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Anion binding of tris-(thio)urea ligands†

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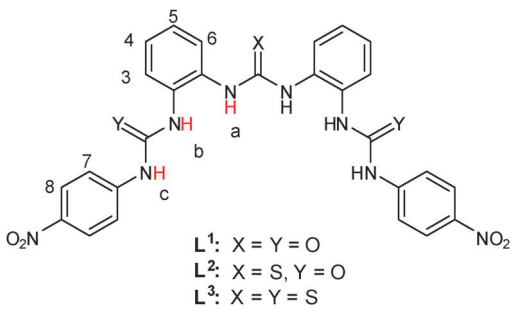
Two tridentate tris-(thio)urea ligands (L^2 and L^3) have been synthesized. Ligand L^2 forms a 2 : 2 complex (1) with the $(H_2PO_4{\cdot}HPO_4)^{3-}$ dimer. ^1H NMR and UV-vis titrations revealed that the mixed urea–thiourea ligand, L^2, shows considerable anion binding affinities, while the tris-thiourea ligand, L^3, undergoes deprotonation in the presence of basic anions.

Anion coordination chemistry has been an active field of research in the past several decades.[1] The design and synthesis of abiotic receptors for biologically and/or chemically important anions are of great importance and many elaborately designed anion ligands have been reported.[2] Among the various anion binding functionalities, the urea and thiourea groups are excellent candidates because they can establish two directional hydrogen bonds with an oxoanion or chelate a spherical anion.[3] Following the primary work of Wilcox[4] and Hamilton,[5] a variety of anion receptors have been reported in which one or more urea/thiourea fragments are incorporated into acyclic, cyclic or polycyclic backbones to achieve efficient anion binding.[6]

We have recently reported a series of *o*-phenylene-bridged[7] oligourea receptors, which exhibit high affinity and selectivity toward tetrahedral anions.[8] For example, the tris(urea) receptor, L^1, can form a 2 : 1 (host-to-anion) complex with the orthophosphate ion in a highly complementary coordination mode.[8d] In order to further explore the anion coordination behavior of such ''tridentate'' ligands, in the present work we modified the trisurea L^1 ligand by replacing one (the central) or three of the urea groups by the more acidic thiourea group(s) (pK_a = 21.1 for thiourea and 26.9 for urea, respectively, in DMSO)[9] and synthesized two thiourea analogues, L^2 and L^3 (Scheme 1). Herein we report the synthesis of the bisurea–thiourea L^2 and tris(thiourea) L^3 ligands and an anion complex of L^2, $(TBA)_3[(L^2)_2{\cdot}HPO_4{\cdot}H_2PO_4]{\cdot}2.9CH_2Cl_2$ (**1**), as well as their anion binding properties in solution.



Scheme 1 Structures of ligands L^1–L^3.

Ligands L^2 and L^3 were synthesized by the reaction of *p*-nitrophenylisocyanate or *p*-nitrophenylisothiocyanate, respectively, with 1,3-bis(2-aminophenyl)thiourea (see the ESI† for details). Crystals of the anion complex, $(TBA)_3[(L^2)_2{\cdot}HPO_4{\cdot}H_2PO_4]{\cdot}2.9CH_2Cl_2$ (**1**), were obtained by slow diffusion of diethyl ether into a dichloromethane solution of ligand L^2 in the presence of an excess of $(TBA)H_2PO_4$ (TBA = tetrabutylammonium).

Complex **1** crystallizes in the space group *P*2/*c*. The asymmetric unit contains one L^2 ligand, one CH_2Cl_2 molecule and two TBA^+ cations all in general positions, as well as one half TBA^+ cation lying about a twofold axis (with N9 atoms on the twofold axis) and one phosphate anion in a general position adjacent to a twofold axis. Notably, although complex **1** was obtained from the dihydrogen phosphate salt $(TBA)H_2PO_4$, it displays a 2 : 2 coordination mode in which two phosphate ions in different protonation states (HPO_4^{2-} and $H_2PO_4^-$) are

