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# Oligozwitterions in coordination polymers and frameworks – a structural view

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Zwitterions may take many forms and have found many applications, some of which are based on their capacity to act as ligands for a wide variety of metal ions. This brief review describes recent developments in this coordination chemistry involving oligozwitterion species, as reflected in solid state X-ray structural studies of the coordination polymers and frameworks formed and with a particular focus on uranyl ion systems.

## 1. Introduction

Zwitterions are neutral molecules in which the electronic structure is such that they can be considered to contain equal numbers of sites with, at least formally, opposite charges of unity. One of the simplest examples of such a species is that of trimethylammonioacetate,  $[(\text{CH}_3)_3\text{NCH}_2\text{CO}_2]$ , originally termed “betaine” due to its ready isolation from sugar beet,<sup>1</sup> with one positive centre, N(+), and one negative,  $\text{CO}_2(-)$ . A large family of “betaines”, some, like trimethylammonioacetate, of natural origin<sup>2</sup> and others purely synthetic, is now recognised.<sup>1</sup> The naturally occurring betaines have important biological roles in the regulation of osmotic pressure across cell membranes and as methylation agents but their capacity to act as metal ion binding ligands has rendered them and many analogues of much broader interest. Although the  $\text{pK}_a$  of  $[(\text{CH}_3)_3\text{NCH}_2\text{CO}_2\text{H}]^+$ , (1.8<sup>1</sup>), indicates that the carboxylate centre of trimethylammonioacetate is an approximately 1000-fold weaker base than acetate, early structural studies<sup>3–10</sup> involving a wide range of transition and main-group metal ions showed that trimethylammonioacetate and various similar mono-zwitterions (Fig. 1)<sup>11,12</sup> readily formed isolable complexes and could be considered comparable in their donor capacity to anionic carboxylates, an issue discussed in more detail ahead. There is of course no necessity to limit the Lewis base site of a zwitterion to a carboxylate group, nor to limit the positive site to an ammonium centre and the applications of zwitterion complexes in catalysis have been considerably developed through synthetic variations in these regards.<sup>13</sup> Further, multiple zwitterion units can be incorporated in a single ligand, offering particular advantages in the synthesis of coordination polymers and frameworks.<sup>14–17</sup> It is this last, recent

development of zwitterion coordination chemistry that is the principal focus of this Perspective.

## 2. Simple zwitterions where a single carboxylate group is the metal–ion binding site

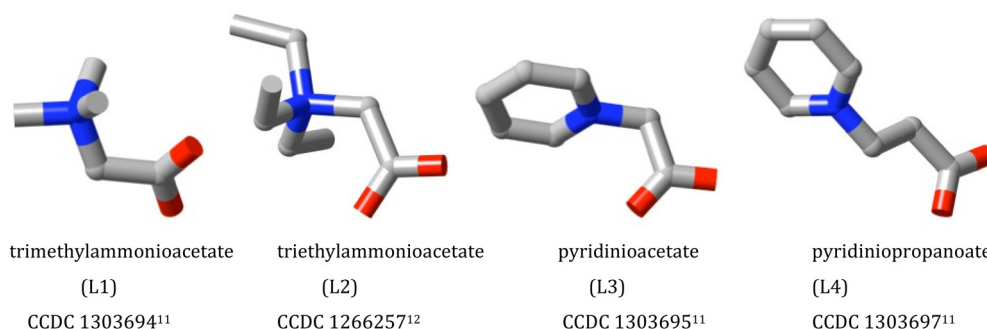
An obvious omission in the introductory remarks above is that of the zwitterion chemistry of amino acids, formally a matter for inclusion in this section. This, however, is a vast<sup>18–21</sup> and exceptionally important topic demanding separate treatment and, as well, is excluded here by limiting considerations to where the N-atom of the positive site of the zwitterion cannot become involved, through deprotonation, in metal ion coordination.

Although very little information is available concerning comparison of stability constants for complexes of betaine zwitterions and non-zwitterion analogues,<sup>22</sup> the broad early structural studies<sup>3–10</sup> of transition and main group metal ion complexes of various carboxylato-betaines established that M–O bond lengths for analogous species generally overlapped, indicating that in the absence of solvent effects (as in solid crystals), no real distinction of the donor strengths could be drawn. These studies did reveal some subtle differences (Fig. 2),<sup>23–25</sup> for example, in that the OCO bond angles in betaines are usually 1–2° larger than in anionic carboxylates, possibly favouring their action as bridging ligands, though the versatility of both types is expressed in the same range of unidentate ( $\kappa^1\text{O}$ ), chelating ( $\kappa^2\text{O},\text{O}'$ ), bridging ( $\kappa^1\text{O};\kappa^1\text{O}'$ ) and chelating–bridging ( $\kappa^2\text{O},\text{O}';\kappa^1\text{O}'$ ) bonding modes being shown. It is possible<sup>5,6</sup> to qualify these designations of bonding modes with the terms *syn* and *anti* based upon the assumption that the O-donor atom is trigonal and that there are two disposition of its lone pairs, leading to the description of the  $\kappa^1\text{O};\kappa^1\text{O}'$  mode, for example, as *syn;anti* in most cases, but it is not always clear in general that this assumption is justified.<sup>26</sup>

