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Coordination Chemistry Reviews
222 (2001) 103–126

COORDINATION CHEMISTRY REVIEWS

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Macrocyclic and open-chain ligands with the redox switchable trithiadiazapentalene unit: synthesis, structures and complexation phenomena

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Received 25 October 2000; received in revised form 25 May 2001; accepted 7 June 2001

Dedicated to Professor Eberhard Hoyer (Leipzig) on the occasion of his 70th birthday

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Abstract

This review focuses on synthesis, structure and binding properties of crown compounds and their open-chain analogues containing a trithiadiazapentalene building block. This

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PII: S0010-8545(01)00397-6

heterocyclic unit favours in particular the complexation and solvent extraction of the soft transition metal ions Ag(I), Pd(II), Hg(II) and Au(III). The redox active system trithiadiazapentalene/trithiotriuret introduced into a crown ring allows the control of Ag(I) and Hg(II) phase transfer in solvent extraction experiments. Crystal structures of metal complexes with these pentaleno crown compounds show significant differences of both S–S bond lengths of the trithiadiazapentalene unit and package arrangements in the cell.

Keywords: Crown compounds; Trithiadiazapentalene systems; Redox switch; Metal extraction; Crystal structures; Molecular modelling

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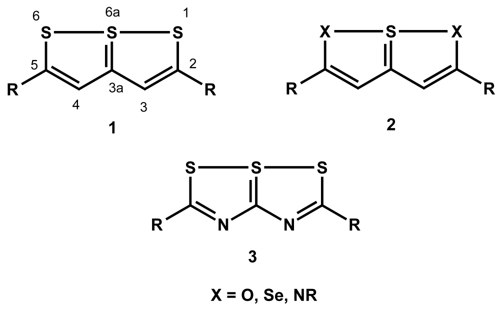
1. Introduction

The design and synthesis of novel supramolecular ligand architectures are connected closely to promising application options in different areas [1]. Up to now, various macrocyclic and spherical ligands as well as their open-chain counterparts were synthesised and characterised with a view to species separation, analytical detection, material preparation, catalytic functions, medical use and nanoscopic devices [2]. Crown ethers allow the possibilities to vary selected properties, especially the stability of corresponding complexes [3]. Introducing heterocyclic functions into the crown ring leads to a greater rigidity of the ligand architecture and provides additional soft donor atoms. Therefore, pyridino macrocycles with unsaturated nitrogen atoms give much greater affinity for most transition and post-transition metal ions in comparison with the pure crown ethers [3,4]. One goal in the control of binding selectivity and reversibility is the use of switchable functionalities fixed in larger supramolecular moieties [5,6]. In this regard the well-known photoisomerisable azobenzene system [7], also the redox active units as the biological relevant dithiol–disulphide couple [8], ferrocenes [9], tetrathiofulvalenes [10], biindolizines [11] or thiadiazoles [12] were discussed in this connection. Heterocyclic building blocks on the basis of 1,6,6aλ^4-trithiapentalenes (**1**) and its heteroanalogues **2** and **3** [13–17] represent another interesting approach to modify the complexation properties of both macrocyclic and structure related open-chain systems which lead to switchable ionophores (Scheme 1).

In this work we summarise the experimental and theoretical results with ligands containing the 1,6,6aλ^4-trithia-3,4-diazapentalene unit (**3**) and the corresponding trithiotriuret form **4** in different structural arrangements (Scheme 2). The presence of unsaturated nitrogen donor atoms [18–20] in the pentalene derivatives and of thiocarbonyl functions [21–23] in the reduced thiourea form should especially enhance the binding strength and binding selectivity towards soft metal ions.



Scheme 1.

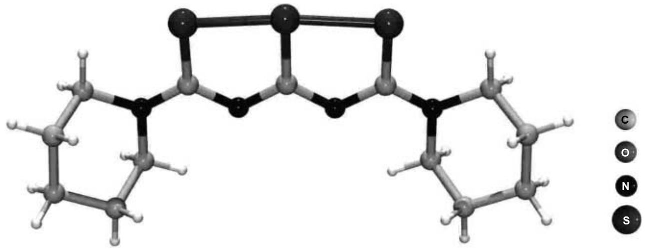
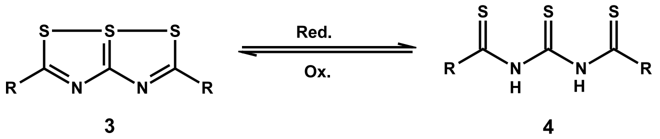


Fig. 1. The X-ray structure of ligand **9a** [26].



Scheme 2.

2. The 1,6,6aλ^4-trithia-3,4-diazapentalene unit

The 1,6,6aλ^4-trithia-3,4-diazapentalenes (**3**) are heteroanalogues of the extensively studied 1,6,6aλ^4-trithiapentalenes (**1**). These systems have attracted much attention, because of their unusual binding behaviour [13–17]. The theoretical situation is quite clear from selected first-principles quantum calculations, which is in agreement with the experimental results that the symmetric and planar arrangement of the bicyclic ring is an aromatic 10π-electronic system with a three-atom sulphur bridge [24–26]. Generally, the two S–S distances found between 2.25 and 2.50 Å are exceedingly long compared to the S–S bonds of monocyclic conjugated disulphides (about 2.1 Å), but substantially shorter than the sum of the corresponding van der Waals radii (3.60 Å). In this sense the formulae **1** and **3** reflect the correct symmetry but are misleading in suggesting hypervalency of the central sulphur by octet expansion. It is well known that the d-orbital model participation of sulphur is not substantiated for compounds containing higher-coordinated sulphur atoms [27]. Thus the λ^4-nomenclature generally does not reflect the bonding nature and the real valency of the central sulphur atom.

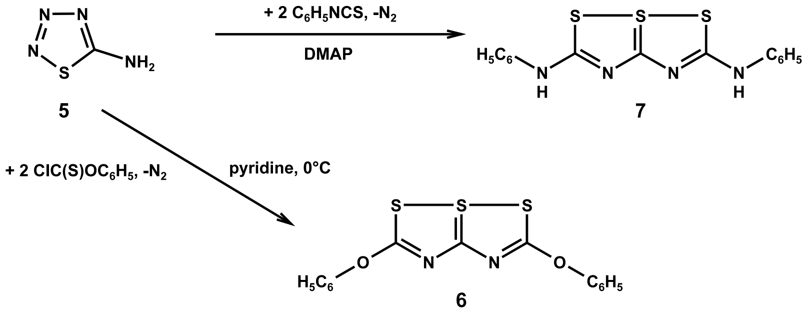
In contrast to the calculations, which always leads to symmetric structures in the case of uniform substitution in **3**, the crystal structures give some differences in dependence on the substitution apparently caused by intra- and intermolecular hydrogen bonds [26]. This is illustrated by the crystal structure of compound **9a** in Fig. 1. In this case the S–S bond lengths of 2.328 [S(1)···S(6a)] and 2.346 Å [S(6)···S(6a)] are observed together with hydrogen bonds of the type CH···N and CH···S. Further interesting facts of the structure are the short and different C–N bond lengths between the carbon atoms of the pentalene unit and the amine nitrogen in the 2- and 5-position. This significant behaviour was also confirmed by solid state ^{13}C-NMR experiments, which give different chemical shifts for these two carbon atoms. Because this splitting cannot be observed in solution, there is clear evidence of a crystal effect caused by four molecules being present in the unit cell [28].

The calculated atomic charges of about -0.5 at the ring nitrogen atoms in **9a** point to their strong basic character, and useful donor ability for complexation processes can be expected. Compared with this, the donor strength of the sulphur atoms in the molecule should be markedly lower, which agrees with the corresponding calculated atomic charges [26].

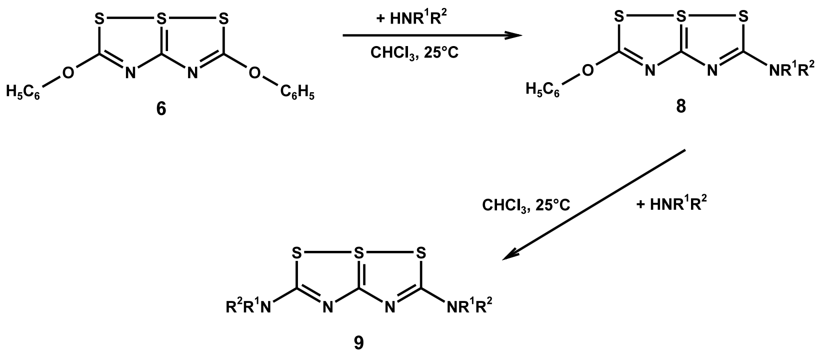
The 1,6,6aλ^4-trithia-3,4-diazapentalenes (**3**) can be reduced by weak reduction agents, e.g. by Zn/acetic acid mixtures. The resulting trithiotriuret compounds **4** are reasonably stable especially in the solid state. The reoxidation in solution is done easily in the presence of atmospheric oxygen [29,30]. The thioureas **4** possess three thiocarbonyl sulphur atoms, which should give very strong interactions with soft metal ions. The observed complexation properties will be discussed in more detail in Section 4.

3. Synthesis

During the last four decades several synthesis methods for substituted 1,6,6aλ^4-trithia-3,4-diazapentalenes have been reported [31]. An easy route to synthesise 2,5-aryloxy or 2,5-amino substituted 1,6,6aλ^4-trithia-3,4-diazapentalenes is to start with 5-amino-1,2,3,4-thiatriazole (**5**). The reaction of **5** with chlorothioformates gives the corresponding trithiadiazapentalenes **6** [32] with about 50% yields and with arylisothiocyanates produces the amino substituted compounds **7** [33]. The trithiadiazapentalene **6** can be easily functionalised further at the aroxy group. So the aminolysis with secondary amines leads stepwise to the 2-monoamino **8** and 2,5-diamino heteropentalenes **9** (yields of about 80%) [34,35]. By analogy, the reaction of **6** with secondary diamines [35], among them open-chain [30] and cyclic polyether diamines [36], gives a great variety of derivatives such as **11**–**18** having different binding potential for cationic guest species. Typical yields for the crown compounds **11** are between 20 and 30% (Schemes 3–8).



