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## Dual-host approach for liquid–liquid extraction of potassium fluoride/ chloride *via* formation of an integrated 1-D polymeric complex<sup>†</sup>

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Extraction of KF/KCl from aqueous solution by distinct cationic and anionic receptors is demonstrated. Structural studies of the extracted complexes showed 1D-polymers of the receptors containing respective ions in their cavities.

Ion-pair recognition and extraction by synthetic hosts is an area of general interest, with promising analytical, industrial and environmental applications.<sup>1</sup> In particular, the selective liquid-liquid extraction of alkali metal salts is important due to its applications in separation technology, production of common living materials, medicine and maintenance of osmotic balances in cells.<sup>2</sup> Recently, Sessler et al. demonstrated extraction of KF or KCl from water using polymeric extractants with calixpyrroles and crown ether pendants.<sup>3</sup> In the literature, a *dual-host* (using separate anion and cation hosts) approach has also been demonstrated for extraction of different alkali salts.<sup>4</sup> Fluoride recognition by synthetic receptors mostly takes place in organic solvents, which greatly limits the scope of their use,<sup>5</sup> though fluoride recognition in aqueous media is known in polyammonium cryptands.6 Herein we show a simple tripodal neutral receptor,  $L^2$  (which has previously shown anion binding ability in organic solvents),<sup>7</sup> as a suitable receptor for encapsulation of F<sup>-</sup>/Cl<sup>-</sup> in water that also acts as a partner in dual-host systems with crown ether, L<sup>1</sup> for extraction of KF/KCl from water. Further we successfully demonstrate the single crystal X-ray structure of the extracted species as integrated 1-D polymeric complexes of KF/KCl. To the best of our knowledge this represents the first dual-host system capable of liquid-liquid extraction of KF from aqueous media and the first single crystal X-ray structure of any extracted ion-pair in a dual host approach.

The 18-Crown-6,  $L^1$  and tripodal amide,  $L^2$  (Fig. 1a and b) is our choice of cation and anion receptors respectively because of high selectivity of  $L^1$  toward potassium ion,<sup>8</sup> and solubility of  $L^2$  in most of the common organic solvents even in water. Water solubility of  $L^2$  gave us the opportunity to attempt complexation of  $F^-$  and  $Cl^-$  in an aqueous medium

and we isolated single crystals of  $[L^{2}(F)(H_{2}O)][N(Bu)_{4}](1)$  and  $[L^{2}(Cl)][N(Bu)_{4}]$  (2) from water upon reaction of  $L^{2}$  with *n*-Bu<sub>4</sub>NF and *n*-Bu<sub>4</sub>NCl respectively. Single crystal X-ray studies of 1 showed recognition of mono hydrated F<sup>-</sup> inside the  $C_{3v}$  symmetric cleft of  $L^2$ .<sup>‡</sup> Fig. 1c shows that encapsulated  $F^-$  is bound strongly via three (N-H···F<sup>-</sup>) bonds and one  $(O-H \cdot \cdot \cdot F^{-})$  hydrogen bond with all three amide hydrogens of  $L^2$  and encapsulated water molecule O4 respectively in a distorted tetrahedral fashion (Fig. 7S and Table 5S, ESI<sup>†</sup>). Further, the oxygen atom of the encapsulated water (O4) is in strong contact with the all three  $-C_6F_5$  moieties of L<sup>2</sup> with O4···Cg1, O4···Cg2 and O4···Cg3 (Cg1, Cg2 and Cg3 are the centroids of three  $-C_6F_5$  moieties) distances of 3.060, 3.161 and 3.169 Å respectively (Fig. 1c). The strong  $H_2O \cdots \pi$  contacts in 1 could be the consequence of ditopic recognition of  $F^-$  and H<sub>2</sub>O inside the small cavity of the receptor. The monotopic recognition of Cl<sup>-</sup> inside the  $C_{3v}$  symmetric cleft of L<sup>2</sup> is observed in case of 2 where Cl<sup>-</sup> has a strong hydrogen bonding interaction with all three amide hydrogens of  $L^2$ (Fig. 10S, Table 6S, ESI<sup>†</sup>).