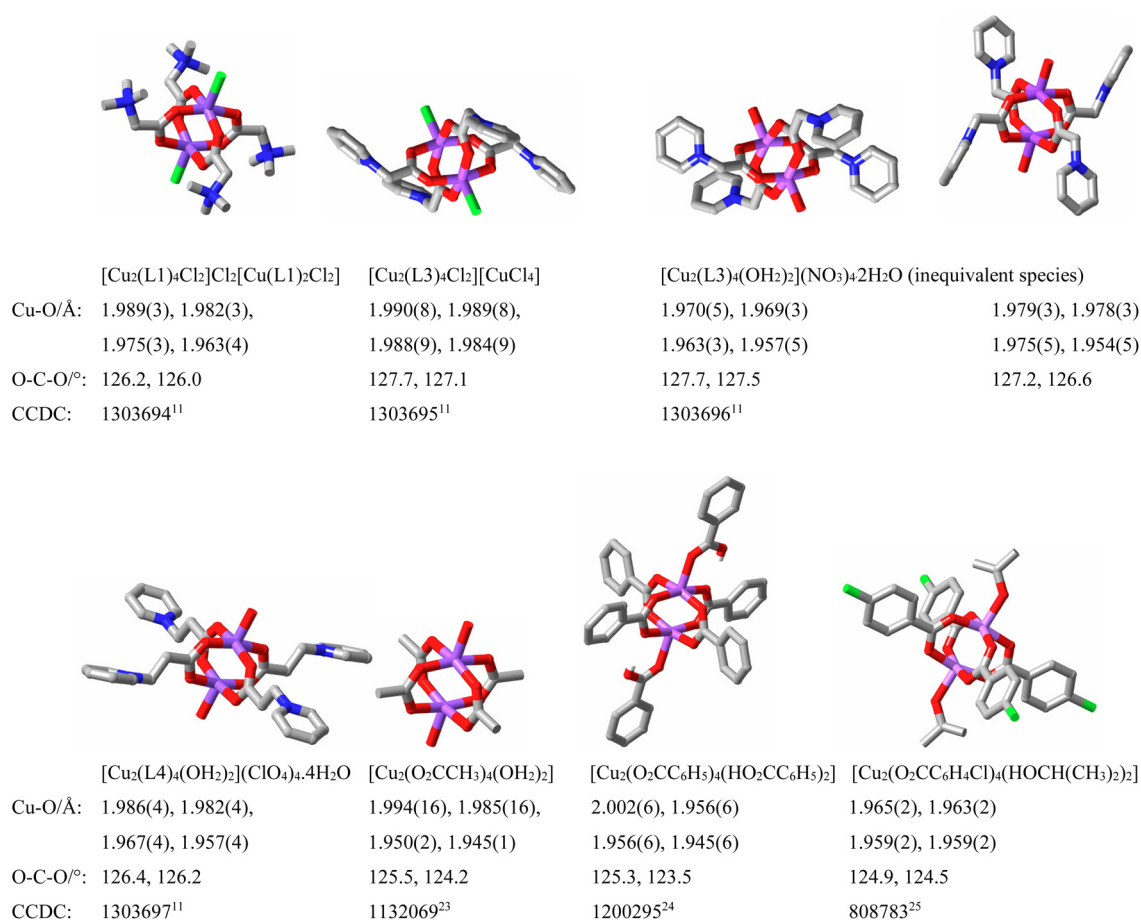
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**Fig. 1** Trimethylammonioacetate (betaine) and three related species used in early studies of zwitterion coordination chemistry with transition and main group metals. The ligands are shown in the conformations observed in crystal structures with the indicated CCDC deposition numbers. In most cases, H-atom coordinates are not available, so for consistency all are shown as stick representations without hydrogen atoms (C = grey, N = blue, O = red).



**Fig. 2** Structural parameters for some binuclear Cu(II) carboxylate species (involving  $\mu_2$ -syn,syn- $\kappa^1\text{O};\kappa^1\text{O}'$  bridging) derived from both anionic and zwitterionic donors, illustrating their generally very close character. Ligand numbering is as in Fig. 1. (C = grey, blue = N, red = O, violet = Cu.)

A notable feature of simple betaine (and monocarboxylate) metal ion complexation is the fact that coordination polymers can be obtained (*e.g.* ref. 5, 6a, 9 and 10) even when only one carboxylate site is available, reflecting the rather special nature of the carboxylate group. Such materials involving paramagnetic metal ions have proven to be of particular interest for

their magnetic behaviour and physical properties.<sup>27</sup> More recent interest in betaine chemistry, however, has been concerned with their application in “task specific” ionic liquids.<sup>28–32</sup> Protonation of trimethylammonioacetate, for example, produces a cation which can be paired with an appropriate anion, *e.g.* bis(trifluoromethylsulfonyl)amide to give an



ionic liquid highly efficient in the dissolution of metal oxides both because of its acidity and the complexing ability of the zwitterion released by the consumption of acid by the oxide. This work has led in particular to the structural characterisation of uranyl ion complexes of simple zwitterions,<sup>28b,29–31</sup> these structures serving to illustrate all four coordination modes of the carboxylate units referred to above (Fig. 3). As found for transition and main group metal ions, examination of U–O bond lengths provides no clear evidence that zwitterion carboxylate-O should be considered to differ in donor capacity towards U(vi) from an anionic carboxylate. Such comparisons are complicated by the fact that the nature and symmetry of

the environment of any U–O unit must differ in the two types of complex but in the complexes  $[\text{UO}_2(\text{imbet})_3][(\text{CF}_3\text{SO}_2)\text{N}]_2$ ,<sup>28b</sup> (imbet = 3-methylimidazoliumacetate = L5) (MeImH)  $[\text{UO}_2(\text{O}_2\text{CCH}_3)_3]$ ,<sup>33</sup> (MeImH = protonated 2-methylimidazole) and  $\text{Na}[\text{UO}_2(\text{O}_2\text{CCH}_3)_3]$ ,<sup>34</sup> for example, the mean equatorial U–O bond lengths of 2.471(3), 2.47(1) and 2.469(9) Å, respectively, are identical within experimental uncertainty.

In the complexes shown in Fig. 3, further possible variations in the betaine structure are exemplified and others are certainly known,<sup>13,35</sup> including those where aromatic thiolate replaces the carboxylate group.<sup>36</sup> In nearly all such cases the positive and negative charge centres are insulated from one



**Fig. 3** Coordination modes observed for simple betaines in uranyl ion complexes: (a)  $\kappa^2\text{O},\text{O}'$  chelation in mononuclear  $\text{K}[\text{UO}_2(\text{L1})\text{Cl}_3]$ ; (b) part of the polymer chain present in  $[\text{UO}_2\text{Cl}_2(\text{L1})(\text{OH}_2)]$ , showing  $\kappa^1\text{O};\kappa^1\text{O}'$  bridging (*syn/anti*); (c) the dimeric species present in  $[(\text{UO}_2)_2\text{Cl}_2(\text{L5})_4][\text{N}(\text{SO}_2\text{CF}_3)_2]_2$  (L5 = imbet = 3-methylimidazoliumacetate) where both  $\kappa^2\text{O},\text{O}'$  chelation and  $\kappa^1\text{O};\kappa^1\text{O}'$  bridging occur; (d) the trinuclear unit present in  $[(\text{UO}_2)_3(\text{L1})_2(\text{NO}_3)_6(\text{OH}_2)_2]\cdot\text{H}_2\text{O}$  where  $\kappa^1\text{O}$  coordination accompanies  $\kappa^1\text{O};\kappa^1\text{O}'$  bridging; (e) part of the polymer chain of heterometallic  $[\text{UO}_2\text{Li}(\text{L1})_4][\text{N}(\text{SO}_2\text{CF}_3)_2]_3$  where bridging of the two metal ions involves both  $\kappa^1\text{O};\kappa^1\text{O}'$  and  $\kappa^2\text{O},\text{O}';\kappa^1\text{O}'$  coordination; (f) tris  $\kappa^2\text{O},\text{O}'$  chelation in  $[\text{UO}_2(\text{L5})_3][\text{N}(\text{SO}_2\text{CF}_3)_2]_2$ , showing U(vi) is not limited to pentagonal-bipyramidal coordination in betaine complexes; (g) part of the polymer chain in  $[(\text{UO}_2)_2(\text{L6})_4(\text{OH})][\text{N}(\text{SO}_2\text{CF}_3)_2]_3$ , (L6 = pyrmbet = *N*-methylpyrrolidiniumacetate), where both  $\kappa^2\text{O},\text{O}'$  and  $\kappa^1\text{O};\kappa^1\text{O}'$  binding occur together; (h) exclusive  $\kappa^1\text{O}$  coordination in  $[\text{UO}_2(\text{L7})_3(\text{OH}_2)_2][\text{N}(\text{SO}_2\text{CF}_3)_2]_2$  (L7 = phosbet = trimethylphosphonioacetate); (i) the binuclear unit found in  $[(\text{UO}_2)_2(\text{L7})_6][\text{N}(\text{SO}_2\text{CF}_3)_2]_4$ , where three different coordination modes,  $\kappa^1\text{O}$ ,  $\kappa^2\text{O},\text{O}'$  and  $\kappa^1\text{O};\kappa^1\text{O}'$  occur together. (C = grey, blue = N, red = O, green = Cl, violet = P, yellow = U.)



