Redox Switchable Ionophores for Heavy and Transition Metal Cations

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First examples of new, modular, redox switchable ionophores for heavy and transition metal cations are presented. These systems are based on a crown ether or polyethylene glycol unit substituted by the 1,2,4-thiadiazole/iminoylthiourea redox system (**2a**−**4a**, **2b**−**4b**). The syntheses via a Boulton-Katritzki rearrangement are described and their cation selectivities, studied by extraction experiments, proved to be determined by the systems' redox state. Additionally, simple 5-anilino-3-phenyl-1,2,4-thiadiazole (**5a**) and the corresponding iminoylthiourea (**5b**), which do not contain a potential cation binding polyether substituent were also tested to investigate the complexation property of the redox active building block itself.

Introduction

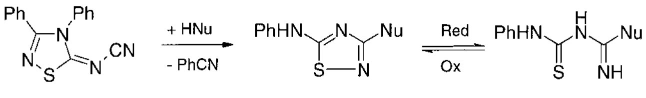
The development of macrocyclic and related acyclic ligand systems for metal cations, especially for environmentally relevant heavy and transition metal ions, is a subject of intense study.[1] For the selective recognition of these analytes, the design of receptor molecules containing a redox-switchable complexation site is a promising approach,[2] ideally leading to systems whose cation selectivity can be controlled by the redox state of the molecule.[3] Previously, we studied the complexation behaviour of such a redox active, 1,2,4-thiadiazole-based fluoroionophore and found excellent selectivities in heavy metal cation recognition.[4] A major field of application of ionophores is their use as carriers, aiming selectively for one distinct metal ion or for the total extraction of a number of different hazardous transition and heavy metal cations. Furthermore, cation receptors are also being established as integral parts of functional materials or as modular building blocks in molecular devices for analytical purposes.[5]

Here, some new ion-responsive molecules are presented which contain both a conventional cation complexation unit with well investigated cation binding properties such as a polyethylene glycol or a crown ether moiety, and a redox-active thiadiazole heterocycle. The heterocycle provides the possibility of reversible redox-switching between the thiadiazole form (oxidised) and the corresponding iminoylthiourea form (reduced). The high affinity of nitrogen and sulfur heteroatoms for heavy and transition metal ions makes it a useful complexation unit itself[6] which should enable the system to overcome the poor selectivity in cation complexation that conventional coronands and podands suffer from. The syntheses of these molecules is presented and the efficiency and selectivity of cation complexation is monitored via extraction experiments.

Results and Discussion

Syntheses

Recently, we reported the syntheses of 1,2,4-thiadiazoles[7] by the reaction of 5-cyanimino-1,2,4-thiadiazoline (**1**) with nucleophiles.[8] Here, the Boulton-Katritzki rearrangement proved to be a useful synthetic tool for the easy functionalisation of crown ethers and polyethylene glycol derivatives. The reaction additionally offers the opportunity of 1:1 or 1:2 conversion of bifunctional nucleophiles, e.g. diols or diamines, depending on the molar ratio of the starting compounds. The reduction of the thiadiazoles, leading to the corresponding iminoylthioureas, is achieved in good yields in a simple procedure, as is the back oxidation of the iminoylthioureas (Figure 1).[9]



1 **2a – 5a** **2b – 5b**

Figure 1. General scheme for the syntheses of **2a**, **3a** and **4a** and the reduction leading to the iminoylthioureas **2b**, **3b** and **4b**

The reaction of the α-ω-diaminotetraethylene glycol with a two fold excess of **1** yields the dithiadiazole product **2a**, (30%) and the mono-substituted product (20%). By reaction of **1** with equimolar amounts of 1-aza-18-crown-6, added portionwise, the corresponding crown ether derivative **4a** is obtained in 41% yield. The conversion of **1** with a 3.8-fold excess of 3,4-diaza-18-crown-6 leads exclusively to the bis-adduct **3a** (40%). The 1,2,4-thiadiazoles **2a**, **3a** and **4a** are converted into the corresponding iminoylthiourea derivatives by reaction with zinc in glacial acetic acid with yields of 61% (**2b**), 65% (**3b**) and 72% (**4b**).