Scheme 3.

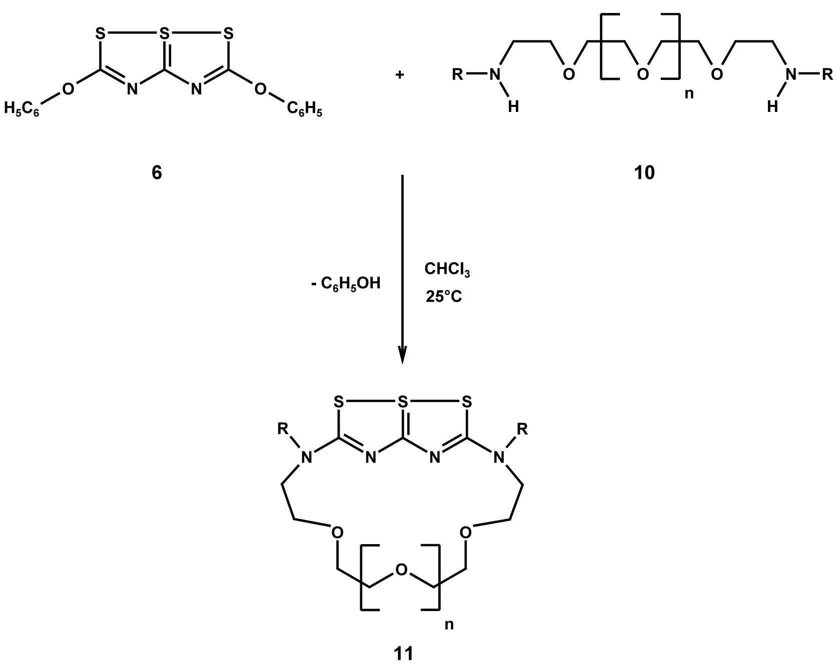


9a: $R^1, R^2 = C_5H_{10}$
9b: $R^1 = CH_3$; $R^2 = C_2H_4OH$
9c: $R^1 = C_2H_5$; $R^2 = C_2H_4OH$
9d: $R^1 = CH_2C_5H_{10}$; $R^2 = CH_3$

Scheme 4.

In particular the introduction of the redox switchable heteropentalene building block in macrocyclic systems allows systematic modifications of the complexation properties and the control of selectivity [30,37]. The X-ray crystal structure of one pentaleno crown derivative **11b** is shown in Fig. 2 [30]. The trithiadiazapentalene unit possesses similar structural parameters as in the corresponding open-chain compound **9a**. However, the S–S distances show greater differences for **11b** (2.308 and 2.379 Å) compared to the case of **9a**. Generally, the crown compound is pre-organised for the inclusion of a guest species by a cleft-like arrangement of the heteropentalene block and the ether ring system in the molecule.

The reduction of the pentaleno crown compounds **11** by zinc in glacial acetic acid gives the corresponding thioureas **19**, which can be reconverted quantitatively by atmospheric oxygen into the system's oxidised form **11** (Scheme 9).



11a: R = $CH_2C_6H_5$; n = 1

11b: R = CH_3; n = 2

11c: R = CH_3; n = 3

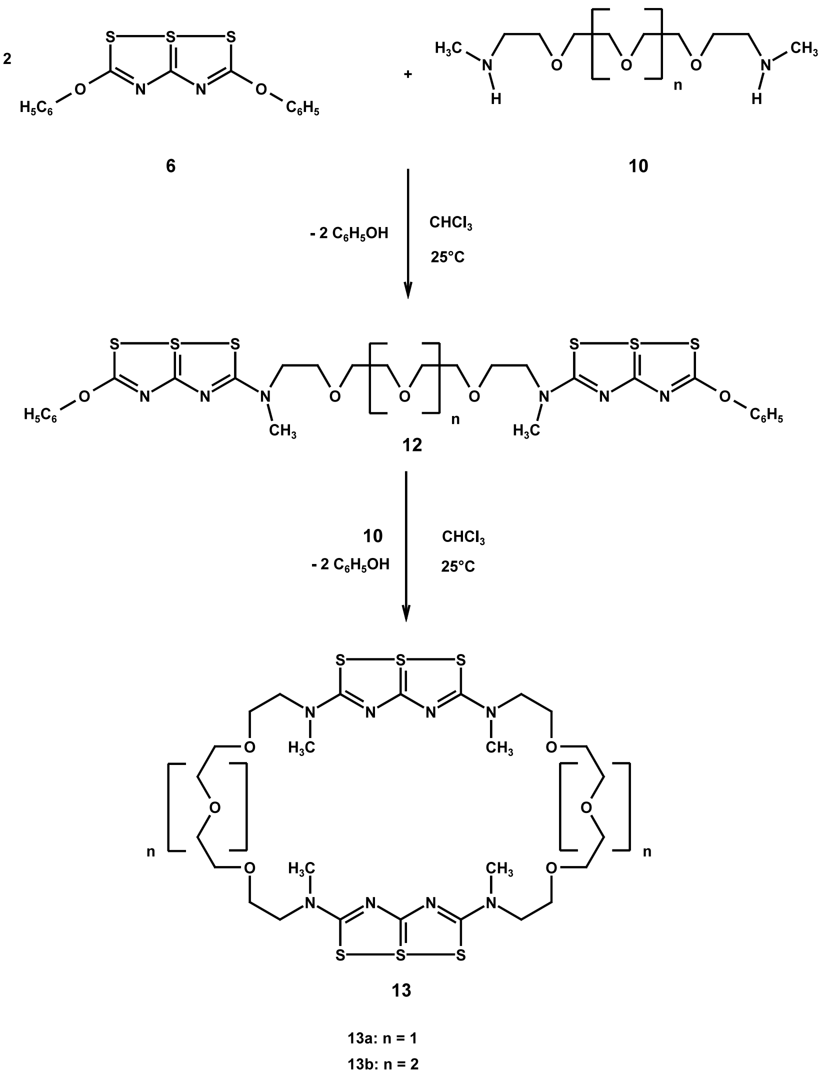
Scheme 5.

4. Liquid–liquid extraction studies

Liquid–liquid extraction carried out as a microtechnique with radionuclide labelling of the interesting species represents a very fast and accurate method [38] to determine the complexation behaviour of new ligand types in solution [39,40]. Furthermore this method also gives a general message about the applicability of the systems investigated for species separation or detection using extraction methods. The ligands studied in this review are neutral ligands and therefore the extraction equilibria are described by the following equation:

$$M^{n+}_{(w)} + nA^{-}_{(w)} + sL_{(org)} \overset{K_{ex}}{\rightleftharpoons} ML_sA_{n(org)} \qquad (1)$$

In this case the corresponding extraction constant K_{ex} is a function of the complex stability of the complexes formed and both of their distribution and of the distribution of the ligands between the two phases [38–40]. Characteristic extraction experiments allow the determination of the relevant complex species and conclusions on the acting structure extractability (and complexation ability) relationships [38–40]. The easily accessible experimental parameter in liquid–liquid

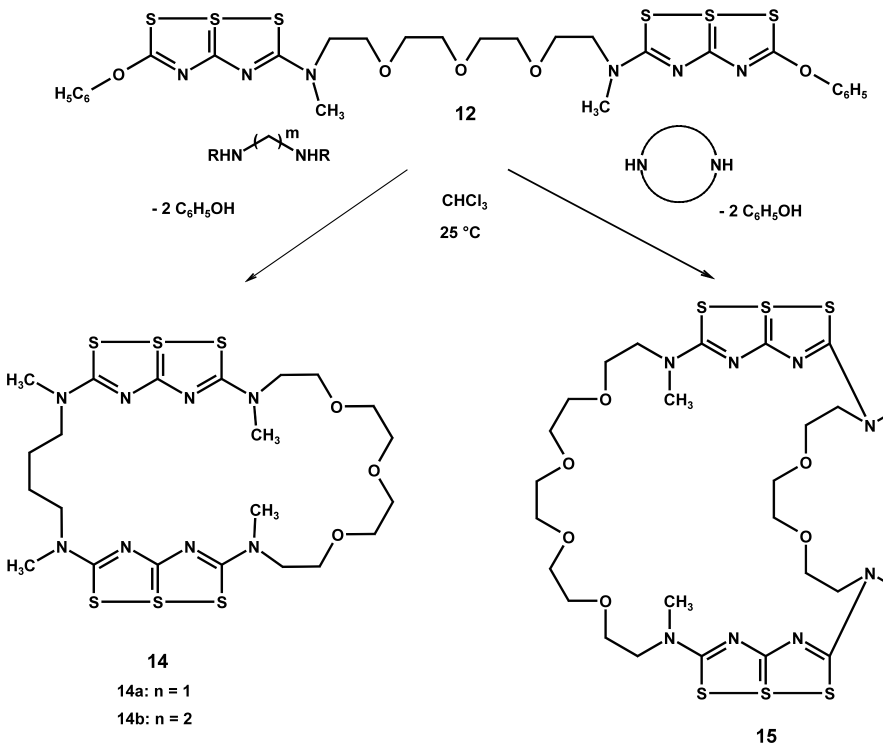


Scheme 6.

