Extraction Studies of Heavy Metal Ions Employing Benzothiaoxacrown Compounds

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(Received May 9, 2015; Accepted August 21, 2015)

Benzothiaoxacrown compounds with different numbers of sulfur and oxygen donor atoms (between 4 to 7 donors) dissolved in an organic diluent selectively extract the soft metal ions Ag(I) and Hg(II) from a mixture of Co(II), Ni(II), Cu(II), Zn(II), Ag(I) and Hg(II) present in an aqueous phase. Generally, the extraction efficiency depends on the specific structure of the benzothiaoxacrowns, on the organic diluent employed, as well as on the counter ion present in the aqueous phase. High extractions of Ag(I) and Hg(II) were achieved with all ligands from perchlorate and picrate aqueous media into nitrobenzene organic solutions. In the case of Cu(I) the extraction is significant lower; only ligand **5** with the O₂S₄ donor atom set gives a moderate extractability. The composition of the extracted complexes depends on the crown ring size and ranges from 1:1 to 1:2 (M:L). Polarographic, UV-Vis and ESI mass spectrometric studies provide a further insight into the complex formation behavior.

1. Introduction

The separation of toxic and valuable heavy metals from process solutions or waste water is of great importance for both the recovery of such metals and the protection of the environment. Solvent extraction is a very efficient separation process for metal ions in solution and is widely used in industry [1,2]. The success of the separation strongly depends on the individual properties of the employed extractant. Although many different extractants are known and a number have been commercialised, there is still a further need to search for more selective reagents [3]. In this context, macrocyclic crown compounds with N,O,S-donor functions are an interesting class of compounds with different options to control their selectivity towards metal ions [4,5]. Generally, the strong affinity of thiacycrowns especially for Cu(I), Ag(I), Hg(II) and Pd(II) is well-known and was tested for different practical purposes [6-17].

Over the years we have been involved in the design, synthesis and testing of novel thiacycrown and structure-related open-chain extractants [18-21]. In several papers we have discussed the extraction properties and structure-extractability relationships of different benzothiaoxacrown compounds towards soft metal ions like Ag(I) and Hg(II) [22-24]. We have also reported the synthesis routes [25-27] and some structural data [28-30] for the benzothiaoxacrown compounds **1-6** (Scheme 1) studied in the present paper. This series of benzothiaoxacrown compounds, varying in both the macrocyclic ring size and the

combination of O and S donor atoms, Scheme 1.

were investigated in single and competitive metal ion liquid-liquid extraction experiments. For comparison, the benzothiazolium substituted benzothiaoxacrowns **7** and **8** (Scheme 1) were included. Furthermore complementary polarographic, UV-Vis and ESI-MS spectrometric measurements have been undertaken in order to obtain additional information on the complex formation process involved.

2. Experimental

The benzothiaoxacrown compounds were prepared as described previously [25-27]. All the chemicals used were of analytical grade.

2.1 Liquid-liquid extraction

The liquid-liquid extraction experiments were performed at $22 \pm 1^\circ C$ in micro centrifuge tubes (2 mL) by means of mechanical shaking for 30 min. The phase ratio $V_{(w)}:V_{(org)}$ was 1:1 (0.5 mL each). Chloroform, 1,2-dichloroethane and nitrobenzene were used as diluents.

The concentration of the ligands in the organic phase was 5×10^{-4} - 5×10^{-3} M; the metal salt concentration in the aqueous phase was 1×10^{-4} - 5×10^{-4} M. Furthermore, the aqueous phase contained picric, perchloric or nitric acid at a concentration of 5×10^{-3} M. All samples were centrifuged after the extraction. The metal concentration in single metal ion experiments was determined radiometrically in both phases [31] by employing the γ -radiation of ^{110m}Ag , ^{64}Cu , and ^{203}Hg using a NaI(Tl) scintillation counter Cobra(II) (Canberra Packard).

In competitive metal ion extraction experiments and, in the case of Hg(II) extraction from perchlorate solution, the metal concentration was measured only in the aqueous phase using ICP-MS (ELAN 5000/Perkin-Elmer). Nitric acid (1%) and potassium dichromate (0.5%) solutions were added to stabilize the aqueous phase. Samples were diluted before measurement by a factor of 1:1000.

