Supramolecular Chemistry

Calix[4]pyrrole: An Old yet New Ion-Pair Receptor**

Radu Custelcean, Lætitia H. Delmau, Bruce A. Moyer, Jonathan L. Sessler,* Won-Seob Cho, Dustin Gross, Gareth W. Bates, Simon J. Brooks, Mark E. Light, and Philip A. Gale**

In memory of Carlo Floriani

The development of ion-pair receptors, with the goal of achieving a higher level of control over recognition than that obtainable from simple ion binding, has intrigued researchers in supramolecular chemistry over the past decade.[1] Many reports have appeared during this period that describe the synthesis and study of very sophisticated receptor designs incorporating a range of electron-pair donor and acceptor groups. Most, if not all, of this work has been performed in the context of creating so-called ion-pair or salt hosts that will bind cation–anion pairs in homogeneous solution or enhance their extraction or transport under interfacial conditions. Whether the ditopic architecture in such systems confers real advantages over simpler combinations of single-ion receptors remains an open question. However, the utility of ion-pair receptors has been demonstrated in several systems incorpo-

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[*] Dr. R. Custelcean, Dr. L. H. Delmau, Dr. B. A. Moyer
Chemical Sciences Division
Oak Ridge National Laboratory
P.O. Box 2008, Oak Ridge, TN 37831-6119 (USA)
Fax: (+1) 865-574-4939
E-mail: moyerba@ornl.gov

Prof. J. L. Sessler, W.-S. Cho, D. Gross
Department of Chemistry and Biochemistry
Institute for Cellular and Molecular Biology
University of Texas at Austin
1 University Station–A5300, Austin, TX 78712-0165 (USA)
Fax: (+1) 512-471-7550
E-mail: sessler@mail.utexas.edu

G. W. Bates, S. J. Brooks, Dr. M. E. Light, Dr. P. A. Gale
School of Chemistry
University of Southampton
Southampton SO171WD (UK)
Fax: (+44) 23-8059-3332
E-mail: philip.gale@soton.ac.uk

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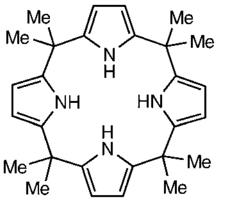
rating engineered steric constraints. Particular success has been encountered with receptors bearing cavities of limited dimensionality and directionality for contact ion pairs,[2] as well as with receptors that embody allosteric effects such that the binding of one ion organizes the receptor to accept the counterion.[3]

In spite of this progress, there remains a need to develop new ion-pair systems and to study the underlying effects that either promote or preclude concurrent anion–cation binding within a given receptor class. This need has prompted us to study the calix[4]pyrroles, a well-recognized class of anion receptors, in greater detail. We examined these systems as anion receptors for the extraction of cesium salts and observed anomalous behavior for the simple *meso*-octamethylcalix[4]pyrrole (**1**) which suggested exceptionally strong ion pairing of Cs$^+$ ions with complexes formed between **1** and Cl$^-$ or Br$^-$ ions in the organic phase. These anomalies could be best, and most interestingly, interpreted in terms of small halide ions organizing **1** into the cone conformation, which then in turn provides an electron-rich cup that putatively binds the Cs$^+$ ion.[4] Previous studies of ours have demonstrated that the binding of halide anions by **1** and other calix[4]pyrrole derivatives does indeed organize the receptors into the cone conformation.[5] However, this induced cup, or conelike cavity, has not yet been observed to serve as a receptor for electropositive species.



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Although the solution chemistry remains under investigation, the exciting implication that **1** could function as a ditopic ion-pair receptor led us to study this easily prepared parent system in the solid state, in which any such potential behavior is expected to be most strongly manifested. Thus, we have carried out a crystallographic analysis of the anion-recognition behavior of calix[4]pyrrole in the presence of two large, polarizable cations, namely the cesium and imidazolium ions, and observed ditopic cation–anion binding in both cases.[6]

X-ray quality crystals of cesium halide/calix[4]pyrrole complexes were obtained by slow diffusion of a solution of cesium fluoride in ethanol into a solution of the calix[4]pyrrole in dichloromethane and by slow evaporation of solutions of cesium chloride or cesium bromide and calix[4]pyrrole in a dichloromethane/methanol mixture. The cesium fluoride/calix[4]pyrrole complex reveals that the cation is symmetrically included in the conelike cavity of the calix[4]pyrrole unit (Figure 1 a),[7] with an observed distance of 3.39 Å between the Cs$^+$ ion and the centroids of the pyrrole rings. The F$^-$ ion is symmetrically bound to the four NH groups of the calix[4]pyrrole, with a distance of 2.79 Å for the N···F interaction (a similar distance to that observed previously in fluoride/calix[4]pyrrole complexes[5] and slightly shorter than those seen in a recently reported polyamide-based fluoride/cryptand complex[8]). The F$^-$ ion is associated with the Cs$^+$ ion within the same complex (Cs···F contact distance of 3.69 Å), as well as with a Cs$^+$ ion in an adjacent complex (Cs···F contact distance of 2.77 Å), thus leading to the formation of a one-dimensional coordination polymer.