extraction systems represents the distribution ratio D_{M}, the quotient of the metal concentrations in the organic and aqueous phase, or the percentage extractability E:

$$D_{\mathrm{M}} = \frac{c_{\mathrm{M(org)}}}{c_{\mathrm{M(w)}}} \tag{2}$$

$$E[\%] = \frac{D}{D+1} \cdot 100 \tag{3}$$

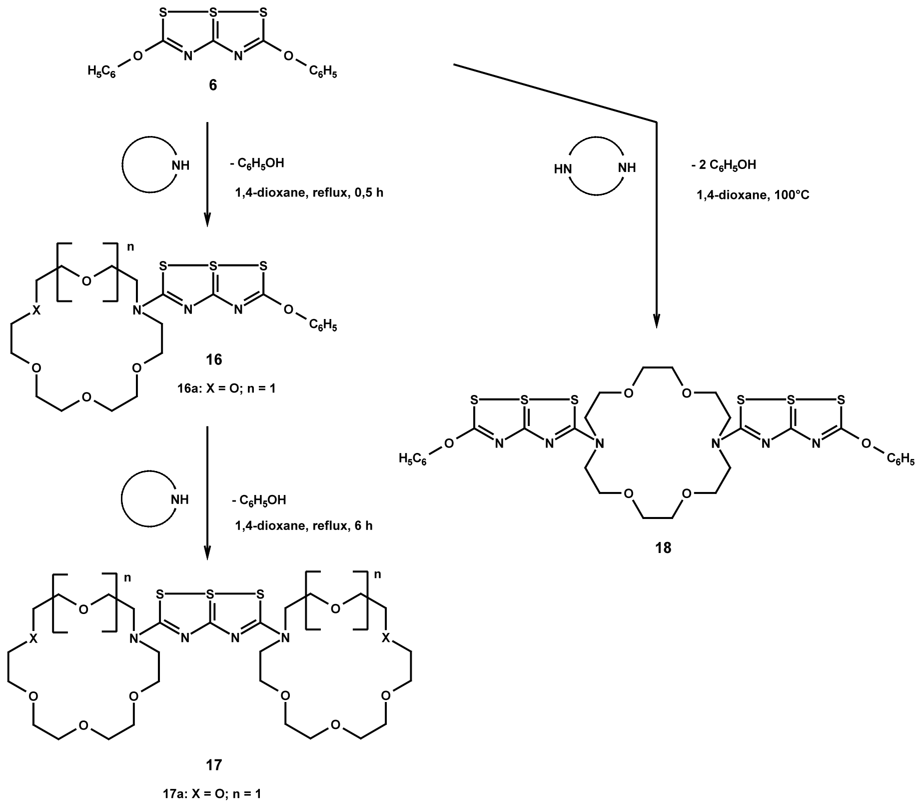


Scheme 7.

To support the transfer of the complexed positively charged metal species from the aqueous into the organic phase the slightly hydrated picrate anion has been used. The liquid–liquid extraction behaviour of selected open-chain trithiadiazapentalenes and their macrocyclic counterparts was studied in the system metal salt–picric acid–water/ligand–$CHCl_3$.

4.1. Open-chain ligands

Extraction results for two different species, in the 2- and 5-substituted positions for trithiadiazapentalenes, are presented. As can be seen from Fig. 3 the extractabilities of Ag(I), Hg(II), Pd(II) and Au(III) with the bisphenoxy derivative **6** are generally very low. In this case the electron withdrawing effect of the phenoxy group should decrease the donor strength of the ring nitrogens. Significant higher values were determined for the metal extraction with the 2,5-bisamino compounds **9a**–**d** and this was obviously caused by a favourable mesomeric influence of the amino nitrogen on the aromatic pentalene system. This fact has been confirmed by the short C–N bond lengths. In comparison with Ag(I), Hg(II) and Pd(II) the highest extractabilities have been observed for Au(III). At present the reason for



Scheme 8.

this result is not yet clear, although the strong complexation of Au(III) by nitrogen containing ligands is well known [41] and the small 'bite' distance between the two chelating N donors should favour the relatively small Au(III) cation. On the other hand an interaction of Au(I) with a sulphur atom in a trithiapentalene derivative was also reported in the literature [42].

With Ag(I) AgL_2^+ complexes were extracted, whereas in contrast for Hg(II), the 1:1 species $HgCl_2 \cdot L$ were found. For Pd(II) and Au(III), both 1:1 and 1:2 complexes are formed simultaneously with ligands **9a**–**d** in the organic phase [37].

4.2. Macrocyclic ligands

The results of the extraction studies with three pentaleno crown compounds are shown in Fig. 4. The introduction of the trithiadiazapentalene unit into a macrocyclic polyether ring (compounds **11a**–**c**) results in a graduated increase of transition metal ion extraction compared with both the heterocyclic building block (compounds **9a**–**d** in Fig. 3) and crown ethers [43]. Whereas the high extraction of Pd(II) and Au(III) do not depend on the ring size of the heterocrown compounds,

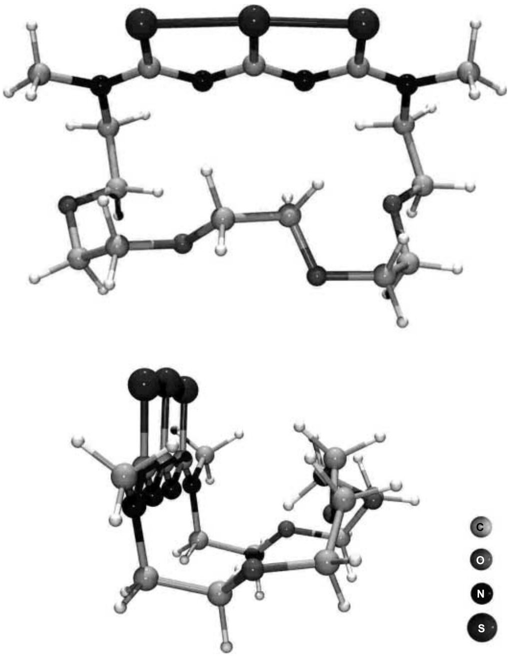
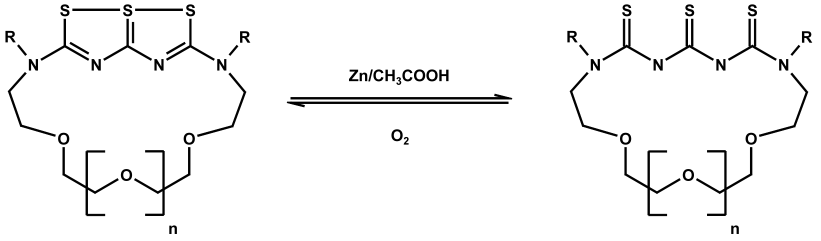


Fig. 2. The X-ray structure of ligand **11b** (view on the top and on the side) [30].



11a - c

19

19a: R = CH$_2$C$_6$H$_5$; n = 1
19b: R = CH$_3$; n = 2
19c: R = CH$_3$; n = 3

Scheme 9.

the graduated extractabilities for Ag(I) and Hg(II) show a clear ring size effect. The smallest crown **11a**, an 18-membered macrocycle, extracts Ag(I) quantitatively into the organic phase, whereas the larger compounds **11b** and **11c** give silver extractabilities of about 20% only. In contrast, Hg(II) used as HgCl$_2$, has an optimum extraction with the medium sized compound **11b**. These differences in the extraction behaviour can be attributed to different structures of Ag(I) and Hg(II) complexes

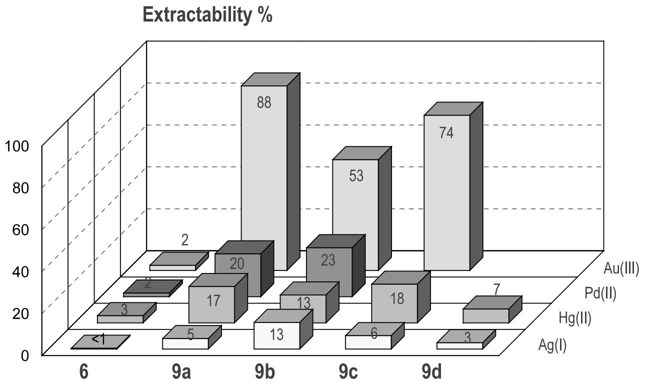


Fig. 3. Extractabilities of soft metal ions with 2,5-bisphenoxy (**6**) and 2,5-diamine (**9a**–**d**) substituted trithiadiazapentalene derivatives (1×10^{-4} M metal salt, 5×10^{-3} M picric acid, 1×10^{-3} M ligand in $CHCl_3$).

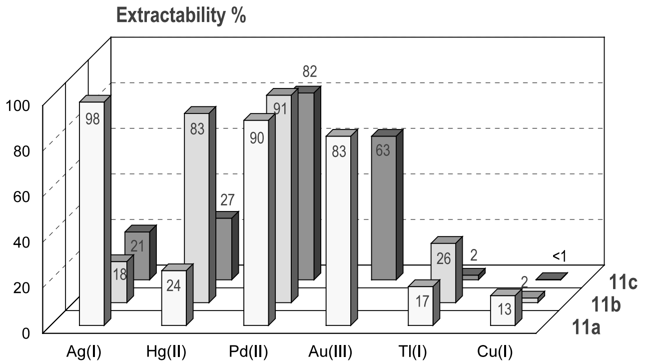


Fig. 4. Extractabilities of soft metal ions with the pentaleno crowns **11a**–**c** (1×10^{-4} M metal salt, 5×10^{-3} M picric acid, 1×10^{-3} M ligand in $CHCl_3$).

formed during extraction even though their ion size is comparable. This has been confirmed by molecular modelling calculations of the 1:1 complexes formed [30]. Only in the case of **11a** and Ag(I) as well as for **11b** and Hg(II) a stable symmetric arrangement of the metal centre in the cavity was observed. This is also in agreement with the graduated order of stability constants of the metal complexes in organic solution [30]. The log K values for the AgL^+ complexes of **11a–c** in acetone are 6.84, 4.51 and 4.50, respectively. In order to illustrate this fact the complex structure of Ag(**11a**)$^+$ based on DFT calculations is shown in Fig. 5 [44]. The small differences in the typical bond lengths and angles of ligand **11a** and its complex support the high degree of pre-organisation of the ligand structure for Ag(I) complexation. A similar interpretation of optimum structure formation can be used for the Hg(II) extraction with **11b**. Accordingly the extraction selectivity of Ag(I) over Hg(II) for **11a** is reversed for **11b**. This is an interesting observation, because