The percentage extraction E (%) was calculated from the experimentally determined distribution ratio D_M :

$$D_M = c_{M(org)}/c_{M(w)} \quad (1)$$

$$E[\%] = 100 \cdot D_M / (D_M + 1) \quad (2)$$

2.2 ESI-MS measurements

Solutions containing **2-6** (0.5 mL, 5 mM) in chloroform were mixed with CF_3SO_3Ag in acetone (0.5 mL, 5 mM). In the case of ligand **1**, a ratio of 1:2 (Ag(I):L) was employed due to the fact that both 1:1 as well as 1:2 (M:L) complex species were observed in preliminary extraction experiments. An aliquot of each sample (100 μ L) was diluted with ammonium acetate solution (1 mL, 0.1%) in methanol in order to

promote ionization prior to the measurement. For the mass determination ESI-MS (Esquire-LC/Perkin-Elmer) has been used.

2.3 UV-Vis measurements

Aliquots (0.3 mL) from the aqueous and organic phases of Ag(I) extraction with **2**, **3** or **5** were diluted with 2.7 mL water or 2.7 mL 1,2-dichloroethane, respectively. These solutions have been used for UV-Vis measurements with a Perkin-Elmer Lambda 2 spectrometer.

2.4 Stability constant determinations

The stability constants were determined polarographically in acetonitrile at 20°C using a 263A potentiostat/galvanostat with a 302A Static Mercury Drop Electrode (Princeton Applied Research) as described previously [27]. The potential scanning rate was 2 mV/s and the dropping time was 1 s. The supporting electrolyte was 0.01 M Et₄NClO₄.

3. Results and Discussion

The extraction capabilities of the benzothioxacrown compounds were investigated for a range of d-block metal ions, different counter ions and diluents. Figure 1 gives an overview of the extraction properties of ligands **2**, **7** and **8** having the same S₂O₃ benzothioxocrown donor set towards Co(II), Ni(II), Cu(II), Zn(II), Hg(II) and Ag(I). The results are based on competitive extraction experiments employing a mix of these metals and using a metal perchlorate-HClO₄-H₂O/ligand-nitrobenzene extraction protocol.

As expected, the thiophilic soft metal ions Ag(I) and Hg(II) show a high degree of extraction with the benzothioxacrowns. Whereas Ag(I) is quantitatively extracted with all three ligands, a graded extraction in the order **2** (41%) < **7** (91%) < **8** (97%) has been observed for Hg(II). The differences between **2**, **7** and **8** are most likely caused by the higher lipophilicity of the benzothiazolium substituted ligands **7** and **8** in comparison with **2**. The borderline metal ions Co(II), Ni(II), Cu(II) and Zn(II) are not extracted by these three ligands. In order to study the extraction of the thiophilic metal ions in more detail, single metal ion extraction experiments were carried out for Ag(I), Hg(II), Cu(I) and Cu(II) with the benzothioxacrown ligands **1-6** (Figure 2). Under changed experimental conditions - picrate was used in place of perchlorate as the counter ion and chloroform instead of nitrobenzene as the diluent - again a strong preference of Ag(I) was observed, whereas only a low extraction of Cu(I) and Hg(II) has been detected. In agreement with the competitive extraction experiment Cu(II) was not extracted. The thioxacrowns **2-5** with 5, 6 or 7 donor atoms and at least 2 sulfur atoms give nearly a quantitative extraction of Ag(I) (99%). In the case of ligand **1** the lower extraction (84%) is possibly attributed to the poor size match between the small cavity ($d_{(12\text{-crown-4})} \leq 1.5 \text{ \AA}$) [8] of this ligand with the O₂S₂ donor set and the large Ag(I) ion ($d_{\text{Ag(I)}} = 2.04 \text{ \AA}$) [32].