Likewise, the cesium chloride (Figure 1 b) and cesium bromide (Figure 1 c) salts are bound by the calix[4]pyrrole units as ion pairs in the solid state. The Cs$^+$ ion is tightly bound by the cone-shaped calix[4]pyrrole, with observed distances to the centroids of the pyrrole rings in the ranges 3.32–3.79 and 3.34–3.51 Å for the cesium chloride/calix[4]pyrrole and cesium bromide/calix[4]pyrrole complexes, respectively. The Cl$^-$ and Br$^-$ ions are bound to the four NH groups of the calix[4]pyrrole by hydrogen bonds, with distances of 3.27–3.32 and 3.45–3.52 Å for the N···Cl and N···Br interactions, respectively. Like the cesium fluoride/calix[4]pyrrole complex, both the cesium chloride/calix[4]pyrrole and cesium bromide/calix[4]pyrrole complexes form coordination polymers, with intermolecular Cs···X contact

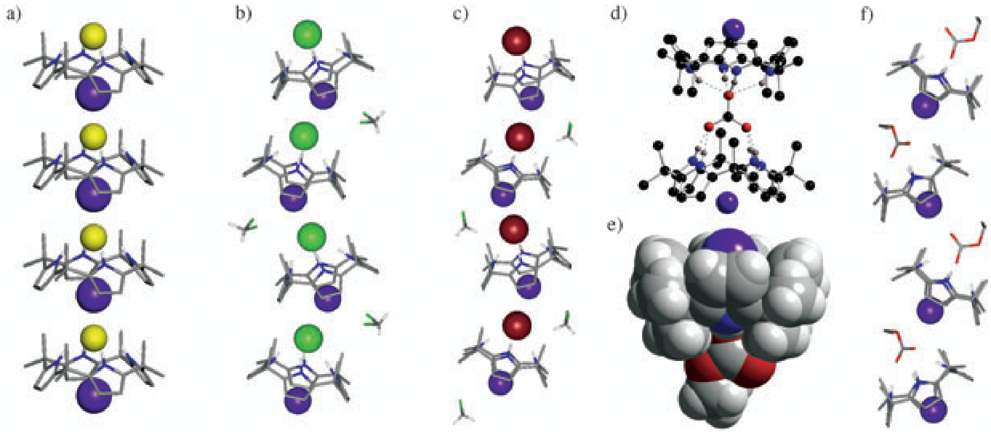


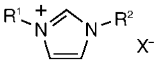
Figure 1. The X-ray crystal structures of a) the CsF, b) CsCl, and c) CsBr complexes of **1** showing inclusion of the Cs$^+$ ion in the cavity of the calix[4]pyrrole, thus leading to formation of a coordination network. d) The Cs$_2$CO$_3$ complex of **1** showing dimerization in the solid state (note that in this structure two different carbonate/calix[4]pyrrole binding modes exist). e) Space-filling representation of the CsEtOCO$_2$ complex of **1**, which illustrates inclusion of a Cs$^+$ ion in the calix[4]pyrrole cavity and f) the coordination network in this complex. The solvent has been removed for clarity in (d)–(f), and certain hydrogen atoms have been omitted for clarity in the non-space-filling representations. The Cs$^+$ ions are shown in purple, F$^-$ ions in yellow, Cl$^-$ ions in green, Br$^-$ ions in orange/brown, O atoms in red, and C atoms in gray or black.

distances of 3.38 and 3.59 Å for X = Cl and Br, respectively. However, dichloromethane is also included in the crystals for the bromide and chloride complexes, with solvent molecules associating with the cation in the chloride complex and both the cation and the anion in the bromide complex. The coordination chains adopt a zig-zag shape as a result.[9]

The attempted complexation of the calix[4]pyrrole with cesium hydroxide in an ethanol/dichloromethane mixture in air resulted in crystals of cesium carbonate and ethyl carbonate complexes being obtained, apparently by CO_2 fixation by the OH^- or EtO^- ions present in solution. Interestingly, the cesium carbonate/calix[4]pyrrole complex is a dimer consisting of a central anion bound through one oxygen atom to one calix[4]pyrrole unit (N···O separations of 2.82–2.89 Å) and through the other two oxygen atoms to the other macrocycle (in this case, each oxygen atom is bound by two hydrogen-bonding interactions, N···O distances of 2.78–2.84 Å). This dimer is of special interest because, to the best of our knowledge, it represents the first well-characterized "sandwich" complex reported to date[10] wherein a single anion serves to bridge two neutral pyrrole-based anion receptors. This complex is also of interest because the cesium counterions are found to reside in the cavity of each calix[4]pyrrole unit, thus balancing the charge (Figure 1 d).