another by saturated organic links but are sufficiently close for these zwitterions to be considered, for example, as models for ion pairs.<sup>37</sup> A much closer approach of the charge centres is possible in non-betaine species such as pyridine *N*-oxide, where a major canonical form is considered to be that where N(+) and O(−) are directly linked by a single bond.<sup>38</sup> The high electron density on the O centre is considered as a crucial factor giving rise to the extended studies that have been made of the coordination chemistry of pyridine *N*-oxide.<sup>39</sup> To consider pyridine *N*-oxide as zwitterion is to foreshadow similar consideration of a substantial number of other ligands of much greater importance due to their widespread utility in contemporary chemistry, taken thus as a major advance in zwitterion chemistry.<sup>21</sup>

### 3. Zwitterions with negatively charged donor atoms located in close proximity to the positive centres – “vicinal zwitterion ylides”

The valence-bond canonical forms for a broad range of neutral ligands such as borylenes,<sup>40</sup> carbenes,<sup>41</sup> nitrenes,<sup>42</sup> sydnonnes<sup>43</sup> and phosphorus ylides<sup>44</sup> include species involving charge separation.<sup>21</sup> Even a ligand as simple as carbon monoxide can be considered to involve the canonical form (−)C≡O(+), a form which, with its opposite charges being located on adjacent atoms, can be termed a “vicinal zwitterion”, a description applicable also to more complicated ligands.<sup>21</sup> Whether or not the charge-separated forms should be considered to be dominant and the molecules therefore considered as true zwitterions is a matter to be resolved through structural, spectroscopic and theoretical studies<sup>45</sup> but with the probable exception of borylenes,<sup>21</sup> this appears to be true in many cases of the four other categories just mentioned. Carbenes and in particular *N*-heterocyclic carbenes (NHCs) have an extensive and well-developed coordination chemistry involving numerous applications in catalysis,<sup>41,45,46</sup> whereas sydnonnes, although

much longer known<sup>43a,b</sup> than NHCs, have only relatively recently come under deliberate study as metal ion complexing agents<sup>43c</sup> and so serve as a subject of greater novelty for the present discussion. Interestingly, metal-catalysed reactions of some sydnonnes have been used to provide new NHCs.<sup>47</sup>

While structural studies of singlet carbenes as free ligands are much less common than those of carbene complexes (Fig. 4),<sup>41,45,48–51</sup> the opposite is true for sydnonnes. This is due to the ready synthesis and stability of functionalised sydnonnes<sup>52</sup> as well as to their versatility as synthetic intermediates, their biological activity and their numerous applications.<sup>43,47</sup> The family of sydnonnes consists of derivatives of 5-oxo-1,2,3-oxadiazole (Fig. 5(a and b)), the parent usually being considered to be the 3-phenyl derivative (obtained by cyclisation of *N*-nitroso-*N*-phenyl glycine), as the unfunctionalised molecule is unknown. The term “mesoionic” was proposed as a descriptor for sydnonnes,<sup>43b</sup> since the valence bond canonical representations for the 5-oxo-1,2,3-oxadiazole ring involve charge separations of various forms (Fig. 5(c)) where both directly bonded N<sup>(+)</sup>–N<sup>(−)</sup>, N<sup>(+)</sup>–C<sup>(−)</sup> and more remote N<sup>(+)</sup>–O<sup>(−)</sup> pairs appear. The crystal structure of a simple sydnone, 3-tolylsydnone,<sup>53</sup> shows (Fig. 5(d)) bond lengths of this ring which all lie between single and double bond values, indicating that the charges must be significantly delocalised, although calculations of charge distributions in 3-phenylsydnone<sup>54</sup> have shown that most of the negative charge resides on the exocyclic O-atom, with some on N2 and very little on C4. Consistent with this, examination of the weak interactions within the crystal of 3-tolylsydnone using CrystalExplorer<sup>55</sup> shows that the only interactions exceeding dispersion are O⋯HC type, the shorter involving the exocyclic-O and both phenyl and sydnone H atoms (Fig. 5(e)).

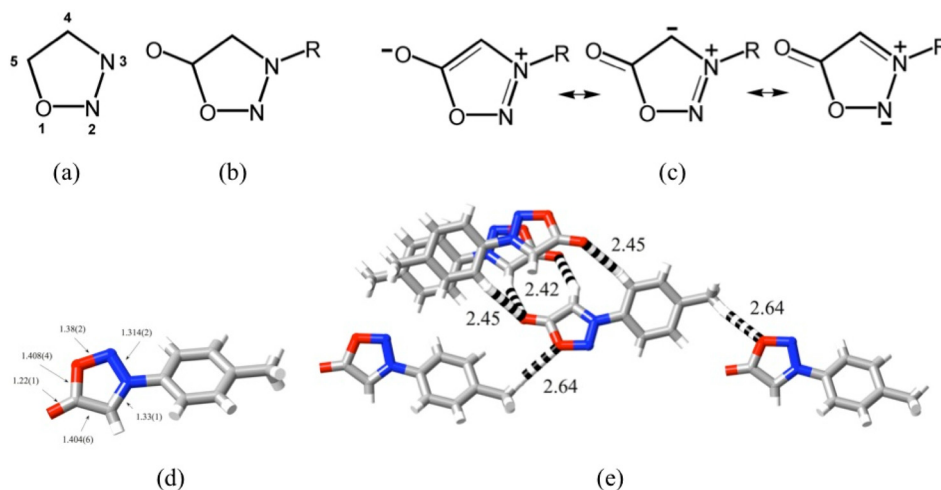
While it appears that in principle a sydnone might act as a C-, N- or O-donor ligand, early attempts to form transition metal complexes through solid state reactions were of limited success and any complexes formed were found to dissociate completely in polar solvents,<sup>56</sup> indicating that neutral sydnonnes, unlike NHCs, must be rather weak ligands (though dissociation in water may have been assisted by the low aqueous



**Fig. 4** (a) The first structurally characterised free *N*-heterocyclic carbene (CCDC 1283830;<sup>49</sup> only H-atoms bound to the five-membered ring are shown); (b) the Pd(II) dibromide complex of a macrocyclic *N*-heterocyclic dicarbene (CCDC 726625<sup>50</sup>); (c) an example of a Grubbs catalyst with [Ru(II)(Cp\*)Cl] bound to a monocarbene (CCDC 1170467<sup>51</sup>). (C = grey, N = blue, O = red, violet = Br, light blue = Pd, pink = Ru.)