Extraction Experiments

The podands **2a**/**2b** and the coronand systems **3a**/**3b** and **4a**/**4b** were tested for their potential application as cation carriers for the metal ions Li^+, Na^+, K^+, Pb^{2+}, Tl^+, Cu^{2+}, Ni^{2+}, and Cd^{2+} using a picrate coextraction method. The concentration of the cations in the organic phase after their

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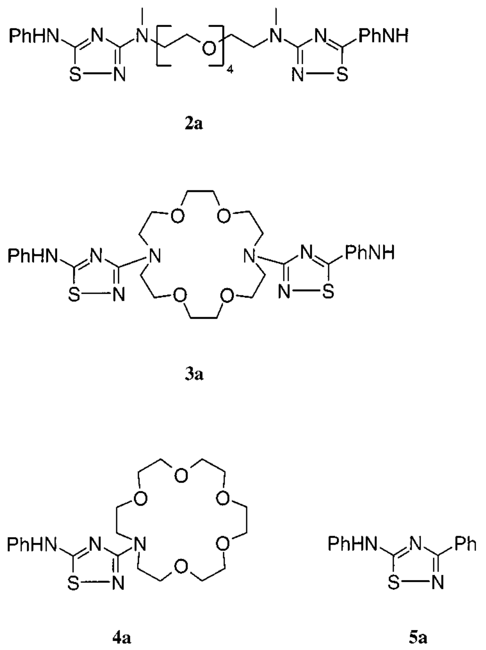

Figure 2. 1,2,4-thiadiazole ionophores **2a**−**5a**

extraction from the aqueous phase was measured indirectly by determining the picrate ion concentration in the aqueous phase by absorption spectroscopy. To estimate the contribution of only the heteroatomic redox-active thiadiazole/iminoylthiourea unit to the system's complexation properties, the same extraction experiments were performed with 5-anilino-3-phenyl-1,2,4-thiadiazole (**5a**) and the corresponding *N*-benziminoyl-*N*′-phenylthiourea (**5b**).[10] Starting with the system **5a/5b**, *N*-benziminoyl-*N*′-phenylthiourea (**5b**) proved to be a highly selective ionophore for Cu^{2+} leading to almost quantitative extraction (92%). The compound's coordination chemistry properties are likely to be comparable to those of the well investigated *N*-acylthioureas which are know as excellent chelation ligands for transition metal cations.[11] Additionally, slightly enhanced extraction efficiencies using **5b** are found only for Ni^{2+} (10%) and Cd^{2+} (12%) while for the oxidised **5a** virtually none of the cations studied is extracted (Figure 3).

For the redox system **2a/2b** containing two thiadiazole heterocycles, considerably larger extraction efficiencies are found for the reduced form **2b** for all the cations studied, the extraction ability of **2a** generally being rather poor (Figure 4). The extraction efficiencies observed for **2b** were very small (7%) for alkali metal ions but larger effects are found for Pb^{2+} (50%), Tl^{+} (46%), Ni^{2+} (32%) Cd^{2+} (68%) and especially for Cu^{2+} (93%). This, along with the generally poor efficiency measured for **2a**, implies that the polyethylene glycol moiety plays only a minor role in the complexation reaction whereas the thiourea subunits of **2b** are mainly responsible for the coordination of the heavy and transition metal ions. Taking also the results of the previous investigation of **5a/5b** into consideration, it is obvious that the overall enhancement of the extraction efficiencies observed for **2a/2b**, mainly for Pb^{2+}, Tl^{+}, Ni^{2+} and Cd^{2+} is the result of linking two of the iminoylthiourea units by the tetraethylene bridge (Figure 4).

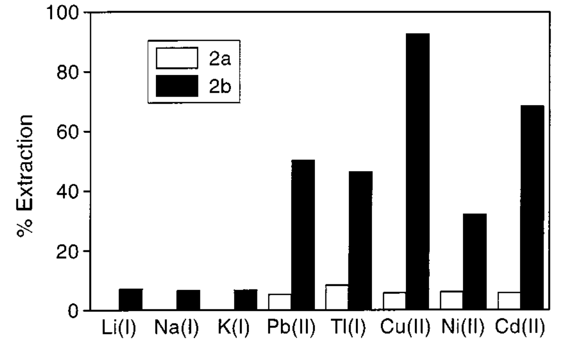

Figure 4. Metal cation coextraction with picric acid by **2a/2b**; $c = 10^{-3}$ M in $CHCl_3$, $c_M = 0.1$ M, $c_{PicOH} = 1.5 \times 10^{-4}$ M in water