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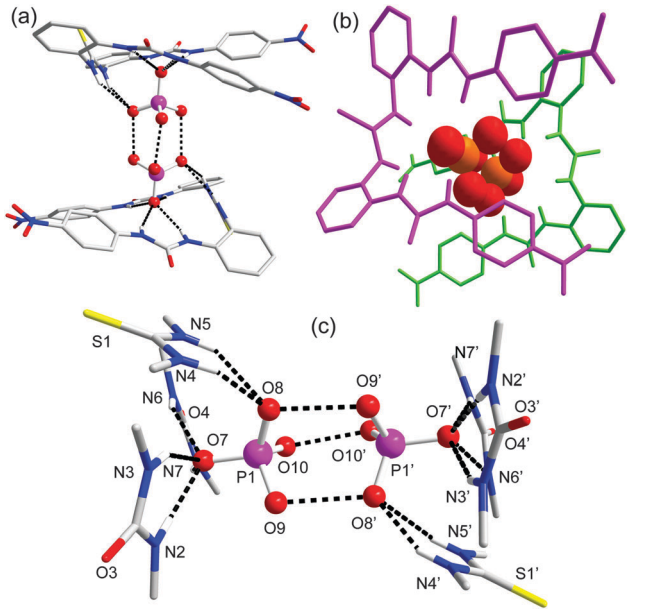

Fig. 1 Crystal structure of complex **1**. (a) Side view; (b) top view; (c) hydrogen bonds around the $(HPO_4{\cdot}H_2PO_4)^{3-}$ dimer (solvents and non-acidic hydrogen atoms are omitted for clarity). Symmetry code ('): $1 - x, y, 1/2 - z$.

sandwiched by two L^2 molecules (Fig. 1a). The two phosphate ions are essentially indistinguishable due to the crystal-imposed C_2 symmetry, and the hydrogen atoms on them were not added. The existence of the mixed states of the anions was proven by the number of TBA^+ countercations (three TBA^+ ions per two phosphate ions) and the close contact of three pairs of oxygen atoms belonging to two distinct anions (O···O distances: 2.469(6)–2.579(5) Å). This binding mode is different from that in the complex of the trisurea ligand L^1, which coordinates to the fully deprotonated phosphate (PO_4^{3-}) ion in the 2 : 1 mode,[8d] although both complexes were isolated from the initial $H_2PO_4^-$ ion. Attempts to grow crystals of the analogous 2 : 1 complex of the orthophosphate ion by using other phosphate salts, such as Na_3PO_4, K_3PO_4, $\{K([18]crown\text{-}6)\}_3PO_4$, and $(TBA)_3PO_4$, have not yet been successful.

In complex **1**, the two anions are in close proximity, joined by three hydrogen bonds between HPO_4^{2-} and $H_2PO_4^-$ to form a $(HPO_4{\cdot}H_2PO_4)^{3-}$ dimer with a P–P distance of 3.586 Å (Fig. 1a and c). The dimerization (or oligomerization and polymerization) of phosphate ions in their different protonation states has been observed in many cases.[10] Very recently, an unusual phosphate dimer, $[H_3PO_4{\cdot}PO_4]^{3-}$, was obtained by Jurczak *et al.*, in which the two phosphate anions are also linked by three hydrogen bonds and the P–P distance is 3.68 Å.[11] We recently reported a $[(HPO_4)_2]^{4-}$ dimer coordinated by two bis-bisurea ligands, wherein the phosphate anions are dimerized by two hydrogen bonds.[12] The sandwich structure of **1** is similar to that of this bis-bisurea complex of $[(HPO_4)_2]^{4-}$, with the two ligand molecules being arranged in a head-to-tail manner (Fig. 1b). On the other hand, the aggregation of phosphate ions with water molecules has also been reported, such as the 1D dihydrogenphosphate–water polymers $(H_2PO_4{\cdot}H_2O)_n^{n-}$ with reduced Schiff base ligands[13] and the hydrogenphosphate–water chain bound by protonated polyamines.[14]

In the dimeric structure, each of the protonated phosphate ions in the $(HPO_4{\cdot}H_2PO_4)^{3-}$ unit is coordinated by the urea and thiourea groups of a ligand molecule *via* six N–H···O hydrogen bonds. Thus, each phosphate ion indeed forms a total of nine hydrogen bonds, including six N–H···O and three P–O···HO–P bonds (Table S1, ESI†). For both of the HPO_4^{2-} and $H_2PO_4^-$ ions, the four NH donors of the two urea groups chelate one oxygen atom (O7) of a phosphate ion, while the central thiourea NH groups bind one oxygen (O8) through two hydrogen bonds and this oxygen atom forms also an O···H–O contact. The remaining two oxygen atoms (O9 and O10) participate in a pair of $HPO_4{\cdot}\cdot\cdot H_2PO_4$ associations (Fig. 1c). The hydrogen bond parameters of the urea and thiourea groups are comparable, with an average N···O distance of 2.916 Å and N–H···O angle of 152°. In addition, the solvent CH_2Cl_2 molecule forms C–H···O and C–H···S hydrogen bonds with the terminal nitro groups and the sulfur atoms of the ligands (Table S1, ESI†).