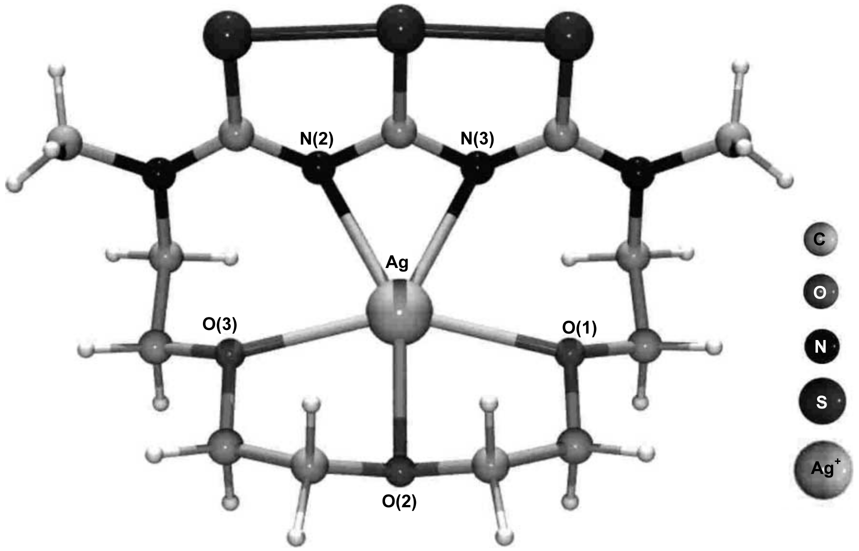


Fig. 5. The calculated structure [DFT-BP86/IV(TZ + P)] of complex cation [Ag**11a**]$^+$; selected bond lengths (Å): Ag···N(2,3), 2.45; Ag···O(1,3), 2.55; Ag···O(2), 2.52; S(1,6)···S(6a), 2.38.

only a few examples are known with changing selectivity order for these metal ions [45].

The extractabilities of Cu(I) and Tl(I) are rather low with some preferences depending on the size ratio of metal ion to pentaleno crown (Fig. 4). Other metal ions, as the border line transition metals Co(II), Cu(II), Zn(II) and the hard metals Eu(III), Na(I), K(I), Cs(I), Ca(II), Sr(II), are not or only slightly extracted. However, at higher ligand concentrations of **11a** the extractability of Na(I) increases and is amazingly, significantly higher than K(I), Cs(I), Ca(II) and Sr(II). This result is also interesting in comparison with 18-crown-6, because the order of selectivity is changed completely by the introduction of the heteropentalene function. Furthermore, there is some evidence for complexation of the ammonium ions by the pentaleno crowns. But the extractabilities are generally low with **11a**–**c**.

The preferred complex composition of the extracted metal complexes is 1:1 (M–L). This is shown in Fig. 6 for **11a** and **b**. The slopes in this $\log D_M - \log c_{L(org)}$ diagrams are mostly 1 for the transition metals investigated. The tendency also to simultaneously form complex species of 1:2 (M–L) is limited to higher ligand concentrations, as for example in the case of Pd(II) and Ag(I) with **11b**.

Liquid–liquid extraction results with the pentaleno crown derivatives **13**–**18** are shown in Figs. 7 and 8. The extractability of Ag(I) is high for all pentaleno macrocycles **13**–**15**. With the exception of **14a** and **15**, Hg(II) has been extracted on a significantly lower level. Other selected metal ions — Co(II), Ni(II), Zn(II), Eu(III), Na(I), Cs(I), Tl(I), Ca(II) and Sr(II) — are not extracted under the conditions chosen. The first experimental data point to the formation of 1:1 complexes for Ag(I) and both 1:1 and 2:1 (M–L) complexes in case of Hg(II).

In contrast to these macrocycles the functionalised azacrown compounds **16** and **17** give remarkable lower extractabilities, both for Ag(I) and Hg(II), whereas the *N*,*N′*-disubstituted azacrown (**18**) again produces high extractabilities. To understand the extraction behaviour discussed, further investigations are necessary especially in view of specific structural features of the ligand and complex molecules. Besides the pentaleno crown derivatives, and also their reduced analogues, the thioureas **19a**–**c**, were characterised by liquid–liquid extraction investi-

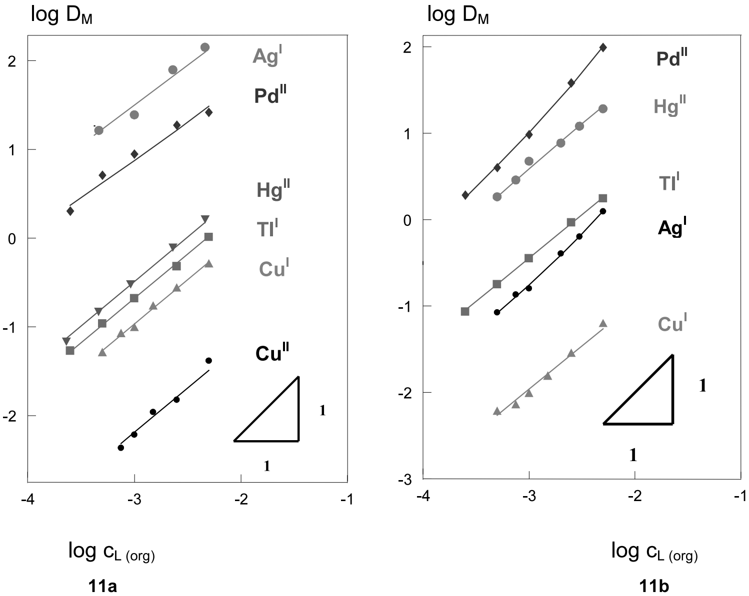


Fig. 6. Extraction of different metal ions with the pentaleno crowns **11a** (left) and **11b** (right) (1×10^{-4} M metal salt, 5×10^{-3} M picric acid, 5×10^{-4} M–5×10^{-3} M ligand in CHCl$_3$).

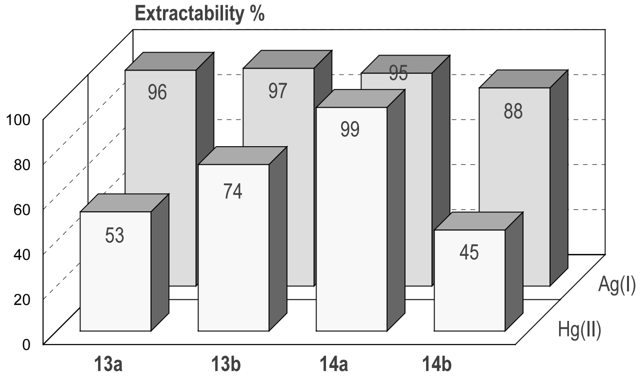


Fig. 7. Extractabilities of Ag(I) and Hg(II) with the pentaleno macrocycles **13a**, **b** and **14a**, **b** (1×10^{-4} M metal salt, 5×10^{-3} M picric acid, 1×10^{-3} M ligand in CHCl$_3$).

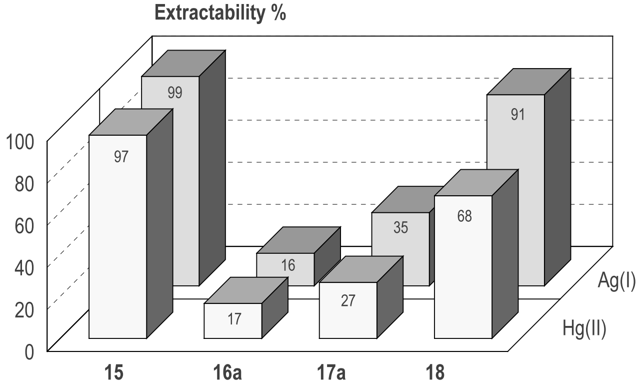


Fig. 8. Extractabilities of Ag(I) and Hg(II) with azacrown containing derivatives of trithiadiazapentalene (1×10^{-4} M metal salt, 5×10^{-3} M picric acid, 1×10^{-3} M ligand in $CHCl_3$).

gations. The results are represented in Fig. 9. As is shown, the soft metal ions Ag(I), Hg(II) and Pd(II) are extracted quantitatively in all cases and in contrast to the oxidised species **11a**–**c** no Ag/Hg selectivity is observed. Other metal ions like Tl(I) and Na(I) give only low extractabilities. The changing Ag/Hg selectivity is dependent on the form and the macrocyclic cavity size of the redox pair trithiadiazapentalene–trithiotriuret allows the control of complexation for Ag(I) and Hg(II). Therefore the binding and extraction efficiency can be switched on/off for Ag(I) using the redox pair **19b**/**11b** and for Hg(II) using **19a**/**11a**. In both cases the trithiadiazapentaleno crown is responsible for the non-binding and the corresponding trithiotriuret derivative for the binding properties. Because the stability of the complex is very high and the phase transfer is complete also under changing conditions, there is no information about the composition of the complex in

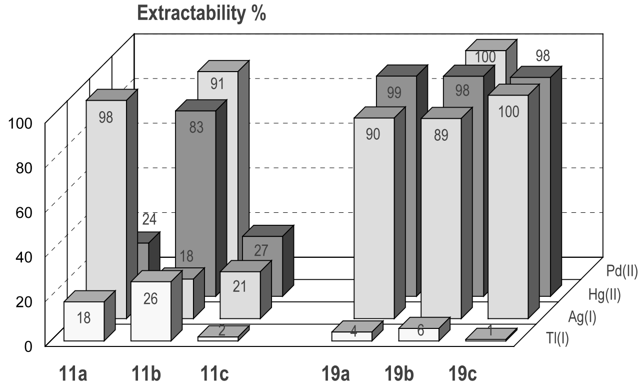


Fig. 9. Comparison of the extraction properties of pentaleno crowns **11a**–**c** with their reduced trithiotriuret counterparts **19a**–**c** (1×10^{-4} M metal salt, 5×10^{-3} M picric acid, 1×10^{-3} M ligand in $CHCl_3$).

solution. The reason for the pronounced complexation properties of the ligands **19** lies in the presence of the strong thiocarbonyl sulphur donor site in the molecule which obviously leads to complex formation outside the macrocyclic cavity in **19**. Molecular modelling studies using the DFT method are in agreement with this consideration [44]. The relevant lowest found minimum structures of a 1:1 and a 2:1 silver complexes with **19a** are given in Figs. 10 and 11, respectively. In both cases Ag(I) is coordinated tetrahedrally by thiocarbonyl sulphur and the calculated Ag···S distances are between 2.52 and 2.76 Å which are similar to other comparable structures [46].