Figure 1. Competitive extraction of Co(II), Ni(II), Cu(II), Zn(II), Hg(II) and Ag(I) with ligands **2**, **7** and **8**; $[M^{n+}] = 2 \times 10^{-4}$ M, $[HClO_4] = 5 \times 10^{-3}$ M; $[ligand] = 5 \times 10^{-4}$ M in nitrobenzene.

Figure 2. Extraction of Ag(I), Cu(I), Cu(II) and Hg(II) with ligands **1-6**; $[M^{n+}] = 1 \times 10^{-4}$ M, $[HPic] = 5 \times 10^{-3}$ M; $[ligand] = 1 \times 10^{-3}$ M in $CHCl_3$; $*[ascorbic\ acid] = 1 \times 10^{-2}$ M as reducing agent for Cu(II).

In this context it should be pointed out that Ag(I) frequently forms exocyclic complexes with thiacyclones [6, 10, 17, 24].

The significantly lower Ag(I) extraction with **6** (58%) is most likely due to the presence of only one sulfur donor atom in this ligand. This ligand (**6**) gives also the lowest Cu(I) extraction. In comparison the extraction of Cu(I) with **1-4** falls in the range 12-20%. The highest Cu(I) extraction of 51% was achieved with **5**, which contains the largest number of sulfur donor atoms (4 S-donor atoms). Under the conditions employed, the extraction of Hg(II) is generally low. The highest extraction (16%) was obtained with ligand **4**, which has the largest ring size. In spite of the similar thiophilic character and size of Hg(II) and Ag(I) – $d_{Hg(II)} = 2.06$ Å and $d_{Ag(I)} = 2.04$ Å [32] – this result for Hg(II) is quite unexpected and especially different to the competitive experiment (see Figure 1). However, the single ion experiments were performed using Hg(II) in the form of $HgCl_2$, which is only a slightly dissociated species and can hamper the phase transfer.

Comparable experiments with $Hg(ClO_4)_2$ as the mercury source in the aqueous phase and nitrobenzene as the organic diluent support this interpretation (Figure 3). Under these experimental conditions the extraction of Hg(II) by **1-6** achieves in all cases more than 50%. The increasing extraction of Hg(II) follows the order **2** (55%) < **3** (60%) < **4** (76%) < **6** (80%) < **5** (83%) < **1** (94%). For the ligands **1-5** this order is in agreement with the order of respective stability constants determined polarographically in acetonitrile (Table 1).

Figure 3. Extraction of Hg(II) by ligands **1-6**; $[\text{Hg}(\text{ClO}_4)_2] = 4 \times 10^{-4} \text{ M}$, $[\text{HClO}_4] = 5 \times 10^{-3} \text{ M}$; $[\text{ligand}] = 5 \times 10^{-4} \text{ M}$ in nitrobenzene.

Table 1. Stability constants of $[\text{HgL}]^{2+}$ and $[\text{HgL}_2]^{2+}$ complexes with ligands **1-6**.

Ligand	$\log K$
1	22.7 ^{a,b}
2	18.0 ^a
3	19.5 ^a
4	20.1
5	21.0
6	14.7 ^b

$\log K$ values were determined polarographically in MeCN (0.01 M Et_4NClO_4) at 20 °C; ^adata from ref. [27]; ^bdata for $[\text{HgL}_2]^{2+}$.

Figure 4 shows that Ag(I) extraction with the ligands **2-5** clearly depends on the counter ion. According to the Hofmeister series the hydrophobic picrate anion favors the extraction in comparison with the more hydrophilic nitrate. It is interesting to note, that Ag(I) extraction with ligands **2-5** from nitrate medium is significantly graded in the order **2** (18%) < **5** (31%) < **4** (57%) < **3** (82%). This result is quite different in comparison with the Hg(II) extraction from perchlorate solution (see Figure 3) and a clear indication of the subtle differences in the extraction behavior of both soft metal ions. For a better understanding of the underlying reasons further studies are necessary with a focus on structural and binding aspects.