^{1}H NMR studies

The anion coordination properties of ligand L^2 with different anions in solution were studied using ^{1}H NMR spectroscopy in DMSO-d_6–0.5% water. When 1.0 equiv. of PO_4^{3-}, SO_4^{2-}, or $H_2PO_4^-$ ions (as TBA^+ salts) was added, the NH protons of the urea and thiourea groups displayed significant downfield shifts. Addition of AcO^- also induced some downfield shifts of the NH signals, due to the high basicity and complementary Y shape of AcO^-, as in the case of other (thio)urea ligands.[15] The very alkaline F^- ions caused the NH signals to broaden (at lower equivalents of the anion) and disappear (at more F^- ions), which has also been discussed in the literature.[16] Other anions (HSO_4^-, Br^-, I^-, NO_3^-, PF_6^-, and ClO_4^-) resulted in only slight or no changes (Fig. S1, ESI†).

^{1}H NMR titration experiments were subsequently carried out for L^2 and selected anions, and the association constants were determined using the WinEQNMR program (errors are less than 10% in all cases).[17] The association constant of L^2 to acetate ions was calculated to be $\log K = 3.06$ M^{-1} based on the 1 : 1 binding mode (Fig. S2–S4, ESI†). For SO_4^{2-}, the association constant ($\log K = 3.54$ M^{-1}) was also obtained by fitting the titration curves to a 1 : 1 binding mode (Fig. S5 and S6, ESI†) which was further confirmed from the Job plot. This binding affinity is somewhat smaller than that of the trisurea L^1 ligand for SO_4^{2-} ($\log K = 4.60$ M^{-1} in DMSO). The binding constant for $H_2PO_4^-$ could not be calculated because it is unable to determine the binding mode due to the coexistence of multiple equilibria, possibly caused by the different protonation states of the phosphate ion.

Notably, when 0.1 equiv. of PO_4^{3-} ions (as Na^+ salt, in DMSO-d_6–5% water) was added to the solution of L^2, a slow exchange process was observed in the ^{1}H NMR spectrum. A new set of signals appeared besides those of the ligand L^2.[8d] The intensity of the new signals increased gradually with the addition of PO_4^{3-} ions, while the signals of free L^2 decreased and disappeared completely after 0.5 equiv. of the PO_4^{3-} ions were added.

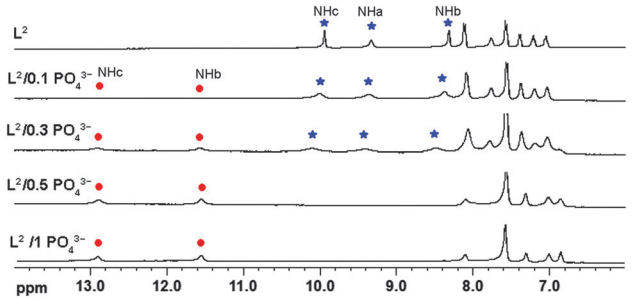

Fig. 2 ^{1}H NMR titration of L^2 (5 mM) with Na_3PO_4 (DMSO-d_6-5% water, 400 MHz).

There were no further changes with the addition of more anions, indicating that the ligand (L^2) and PO_4^{3-} ions adopt a 2 : 1 binding mode (Fig. 2). This is similar to the phosphate coordination behavior of the analogous ligand L^1. However, the thiourea (NHa) protons disappeared during the titration process, suggesting that the more acidic thiourea may undergo deprotonation in the presence of the basic anion. This phenomenon was observed in a number of thiourea receptors, *e.g.*, Dehaen *et al.* reported a series of oxacalix[2]arene[2]-pyrimidine-based bis(thio)ureido receptors, where the more acidic NH proton resonance disappeared when 1.0 equiv. of $H_2PO_4^-$ or AcO^- ions was added to the host solution.[6f] Fabbrizzi *et al.* reported that a thiourea receptor led to the formation of complexes which are intrinsically stable but are unstable with respect to HX (X = F^-, CH_3COO^-, $H_2PO_4^-$, $C_6H_5COO^-$) release and deprotonation, while for urea the situation is caused only by fluoride.[6g]