5. Liquid-membrane studies

The heteropentalene derivatives discussed in this review can act as carrier for the transport of a large variety of cations across lipophilic barriers [37]. This behaviour was shown by liquid-membrane tests using an Izatt apparatus with an aqueous source phase, a bulk chloroform membrane and an aqueous receiving phase [47]. In contrast to the liquid–liquid extraction experiments significant differences can be expected because kinetic effects play an important role for this separation technique [48]. The results of transport studies are summarised in Fig. 12 for the redox pairs

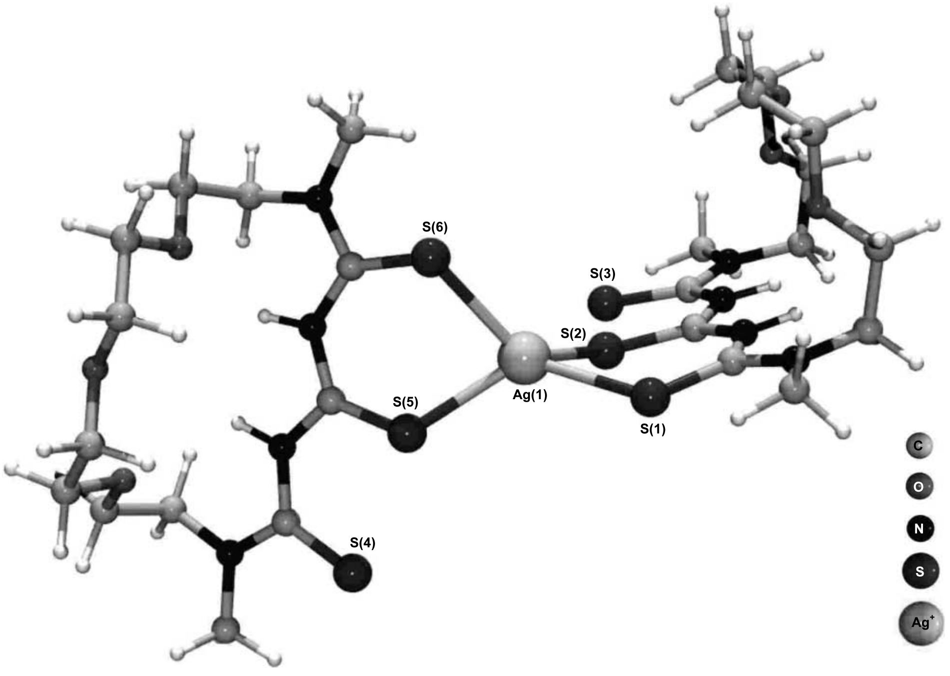


Fig. 10. The calculated structure [DFT-BP86/IV(TZ + P)] of the complex cation $[\mathrm{Ag}(\mathbf{19a})_2]^+$; selected bond lengths (Å): Ag(1)···S(1), 2.53; Ag(1)···S(2), 2.56; Ag(1)···S(5), 2.52; Ag(1)···S(6), 2.57.

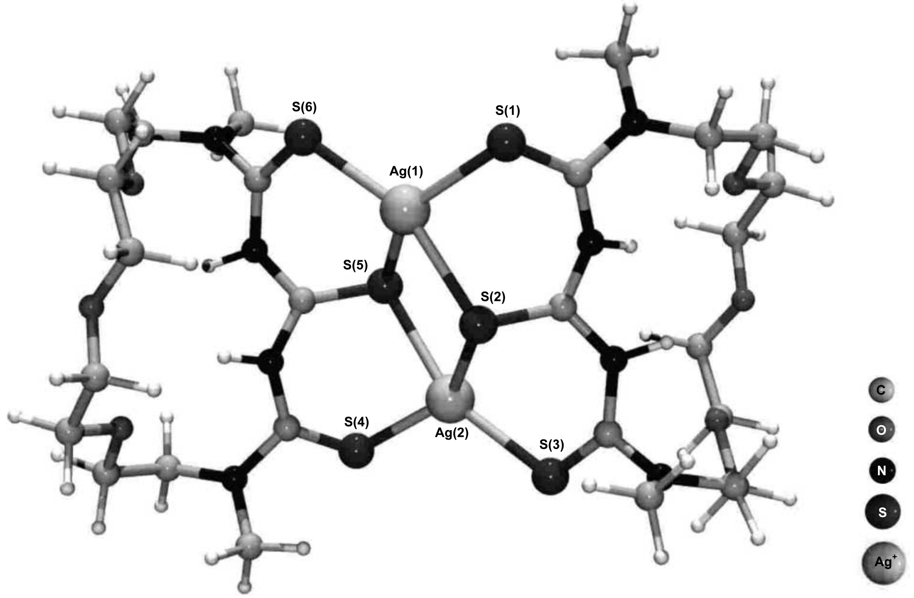


Fig. 11. The calculated structure [DFT-BP86/IV(TZ + P)] of the dimeric complex $[Ag_2(\mathbf{19a})_2]^{2+}$; selected bond lengths (Å): Ag(1)···S(1), 2.52; Ag(1)···S(2), 2.74; Ag(1)···S(5), 2.66; Ag(1)···S(6), 2.58; Ag(2)···S(2), 2.64; Ag(2)···S(3), 2.61; Ag(2)···S(4), 2.51; Ag(2)···S(5), 2.76; Ag(1)···Ag(2), 4.00.

11a/**19a** and **11b**/**19b**. It is shown clearly that Ag(I) selectivity exists only for **11a**. In all other cases the metal ions investigated are transported efficiently. Therefore a clear switch of the transport properties can be realised only for the redox pair **11a**/**19a** with the metal ions Mn(II), Co(II), Ni(II), Cu(II), Cd(II) and Gd(III). In this case the binding is based on the thiourea derivative **19a**.

For the amino acid L-phenylalanine the liquid-membrane transport was investigated in the presence of 3,5-bis(trifluoromethyl)phenylboronic acid as synergist [49]. Here it was observed that the transport rate of L-phenylalanine with **11b** is of the same order of magnitude as with 18-crown-6 [30].

6. Synthesis and structure of solid ammonium and metal complexes

On the basis of the extraction studies discussed, we have attempted to synthesise the corresponding solid metal complexes of the pentaleno crowns [50]. These investigations led to a variety of Ag(I) complexes with **11a**–**c** of the composition $AgLClO_4$ and $AgLPF_6$, which were identified by elemental analysis and FAB mass spectroscopy.

Two complexes, Hg(**11b**)$(SCN)_2$ and Hg(**11c**)$(SCN)_2$, could be isolated with Hg(II). The structure of the first one is shown in Fig. 13. Hg(II) is incorporated as the $Hg(SCN)_2$ species nearly perpendicular to the cavity plane of **11b** by four weak

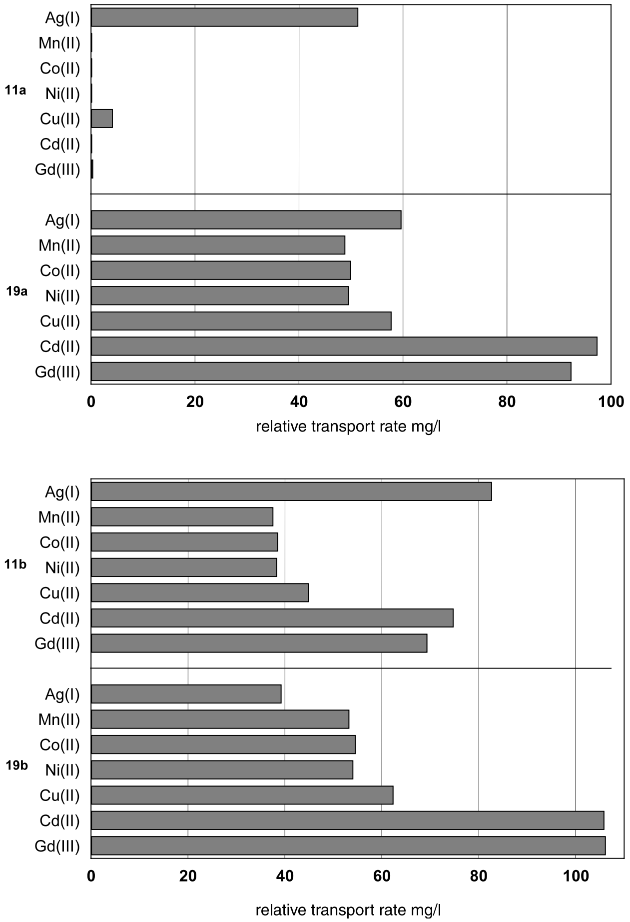


Fig. 12. Relative transport rates for different metal ions from 10^{-2} M metal nitrate solution across a bulk $CHCl_3$ membrane (10^{-2} M **11a**, **b** and **19a**, **b**) into H_2O [50].