In this respect, 4,13-diaza-18-crown-6 appears to be an even better linker group, preorganising the two heteroatomic redox active units in the system **3a/3b** towards the cation to be analysed. The reduced form **3b** displays very efficient extraction of the transition and heavy metal cations Pb^{2+}, Tl^{+}, Ni^{2+} and Cd^{2+} with efficiencies of 70%, 82%, and even 100% for Cu^{2+} (Figure5); significant amounts of Li^{+} (19%) and K^{+} (18%) are also extracted. For the oxidised form **3a**, the efficiencies are again relatively low with only Tl^{+} (16%) and Ni^{2+} (17%) reaching a value higher than 10%.

The extraction of Cu^{2+} by **4b** is again very efficient with a value of 89%. Additionally, for K^{+} (15%), Ni^{2+} (18%)

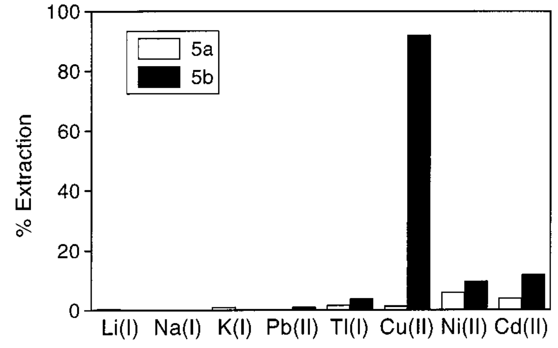

Figure 3. Metal cation coextraction with picric acid by **5a/5b**; $c = 10^{-3}$ M in $CHCl_3$, $c_M = 0.1$ M, $c_{PicOH} = 1.5 \times 10^{-4}$ M in water

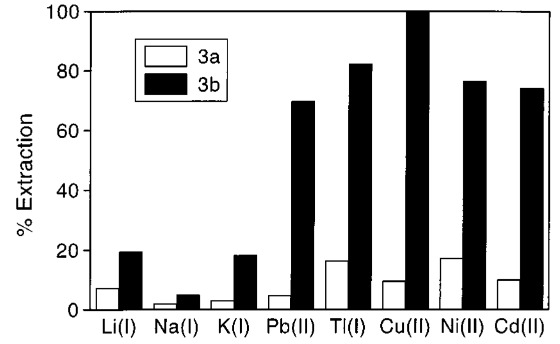

Figure 5. Metal cation coextraction with picric acid by **3a/3b**; $c = 10^{-3}$ M in $CHCl_3$, $c_M = 0.1$ M, $c_{PicOH} = 1.5 \times 10^{-4}$ M in water

and Cd^{2+} (15%), enhanced extraction efficiencies are found for **4b** (Figure 6). The aza crown derivative **4a** shows small extraction efficiencies for the cations studied, Li^+ not being extracted at all, Pb^{2+} and Tl^+ showing the largest efficiencies of 37% and 24%, respectively. In contrast to the other systems investigated, these two ions are extracted even more efficiently by the oxidised form **4a** than the reduced form **4b**. The extraction behaviour of **4a** can be correlated with the complexation behaviour of the 1-aza-18-crown-6 ligand. A comparison of the cavity size (2.6−3.2 Å) and ionic radii along with published complexation constants for the related ligands 18-crown-6 and 1,4-diaza-18-crown-6 suggests that the observed order of the extraction efficiencies $Pb^{2+} > Tl^+ > Cu^{2+} > K^+ > Na^+ > Ni^{2+} \approx Cd^{2+} > Li^+$ of **4a** is due to complexation of these ions to 18-crown-6.[12]