^{1}H NMR titration of Cl^- ions to ligand L^2 indicated interesting interactions between the ligand and the anion. When up to 1.0 equiv. of chloride ions were added to L^2, the NH signals of the two terminal urea groups showed significant downfield shifts (Fig. 3), while the central thiourea NH peaks displayed almost no change, suggesting that the Cl^- ion was firstly bound by the two urea groups (NHb and NHc). Then, when more chloride ions were added, the urea NHb and NHc signals continued to move to a lower field and reached a plateau after addition of about 10 equiv. of the anion. Meanwhile, the thiourea NHa protons also began to change after 1.0 equiv. of Cl^- ions was added, indicative of a second chloride ion being bound by the thiourea group. The change in the thiourea was not complete even after addition of 100 equiv. of the chloride ions. This binding mode is similar to that of the oligo(thiourea) receptors designed by Pfeffer *et al.*[18]

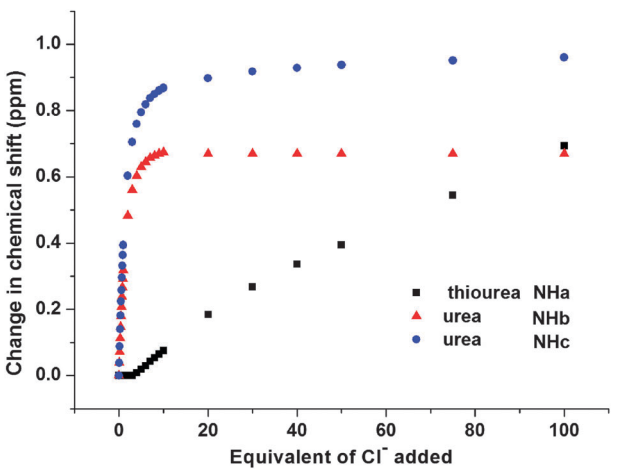

Fig. 3 Change in the chemical shifts of NH signals upon titration of L^2 with Cl^- ions.

Table 1 Association constants K_a (M^{-1}) for receptors L^2 and L^3 toward various anions in DMSO-d_6-0.5% water at 298 K (errors < 15%)

	SO_4^{2-}	$H_2PO_4^-$	PO_4^{3-}	AcO^-	Cl^-
L^2	3.54	—[a]	5.85[b]	3.06	2.47
L^3	3.17	—[a]	—[c]	—[c]	—[d]

[a] Data could not be fitted to any model. [b] Data for DMSO-25% water by UV-vis titration (the data for DMSO-d_6-0.5% water could not be fitted). [c] Peak broadening. [d] No significant shift of NH peaks.

The changes in the urea NHb and NHc protons were fitted to the 1 : 1 binding mode, with a binding constant of $\log K_1$ = 2.47 M^{-1} (Table 1, Fig. S7 and S8, ESI†). The titration results are consistent with the preliminary crystal structure of a dichloride complex of L^2, in which one chloride ion is coordinated by the two urea groups while the other chloride is bound by the central thiourea group. Unfortunately, the crystal data are too poor to allow for further refinement (Fig. S18, ESI†). Moreover, this 1 : 2 binding is different from that of the trisurea analogue L^1, which binds only one chloride ion by using all of the three urea groups. The difference may be attributed to the weaker tendency of the thiourea sulfur to form hydrogen bonds with the aryl rings, thus leading the NH donors to twist away and bind another Cl^- ion. On the other hand, the results also demonstrated the interesting binding behavior of the mixed urea–thiourea ligand L^2 toward different anions, which shows considerable affinity to less basic anions but deprotonation of thiourea with strongly basic anions.