bonds to two nitrogens of the thiaazapentalene and two ether oxygens of the ring. The bond lengths are between 2.88 and 3.07 Å. The distances to the two further oxygen atoms O(1) and O(4) in the macrocyclic ring are 3.35 and 3.24 Å well beyond typical Hg···O bond lengths [51]. ^1H- and ^{13}C-NMR spectroscopic investigations of the complex in solution ($CDCl_3$) show that all of the macrocyclic hydrogen and carbon resonances are shifted relative to the free ligand [37]. In solution therefore all six heteroatoms interact with the metal ion in the complex. Furthermore, it is noteworthy that in this Hg(II) complex both S–S distances [S(1)···S(6a), 2.43 Å; S(6)···S(6a), 2.66 Å] of the trithiadiazapentalene unit are much larger than in the free ligand or in the other complexes. This fact is a clear evidence for the strong influence of the metal centre on the heterocyclic subunit of the macrocycle. A ring opening reaction of the trithiadiazapentalene function [52]

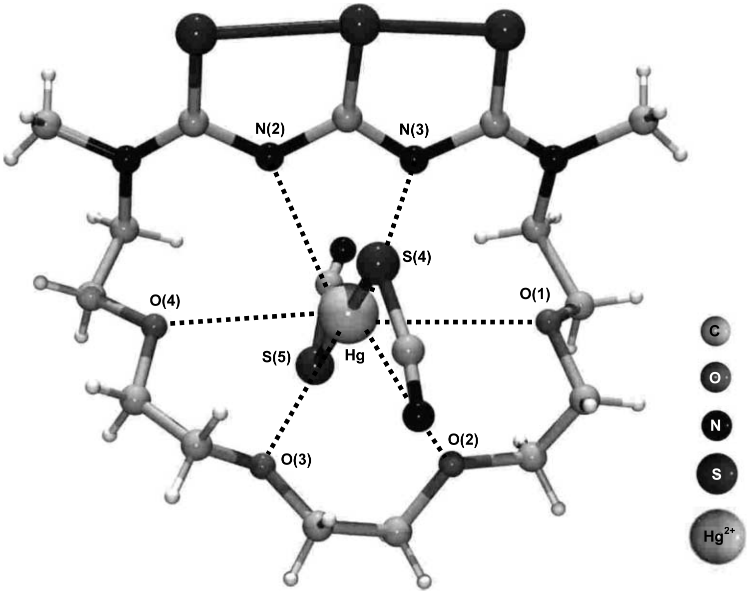


Fig. 13. The X-ray structure of complex [Hg(SCN)$_2$**11b**] [50]; selected bond lengths (Å): Hg···N(2), 2.98; Hg···N(3), 2.88; Hg···O(1), 3.35; Hg···O(2), 3.07; Hg···O(3), 2.96; Hg···O(4), 3.24; Hg···S(4), 2.49; Hg···S(5), 2.47, S(1)...S(6a), 2.43; S(6)...S(6a), 2.66.

which gives a sulphur–oxygen exchange in ethanol under the influence of Hg(II) acetate at a temperature of 50 °C seems possible.

A further complex of a pentaleno crown with a d-block element, [Cd(ClO$_4$)(**11a**)(H$_2$O)]ClO$_4$, is shown in Fig. 14 [50]. In this case the Cd(II) occupies the central position in the macrocyclic ring with similar bond lengths which are between 2.32 and 2.43 Å to the two nitrogen atoms of the heterocyclic unit and the three ether ring oxygens. The axial positions 6 and 7 for the cadmium centre resulting in a pentagonal bipyramidal structure are occupied by an oxygen both of a water molecule and a perchlorate anion. The coordination pattern is comparable with a corresponding Cd(II) complex with 15-crown-5 [53]. In analogy to the Hg(II) complex the S–S distances of the trithiadiazapentalene unit are also quite different with 2.48 Å for S(1)···S(6a) and 2.27 Å for S(6a)···S(6). At present it is not yet clear what causes the asymmetry in the two S–S bonds of both complex molecules.

In contrast to the complexes discussed changes of the S–S bond distances in the trithiadiazapentalene unit are significantly smaller in the pentaleno crown complexes with alkali metal ions and the ammonium ion. The sodium complex with **11a**, [NaSCN(**11a**)] · H$_2$O is shown in Fig. 15. In this case the bond lengths to the ring donor sites N and O are comparable (between 2.39 and 2.55 Å), however, the shorter distances are directed to the ether oxygens. Also the S–S distances are 2.36 Å [S(1)···S(6a)] and 2.34 Å [S(6)···S(6a)] which are nearly uniform. Based on the nature of the cation the thiocyanate anion is bonded strongly via its nitrogen atom.

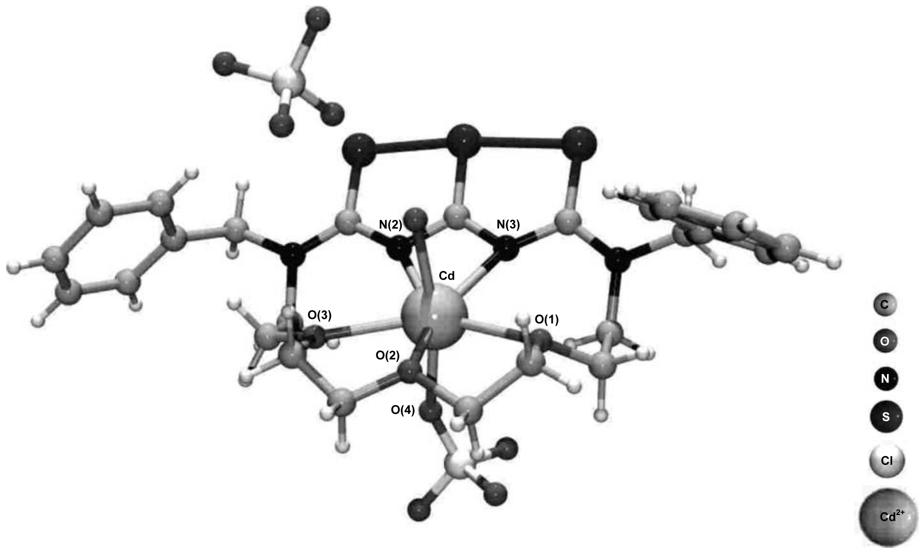


Fig. 14. The X-ray structure of complex [Cd(ClO$_4$)(H$_2$O)**11a**]ClO$_4$ [50]; selected bond lengths (Å): Cd···N(2), 2.43; Cd···N(3), 2.36; Cd···O(1), 2.38; Cd···O(2), 2.32; Cd···O(3), 2.39; Cd···O(4), 2.28; Cd···O(H$_2$O), 2.29; S(1)···S(6a), 2.48; S(6)···S(6a), 2.27.

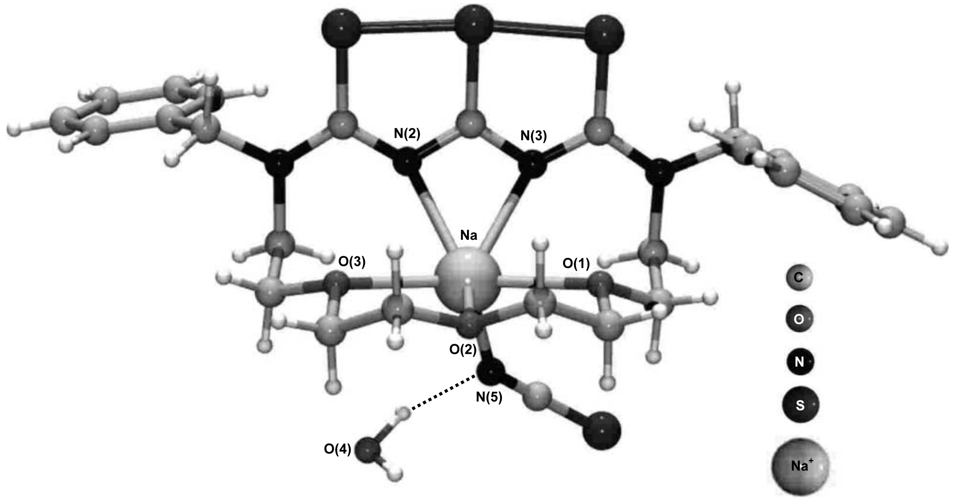


Fig. 15. The X-ray structure of complex [Na(NCS)**11a**]H$_2$O [50]; selected bond lengths (Å): Na···N(2), 2.54; Na···N(3), 2.55; Na···O(1), 2.47; Na···O(2), 2.39; Na···O(3), 2.47; Na···N(5), 2.36; S(1)···S(6a), 2.36; S(6)···S(6a), 2.33; N(5)···H(H$_2$O), 1.70.

It is quite interesting that this nitrogen donor gives a second interaction in the molecule via one hydrogen bond to a water molecule (H(O)H···N, 1.70 Å). The resulting package motive is presented in Fig. 16 showing a channel-like structure containing the water molecules.