The extracted complexes of **3** and **4** were obtained by the liquid–liquid extraction of an aqueous phase containing KF (100 mM) or KCl (100 mM) with equimolar amounts of  $L^1$  and  $L^2$  (10 mM) in CHCl<sub>3</sub>. Details of extraction and crystallization of **3** and **4** are given in the ESI.† Complex **3**,  $[L^2(F)(H_2O)][L^1(K)]$  was subjected to various studies like <sup>1</sup>H-NMR, <sup>19</sup>F-NMR, IR, SEM-EDX, PXRD and Single crystal X-ray diffraction.‡Similar experiments and characterization were carried out with the exception of <sup>35</sup>Cl-NMR instead of <sup>19</sup>F-NMR studies for **4**,  $[L^2(Cl)(H_2O)][L^1(K)]$ .‡ Competitive extraction from aqueous solutions containing mixtures of KF (100 mM) and KNO<sub>3</sub> (100 mM) or KCl



**Fig. 1** (a)  $L^1$ , (b)  $L^2$  and (c) single crystal structure of encapsulated  $F^-$  in the cavity of  $L^2$ .

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**Fig. 2** Partial <sup>1</sup>H-NMR spectra of free L<sup>2</sup> and complexes 1, 2, 3 and 4 in CDCl<sub>3</sub> at 298 K.  $\alpha$  and  $\beta$  denote the existence of *n*-Bu<sub>4</sub>N<sup>+</sup> and K<sup>+</sup> · L<sup>1</sup> cations in complexes 1, 2 and 3, 4, respectively.

(100 mM) and KNO<sub>3</sub> (100 mM) has also resulted in 3 and 4 respectively. Fig. 2 shows  ${}^{1}$ H-NMR studies on  $L^{2}$  and complexes 1-4. In 1 and 2 a large downfield chemical shift of the -NH signal ( $\Delta \delta = 4.52$  and 2.49 ppm respectively) w.r.t.  $L^2$  is observed, indicative of halide encapsulation inside the cleft of L<sup>2</sup> and its strong interactions with the -NH protons. In the cases of **3** and **4**, a similar downfield shift of -NH signals are observed as in the cases of 1 and 2 respectively, indicating the presence of  $F^-$  and  $Cl^-$  encapsulated  $L^2$  in the extracted products. Though, 1 and 3 showed similar shifts in the -NH resonance of  $L^2$ , a major noticeable upfield shift of 0.17 and 0.20 ppm of -CH2<sup>a</sup> and -CH2<sup>b</sup> resonances respectively in the aliphatic region of  $L^2$  are observed in case of 3 whereas in case of 1 -CH<sub>2</sub> resonances are matched with  $L^2$ . Similar upfield shifts in the aliphatic region (0.16 and 0.21 ppm) are also observed in 4 whereas in 2, no such shifts are present. The -CH<sub>2</sub> chemical shifts observed in **3** and **4** could be attributed to the strong interaction of  $F^{-}/Cl^{-}$  encapsulated  $L^{2}$  with cationic counter part of complexes. In 3 and 4, a new peak at 3.6 ppm clearly indicated the presence of a crown-ether moiety in the extracted complexes. Detailed analyses of <sup>1</sup>H-NMR spectra of **3** and **4** upon calculating  $-CH_2^a$  or  $-CH_2^b$  integration of  $L^2$  to the  $\beta$  protons of L<sup>1</sup> indicated a 1:1 involvement of L<sup>1</sup> and L<sup>2</sup> (Fig. 12S and 14S, ESI<sup>†</sup>).

In the <sup>19</sup>F-NMR and <sup>35</sup>Cl-NMR studies (Fig. 16S, ESI<sup>†</sup>) hydrated F<sup>-</sup> and Cl<sup>-</sup> resonances for KF and KCl in D<sub>2</sub>O are observed at -125.08 and 0.00 ppm respectively. Complexes 1 and 3 both showed a sharp resonance with a downfield chemical shift of 14.86 ppm that represents encapsulation of  $F^-$  in the cavity of  $L^2$  in both the cases. In 2 and 4 a 14.84 ppm downfield shift of Cl<sup>-</sup> resonance is observed where Cl<sup>-</sup> signals showed broadening, indicative of Cl- encapsulation and complexation. As control experiments, extractions were also performed in an analogous manner using  $L^1$  and  $L^2$ , separately. No quantifiable fluorine or chlorine signal in <sup>19</sup>F- and <sup>35</sup>Cl-NMR was observed in the organic phase when  $L^1$  was used as an extractant. There is no observable change in the -NH resonance in <sup>1</sup>H-NMR of L<sup>2</sup> obtained from the organic phase when  $L^2$  is used alone as an extractant for KF or KCl (Fig. 22S, 23S and 27S, ESI<sup>†</sup>). These studies indeed

show the necessity of dual receptors towards the extraction of the salt from aqueous media. To determine the effect of pH towards KF/KCl extraction by  $L^1$  and  $L^2$ , experiments were carried out at three different pH, 4.5, 6.3 and 9.3. The maximum extraction of KF (48%) and KCl (44%) is observed at pH ~6.0 whereas no extraction of KF and KCl is observed at pH ~9.0 (Table 10S, ESI<sup>†</sup>).