The anion binding behavior of the tristhiourea ligand L^3 was also tested (Fig. S9, ESI†). When 1.0 equiv. of AcO^-, $H_2PO_4^-$, or F^- ions (as TBA^+ salt) was added to the solution of L^3, the NH signals of ligand L^3 broadened or disappeared. During the titration of PO_4^{3-} ions, the NHa, NHb and NHc proton signals broadened, and these signals disappeared completely after 0.5 equiv. of PO_4^{3-} ions (as TBA^+ salt) were added (Fig. S10, ESI†), suggesting that the acidic thiourea NH protons were deprotonated in the presence of the basic anion. Meanwhile, the H3, H6 and H7 protons on the aromatic rings (see Scheme 1 for the numbering of the protons) showed significant downfield shifts, which may result from the enhanced intramolecular C–H···S interactions caused by the increased electron density on sulfur upon the deprotonation of the thiourea groups. Besides, there is an obvious color change from yellow to red (Fig. S11, ESI†). Addition of sulfate ions (as TBA^+ salt) to ligand L^3 resulted in downfield shifts of the NH signals up to 1.0 equiv. of SO_4^{2-} (Fig. S12 and S13, ESI†). However, it is noticeable that the NH protons of L^3 also showed complete deprotonation after 2.0 equiv. of the SO_4^{2-} ions were added, which is accompanied by the downfield shifts of the H3, H6 and H7 protons as in the case of

the phosphate ion. The association constant of L^3 in the binding of the first equivalent of SO_4^{2-} (1:1 binding mode) was calculated to be $\log K = 3.17\ M^{-1}$ (Table 1).

UV-vis studies

The anion binding properties of the ligands L^2 and L^3 were further studied using UV-vis titration experiments in DMSO. Among the various anions examined (added as TBA^+ salts), only PO_4^{3-}, SO_4^{2-}, F^-, $H_2PO_4^-$ and AcO^- induced bathochromic shifts. Other anions (Cl^-, Br^-, I^-, PF_6^-, NO_3^-, HSO_4^-, ClO_4^-) resulted in slight or no changes (Fig. 4, Fig. S14, ESI†), which is in agreement with the NMR results.

The interaction between L^2 and PO_4^{3-} (as Na^+ salt) was investigated using the UV-vis titration method. The Job plot curve indicates a 2:1 (host–guest) binding mode (Fig. S15, ESI†), which is consistent with the results of NMR titration (in DMSO-d_6–5% water). However, in a more competitive environment (DMSO–25% water), the spectrum reached a plateau after 1.0 equiv. of PO_4^{3-} ions (as Na^+ salt) were added (Fig. S16, ESI†), with an association constant of $\log K = 5.85\ M^{-1}$ by fitting the titration curve to a 1:1 binding mode (Table 1).

For the tristhiourea L^3 ligand, addition of PO_4^{3-}, F^-, $H_2PO_4^-$, SO_4^{2-}, and AcO^- ions resulted in a clear red-shift of the low-wavelength band, from 357 nm to about 402 nm (Fig. 4), with a concomitant color change. This is consistent with the deprotonation of the thiourea groups by the basic anions. Such deprotonation processes of the acidic thiourea protons have been reported for many thiourea-based receptors.[6f,g] In contrast, no deprotonation was observed for the bisurea–monothiourea ligand L^2 even in the presence of the strongly basic phosphate anion. Fig. S17 (ESI†) shows [A(335 nm)/A(410 nm)] upon the addition of 1.0 equiv. of various anions into the DMSO-d_6–0.5% water solution of ligands L^2 and L^3.

In summary, the tridentate monothiourea–bisurea ligand, L^2, and tris(thiourea) ligand, L^3, have been synthesized and their anion coordination properties investigated. Both the solid-state and solution binding modes of the two ligands (and the trisurea L^1 ligand reported previously) show significant differences. The crystal structure of the 2:2 anion complex **1** with ligand L^2 shows an unusual $(H_2PO_4{\cdot}HPO_4)^{3-}$ dimer sandwiched between two ligand molecules. ^{1}H NMR and UV-vis titration experiments demonstrated that the mixed urea–thiourea ligand L^2 can form a 2:1 complex with an orthophosphate ion as in the case of the tris(urea) analogue. However, the tris(thiourea) L^3 ligand undergoes deprotonation in the presence of basic anions accompanied by color change of the solution, while the urea analogues show deprotonation only in the presence of an excess of the strongly basic anions (*e.g.* PO_4^{3-}).