**Fig. 5** (a) Atom numbering in the oxadiazole ring; (b) substitution pattern of a sydnone core; (c) zwitterionic canonical forms of a sydnone; (d) bond lengths/Å within a simple sydnone species, 3-tolylsydnone (CCDC 1125215<sup>53</sup>); (e) local CH...O contacts/Å (dashed lines) of a single 3-tolylsydnone molecule (central in the figure) within its crystal. (All molecules are equivalent, so in fact these interactions extend throughout the structure.) (H = white, C = grey, N = blue, O = red.)

solubility of simple sydnones<sup>43d</sup>). Later work<sup>57</sup> employing more sophisticated ball-milling techniques for solid state reactions did provide structurally characterised stable complexes involving sydnone exocyclic-O coordination in chelate rings resulting from N-coordination of a pyridyl substituent. Similar coordination was observed in a sydnone with a larger thiasemcarbazono substituent providing the chelation assistance.<sup>58</sup> A sydnone doubly substituted with diphenylphosphino groups, however, provided only a Pd(II) complex involving phosphorus coordination,<sup>59</sup> while an alkynylaryl sydnone gave a Pt(II) complex where again the oxadiazole unit was not bound to the metal, although it did have an influence on the optical properties of the complex.<sup>60</sup> This small number of X-ray structures known for complexes involving neutral sydnone groups is shown in Fig. 6. In all cases where the sydnone unit is coordinated, it binds in a  $\kappa^1\text{O}$  manner and the M–O bond lengths (Fig. 6), are all significantly longer (by  $\sim 0.06$  Å on average) than those for comparable betaine complexes.<sup>5–7</sup> Considering also that the sydnone species involve chelation which may enhance the M–O interactions, it appears that indeed sydnone-O is a relatively weak donor.

C4-bound sydnone complexes of Hg(II)<sup>61</sup> have been well characterised by spectroscopic and analytical methods but although described as nicely crystalline have not been studied by X-ray crystallography. They are of course complexes of the sydnone anion and not the neutral species and have been used to prepare Ni, Pd and Pt complexes of the same anion.<sup>62</sup> Metallation at C4 has also been achieved for Li, Cu and Zn,<sup>43c</sup> though only in reaction intermediates used for the synthesis of sydnone derivatives. It has been suggested the mechanism of the Cu-catalysed reaction between sydnones and acetylides may involve sydnone N2 coordination to copper(I), this reaction being a useful variant of click chemistry.<sup>63</sup> Overall, while it is apparent that many reactions of sydnones involve metal

ion catalysis and pass through complex formation, details of the coordination chemistry involved remain open to structural study.

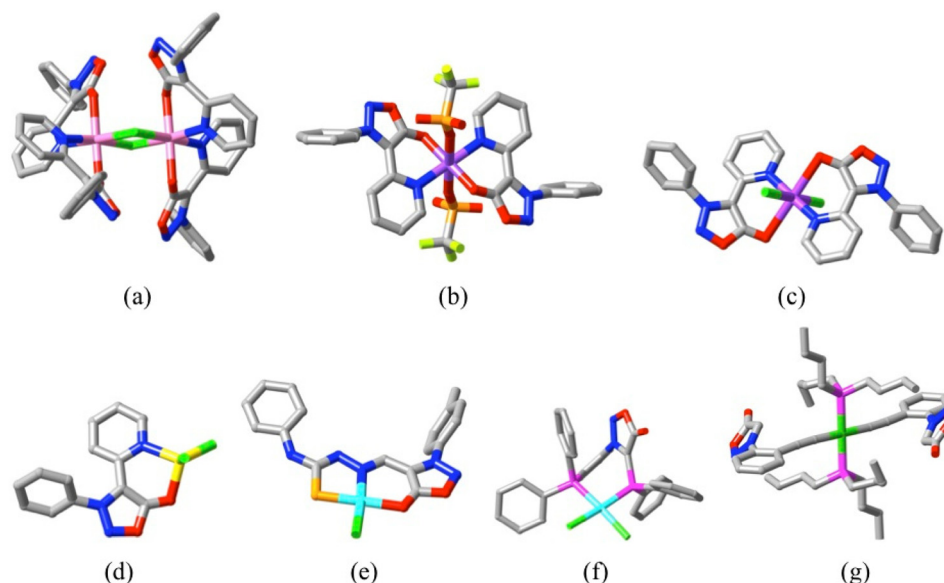
#### 4. Oligo-zwitterions and the formation of coordination polymers and frameworks

Polymeric zwitterion species, mainly based on the full variety of betaine subunits (ammonio, pyridinio and phosphonio acetates, sulfates and phosphates), are long known<sup>64</sup> and have a large number of significant applications,<sup>21,64–66</sup> including metal ion binding. X-ray structure determinations of metal ion complexes, however, are limited to those based on small oligomers in coordination polymers or frameworks. Over the past three decades, research on inorganic coordination polymers and frameworks has become intense and an extraordinary variety of systems has been characterised. For some recent reviews illustrating their diversity, see ref. 67–71, where more comprehensive listing of background material is given. For oligo-zwitterion ligands, at least three points of interest related to their use in the synthesis of coordination polymers and frameworks arise:

(i) Unlike mono-zwitterion ligands, where bridging must bring metal ions into close proximity, oligo-zwitterions should have the capacity to link metal ions at larger separations, thereby having the potential to create more open networks with enhanced porosity.

(ii) Being uncharged, oligo-zwitterions should have the capacity to form cationic coordination polymers associated with small anions and thus the potential to act as anion exchange materials.





**Fig. 6** Structurally characterised complexes formed from sydnone derivatives: (a)  $[\text{Co}_2(\text{L}8)_4\text{Cl}_2][\text{CoCl}_4]$  ( $\text{L}8 = \text{ppsyd} = 3\text{-phenyl-4-(2-pyridyl)sydnone}$ ),<sup>57</sup> CCDC 1913663,  $\text{Co-O}$  2.080(2) Å; (b)  $[\text{Cu}(\text{L}8)_2(\text{O}_3\text{SCF}_3)_2]$ ,<sup>57</sup> CCDC 1913662,  $\text{Cu-O}$  1.967(4) Å; (c)  $[\text{Cu}(\text{L}8)_2\text{Cl}_2]$ ,<sup>57</sup> CCDC 1913667,  $\text{Cu-O}$  2.583(6) Å (here, it is assumed that the sydnone-O atoms occupy the axial sites of a Jahn–Teller distorted Cu(II) coordination sphere, whereas in complex (b) these sites are occupied by triflate-O); (d)  $[\text{Zn}(\text{L}8)\text{Cl}_2]$ ,<sup>57</sup> CCDC 1913665,  $\text{Zn-O}$  2.060(2) Å; (e)  $[\text{Pd}(\text{L}9)\text{Cl}]$ ,<sup>58</sup> CCDC 142604; (f)  $[\text{Pd}(\text{L}10)\text{Cl}_2]$ ,<sup>59</sup> CCDC 264664; (g)  $[\text{Pt}((\text{L}11)_2(\text{P}(\text{nBu})_3)_2)]$ <sup>60</sup> ( $\text{L}11 = \text{pesyd} = 3\text{-(2-ethynylphenyl)-sydnone}$ , CCDC 264664. (C = grey, N = blue, O = red, F = yellow-green, P = deep pink, S = orange, Cl = green, Co = light pink, Cu = violet, Zn = yellow, Pd = sky blue, Pt = dark green.)