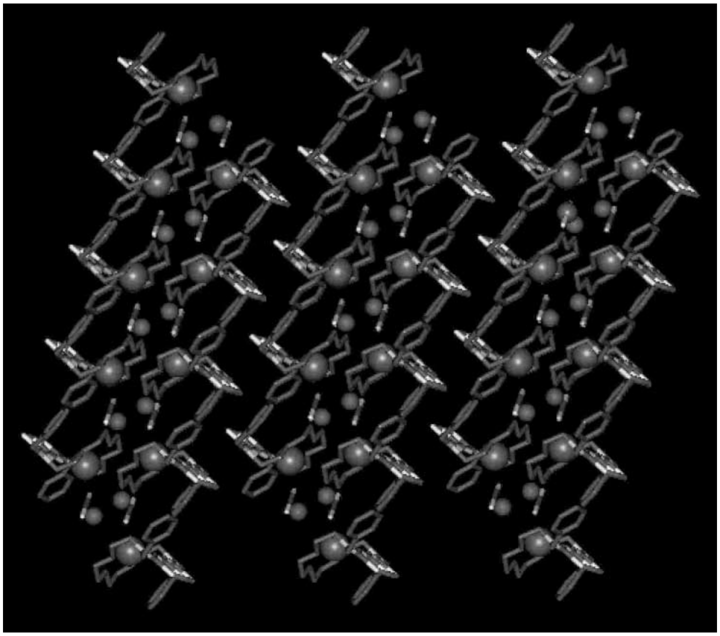


Fig. 16. Crystal packing of complex [Na(NCS)**11a**]H_2O [50]; the small bowls are the H_2O molecules.

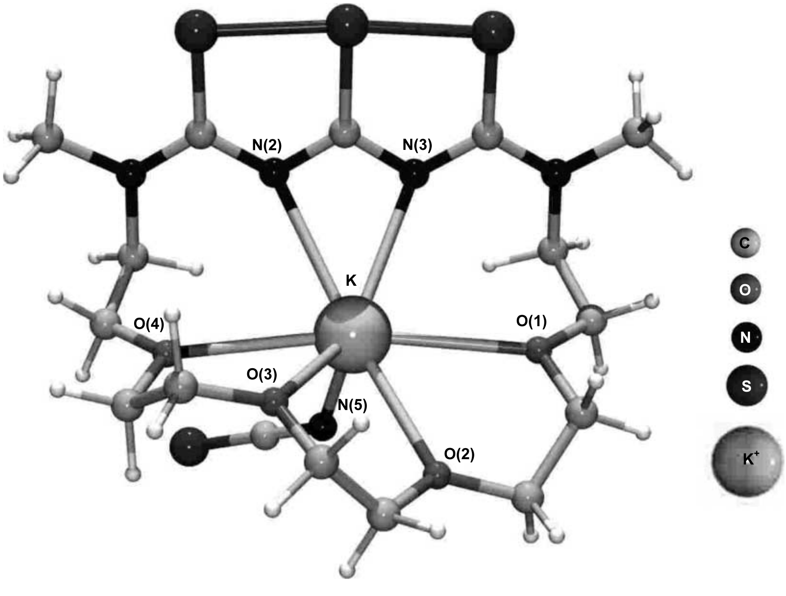


Fig. 17. The X-ray structure of the complex [K(NCS)**11b**] [50]; selected bond lengths (Å): K···N(2), 2.90; K···N(3), 3.00; K···O(1), 2.95; K···O(2), 2.80; K···O(3), 2.75; K···O(4), 2.96; K···N(5), 2.72; S(1)···S(6a), 2.30; S(6)···S(6a), 2.37.

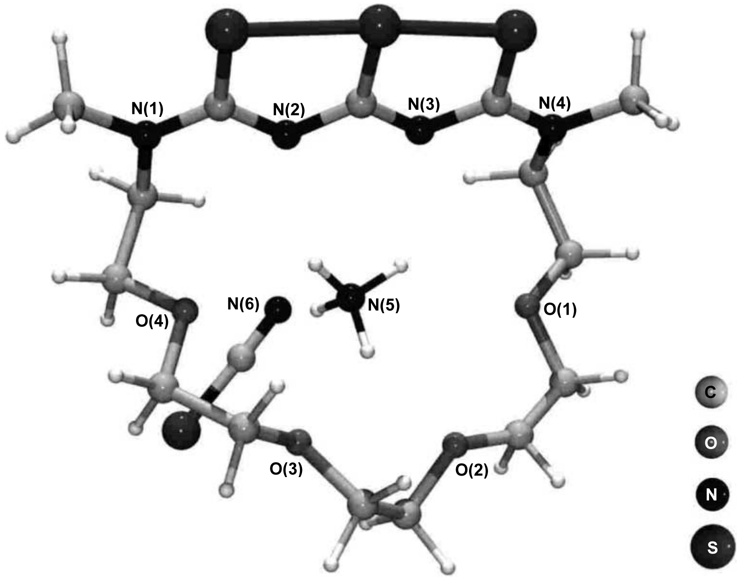


Fig. 18. The calculated structure [DFT-BP86/IV(TZ + P)] of complex [NH$_4$(NCS)**11b**] based on a preliminary X-ray structure analysis [30,50]; selected bond lengths (Å): N(5)···O(1), 3.07; N(5)···O(2), 3.04; N(5)···O(3), N(5)···O(4), 3.07; N(5)···N(2), 3.06; N(5)···N(3), N(5)···N(6), 2.97; S(1,6)···S(6a), 2.37.

Potassium and ammonium thiocyanate 1:1 complexes with **11a** and **b** have been synthesised. The structures of the complexes with **11b** are given in Figs. 17 and 18. In both cases the resulting arrangement in the crown cavity is nearly symmetrical. Two short K···O contacts (2.75 and 2.80 Å) and two longer ones (2.95 and 2.96 Å) are observed; the K···N distances are 2.90 and 3.00 Å. By analogy with sodium also in case of potassium the thiocyanate anion is strongly bound resulting in a short contact to its nitrogen atom (2.72 Å). The two S–S distances in the heterocyclic building block are again comparable (2.30 and 2.36 Å). Because the refinement of the structure of the ammonium thiocyanate complex with **11b** was limited, the structure has been calculated by the DFT method [50] on the basis of the provisional X-ray structure analysis [54]. The ion is fixed in the hole of the crown by three fluctuating hydrogen bonds to the two pentalene nitrogens and the four ether oxygens. An additional hydrogen bond is formed with the nitrogen of the thiocyanate anion. In the structure presented, the two S–S distances in the thiaaza-pentalene function are uniform (2.37 Å)[26]. The bond lengths are of the same order of magnitude as for sodium and potassium.

7. Conclusions

The combination of the redox switchable heterobicyclic trithiadiazapentalene unit with different amine containing building blocks leads to a series of novel open-chain and macrocyclic ligand systems for metal and ammonium ions. The graduated binding of silver(I) and mercury(II) is dependent on the ring size of the crown type materials and the redox state of the thiaazapentalene function. This behaviour allows one to switch the complexation process and therefore to control the selectivity. Both the experimental and the theoretical studies of the systems investigated up until now show the specific feature of the trithiadiazapentalene building block. This aromatic π-system influences on the one hand, the donor capacity of the potential donor sites and on the other the flexibility of the ligand molecule. The resulting binding behaviour depends strongly on the nature and size of the coordinated metal centre. The S–S bond lengths of the trithiadiazapentalene group in the solid state are particularly sensitive to the nature of the bound cation. Therefore the crystal structures of the complexes differ significantly.

The characteristic binding behaviour could be useful for the separation and concentration processes by liquid–liquid extraction and liquid-membrane techniques.

Acknowledgements

The authors thank the Saxon Ministry of Sciences and Arts (Dresden, Germany) and the Fonds der Chemischen Industrie (Frankfurt, Germany) for support of their research program on metal extraction with macrocyclic ligands. M.W. thanks the Studienstiftung des deutschen Volkes for a graduate scholarship.

References

[1] J.-M. Lehn, Supramolecular Chemistry — Concepts and Perspectives, VCH, Weinheim, 1995.
[2] J.L. Atwood, J.E. Davies, D.D. McNicol, F. Vögtle, J.-M. Lehn (Eds.), Comprehensive Supramolecular Chemistry, vols. 1–10, Elsevier, Oxford, 1996.
[3] J.S. Bradshaw, R.M. Izatt, A.V. Bordunov, C.Y. Zhu, J.K. Hathaway, in: J.L. Atwood, J.E. Davies, D.D. McNicol, F. Vögtle, J.-M. Lehn (Eds.), Comprehensive Supramolecular Chemistry, vol. 1, Elsevier, Oxford, 1996, pp. 35–95.
[4] T.W. Bell, S.K. Sahni, in: J.L. Atwood, J.E.D. Davis, D.D. MacNicol (Eds.), Inclusion Compounds: Key Organic Host Systems, Oxford University Press, Oxford, 1991, pp. 325–390.
[5] S. Shinkai, in: J.L. Atwood, J.E. Davies, D.D. McNicol, F. Vögtle, J.-M. Lehn (Eds.), Comprehensive Supramolecular Chemistry, vol. 1, Elsevier, Oxford, 1996, pp. 671–700.
[6] (a) A.F. Kaifer, S. Mendoza, in: J.L. Atwood, J.E. Davies, D.D. McNicol, F. Vögtle, J.-M. Lehn (Eds.), Comprehensive Supramolecular Chemistry, vol. 1, Elsevier, Oxford, 1996, pp. 701–732;
(b) P.L. Boulas, M. Gomez-Kaifer, L. Echegoyen, Angew. Chem. Int. Ed. Engl. 37 (1998) 216.
[7] (a) S. Shinkai, T. Ogawa, T. Nakaji, Y. Kusano, O. Manabe, Tetrahedron Lett. (1979) 4569;
(b) S. Shinkai, T. Nakaji, Y. Nishida, T. Ogawa, O. Manabe, J. Am. Chem. Soc. 102 (1980) 5860.
[8] (a) S. Shinkai, K. Inozuka, O. Miyazaki, O. Manabe, J. Am. Chem. Soc. 107 (1985) 3950;
(b) T. Nabehima, H. Furusawa, Y. Yano, Angew. Chem. Int. Ed. Engl. 33 (1994) 1750;
(c) H. Graubaum, F. Tittelbach, G. Lutze, K. Gloe, M. Mackrodt, J. Prakt. Chem. 339 (1997) 55.
[9] (a) T. Saji, I. Kinoshita, J. Chem. Soc. Chem. Commun. (1986) 716;
(b) A.M. Allgeier, C.S. Slone, C.A. Mikin, L.M. Liable-Sands, G.P.A. Yap, A.L. Rheingold, J. Am. Chem. Soc. 119 (1997) 550.