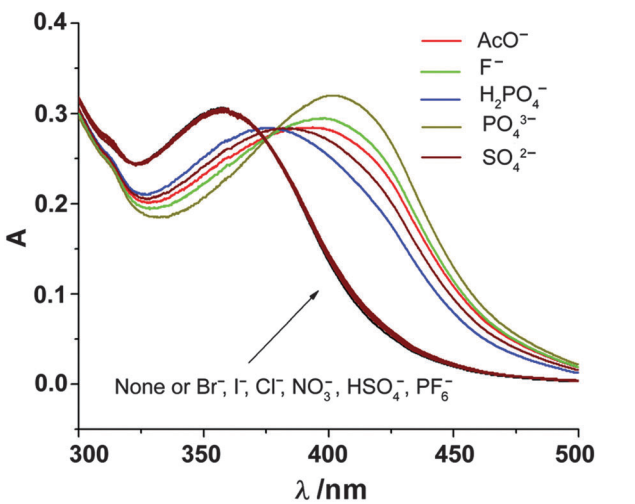

Fig. 4 UV-vis spectra of L^3 (1.0×10^{-5} M) in DMSO-0.5% water (v/v), alone and in the presence of 1.0 equiv. of various anions (added as TBA salts, PO_4^{3-} as Na^+ salt).

Experimental section

Synthesis of ligand L^2

A solution of 1,3-bis(2-aminophenyl)thiourea (**1b**, see ESI† for the synthesis) (0.26 g, 1.0 mmol) in 100 mL THF was added dropwise into a 130 mL refluxing THF solution of *p*-nitrophenyl isocyanate (0.36 g, 2.2 mmol). The mixture was refluxed for 5 h and the precipitate was filtered off and washed several times with toluene and diethyl ether and then dried under vacuum to yield pure L^2 as a yellow solid (0.46 g, 78%). M.p.: 227 °C. ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ 10.01 (s, 2H, Hc), 9.37 (s, 2H, Ha), 8.323 (s, 2H, Hb), 8.16 (d, J = 8.0 Hz, 4H, H8), 7.81 (d, 2H, H3), 7.64 (d, J = 8.0 Hz, 4H, H7), 7.43 (d, J = 8.0 Hz, 4H, H6), 7.23 (t, J = 4.0 Hz, 4H, H4), 7.23 (t, J = 4.0 Hz, 4H, H5). ^{13}C NMR (100 MHz, DMSO-d_6): δ 157.7 (CS), 151.7 (CO), 146.4 (C), 139.7 (C), 134.0 (C), 132.4 (C), 130.5 (CH), 129.0 (CH), 127.7 (CH), 122.9 (CH). Anal. calcd for $C_{27}H_{22}N_8O_6S$: C, 55.28; H, 3.78; N, 19.10. Found: C, 55.18; H, 3.66; N, 19.02%. ESI-MS: m/z 585.1 (17%), $[L^2 - H]^-$.

Synthesis of ligand L^3

1,3-Bis(2-aminophenyl)thiourea (0.10 g, 0.4 mmol) was added to a solution of *p*-nitrophenyl isothiocyanate (0.17 g, 0.9 mmol) in dry CH_3CN (130 mL). The mixture was stirred at r.t. for about 30 h. The precipitate was filtered off and washed several times with toluene and diethyl ether and then dried under vacuum to yield pure L^3 as a yellow solid (0.20 g, 81%). M.p.: 184 °C. ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ 10.57 (s, 2H, Hc), 9.65 (s, 2H, Ha), 9.44 (s, 2H, Hb), 8.18 (d, J = 8.8 Hz, 4H, H8), 7.88 (d, J = 8.8 Hz, 4H, H7), 7.47 (m, 4H, H3 + H6), 7.25 (m, 4H, H4 + H5). ^{13}C NMR (100 MHz, DMSO-d_6): δ 180.7 (CS), 180.1 (CS), 148.1 (C), 142.7 (C), 134.4 (C), 134.0 (C), 128.3 (CH), 128.0 (CH), 126.9 (CH), 126.7 (CH), 124.5 (CH), 122.0 (CH). Anal. calcd for $C_{27}H_{22}N_8O_4S_3$: C, 52.41; H, 3.58; N, 18.11. Found: C, 52.23; H, 3.43; N, 18.05%. ESI-MS: m/z 619.1 (12%), $[L^3 + H]^+$; 641.1 (100%), $[L^3 + Na]^+$.