The composition of the extracted metal complexes in the organic phase can be determined by slope analysis of the extraction data in a $\log D_M$ - $\log c_{L(\text{org})}$ diagram [31]. The results for Ag(I) with **1-6** using CHCl_3 as the diluent show linear relationships in each case (Figure 5). Nitrate was chosen as the counter ion for ligands **2-5** and in the case of ligands **1** and **6** picrate was used, in order to keep the Ag(I) extraction in a suitable range for this determination.

A slope of approximately one in a $\log D_{\text{Ag}}$ - $\log c_{L(\text{org})}$ diagram for Ag(I) extraction with **6** having an O_4S donor set indicates that 1:1 (M:L) complex species dominate in the organic phase (Figure 5). In contrast the slope of 1.7 for the Ag(I) extraction by **1** is in accordance with the formation of both 1:1 and 1:2 (M:L) complex species. The latter is the smallest crown of the series preferring obviously 1:2 sandwich ($[\text{AgL}_2]^+$) arrangements. The ligands **2-5** show significantly smaller slopes between 0.2 and 0.6 (**3**: 0.2; **2**: 0.3; **4**: 0.4 and **5**: 0.6) which excludes any meaningful conclusion about the speciation.

Figure 4. Dependence of the extraction of Ag(I) with 2-5 on the counter ion; $[\text{AgNO}_3] = 1 \times 10^{-4} \text{ M}$; $[\text{NaNO}_3] = 1 \times 10^{-1} \text{ M}$ or $[\text{HPic}] = 5 \times 10^{-3} \text{ M}$; $[\text{ligand}] = 1 \times 10^{-3} \text{ M}$ in CHCl_3 .

Figure 5. Dependence of the extraction of Ag(I) by 1-6 on ligand concentration; $[\text{AgNO}_3] = 1 \times 10^{-4} \text{ M}$, $[\text{HNO}_3] = 5 \times 10^{-4} \text{ M}$, $[\text{HPic}] = 5 \times 10^{-3} \text{ M}$; $[\text{ligand}] = 5 \times 10^{-4} - 5 \times 10^{-3} \text{ M}$ in CHCl_3 (slopes: **1** 1.7; **2** 0.3; **3** 0.2; **4** 0.4; **5** 0.6; **6** 1.1).

To obtain some further evidence in respect of the composition of the formed Ag(I) complexes, a comparative ESI-MS analysis of complex composition in the organic phase was undertaken. For this purpose the ligands were dissolved in chloroform and mixed in the ratio of 1:1 with a solution of $\text{CF}_3\text{SO}_3\text{Ag}$ in acetone. The resulting ESI-MS spectra are shown in Figure 6.

For ligand **1**, the smallest macrocycle with an O_2S_2 donor set, the complex cations $[\text{Ag} \cdot \mathbf{1}]^+$ (m/z 392.9) and $[\text{Ag} \cdot (\mathbf{1})_2]^+$ (m/z 674.5) can be detected in the chloroform/acetone solution. The larger macrocycles **2**, **3**, **4** and **5**, each with 5, 6 or 7 donor atoms, show the formation of 1:1 complexes as only a signal for the respective 1:1 species $[\text{AgL}]^+$ has been found in the individual spectra. In the case of ligand **5** the major signal at m/z 452.9 is connected with the loss of a thioethylene group through fragmentation during the excitation process. However, the second largest signal at m/z 513.0 indicates the presence of the 1:1 species. For **6**, which contains an O_4S donor set, besides the $[\text{AgL}]^+$ species, the species $[\text{AgL}_2]^+$ is also detected. This is in contrast to the extraction data (see Figure 5) where only 1:1 species have been detected. In spite of the different experimental conditions for extraction and ESI-MS experiments, the results are in good agreement for the observed complex compositions and confirm the interpretation.

Figure 6. ESI-MS spectra for equimolar mixtures (0.5 mL each) of a solution of **1-6** (5 mM) in CHCl_3 and of $\text{CF}_3\text{SO}_3\text{Ag}$ (5 mM) in acetone.