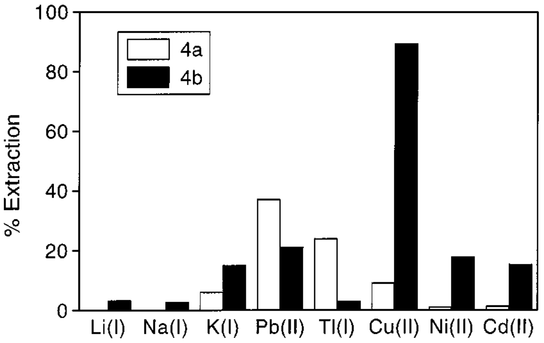

Figure 6. Metal cation coextraction with picric acid by **4a**/**4b**; $c = 10^{-3}$ M in $CHCl_3$, $c_M = 0.1$ M, $c_{PicOH} = 1.5 \times 10^{-4}$ M in water

Conclusions

The cation selectivities of the ionophores presented are clearly dependent on the redox state of the switchable 1,2,4-thiadiazole/iminoylthiourea unit. In their reduced form they show a high affinity towards transition and heavy metal cations, especially towards Cu^{2+} which is extracted almost quantitatively by all the molecules investigated. The cation binding property of the iminoylthiourea function predominates the complexation behaviour of all the receptor molecules studied. A significant influence of the polyether binding sites can only be found in case of the monosubstituted crown ether system **4a**/**4b** where, especially for the oxidised form **4a**, the extraction of Pb^{2+} and Tl^+ is attributed to the complexation property of the aza crown ether. Apart from this exception, the extraction efficiencies by using the ionophores in their oxidised form proved to be poor in general. Finally, the combination of two principles, i.e. combining a heteroatomic chelation unit with a polyether complexation site in one molecule, does not lead to receptors with enhanced cation selectivity. Simple **5b** shows the highest selectively in cation recognition, i.e. it extracts Cu^{2+} exclusively and very efficiently. Nevertheless, the new ionophores, especially **2b** and **3b**, can be regarded as useful reagents for the total extraction of heavy and transition metal ions.

Experimental Section

Methods: Nuclear magnetic resonance data were recorded on a UNITY plus-500 spectrometer and are reported in ppm (Me_4Si as internal standard, J in Hz, coupling constants were taken directly from the obtained spectra). Mass spectra were run on a Hewlett Packard 5985 B mass spectrometer (FAB- and CI-MS). High resolution mass spectra were recorded using a Finnigan MAT-95 mass spectrometer (ESI II/APCI). Melting points are uncorrected (Boetius apparatus). TLC was carried out on plastic silica gel plates 60 F_{254} (5735, Merck) and flash chromatography on silica gel 60 (7731, Merck). Absorption spectra were recorded on a Carl Zeiss SPECORD M500 spectrometer.

Complexation Studies: Spectroscopic experiments were performed with spectroscopic grade solvents from Merck. Extraction studies were carried out using a picrate coextraction method:[13] Cu^{2+}, Ni^{2+}, Cd^{2+}, Pb^{2+}, Tl^+ were introduced as nitrates, Li^+, Na^+, K^+ as hydroxides (metal ion concentration $c_M = 10^{-1}$ mol/L, $c_{PicOH} = 1.5 \times 10^{-4}$ mol/L). After stirring for 1 h at room temperature the respective chloroform/water mixture for every cation [$V(CHCl_3) = V(H_2O) = 3$ mL] was centrifuged, 0.5 mL of the aqueous phase was taken off and diluted with 2 mL water. The concentration of the cations in the organic phase was measured indirectly by determining the picrate ion concentration in the aqueous phase by absorption spectroscopy. The aqueous phase containing only the corresponding metal salt and picric acid was taken as blank solution. The absorptions measured for the solution with the extracted complex were normalised with respect to their corresponding blank value. The possible influence of the different anions, i.e. hydroxide or perchlorate, on the extraction efficiencies was not studied.