(iii) Being uncharged, oligo-zwitterions should also have the capacity to form coordination polymers in association with anionic bridging ligands capable of forming coordination polymers themselves alone, and thus modifying or reinforcing the structures of those simpler polymers.

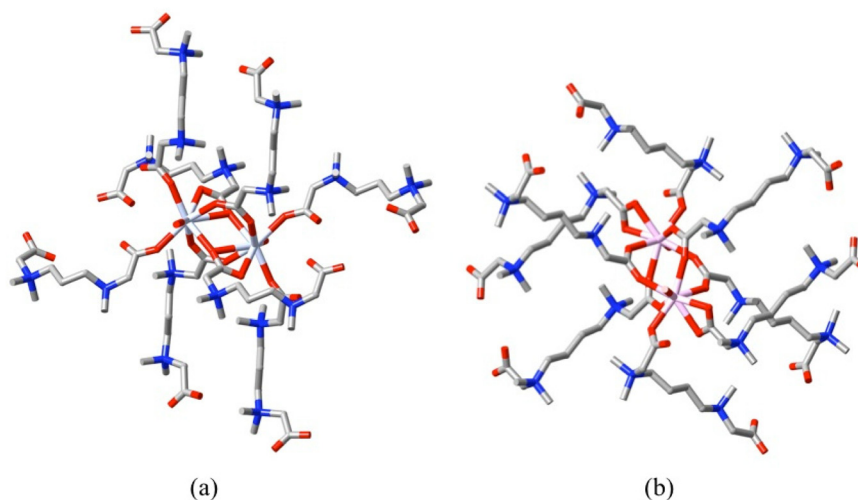
X-ray structural data sufficiently extensive to consider all three points is available in the furthering, beginning with dizwitterion studies,<sup>72</sup> of the work described in section 1 on carboxylate-donor zwitterions and as well in the coordination chemistry of the aza-aromatic *N*-oxide, 4,4'-bipyridine-*N,N'*-dioxide alone.<sup>73–76</sup> Thus, complexes of the double betaine 1,4-diazoniabicyclo[2.2.2]octane-1,4-diacetate (**L12**) with  $\text{Zn}(\text{ClO}_4)_2$  and  $\text{ZnBr}_2$ <sup>72a</sup> are diperiodic and monopерiodic polymers, respectively, though only the former can be regarded as a cationic species, as bromide coordination occurs in the latter. In both cases, the ligand acts as a bis( $\kappa^1\text{O}$ ) bridge. Complexes of the double betaines 3,7-diazonia-3,3,7,7-tetramethylnonane-1,9-dioate (**L13**) and 3,8-diazonia-3,3,8,8-tetramethyldecane-1,10-dioate (**L14**) with one early (Nd) and one late (Er) lanthanide(III) ions<sup>72b</sup> consist of cationic, diperiodic coordination polymers involving in total ( $\kappa^1\text{O}$ ), ( $\kappa^2\text{O},\text{O}'$ ), ( $\kappa^1\text{O};\kappa^1\text{O}'$ ) and ( $\kappa^2\text{O},\text{O}';\kappa^1\text{O}'$ ) bonding modes of the carboxylate groups, with the double betaines alone providing the bridges between the cations, the perchlorate counter anions not being directly bound to them (Fig. 7).

Similar features have been observed in other lanthanide(III) complexes of the dizwitterion 1,4-di(4-carboxylatopyridinium-methyl)benzene (**L15**), where the  $\kappa^1\text{O}$  bonding mode seems to

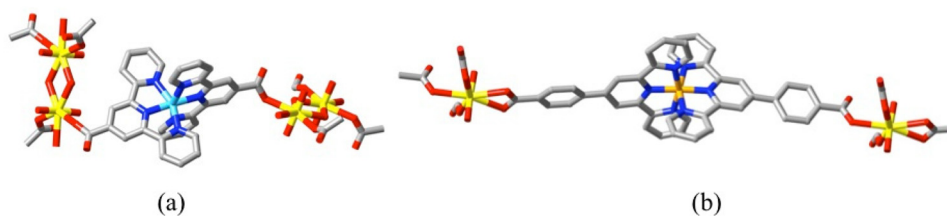
predominate, though accompanied by  $\kappa^1\text{O};\kappa^1\text{O}'$ .<sup>77</sup> An isomer of this ligand, 1,4-di(3-carboxylatopyridinium-methyl)benzene (**L16**) has been shown<sup>16</sup> to form transition metal (Co and Zn) polymer complexes where in the Co(II) species it binds as a bis ( $\kappa^1\text{O};\kappa^1\text{O}'$ ) bridge while in the Zn(II) complex it bridges in a bis ( $\kappa^1\text{O}$ ) fashion. A dizwitterion where the positive centre is a metal ion is  $[\text{Ni}(\text{tpyc})_2]$ , **L17**, ( $\text{tpyc} = 2,2':6',2''\text{-terpyridine-4'-carboxylate}$ ), an “expanded ligand”<sup>78</sup> and a particular member of the broad class of metalloligands,<sup>79</sup> where any charge carried by external substituents on a bound ligand is not necessarily balanced by that of the metal, a factor which certainly does not prevent their acting as bridging species in coordination polymers.<sup>67,68,80</sup> Both this ligand<sup>81</sup> and its further expanded analogues,  $[\text{M}^{\text{II}}(\text{cptpy})_2]$  (**L18**) ( $\text{cptpy} = 4'\text{-(4-carboxylatophenyl)-2,2':6',2''-terpyridine}$ ;  $\text{M} = \text{Fe, Co, Ni}$ )<sup>82</sup> have been shown to form coordination polymers with uranyl ion where both  $\kappa^1\text{O}$  and  $\kappa^2\text{O},\text{O}'$  bonding modes are seen (Fig. 8). (Another large family of organometallic metallazwitterions exists where the metal ion may be regarded in some cases as the positive site and in others as the negative but interest in such species has been largely limited to their applications as solution catalysts.<sup>13</sup>)