One important influencing factor on the extraction equilibria is the nature of the organic diluent employed. In general, nitrobenzene very often enhances the extraction ability of a ligand due to strong solvation effects for the extracted compound. For comparison, Ag(I) extraction experiments were carried out with **2** and **7** both in 1,2-dichloroethane (DCE) or nitrobenzene (NB). As shown in Figure 7, the expected extraction enhancement for nitrobenzene was observed only in case of **2** pointing to a favored solvation of the extracted complex. In the case of **7**, the presence of the lipophilic benzothiazolium substituent may compensate this effect. Ag(I) extraction is comparable in both solvents, 78% (1,2-dichloroethane) and 75% (nitrobenzene), respectively.

Figure 7. Influence of the diluent on the extraction of Ag(I) by **2** and **7**; $[\text{AgNO}_3] = 1 \times 10^{-4} \text{ M}$, $[\text{HNO}_3] = 5 \times 10^{-4} \text{ M}$; $[\text{ligand}] = 1 \times 10^{-3} \text{ M}$ in DCE and NB.

Figure 8. Dependence of the extraction of Ag(I) with **2** and **7** on ligand concentration; $[\text{AgNO}_3] = 1 \times 10^{-4} \text{ M}$, $[\text{HNO}_3] = 5 \times 10^{-4} \text{ M}$; $[\text{ligand}] = 2.5 \times 10^{-4} - 2 \times 10^{-3} \text{ M}$ in DCE and NB; slopes for **2** 0.3 (NB) and 0.4 (DCE); for **7** 1.0 (NB) and 1.6 (DCE).

However, a change of the organic diluent can also have a significant influence on the composition of the extracted Ag(I) complex. Slope analyses employing a $\log D_{\text{Ag}} - \log c_{\text{L(org)}}$ diagram for Ag(I) extraction with **2** and **7** for 1,2-dichloroethane or nitrobenzene diluents are shown in Figure 8. Thus, for **7** both $[\text{AgL}]^+$ and $[\text{AgL}_2]^+$ species are formed in 1,2-dichloroethane (slope 1.6), whereas only a $[\text{AgL}]^+$ species is formed in nitrobenzene (slope 1.0) exclusively. In comparison, experiments for **2** gave very low slopes of 0.3 and 0.4 in 1,2-dichloroethane and nitrobenzene, respectively, and are in agreement with the result obtained when chloroform was used as the diluent (see Figure 5). Obviously, the high water solubility of the Ag(I) complex of **2** (see below) prevents a clear indication of the composition of the extracted species.

In order to probe the assumption that the extracted Ag(I) complex species of the ligands **2**, **3** and **5** possess an enhanced water solubility, UV-Vis spectroscopic analysis of both aqueous and organic phases were carried out after extraction. The results are shown in Figures 9 and 10. In the absence of Ag(I) no characteristic UV absorption could be observed in the aqueous phase. In contrast, after extraction, two absorption bands at 275 nm and 303 nm appear in both phases and indicate similar Ag(I) complexes (Figure 9 and 10). This observation supports the assumption that Ag(I) complexation results in a significant solubility increase of the Ag(I) species in the aqueous phase. Furthermore, the increase of the characteristic absorbance in the aqueous phase in the order $\mathbf{5} < \mathbf{2} < \mathbf{3}$ correlates with the observed decreasing slopes in the corresponding analyses obtained for the respective extraction experiments (Figure 5). In agreement with this tendency, the absorbance of both characteristic UV bands of the extracted Ag(I) complexes in the organic phase increase in the order $\mathbf{3} < \mathbf{2} < \mathbf{5}$ (Figure 10) which is the opposite trend to the absorbance in the aqueous phase.

Figure 9. UV-Vis spectra of the aqueous phase after extraction of Ag(I) with **2**, **3** and **5**; for **3** and **5** $[\text{AgNO}_3] = 5 \times 10^{-4} \text{ M}$, $[\text{HNO}_3] = 5 \times 10^{-3} \text{ M}$; for **2** $[\text{AgClO}_4] = 5 \times 10^{-4} \text{ M}$; $[\text{ligand}] = 5 \times 10^{-4} \text{ M}$ in 1,2-dichloroethane.