1,16-Bis(5-anilino-1,2,4-thiadiazol-3-yl)-1,16-diazo-1,16-dimethyl-4,7,10,13-tetraoxahexadecane (2a): To a solution of 1,16-diazo-1,16-dimethyl-4,7,10,13-tetraoxahexadecane (264 mg, 1.0 mmol) in 10 mL boiling toluene, a solution of **1** (278 mg, 1.0 mmol) in 30 mL toluene was added dropwise over 20 h. After refluxing the mixture for 24 h, the solvent was evaporated. The remaining oily residue was extracted with a mixture of ethyl acetate/hexane (1:1). The eluent was refrigerated for about 12 h to give **2a** as colourless crystals. Yield: 178 mg (29%), m.p. 86−88 °C. − ^1H NMR ($CDCl_3$): δ = 3.09 (6 H, s, $>N-CH_3$), 3.47−3.63 (20 H, m, $-CH_2-O$, $CH_2-N<$), 6.98−7.33 (10 H, m, Ph), 8.45 (2 H, b s, $=NH$). − ^{13}C NMR ($CDCl_3$): δ_C = 37.4 ($>N-CH_3$), 51.0 ($-CH_2-N<$), 69.3, 70.45, 70.6 ($-CH_2-O-$), 118.0, 123.5, 129.6, 139.5 (Ph), 167.4 ($-C=N-$), 179.7 ($-C-S-$). − MS (FAB) *m/z* (%) 637 (57) [M + Na]$^+$, 615 (58) [M + H]$^+$, 382 (22), 307 (18), 233 (96), 219 (83), 206 (17), 176 (35), 154 (100), 136 (84), 121 (24). − $C_{28}H_{38}N_8O_4S_2$ (614): calcd. C 54.70, H 6.23, N 18.22; found: C 54.69, H, 6.26, N 18.20.

1,10-Bis(5-anilino-1,2,4-thiadiazol-3-yl)-1,10-diaza-4,7,13,16-tetraoxacyclooctadecane (3a): 4,13-diaza-18-crown-6 (1.0 g, 3.8 mmol) and **1** (278 mg, 1.0 mmol) were refluxed in toluene for 22 h to leave a yellow oil after evaporation of the solvent. Purification by chromatography (toluene/ethyl acetate 1:1) and finally recrystallisation from methanol of the solid obtained yielded **3a** as colourless crystals. Yield 245 mg (40%), m.p. 88−91 °C. − ^1H NMR ([D_6]DMSO): δ_H = 3.57−3.73 (24 H, m, $-CH_2-O-$, $-CH_2-N<$), 7.01−7.48 (10 H, m, Ph), 10.70 (2 H, s, $>NH$). − ^{13}C NMR ([D_6]DMSO): δ_c = 49.5 ($-CH_2-N<$), 69.1, 70.0 ($-CH_2-O-$), 117.4, 122.4, 129.2, 140.0 (Ph), 166.3 ($-C=N-$), 177.4 ($-C-S-$). − HRMS: $C_{28}H_{36}N_8O_4S_2 + Na^+$: calcd. 635.2199; found 635.2201.

5-Anilino-3-(1-aza-4,7,10,13,16-pentaoxacyclooctadec-1-yl)-1,2,4-tiadiazole (4a): To a solution of 1-aza-18-crown-6 (263 mg, 1.0 mmol) in 15 mL boiling toluene was added **1** (278 mg, 1.0 mmol) in small portions over 12 h. The mixture was kept under reflux for another 12 h. After evaporation of the solvent, purification by chromatography (toluene/ethyl acetate; at first 10:1, then 5:1, finally toluene/methanol 5:1) gave **4a** as a yellow oil. Yield 180 mg (41%). − ^{1}H NMR ([D$_6$]DMSO): δ_H = 3.48−3.74 (24 H, m, $-CH_2-O-$, $-CH_2-N<$), 7.02−7.50 (5 H, m, Ph), 10.75 (1 H, s, $>NH$). − ^{13}C NMR (CDCl$_3$): δ_c = 49.7 ($-CH_2-N<$), 68.7, 69.8, 69.9, 70.0, 70.1 ($-CH_2-O-$), 117.5, 122.6, 129.3, 139.9 (Ph), 166.1 ($-C{=}N-$), 177.1 ($-C-S-$). − HRMS: $C_{20}H_{30}N_4O_5S + H^+$: calcd. 439.2015; found 439.2018.

5-Anilino-3-phenyl-1,2,4-thiadiazole **(5a)** and *N*-benziminoyl-*N'*-phenylthiourea **(5b)** were prepared following a description by Kurzer and Tertiuk.[10]

Reduction of 2a, 3a, 4a. − General Procedure: The thiadiazole derivative (0.5 mmol) was stirred with zinc (1 g) in 5 mL of glacial acetic acid for 4 h. The insoluble components of the suspension were filtered off and washed with chloroform. After addition of 10 mL water to the filtrate, the mixture was neutralised with sodium hydrogen carbonate. The phases were separated and the aqueous phase was extracted with chloroform (4 × 5 mL). The combined organic layers were dried (MgSO$_4$) and the solvent was evaporated. The crude products were purified as described below.