Energy-Dispersion X-ray (EDX) analyses were carried out on the extracted complexes **3** and **4** (Fig. 18S, ESI<sup>†</sup>). In cases of **3** and **4**, the EDX spectrum shows peaks in addition to C, N and O, that can be assigned to K (3.312 KeV), F (0.677 KeV) and K (3.312 KeV), Cl (2.621 KeV), respectively indicating the presence of KF/KCl which are absent in the case of  $L^2$ . Since,  $L^2$  contains pentafluorophenyl moieties, a separate peak for fluoride is not observed in case of **3**.

We have carried out a detailed IR studies for  $L^2$  and complexes 1–4 (Fig. 21S, ESI†). The peak at 1660 cm<sup>-1</sup> in  $L^2$  may be attributed to the -C=O (amide I) stretching frequency. In 1 and 2 -C=O stretching frequency remains unaltered whereas, 3 and 4 showed existence of two different carbonyl stretching frequencies. In the case of 3, two different -C=O stretching frequencies appear at 1683 and 1652 cm<sup>-1</sup> whereas in 4 corresponding frequencies appear at 1681 and 1655 cm<sup>-1</sup>. This suggests that in these two complexes the carbonyl groups are in two different environments.

The single-crystal X-ray structure of 3<sup>‡</sup> revealed the formation of a 1-D coordination polymer composed of  $L^1$ ,  $L^2$  and KF (Fig. 3) where K<sup>+</sup> and F<sup>-</sup> are encapsulated inside  $L^1$  and  $L^2$  respectively. In the case of 4 a similar 1-D coordination polymer is obtained (Fig. 17S, ESI<sup>+</sup>). Structural analyses showed that 3 and 4 are isostructural. Interestingly, two out of the three amide carbonyl oxygen atoms of F encapsulated  $L^2$  form two coordinate covalent bonds with the encapsulated  $K^+$  of  $L^1$ , in the case of 3, which upon propagation form the 1-D polymeric chain. In this metal-organic polymeric complex,  $K^+$  is bound to all six oxygen atoms of  $L^1$  with  $K^+ \cdots O$  distances ~2.8 Å with two more oxygen atoms coordinating from the carbonyl groups of F<sup>-</sup> encapsulated  $L^2$  with  $K^+ \cdots O$  distances 2.73 and 2.77 Å, resulting in eight coordinate covalent bonds. The presence of carbonyl groups in different environments is also evident from the IR analysis. The low energy band in IR analyses of 3 or 4 could be assigned



Fig. 3 Single crystal X-ray structure of (a) monomeric  $L^1 \cdot L^2 \cdot KF$  (complex 3) with partial atom-labeling and (b) a 1-D polymer of complex 3. Non acidic hydrogen atoms and disordered crown ether moieties are omitted for clarity.



Fig. 4 Proposed mechanism of KF/KCl extraction.

to the carbonyl bound to potassium of  $L^1$ . On the other hand, the encapsulated fluoride is hydrogen bonded to all three amide -NH of  $L^2$  with  $N \cdots F^-$  distances ranging from 2.66–2.73 Å and to a molecule of water as observed in the case of 1. The extracted complexes of bulk 1-D polymeric complexes 3 and 4 are obtained in 48% and 44% yield respectively when 0.1 mmol of each  $L^1$  and  $L^2$  are used for extraction, see ESI.†

Experimental powder X-ray patterns of bulk **3** and **4** showed similar powder X-ray patterns simulated from the corresponding single crystal X-ray data of these complexes (Fig. 19S, ESI†), suggesting high purity of the bulk extracted complexes.

The 2D-DOSY has been used as an independent method to propose a suitable mechanism for the extraction of KF/KCl from water (Fig. 20S, ESI<sup>†</sup>) through the measurement of the diffusion coefficients. The <sup>1</sup>H-NMR spectra of all the combinations are shown in the horizontal projection. All signals are well resolved and can be classified according to their self-diffusion coefficients. The DOSY spectrum of an acetonitrile solution of  $L^1 + L^2$  (10 mM) shows two distinct sets of resonances with different diffusion coefficients of  $2.58 \times$  $10^{-9}$  m<sup>2</sup> s<sup>-1</sup> and 5.0 ×  $10^{-9}$  m<sup>2</sup> s<sup>-1</sup>. It is clearly evident from the spectra, that the addition of  $KPF_6$  (10 mM) to this solution showed a single set of resonances with a diffusion coefficient of  $1.03 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ . This indicates the formation of an integrated co-ordination species between potassium encapsulated  $L^1$  and  $L^2$ , whereas there is no change in the -NH resonance of the receptor. The addition of *n*-Bu<sub>4</sub>NF or *n*-Bu<sub>4</sub>NCl to the above solution showed two sets of resonances with different diffusion co-efficients which is attributed to the existence of  $Bu_4N^+$  groups ( $D = 1.334 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ ) and the integrated species of  $L^1$  and  $L^2$  ( $D = 1.03 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ ) in solution, further a downfield shift of the -NH resonances of  $L^2$ , indicated the encapsulation of  $F^{-}/Cl^{-}$  in its cavity.