Figure 10. UV-Vis spectra of the organic phase after extraction of Ag(I) with **2**, **3** and **5**; for **3** and **5** $[\text{AgNO}_3] = 5 \times 10^{-4} \text{ M}$, $[\text{HNO}_3] = 5 \times 10^{-3} \text{ M}$; for **2** $[\text{AgClO}_4] = 5 \times 10^{-4} \text{ M}$; $[\text{ligand}] = 5 \times 10^{-4} \text{ M}$ in 1,2-dichloroethane.

4. Conclusions

The novel benzothiaoxacrown compounds **1-8** show a good extraction ability toward the soft metal ions Ag(I) and Hg(II) in both single and competitive metal ion experiments with a preferred extraction of Ag(I). In contrast, the extraction of the soft Cu(I) ion with these ligands is weak; the metal ions Co(II), Ni(II), Cu(II) and Zn(II) are not extracted at all. It is interesting to note that, in comparison with Ag(I), the extraction behavior of Hg(II) with the ligands studied is more sensitive toward the chosen experimental conditions. This concerns especially the choice of the organic diluent and the counter ion in the aqueous phase. The highest Hg(II) extraction was obtained with ligands **1**, **7** and **8** using nitrobenzene as the diluent and perchlorate as the anion.

For Ag(I) the complex composition in the organic phase varies between 1:2 and 1:1 (M:L) depending on the ring size. This result correlates with the degree of size match between the metal ion and the macrocyclic ring and is in agreement with literature data for relevant complexes [10,15,27,28], suggesting the formation of 1:2 sandwich or 1:2 linear complexes and 1:1 (in or above the macrocyclic ring) structure arrangements with different coordination numbers (Scheme 2). This observation reflects the known variation of the Ag(I) coordination number – with a preference between 2 and 6 – depending on the ligand used [24,33].

Scheme 2.

Of interest is the fact that the lipophilicity of the benzothiaoxacrowns **2**, **3** and **5** decreases upon extraction. UV-Vis measurements reveal that these ligands are exclusively in the organic phase prior to extraction. Afterwards the relevant complexes show a relatively high solubility in water.

Acknowledgments

The research was supported by INTAS program 2001-0267. MW thanks Massey University for a postdoctoral fellowship.