1,16-Bis(*N'*-iminocarbonyl-*N*-phenyl-thioureyl)-1,16-diazo-1,16-dimethyl-4,7,10,13-tetraoxahexadecane (2b): The remaining solid was treated with 2 mL hexane/chloroform/ethyl acetate (1:1:1). After standing overnight in the refrigerator, colourless crystals of **2b** precipitated. Yield 189 mg (61%), m.p. 119−120 C. − ^{1}H NMR (CDCl$_3$): δ_H = 3.02 (6 H, s, $>N-CH_3$), 3.50−3.64 (20 H, m, $-CH_2-O-$, $-CH_2-N<$), 7.02−7.42 (10 H, m, Ph), 7.83 (2 H, $>NH$, bs), 8.1−8.4 (4 H, m, $=NH$, $>NH$). − ^{13}C NMR ([D$_6$]DMSO, 100°C): δ_C = 35.5 ($>N-CH_3$), 48.3 ($-CH_2-N<$), 68.2, 69.4, 69.5 ($-CH_2-O-$), 121.8, 122.3, 127.4, 139.9 (Ph), 160.1 ($-C{=}NH$), 182.2 ($-C{=}S$). − MS (FAB) *m/z* (%) 619 (94) [M + H]$^+$, 526 (90), 484 (38), 467 (23), 450 (41), 433 (48), 374 (55), 349 (78), 332 (100), 307 (57).

1,10-Bis(*N'*-iminocarbonyl-*N*-phenyl-thioureyl)-1,10-diaza-4,7,13,16-tetraoxacyclooctadecane (3b): The remaining solid was recrystallised from chloroform to give colourless crystals of **3b**. Yield 200 mg (65%), m.p. 164−166°C. − ^{1}H NMR ([D$_6$]DMSO): δ_H = 3.49−3.59 (24 H, m, $-CH_2-O-$, $-CH_2-N<$), 6.95−7.44 (10 H, m, Ph), 8.8 (4H, br. s, $>NH$, $=NH$), 9.46 (2 H, s, $>NH$). − ^{13}C NMR ([D$_6$]DMSO): δ_c = 48.0 ($-CH_2-N<$), 69.9, 68.7 ($-CH_2-O-$), 122.3, 122.8, 128.0, 140.2 (Ph), 159.9 ($-C{=}N-$), 181.8 ($-C{=}S$). − HRMS: $C_{28}H_{36}N_8O_4S_2 + Na^+$: calcd. 639.2512; found 639.2506.

***N*-Phenyl-*N'*-[(1-aza-,4,7,10,13,16-pentaoxacyclooctadec-1-yl)-iminocarbonyl]thiourea (4b):** The remaining solid was purified by chromatography (toluene/ethyl acetate; at first 5:1, then 1:1) **4b** was obtained as colourless crystals. Yield 158 mg (72%), m.p. 119−121°C. − ^{1}H NMR ([D$_6$]DMSO): δ_H = 3.55−3.59 (24 H, m, $-CH_2-O$, $-CH_2-N<$), 6.96−7.46 (5 H, m, Ph), 8.57−8.62 (2 H, b m, $>NH$, $=NH$), 9.06 (1 H, b s, $>NH$) − ^{13}C NMR ([D$_6$]DMSO, 100°C): δ_C = 48.0 ($-CH_2-N<$), 68.6, 69.6, 69.7 ($-CH_2-O-$), 122.0, 122.4, 127.4, 139.8 (Ph),159.9 ($-C{=}N-$), 182.6 ($-C{=}S$). − MS (FAB) (%) *m/z* 463 (100) [M + Na]$^+$, 441 (68) [M + H]$^+$, 429 (20), 407 (27), 348 (57), 311 (36), 286 (17), 264 (20), 176 (15), 154 (24), 137 (29), 123 (19), 109 (29). − $C_{20}H_{32}N_4O_5S$ (440): calcd. C 54.52, H 7.32, N, 12.72; found: C 54.62, H 7.42, N 12.57.

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