Synthesis of $(TBA)_3[(L^2)_2{\cdot}HPO_4{\cdot}H_2PO_4]{\cdot}2.9CH_2Cl_2$ (1)

L^2 (10 mg, 0.02 mmol) was mixed with $(TBA)H_2PO_4$ (0.05 mmol) in CH_2Cl_2 (4 mL). After stirring for 1 h at room temperature, a clear light yellow solution was obtained. Slow vapor diffusion of diethyl ether into this solution provided yellow crystals of complex **1** within 3 days (11 mg, 51%). Anal. calcd for

$(TBA)_3[(L^2)_2{\cdot}HPO_4{\cdot}H_2PO_4]{\cdot}2CH_2Cl_2$ ($C_{104}H_{159}Cl_4N_{19}O_{20}P_2S_2$): C, 55.19; H, 7.08; N, 11.76%. Found: C, 55.10; H, 7.02; N, 11.68%.

Crystal data for **1**: $C_{104.9}H_{160.8}Cl_{5.8}N_{19}O_{20}P_2S_2$, M = 2339.80, monoclinic, space group $P2/c$, a = 17.251(3), b = 12.4954(19), c = 28.007(4) Å, β = 97.612(3)°, V = 5984.0(15) Å^3, Z = 2, T = 293(2) K, D_{calc} = 1.299 g cm^{-3}, $F(000)$ = 2488, μ = 0.272 mm^{-1}, R_1 [$I > 2\sigma(I)$] = 0.0845, wR_2 [$I > 2\sigma(I)$] = 0.2508.

Notes and references

1 (*a*) J.-M. Lehn, *Acc. Chem. Res.*, 1978, **11**, 49–57; (*b*) J.-M. Lehn, *Supramolecular Chemistry: Concepts and Perspectives*, VCH, Weinheim, 1995; (*c*) K. Bowman-James, *Acc. Chem. Res.*, 2005, **38**, 671–678; (*d*) *Anion Coordination Chemistry*, ed. K. Bowman-James, A. Bianchi and E. García-España, Wiley-VCH, Weinheim, 2011.

2 For selected reviews and articles, see: (*a*) P. D. Beer and P. A. Gale, *Angew. Chem., Int. Ed.*, 2001, **40**, 486–516; (*b*) P. A. Gale and T. Gunnlaugsson, *Chem. Soc. Rev.*, 2010, **39**, 3595–3596; (*c*) T. Shioya, S. Nishizawa and N. Teramae, *J. Am. Chem. Soc.*, 1998, **120**, 11534–11535; (*d*) R. Custelcean, *Chem. Commun.*, 2008, 295–307; (*e*) S. O. Kang, R. A. Begum and K. B. James, *Angew. Chem., Int. Ed.*, 2006, **45**, 7882–7894; (*f*) For latest reviews on anion chemistry, see a thematic issue: *Chem. Soc. Rev.*, 2010, 3581–4008.

3 (*a*) R. Custelcean, *Chem. Soc. Rev.*, 2010, **39**, 3675–3685; (*b*) M. C. Etter, *Acc. Chem. Res.*, 1990, **23**, 120–126; (*c*) M. C. Etter, Z. Urbakzyk-Lipkowska, M. Zia-Ebrahimi and T. W. Panunto, *J. Am. Chem. Soc.*, 1990, **112**, 8415–8426.

4 P. J. Smith, M. V. Reddington and C. S. Wilcox, *Tetrahedron Lett.*, 1992, **31**, 6085–6088.

5 E. Fan, S. A. V. Arman, S. Kincaid and A. D. Hamilton, *J. Am. Chem. Soc.*, 1993, **115**, 369–370.

6 (*a*) R. Martínez-Máñez and F. Sancenón, *Chem. Rev.*, 2003, **103**, 4419–4476; (*b*) A. E. Hargrove, S. Nieto, T. Z. Zhang, J. L. Sessler and E. V. Anslyn, *Chem. Rev.*, 2011, **111**, 6603–6782; (*c*) J. W. Steed, *Chem. Soc. Rev.*, 2009, **38**, 506–519; (*d*) M. Wenzel, J. R. Hiscock and P. A. Gale, *Chem. Soc. Rev.*, 2012, **41**, 480–520; (*e*) I. Ravikumar and P. Ghosh, *Chem. Soc. Rev.*, 2012, **41**, 3077–3098; (*f*) W. V. Rossom, J. Caers, K. Robeyns, L. V. Meervelt, W. Maes and W. Dehaen, *J. Org. Chem.*, 2012, **77**, 2791–2797; (*g*) D. E. Gómez, L. Fabbrizzi, M. Licchelli and E. Monzani, *Org. Biomol. Chem.*, 2005, **3**, 1495–1500.