References

- 1) Solvent Extraction Principles and Practice, J. Rydberg, M. Cox, C. Musikas, G.R. Choppin, Eds., Marcel Dekker, NewYork, 2004.
- 2) A.M. Wilson, P.J. Bailey, P.A. Tasker, J.R. Turkington, R.A. Grant, J.B. Love, *Chem. Soc. Rev.*, **43**, 123-134 (2014).
- 3) R.M. Izatt, S.R. Izatt, R.L. Bruening, N.E. Izatt, B.A. Moyer, *Chem. Soc. Rev.*, **43**, 2451-2475 (2014).
- 4) Macrocyclic Compounds in Analytical Chemistry, Y.A. Zolotov, Ed., Wiley, NewYork, 1997.
- 5) Macrocyclic Chemistry: Current Trends and Future Perspectives, K. Gloe. Ed., Springer, Dordrecht, 2005.
- 6) D. Sevdic, H. Meider, *J. Inorg. Nucl. Chem.*, **39**, 1409-1413 (1977).
- 7) D. Sevdic, L. Fekete, H. Meider, *J. Inorg. Nucl. Chem.*, **42**, 885-889 (1980).
- 8) I.M. Kolthoff, *Anal. Chem.*, **51**, 1-22 (1979).
- 9) K. Saito, Y. Masuda, E. Sekido, *Anal. Chim. Acta*, **151**, 447-455 (1983).
- 10) E. Sekido, K. Saito, Y. Naganuma, H. Kumazaki, *Anal. Sci.*, **1**, 363-368 (1985).
- 11) E. Sekido, K. Chayama, M. Muroi, *Talanta*, **32**, 797-802 (1985).
- 12) M. Muroi, A. Hamaguchi, E. Sekido, *Anal. Sci.*, **2**, 351-356 (1986).
- 13) M. Oue, K. Kimura, T. Shono, *Anal. Chim. Acta*, **194**, 293-298 (1987).
- 14) W.J. McDowell, *Sep. Sci. Technol.*, **23**, 1251-1268 (1988).
- 15) A.J. Blake, M. Schröder, *Adv. Inorg. Chem.*, **35**, 1-80 (1990).
- 16) G. Wu, W. Jiang, J.D. Lamb, J.S. Bradshaw, R.M. Izatt, *J. Am. Chem. Soc.*, **113**, 6538-6541 (1991).
- 17) S. Kim, L.F. Lindoy, S.S. Lee, *Coord. Chem. Rev.*, **280**, 176-202 (2014).
- 18) K. Gloe, P. Mühl, L. Beyer, M. Mühlstädt, E. Hoyer, *Solvent Extr. Ion Exch.*, **4**, 907-925 (1986).
- 19) K. Gloe, P. Mühl, J. Beger, *Z. Chem.*, **28**, 1-14 (1988).
- 20) F. Dietze, K. Gloe, R. Jacobi, P. Mühl, J. Beger, M. Petrich, L. Beyer, E. Hoyer, *Solvent Extr. Ion Exch.*, **7**, 223-247 (1989).
- 21) M.C. Aragoni, M. Arca, A. Bencini, S. Biagini, A.J. Blake, C. Caltagirone, F. Demartin, G. De Filippo, F.A. Devillanova, A. Garau, K. Gloe, F. Isaia, V. Lippolis, B. Valtancoli, M. Wenzel, *Inorg. Chem.*, **47**, 8391-8404 (2008).
- 22) O. Heitzsch, K. Gloe, H. Stephan, E. Weber, *Solvent Extr. Ion Exch.*, **12**, 475-496 (1994).
- 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**, 152-158 (1998).
- 24) T. Rambusch, K. Gloe, K. Gloe, *J. Prakt. Chem.*, **341**, 202-217 (1999).
- 25) M.V. Alfimov, A.I. Vedernikov, S.P. Gromov, Y.V. Fedorov, O.A. Fedorova, *Russ. Chem. Bull.*, **46**, 967-974 (1997).
- 26) O.A. Fedorova, A.I. Vedernikov, O.V. Yescheulova, Y.V. Pershina, P.V. Tsapenko, S.P. Gromov, *Synthetic Commun.*, **32**, 1909-1915 (2002).

- 27) O.A. Fedorova, Y.V. Fedorov, A.I. Vedernikov, S.P. Gromov, O.V. Yescheulova, M.V. Alfimov, M. Woerner, S. Bossmann, A. Braun, J. Saltiel, *J. Phys. Chem. A*, **106**, 6213-6222 (2002).
- 28) L.G. Kuzmina, A.I. Vedernikov, S.N. Dmitrieva, J.A.K. Howard, S.P. Gromov, *Russ. Chem. Bull.*, **56**, 1003-1012 (2007).
- 29) A.I. Vedernikov, L.G. Kuzmina, Y.A. Strelenko, J.A.K. Howard, S.P. Gromov, *Russ. Chem. Bull.*, **59**, 927-940 (2010).
- 30) S.N. Dmitrieva, N.I. Sidorenko, N.A. Kurchavov, A.I. Vedernikov, A.Y. Freidzon, L.G. Kuzmina, A.K. Buryak, T.M. Buslaeva, A.A. Bagaturyants, Y.A. Strelenko, J.A.K. Howard, S.P. Gromov, *Inorg. Chem.*, **50**, 7500-7510 (2011).
- 31) H. Stephan, M. Kubeil, K. Gloe, K. Gloe, in *Analytical Methods in Supramolecular Chemistry*, Ch. Schalley, Ed., Wiley-VCH, Weinheim, pp. 105-127, 2012.
- 32) Y. Marcus, *Chem. Rev.*, **88**, 1475-1498 (1988).
- 33) B. Antonioli, D.J. Bray, J.K. Clegg, K. Gloe, K. Gloe, O. Kataeva, L.F. Lindoy, J.C. McMurtrie, P.J. Steel, C.J. Sumby, M. Wenzel, *Dalton Trans.*, 4783-4794 (2006).