The relative wealth of dizwitterions available is not matched by that of trizwitterions and studies of their coordination chemistry are therefore more limited. The ligand 1,1',1''-(2,4,6-trimethylbenzene-1,3,5-triyl)-trimethylenetrakis(4-carboxylatopyridinium) (**L19**) forms coordination polymers with Cu(II), Zn(II) and Cd(II)<sup>14</sup> in which both  $\kappa^1\text{O}$  and  $\kappa^2\text{O},\text{O}'$  bonding modes are





**Fig. 7** Perspective views of the dimer units and their dizwitterion ligand environments in (a) the Nd(III) perchlorate complex of 3,7-diazonia-3,3,7,7-tetramethylnonane-1,9-dioate (L13) (CCDC 1251398<sup>72b</sup>), where the carboxylate bonding modes are  $\kappa^1\text{O}, \kappa^1\text{O}; \kappa^1\text{O}'$  and  $\kappa^2\text{O}, \text{O}'; \kappa^1\text{O}'$  and (b) the Er(III) perchlorate complex of 3,8-diazonia-3,3,8,8-tetramethyldecane-1,10-dioate (L14) (CCDC 1251401,<sup>72b</sup> where the carboxylate bonding modes are  $\kappa^1\text{O}, \kappa^1\text{O}; \kappa^1\text{O}'$  and  $\kappa^2\text{O}, \text{O}'$ . (Nd = pale blue-violet, Er = pink.)



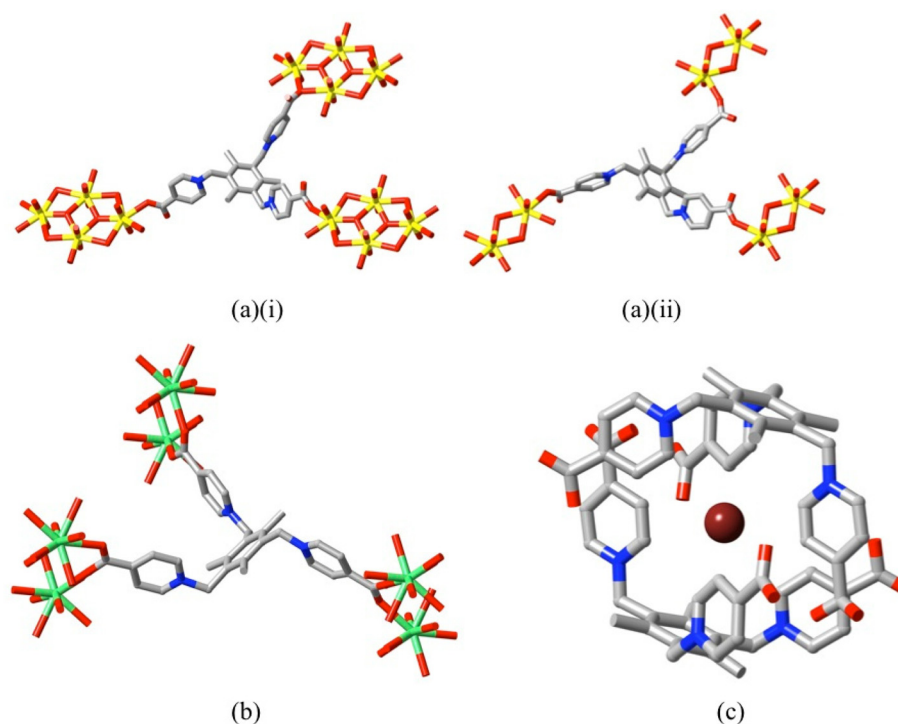
**Fig. 8** Portions of (a) the cationic diperiodic polymer present in  $[\text{UO}_2\text{Ni}(\text{tpyc})_2(\text{OH})(\text{OH}_2)]\cdot\text{NO}_3\cdot 1.5\text{H}_2\text{O}$  (CCDC 2105580<sup>81a</sup>), showing the bis( $\kappa^1\text{O}$ ) mode of bonding of the zwitterion and (b) the neutral monoperic polymer present in  $[(\text{UO}_2)_2\text{Fe}(\text{cptpy})_2(\text{O}_2\text{CH})_4]$  (CCDC 2027199;<sup>82</sup> isostructural with its Co and Ni analogues), showing the mixed  $\kappa^1\text{O}$  plus  $\kappa^2\text{O}, \text{O}'$  mode of bridging by the larger expanded ligand. (Fe = orange, Ni = sky blue.)

again seen, though in two of the four structures reported only two carboxylate groups of the ligand are bound. In linking tetranuclear U(VI) clusters into a diperiodic (layered) polymer structure,<sup>83</sup> however, it functions as a tris( $\kappa^1\text{O}$ ) ligand (giving a complex noted as the first cationic uranyl-organic framework, though it may also be noted that in a related neutral complex involving diuranate units the ligand adopts an otherwise unknown bis( $\kappa^1\text{O}$ ); $\kappa^2\text{O}$  bonding mode; Fig. 9(a)). While the ligand there has a chair-like conformation as seen in the Eu(III) complex polymer,<sup>15</sup> the Eu species is triperiodic and involves tris( $\kappa^1\text{O}; \kappa^1\text{O}'$ ) Eu(III)-carboxylate interactions (Fig. 9(b)). An interesting aspect of the crystal structure of the protonated ligand isolated as the tribromide<sup>14</sup> is the inclusion of one  $\text{Br}^-$  within a capsule formed by two facing ligands in a tripodal form (Fig. 9(c)) and even after deprotonation for the formation of the trizwitterion complexes, the interaction involved appears to have a structural influence (discussed ahead in relation to structures of mixed-ligand complexes involving trizwitterions).

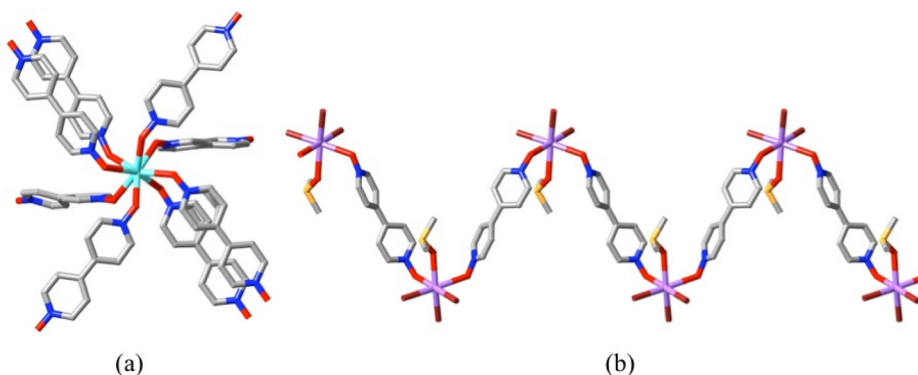
The behaviour of 4,4'-bipyridine-*N,N'*-dioxide (4,4'-bpdo = L20) as a dizwitterionic ligand, especially as seen in coordination to the lanthanides,<sup>76</sup> is remarkably different to that of the polybetaine-related species just discussed. It is a ligand of