[10] (a) Z.-T. Li, P.C. Stein, J. Becher, D. Jensen, P. Mork, N. Svenstrup, Chem. Eur. J. (1996) 624;
(b) W. Devonport, M.A. Blower, M.R. Bryce, L.M. Goldenberg, J. Org. Chem. 2 (1997) 885.

[11] (a) H. Sonnenschein, T. Kreher, E. Gründemann, R.-P. Krüger, A. Kunath, V. Zabel, J. Org. Chem. 61 (1996) 710;
(b) T. Kreher, H. Sonnenschein, B. Costisella, M. Schneider, J. Chem. Soc. Perkin Trans. 1 (1997) 3451.

[12] (a) G. Hennrich, H. Sonnenschein, U. Resch-Genger, J. Am. Chem. Soc. 121 (1999) 5073;
(b) G. Hennrich, H. Sonnenschein, U. Resch-Genger, Eur. J. Org. Chem. (2000) 539.

[13] (a) N. Lozac'h, Adv. Heterocycl. Chem. 13 (1971) 161;
(b) in: A.R. Katritzky, C.W. Rees (Eds.), Comprehensive Heterocyclic Chemistry, vol. 6, Pergamon Press, Oxford, 1984, pp. 1049–1062.

[14] R. Gleiter, R. Gygax, Top. Curr. Chem. 63 (1976) 49.

[15] C.Th. Pedersen, Sulfur Reports 1 (1980) 1.

[16] F. Duns, in: E. Schaumann (Ed.), Houben-Weyl Meth. Org. Chem., Thieme-Verlag, Stuttgart, vol. E8a, part I Hetarene III, 1993, pp. 470–629.

[17] D.M. McKinnon, Sulfur Rep. 15 (1994) 317.

[18] O. Heitzsch, K. Gloe, H. Stephan, E. Weber, Solvent Extr. Ion Exch. 12 (1994) 475.

[19] H. Stephan, T. Krüger, K. Gloe, W. Hasse, B. Ahlers, K. Cammann, K. Rissanen, G. Brodesser, F. Vögtle, Chem. Eur. J. 4 (1998) 434.

[20] C. Chartroux, K. Wichmann, G. Goretzki, T. Rambusch, K. Gloe, U. Müller, W. Müller, F. Vögtle, Ind. Eng. Chem. Res. 39 (2000) 3616.

[21] M. Rosser, D. Parker, G. Ferguson, J.F. Gallagher, J.A.K. Howard, D.S. Yufit, J. Chem. Soc. Chem. Commun. (1993) 1267.

[22] J. Dai, T. Kuroda-Sowa, M. Munakata, M. Maekouva, Y. Suenaga, Y. Ohno, J. Chem. Soc. Dalton Trans. (1997) 2363.

[23] K. Gloe, T. Krüger, H. Stephan, M. Wagner, U. Drutkowski, R.-M. Olk, U. Leckelt, R. Richter, E. Hoyer, Z. Anorg. Allg. Chem. 624 (1998) 152.

[24] R. Cimiraglia, H.-J. Hoffmann, J. Am. Chem. Soc. 113 (1991) 6449.

[25] (a) J. Spanget-Larsen, Ch. Ertring, I. Shim, J. Am. Chem. Soc. 116 (1994) 11433;
(b) K.B. Andersen, J. Abildgaard, J.G. Radziszewski, J. Spanget-Larsen, J. Phys. Chem. 101 (1997) 4475.

[26] J. Fabian, K. Gloe, M. Wüst, T. Krüger-Rambusch, O. Rademacher, H. Graubaum, Phosphorus, Sulfur Silicon 140 (1998) 35.

[27] (a) E. Magnusson, J. Am. Chem. Soc. 112 (1990) 7940;
(b) E. Magnusson, J. Am. Chem. Soc. 115 (1993) 1051;
(c) A.E. Reed, P. von Ragué Schleyer, J. Am. Chem. Soc. 112 (1990) 1434;
(d) J. Cioslowski, P.R. Surján, J. Mol. Struct. 255 (1992) 9.

[28] ^{13}C-NMR of **9a** ($CDCl_3$, δ ppm): 181.8 [C(2), C(5)], 187.7 [C(3a)]; solid: 180.8 [C(2)]; 180.3 [C(5)]; 185. 8 [C(3a)].

[29] F. Tittelbach, unpublished results.

[30] H. Graubaum, F. Tittelbach, G. Lutze, K. Gloe, M. Mackrodt, T. Krüger, N. Krauss, A. Deege, H. Hinrichs, Angew. Chem. Int. Ed. Engl. 36 (1997) 1648.

[31] (a) H. Behringer, D. Weber, Chem. Ber. 97 (1964) 2567;
(b) J.-L. Derocque, J. Vialle, Bull. Soc. Chim. Fr. (1967) 3079;
(c) J.-L. Deroque, M. Perrier, J. Vialle, Bull. Soc. Chim. Fr. (1968) 2062;
(d) R.J. Beer, I. Hart, J. Chem. Soc. Chem. Commun. (1977) 143;
(e) G. L'abbe, G. Verhelst, G. Vermeulen, Angew. Chem. Int. Ed. Engl. 16 (1977) 403;
(f) B. Stelander, H.G. Viehe, M. van Meerssche, G. Germain, J.P. Dechercq, Bull. Soc. Chim. Belg. 86 (1977) 291;
(g) T. Tsuchiya, M. Yasumoto, I. Shibuya, Chem. Lett. (1989) 1357;
(h) D.H. Reid, Y. Ding, L.-L. Lai, B.J. Luh, T.M. Ngoi, Bull. Soc. Chim. Belg. 103 (1994) 539;
(i) N. Matsumura, M. Kusamiya, H. Inoue, J. Heterocycl. Chem. 32 (1995) 1269.

[32] (a) H. Graubaum, H. Seeboth, P. Zalupsky, Monatsh. Chem. 120 (1989) 997;
(b) H. Graubaum, B. Costisella, M. Ramm, D. Schulz, J. Prakt. Chem. 332 (1990) 208.

[33] H. Graubaum, J. Prakt. Chem. 331 (1989) 115.
[34] F. Tittelbach, G. Lutze, H. Graubaum, Chem. Ber. 127 (1994) 2209.
[35] H. Graubaum, G. Lutze, M. Ramm, Phosphorus, Sulfur Silicon 84 (1993) 83.
[36] G. Lutze, F. Tittelbach, H. Graubaum, M. Ramm, Phosphorus, Sulfur Silicon 91 (1994) 81.
[37] M. Wüst, PhD Thesis, TU Dresden, 1999.
[38] (a) K. Gloe, P. Mühl, Isotopenpraxis, 1983;
(b) K. Gloe, P. Mühl, J. Beger, Z. Chem. 28 (1988) 1.
[39] B.A. Moyer, in: J.L. Atwood, J.E. Davies, D.D. McNicol, F. Vögtle, J.-M. Lehn (Eds.), Comprehensive Supramolecular Chemistry, vol. 1, Elsevier, Oxford, 1996, pp. 377–416.
[40] S. Ibach, V. Prautzsch, F. Vögtle, C. Chartroux, K. Gloe, Acc. Chem. Res. 32 (1999) 729.
[41] K. Gloe, P. Mühl, J. Beger, R. Jacobi, A. Urban, Z. Chem. 25 (1985) 99.
[42] S. Wang, J.P. Fackler Jr., J. Chem. Soc. Chem. Commun. (1988) 22.
[43] K. Gloe, P. Mühl, J. Beger, E. Uhlemann, L. Beyer, Wiss. Ber. ZFW Dresden 44 (1990) 83.
[44] T. Rambusch, unpublished results, for details of calculations see T. Rambusch, K. Hollmann-Gloe, K. Gloe, J. Prakt. Chem. 341 (1990) 202.
[45] G. Wu, W. Jiang, J.-D. Lamb, J.S. Bradshaw, R.M. Izatt, J. Am. Chem. Soc. 113 (1991) 6538.
[46] J. Dai, T. Kuroda-Sowa, M. Munagata, M. Maekawa, Y. Suenaga, Y. Ohno, J. Chem. Soc. Dalton Trans. (1997) 2363.
[47] J.D. Lamb, J.J. Christensen, R.S. Izatt, K. Bedtke, M.S. Astin, R.M. Izatt, J. Am. Chem. Soc. 102 (1980) 3399.
[48] (a) G. Gokel, Crown Ethers and Cryptands, The Royal Society of Chemistry, Cambridge, 1991, pp. 81–83, 151–156;
(b) T.M. Fyles, in: T. Osa, J.L. Atwood (Eds.), Inclusion Aspects of Membrane Chemistry, Kluwer Academic, Dordrecht, 1991, pp. 59–110.
[49] M.T. Reetz, J. Huff, J. Rudolph, K. Töllner, A. Deege, R. Goddard, J. Am. Chem. Soc. 116 (1994) 11588.
[50] K. Gloe, M. Wüst, T. Rambusch, H. Graubaum, W. Seichter, Z. Anorg. Allg. Chem., in preparation.
[51] (a) J.W. Sibert, S.J. Lange, C. Stern, B.M. Hoffman, A.G.M. Barrett, J. Chem. Soc. Chem. Commun. (1994) 1751;
(b) K. Kubo, A. Mori, N. Kato, H. Takeshita, Chem. Lett. (1995) 629.
[52] F. Tittelbach, H. Graubaum, unpublished results, see also Ref. [15].
[53] A. Hazell, R.G. Hazell, M.F. Holm, L. Krogh, Acta Crystallogr. B 47 (1991) 234.
[54] N. Krauss, unpublished results, see also Ref. [30].