemental analyser. IR spectra were obtained as KBr disks on a Nicolet 170 SX FT-IR spectrometer. ^{1}H NMR spectra were recorded in $CDCl_3$ with a Varian UNITY-plus 400MHz spectrometer. 1,10-Phenanthroline-2,9-dicarboxaldehyde[10] (**1**), 1,8-diamino-3,6-dithia-octane(**2**), 1,9-diamino-3,7-dithianonane(**3**) and 1,10-diamino-3,8-dithiadecane[11] (**4**) were prepared by reported procedures.

General technique

Compound **1** (1mmol) was dissolved in 50ml of hot CH_3OH and then cooled to room temperature. The solution was slowly dropped into the solution of **2, 3** or **4** (1mmol) in 50ml CH_3OH during 2h, the resulting solution was stirred vigorously overnight at room temperature, respectively. The collected brown rubber-like solid was washed with a small amount of absolute ethanol and dry diethyl ether, and then dried in a desiccator. The yields and physical and spectral properties of **5, 6** and **7** are as follows.

6,9-dithia-3,12,23,26-tetraazatetracyclo-[12.8.4.0.0]hexacosa-1(23),2,12,14(26),15,17(25),18,20(24),21-nonaene **5**: brown solid, yield 63%. Found (%): C, 53.33; H, 6.38; N, 12.18, calc. for $C_{20}H_{20}N_4S_2 \cdot 4H_2O$ (%): C, 53.03; H, 6.19; N, 12.37。 FAB-MS: *m/z* 380.6 (3.51%, M^+). ^{1}H NMR ($CDCl_3$, 400MHz): δ7.82 (d, phen H-3, H-8); δ8.28 (d, phen H-5, H-6); δ8.46 (d, phen H-4, H-7); δ8.91 (d, phen-CH_2=N)。 IR (KBr, cm^{-1}): 3041, 2910, 2838, 1648, 1548, 1497, 1360, 1032, 861, 743, 633.

6,10-dithia-3,13,24,27-tertraazatetracyclo-[13.8.4.0.0]heptacosa-1(24),2,13,15(27),16,18(26),19,21(25),22-nonaene **6**: brown solid, yield 65%. Found (%): C, 54.46; H, 6.03; N, 12.34, calc. for $C_{21}H_{22}N_8S_2 \cdot 4H_2O$ (%): C, 54.01; H, 6.43; N, 12.00。 FAB-MS: *m/z* 394.7 (3.06%, M^+). ^{1}H NMR ($CDCl_3$, 400MHz): δ7.82 (d, phen H-3, H-8); δ8.37 (s, phen H-5, H-6); δ8.40 (d, phen H-4, H-7); δ8.90 (d, phen-CH=N)。 IR (KBr, cm^{-1}) : 3040, 2913, 2842, 1646, 1548, 1497, 1361, 1037, 861, 633.



Scheme 1 Reagents and conditions: CH_3OH, room temperature.

6,11-dithia-3,14,25,28-tertraazatetracyclo-[14.8.4.0.0]octacosa-1(25),2,14,16(28),17,19(27),20,22(26),23-nonaene **7**: brown solid, yield 70%. Found (%): C, 55.31; H, 6.42; N, 11.84, calc. for $C_{22}H_{24}N_4S_2 \cdot 4H_2O$ (%): C, 54.91; H, 6.66; N, 11.65。 FAB-MS: *m/z* 408.7 (2.87%, M^+). ^{1}H NMR ($CDCl_3$, 400MHz): δ7.82 (d, phen H-3, H-8); δ8.37 (d, phen H-5, H-6); δ8.40 (d, phen H-4, H-7); δ8.89 (d, phen-CH_2=N)。 IR (KBr, cm^{-1}): 3040, 2915, 2849, 1646, 1548, 1497, 1360, 1035, 862, 632.

Extraction experiment

5ml of a chloroform solution of a ligand (1×10^{-4}M) and 5ml of an aqueous solution of metal nitrate (1×10^{-2}M) and picric acid (1×10^{-4}M) were placed in a stopped tube, shaken for 5min and then allowed to stand for 10min in a water bath (25±0.1°C). The concentration of picric anion in the aqueous phase was determined by UV–Vis spectroscopy monitoring at 365nm.The extractability was calculated according to equation(1).

$$\text{Extractability}(\%) = ([\text{pic}]_0 - [\text{pic}])/[\text{pic}]_0 \times 100 \qquad (1)$$

Where $[\text{pic}]_0$ is the initial concentration of picric in the aqueous phase (1×10^{-4}M) and [pic] that in the aqueous phase after extraction. All experiments were performed in triplicate

Result and discussion

The IR spectra of the compounds are similar, and reveal the absorptions expected for the proposed structures. IR spectroscopy can provide valuable information as to whether or not condensation to form Schiff base bonds has occurred. Disappearance of the absorption band owing to $\nu_{C=O}$ from 2,9-diformyl-1,10-phenanthroline and the appearance of an absorption band assigned to $\nu_{C=N}$ indicates that the Schiff base has been formed. The carbonyl groups from the 2,9-diformyl- 1,10-phenanthroline occur at 1700 cm^{-1}, and are completely absent in the spectra of the compounds. A significant band at 1646 cm^{-1} in the spectra of the compounds can be assigned to $\nu_{C=N}$ of the Schiff base. A broad diffuse band of medium intensity in the 3040 cm^{-1} region may be assigned to lattice water.

After the induction of soft atoms such as nitrogen and sulfur into macrocycles, this complexation with alkali and alkaline-earth metal ions will degrade while the capability of complexation with transitional metal ions (including d^{10} ions) will be enhanced. The complexation behavior of **5, 6** and **7** has been studied experimentally by liquid-liquid extraction measurements. The results of extractability of the compounds are listed in Table 1. The order of extractability is $Pb^{2+} > Ag^{+} >> Cd^{2+} > Ni^{2+} > Hg^{2+} > Zn^{2+} >> Ca^{2+} \sim K^{+} \sim Na^{+}$ which is particularly notable. The extracting capability of metal ions increases with increase of the macrocyle size as expected.

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Table 1 The extractability(%) result of the compounds **5**, **6** and **7**

	Na(I)	K(I)	Ca(II)	Ag(I)	Pb(II)	Hg(II)	Cd(II)	Ni(II)	Zn(II)
5	2.1	3.3	2.8	63.5	74.2	23.4	40.5	28.4	17.5
6	2.6	3.5	3.4	67.5	79.9	25.7	48.5	30.0	18.1
7	8.5	5.1	7.1	78.5	83.2	27.1	49.5	31.2	26.6

Because Ag^+ ion is a typical soft acid it can strongly bind with macrocyles containing S atoms (typical soft base). Similarly the Pb^{2+} ion is in lower oxidation state and the outer electron cloud of Pb^{2+} ion is easy polarised, therefore it can bind well with macrocyles containing S atoms and the N atoms of phen.

It is expected that Cu^+ and Sn^{2+} ions can very strongly bind with macrocyclic ligands containing S and N atoms of phen and the further investigation proceeds.

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