7 (*a*) S. J. Brooks, P. A. Gale and M. E. Light, *Chem. Commun.*, 2005, 4696–4697; (*b*) S. J. Brooks, P. A. Gale and M. E. Light, *CrystEngComm*, 2005, **7**, 586–591.

8 (*a*) S. Li, M. Wei, X. Huang, X.-J. Yang and B. Wu, *Chem. Commun.*, 2012, **48**, 3097–3099; (*b*) C. Jia, B. Wu, S. Li, X. Huang, Q. Zhao, Q.-S. Li and X.-J. Yang, *Angew. Chem., Int. Ed.*, 2011, **50**, 486–490; (*c*) S. Li, C. Jia, B. Wu, Q. Luo, X. Huang, Z. Yang, Q.-S. Li and X.-J. Yang, *Angew. Chem., Int. Ed.*, 2011, **50**, 5721–5724; (*d*) C. Jia, B. Wu, S. Li, Z. Yang, Q. Zhao, J. Liang, Q.-S. Li and X.-J. Yang, *Chem. Commun.*, 2010, **46**, 5376–5378.

9 F. G. Bordwell, *Acc. Chem. Res.*, 1988, **21**, 456–463.

10 (*a*) P. A. Gale, J. R. Hiscock, C. Z. Jie, M. B. Hursthouse and M. E. Light, *Chem. Sci.*, 2010, **1**, 215–220; (*b*) P. S. Lakshminarayanan, I. Ravikumar, E. Suresh and P. Ghosh, *Chem. Commun.*, 2007, 5214–5216; (*c*) V. Amendola, M. Boiocchi, D. Esteban-Gómez, L. Fabbrizzi and E. Monzani, *Org. Biomol. Chem.*, 2005, **3**, 2632–2639; (*d*) Md. A. Hossain, M. Işıklan, A. Pramanik, M. A. Saeed and F. R. Fronczek, *Cryst. Growth Des.*, 2012, **12**, 567–571; (*e*) A. Rajbanshi, S. Wan and R. Custelcean, *Cryst. Growth Des.*, 2013, **13**, 2233–2237.

11 P. Dydio, T. Zieliński and J. Jurczak, *Org. Lett.*, 2010, **12**, 1076–1078.

12 M. Wei, B. Wu, L. Zhao, H. Zhang, S. Li, Y. Zhao and X.-J. Yang, *Org. Biomol. Chem.*, 2012, **10**, 8758–8761.

13 S. Dalapati, Md. A. Alam, S. Jana and N. Guchhait, *CrystEngComm*, 2012, **14**, 6029–6034.

14 C. A. Ilioudis, D. G. Georganopoulou and J. W. Steed, *CrystEngComm*, 2002, **4**, 26–36.

15 (*a*) P. A. Gale, S. E. García-Garrido and J. Garric, *Chem. Soc. Rev.*, 2008, **37**, 151–190; (*b*) S. I. Sasaki, M. Mizuno, K. Naemura and Y. Tobe, *J. Org. Chem.*, 2000, **65**, 275–283; (*c*) J. M. Benito, M. Gómez-García, J. L. Jiménez Blanco, C. Ortiz Mellet and J. M. García Fernández, *J. Org. Chem.*, 2001, **66**, 1366–1372.

16 (*a*) M. Boiocchi, L. D. Boca, D. Esteban-Gómez, L. Fabbrizzi, M. Licchelli and E. Monzani, *Chem.–Eur. J.*, 2005, **11**, 3097–3104; (*b*) G. W. Bates, P. A. Gale and M. E. Light, *Chem. Commun.*, 2007, 2121–2123; (*c*) E. J. Cho, J. W. Moon, S. W. Ko, J. Y. Lee, S. K. Kim, J. Yoon and K. C. Nam, *J. Am. Chem. Soc.*, 2003, **125**, 12376–12377.

17 M. J. Hynes, *J. Chem. Soc., Dalton Trans.*, 1993, 311–312.

18 A. J. Lowe, B. M. Long and F. M. Pfeffer, *J. Org. Chem.*, 2012, **77**, 8507–8517.