From the above studies, we propose a suitable mechanism for extraction of KF/KCl from water as depicted in Fig. 4. Even though Dual-Hosts are employed for the extraction of these salts, the potassium cation first assists the formation of an integrated species of the dual receptors and participates in the extraction process of fluoride or chloride from water.

In conclusion, a simple tripodal amide acts as a selective fluoride/chloride binding receptor in an aqueous medium in combination with a well known potassium binding crown ether, a dual hosts approach, for the liquid–liquid extraction of potassium fluoride/chloride even in the presence of nitrate. Different solution state studies along with 2D-DOSY-NMR studies have been performed to establish a suitable mechanism for the liquid–liquid extraction of KF/KCl.

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## Notes and references

<sup>‡</sup> The crystals of complexes 2, 3 and 4 are very weakly diffracting at higher Bragg angles. This resulted in poor quality of the data set. However, this is the best possible data set for these complexes. Crystallographic data for complex 1 (CCDC 701763):  $C_{43}H_{52}F_{16}N_5O_4$ , M = 1006.88, monoclinic, space group  $P2_1/n$ , a =16.3394(11), b = 13.3936(9), c = 23.0429(15) Å,  $\beta = 104.689(2)^{\circ}$ ,  $V = 4878.0(6) \text{ Å}^3, D_c = 1.368 \text{ g cm}^{-3}, Z = 4, \lambda = 0.71073 \text{ Å}, T =$ 100(2) K, 28 988 reflections, 6895 independent ( $R_{int} = 0.0293$ ), and 4200 observed reflections  $[I > 2\sigma(I)]$ , 617 refined parameters, R = $0.0665, WR_2 = 0.1883.$  Complex 2 (CCDC 710731):  $C_{43}H_{51}ClF_{15}N_5O_3$ , M = 1006.34, triclinic, space group  $P\bar{1}$ , a =11.7018(18), b = 14.141(2), c = 15.737(2) Å,  $\alpha = 88.438(6)$ ,  $\beta = 77.895(5)$ ,  $\gamma = 74.960(5)^\circ$ , V = 2458.0(7) Å<sup>3</sup>,  $D_c = 1.360$  g cm<sup>-3</sup>,  $Z = 2, \lambda = 0.71073$  Å, T = 298(2) K, 14575 reflections, 4642 independent ( $R_{int} = 0.0379$ ), and 3128 observed reflections  $[I > 2\sigma(I)]$ , 601 refined parameters, R = 0.0624, w $R_2 = 0.1437$ . Complex **3** (CCDC 732760):  $C_{36}H_{41}F_{16}KN_4O_{10}$ , M = 1032.83, monoclinic, space group  $P2_1/n$ , a = 15.591(7), b = 19.049(8), c = 16.196(7) Å,  $\beta = 93.954(6)^{\circ}, V = 4799(4) \text{ Å}^3, D_c = 1.430 \text{ g cm}^{-3}, Z = 4, \lambda =$ 0.71073 Å, T = 100(2) K, 26265 reflections, 4111 independent ( $R_{int} =$ 0.1175), and 2206 observed reflections  $[I > 2\sigma(I)]$ , 574 refined parameters, R = 0.0832,  $wR_2 = 0.2168$ . Complex 4 (CCDC 804542):  $C_{39}H_{41}ClF_{15}KN_4O_{10}, M = 1085.29$ , monoclinic, space group  $P2_1/c$ ,  $a = 10.676(10), b = 24.66(2), c = 18.522(18) \text{ Å}, \beta = 98.094(11)^\circ, V = 4827(8) \text{ Å}^3, D_c = 1.491 \text{ g cm}^{-3}, Z = 4, \lambda = 0.71073 \text{ Å}, T = 298(2) \text{ K},$ 21 302 reflections, 3379 independent ( $R_{int} = 0.0777$ ), and 2565 observed reflections  $[I > 2\sigma(I)]$ , 631 refined parameters, R = $0.0738, wR_2 = 0.1931.$ 

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