very limited flexibility and can be considered as a linear rod, though some degree of twisting of one pyridine ring relative to the other is usually seen and binding by the O-donors involves bent M–O–N bond angles, so that convergent (*syn*) and divergent (*anti*) bridging modes are possible.<sup>76</sup> Like dibetaines, it is a good bridging ligand and favours solid state polymerisation but its capacity to exploit the high coordination numbers of the lanthanides results in species of exceptionally high connectivity involving La(III), for example, in 8-coordination by bpdo only (Fig. 10(a)), better described as frameworks<sup>84</sup> rather than simply as coordination polymers, though not all are strictly triperiodic.<sup>85</sup> In contrast, transition metal ions generally provide solid complexes with low metal-ion:4,4'-bpdo ratios, resulting in polymers which are monoperic (chains) or diperiodic (sheets) showing little or no porosity.<sup>75,86</sup> Units such as  $[\text{Cu}(4,4'\text{-bpdo})_6]^{2+}$  and  $[\text{Cd}(4,4'\text{-bpdo})_6]^{2+}$  are known but simply as mononuclear, non-polymeric complexes.<sup>75</sup> Even with very heavy metal ions such as Bi(III), which otherwise shows many similarities to the lanthanides in its coordination chemistry, species with a 1 : 1 metal-ion : 4,4'-bpdo ratio where just monoperic polymer chains are present can be isolated (Fig. 10(b)).<sup>73</sup>





**Fig. 9** (a) A 1,1',1''-(2,4,6-trimethylbenzene-1,3,5-triyl)-trimethylenetris(4-carboxylatopyridinium) ligand (L19) and its interactions with uranate clusters in (i) the neutral complex  $[(\text{UO}_2)_2(\text{L19})(\text{OH})\text{O}(\text{O}_2\text{CH})]$  (CCDC 1500076<sup>83</sup>), where two arms bind in a  $\kappa^1\text{O}$  fashion and one as  $\kappa^2\text{O}$ , and in (ii) the cationic species  $[\text{UO}_2(\text{L19})(\text{OH})]\text{Br}$  (CCDC 1500077<sup>83</sup>), where the bonding is tris( $\kappa^1\text{O}$ ) (U = yellow); (b) interactions of the ligand in  $[\text{Eu}(\text{L19})(\text{OH})_2](\text{NO}_3)_3$  (CCDC 1015226<sup>15</sup>) where a tris( $\kappa^1\text{O};\kappa^1\text{O}'$ ) mode is adopted (Eu = green); (c) encapsulation of a bromide ion within the structure of  $[\text{H}_3\text{L19}]\text{Br}_3$  (CCDC 819126<sup>14</sup>) (Br = brown).



**Fig. 10** Differing stoichiometry in complexes of 4,4'-bpdo: (a) the eight-coordinate La(III) centre in the diperiodic polymer  $[\text{La}(\text{L20})_4](\text{ClO}_4)_3$  (CCDC 239608<sup>85</sup>) where all ligands bridge in a bis( $\kappa^1\text{O}$ ) manner to other La(III) ions (not shown). (La = sky blue); (b) similar bridging of Bi(III) centres in the monoperic polymer  $[\text{BiBr}_3(\text{dmsO})(\text{L20})]$  (CCDC 2008674<sup>73</sup>). (Bi = violet, Br = brown, S = orange; partial disorder of the dmsO ligands not shown.)

The essential message to be gleaned from the discussion above is that oligo-zwitterions with a variety of functional groups can give rise alone to coordination polymers and frameworks. It is misleading to conclude that this means that metal ion separations in these materials must be large, since one carboxylate group alone can still serve as a bridge, as can (but rarely<sup>76</sup>) one oxygen of 4,4'-bpdo. In the Eu(III) complex of 1,1',1''-(2,4,6-trimethylbenzene-1,3,5-triyl)-trimethylenetris(4-carboxylatopyridinium) (L19), for example,<sup>15</sup> the Eu...Eu separ-

ation of the pair linked by the ligand arm which binds in the  $\kappa^1\text{O};\kappa^1\text{O}'$  manner is 4.47(1) Å, while the Eu...Eu separations between cations on separate arms range from 12.788(3) to 19.4(5) Å. In the mixed-ligand complex  $[\text{La}_4(4,4'\text{-bpdo})_3(\text{bztfacac})_6]\cdot 3\text{H}_2\text{O}$ ,<sup>87</sup> (bztfacac<sup>2-</sup> = benzoyltrifluoroacetate) the La(III) centres bridged by  $\kappa^2\text{O}$  bonding of one 4,4'-bpdo oxygen are 4.225(1) Å apart, while other close La...La separations range between 11.320(7) and 13.123(2) Å. A feature of all the complexes discussed above is that there is very little





evidence, from either direct experimentation<sup>75</sup> or estimates of the Kitaigorodsky porosity index (KPI) (calculated with PLATON<sup>88</sup>) cited in numerous publications (*e.g.* ref. 81*a*), of their capacity to undergo reversible absorption of small molecules or of the presence of cavities large enough to accommodate organic molecules, in part a consequence of the common observation of interpenetration.<sup>76,81</sup> This is a situation perhaps in the process of being redressed,<sup>89</sup> with the implication that success in creating a coordination polymer showing reversible gas absorption resulting from the use of the very rigid dizwitterion 1,4-di(4-carboxylatophenyl)-1,4-bipyridinium (L21) (Fig. 11), being that the flexibility of the systems discussed above may have been a disadvantage. Nonetheless, these are systems in which the magnetic, spectroscopic and ion exchange properties have provided numerous aspects of interest.<sup>73,77,90,91</sup> Note that in the structure<sup>83</sup> of the uranyl ion complex of the trizwitterion L19, 1,1',1''-(2,4,6-trimethylbenzene-1,3,5-triyl)-trimethylenetris(4-carboxylatopyridinium), shown to undergo anion exchange with retention of the coordination polymer structure, the counter anions are not coordinated to the metal ion, so that the polymer is truly cationic and the system can be regarded as equivalent to conventional organic ion exchangers. Given the lability of equatorial sites on U(vi),<sup>92</sup> it might be anticipated that non-bridging counter-anions coordinated to U(vi) sites of a zwitterion coordination polymer, thus making it a neutral species, would also undergo exchange. While such exchange has not been directly demonstrated for any uranyl

ion complex of the metallazwitterion [Ni(tpyc)<sub>2</sub>], it has been found possible to isolate complexes with different counter-anions, some (F<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, CH<sub>2</sub>(SO<sub>3</sub>)<sub>2</sub><sup>2-</sup>) proving to be coordinated, others (CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>, I<sub>3</sub><sup>-</sup>) not.<sup>93</sup> Here, however, the form of the coordination polymer varies with each anion, indicating that direct exchange reactions would probably not be reversible.

The observations that coordination polymers in which oligo-zwitterions are the principal bridging units are usually of negligible porosity and may not always be suitable for ion exchange reactions appear to pose limits on their applications. It has long been recognised, at least for uranyl ion complexes in general,<sup>94,95</sup> however, that mixed-ligand species can have novel properties<sup>96</sup> and this approach has been the basis of recent developments in oligo-zwitterion chemistry in this domain. Luminescence is a fundamental aspect of U(vi) chemistry<sup>97</sup> and in mixed-ligand complexes where both 4,4'-bpdo and polycyanometallates function as bridging ligands to give both di- and triperiodic polymer networks (Fig. 12), the usual green emission<sup>97</sup> from uranyl ions has been shown to be modifiable over a range of colours from green to orange depending upon the cyanometallate.<sup>98</sup> This is viewed as having possible application in new light-emitting devices. The more obvious potential applications of uranyl ion complexes are of course those based on the photo-oxidation capacity of U(vi) centres<sup>97,99</sup> and it has been shown, for example, that uranyl ion coordination polymers can be used for removal and



Fig. 11 The rigid ligand 1,4-di(4-carboxylatophenyl)-1,4-bipyridinium (L21) and a fragment of the triperiodic polymer formed with CdCl<sub>2</sub>, [Cd<sub>4</sub>(L21)<sub>3</sub>Cl<sub>6</sub>][CdCl<sub>4</sub>]·8H<sub>2</sub>O (CCDC 1473082<sup>89</sup>), showing the bis(κ<sup>2</sup>O,O') bonding mode to Cd(II). (Cd = light blue, Cl = green.)



Fig. 12 Partial views of the components of the triperiodic coordination framework found in [(UO<sub>2</sub>)<sub>2</sub>(OH)(L20)<sub>2</sub>][Ir(CN)<sub>6</sub>] (CCDC 1857916<sup>98</sup>) showing (a) a section of the diperiodic network formed by bis(κ<sup>4</sup>N) bridging of uranyl centres by four of the cyano groups of each [Ir(CN)<sub>6</sub>]<sup>3-</sup> unit and (b) the double-chain of uranyl centres linked by bis(κ<sup>4</sup>O) coordination of 4,4'-bpdo ligands and crosslinked by hydroxido bridges that, through connection further to [Ir(CN)<sub>6</sub>]<sup>3-</sup> units, generates the full 3-dimensional structure.





**Fig. 13** Partial views of the ionic components of the mixed-ligand uranyl ion complex of  $L'' = 1,1'-[(2,3,5,6\text{-tetramethylbenzene-1,4-diyl})\text{bis(methylene)}]\text{bis(pyridin-1-ium-3-carboxylate)}$  and thiophene-2,5-dicarboxylate (TDC),  $[(\text{UO}_2)_2(\text{L}')_3(\text{H}_2\text{O})_2][(\text{UO}_2)_2(\text{TDC})_3]_2 \cdot 10\text{H}_2\text{O}$  (CCDC 2202990<sup>101</sup>) showing (a) a section of the diperiodic, distorted honeycomb annionic polymer involving  $\text{TDC}^{2-}$  only and (b) portion of the undulating cationic polymer formed by  $\kappa^1\text{O}$  plus  $\kappa^1\text{O};\kappa^2\text{O}'$  bridging by  $L''$  only.

visible-light photoactivated destruction of rhodamine B present as an environmental contaminant.<sup>100</sup> Any use of a radioactive material for such purposes must involve rather stringent requirements concerning security, the scale of usage and recovery and recyclability of the catalyst,<sup>69</sup> so that small-scale use of uranyl ion coordination polymers or frameworks as heterogeneous catalysts for selective synthetic transformations would seem to be a more realistic prospect.

Although as yet unexplored in regard to any possible applications, it has been demonstrated<sup>17,82,101–104</sup> that carboxylate di- or tri-zwitterions and anionic polycarboxylates can form mixed ligand coordination polymers in which both ligands act as bridges, seemingly consistent with the different donor species having almost identical bonding interactions. Bond lengths to zwitterion carboxylate-O and anionic carboxylate-O are similar but the common adoption of a bis or tris( $\kappa^1\text{O}$ ) mode of bonding by the zwitterions may indicate that they have a weaker structural influence and in the particular case of thiophene-2,5-dicarboxylate as the anion,<sup>103</sup> the isolated crystals have the composition of a mixed-ligand species but the structure in fact involves independent polymer networks of the two ligands (Fig. 13), meaning that the solid is ionic, where a cationic polymer formed by the zwitterion 1,1'-[(2,3,5,6-tetramethylbenzene-1,4-diyl)bis(methylene)]bis(pyridin-1-ium-3-carboxylate), L22, is accompanied by an anionic polymer formed by the dicarboxylate. Thus, it is not clear that a true mixed ligand species must be obtained rather than separate species, each with a unique bridging component. While there is little indication of significant porosity in any of the complexes, the complex formed<sup>101</sup> from adamantane-1,3-dicarboxylate and 1,1',1''-(2,4,6-trimethylbenzene-1,3,5-triyl)-trimethylenetris(4-carboxylatopyridinium) (L19) actually contains an encapsulated bromide ion bound (through  $\text{Br}\cdots\text{HC}$  interactions) in a manner similar to that found in the bromide salt of the protonated trizwitterion, this cation also being a component of the structure. Hence, the appropriate choice of zwitterion might be a means of controlling guest inclusion in such complexes. Added to these considerations, it has also been

shown recently<sup>104</sup> that the moderately flexible dizwitterion 4,4'-bis(carboxylatoethyl)-4,4'-bipyridinium (L23) in combination with 1,3-phenylenediacetate ( $1,3\text{-pda}^{2-}$ ) can form a chiral, binuclear cage species  $[(\text{UO}_2)_2(\text{L23})(1,3\text{-pda})_2]$ . Cage complexes are relatively rare in U(VI) coordination chemistry<sup>105</sup> but they bring with them the possibility of selective inclusion of substrates susceptible to reaction with photoexcited U(VI) as well as the possibility of sufficient solubility for use as homogeneous catalysts. Little is presently known in these regards.

This is far from a comprehensive review of zwitterion coordination chemistry, its focus on solid state structures being intended only to define the benefits that may derive from the use of oligozwitterions in the generation of coordination polymers and frameworks, particularly in the formation of mixed-ligand species. Although only two binding units (*N*-oxide and carboxylate-O) have been considered in any detail as components of oligozwitterions, their properties are such as to make such zwitterions efficacious as ligands in a variety of novel materials. The differences observed between di- and tri-zwitterions indicate that extension of the list to higher species offering something approaching the extraordinary variety of known polycarboxylates could give rise a considerable expansion of the area and a range of surprises in the structures obtained.

## Conflicts of interest

There are no conflicts to declare.

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