Similarly, the ethyl carbonate anion forms hydrogen bonds with the calix[4]pyrrole unit in two distinct ways: one $EtOCO_2^-$ ion is bound through one oxygen atom (N···O distances of 2.89–3.00 Å), while the second crystallographically different $EtOCO_2^-$ ion is bound by hydrogen bonds through two oxygen atoms (N···O distances of 2.87–3.04 Å). A space-filling representation of one of the two distinctive ethyl carbonate/calix[4]pyrrole pairs found in this structure is shown in Figure 1 e, which illustrates the fit of the Cs^+ ion within the cuplike calix[4]pyrrole cavity. The ethyl carbonate anions in this structure act as a bridge between the four NH hydrogen-bond donors of one calix[4]pyrrole unit and a Cs^+ ion bound within the cavity of an adjacent complex (Cs···O contact distances of 2.84–3.17 Å). The net result of this anion–cation binding behavior is, once again, the formation of a one-dimensional coordination polymer in the solid state (Figure 1 f).

High-quality crystals of the imidazolium salt complexes were prepared by evaporation of a solution of **1** in dichloromethane in the presence of 1-butyl-3-methylimidazolium chloride (**2**), 1-butyl-3-methylimidazolium bromide (**3**), 1-ethyl-3-methylimidazolium bromide (**4**), or 1,3-dimethylimidazolium methylsulfate (**5**).



2: $R^1 = n$Bu, R^2 = Me, X = Cl^-
3: $R^1 = n$Bu, R^2 = Me, X = Br^-
4: R^1 = Et, R^2 = Me, X = Br^-
5: $R^1 = R^2$ = Me, X = $MeSO_4^-$

Complexes **1**·**2**·CH_2Cl_2·2 H_2O and **1**·**3**·CH_2Cl_2·2 H_2O were found to be isostructural. In the complex **1**·**2**, the Cl^- ion is bound by four NH hydrogen bonds from the pyrrole groups with N···Cl distances of 3.30–3.35 Å. The imidazolium cation is bound to the Cl^- ion by two CH···Cl hydrogen bonds (C31···Cl1 and C32···Cl1 distances are 3.47 and 3.66(3) Å). In the analogous bromide/calix[4]pyrrole complex, where NH···Br and CH···Br interactions were formed, the N···Br separations were 3.40–3.47 Å and the C31···Br1 and C32···Br1 separations were 3.52 and 3.71 Å, respectively. Interestingly, the imidazolium cations in these structures are included in the anion-induced cone-shaped cavity of an adjacent calix[4]pyrrole. The CH groups in the 4- and 5-positions of the imidazolium ring are close enough to have hydrogen-bonding interactions with the π-electron clouds of two of the pyrrole rings in the macrocycle. These interactions lead to the formation of one-dimensional chains in the solid state in **1**·**2** (Figure 2 a) and **1**·**3** (see the Supporting Information).

Similarly, the anion binds to the four NH groups in the calix[4]pyrrole in the complex of **1** with **4**, with N···Br distances of 3.39–3.47 Å. In this case, two crystallographically distinct calixpyrrole complexes were observed in the solid-state structure. As in the structure of **1**·**2**, the imidazolium cation was found to reside in the calix[4]pyrrole cavity with the 4- and 5-positions of the imidazolium cation oriented within hydrogen-bonding distance of the π-electron clouds of two of the pyrrole rings. However, the orientation of the imidazolium cation differs slightly in the two crystallographically distinct complexes. In one of these calix[4]pyrrole complexes, the imidazolium cation is roughly symmetrically disposed with respect to the macrocycle (the H30···N10 and H31···N8 separations are 2.62 and 2.66 Å, respectively), whereas in the other calixpyrrole complex, the imidazolium cation is closer to one pyrrole ring than the other (the H64B···N2 and H65B···N4 distances are 2.71 and 2.43 Å, respectively). In contrast to the one-dimensional chains formed in **1**·**2** and **1**·**3** through imidazolium CH/anion interactions, the imidazolium CH group in the 2-position is within hydrogen-bonding distance of the π-electron cloud of one of the pyrrole rings of an adjacent calixpyrrole in this complex, as evidenced by the distance of 2.62 Å between the CH hydrogen (H32) and pyrrole nitrogen atoms (N2) (Figure 2 b).

The structure of the 1,3-dimethylimidazolium methylsulfate complex of **1** (**1**·**5**) reveals that a bifurcated hydrogen bond is formed from the calix[4]pyrrole to the oxoanion guest. Three pyrrole NH groups form single NH···O hydrogen-bonding interactions with the O1 atom with separations of 2.95–3.07 Å. In contrast, the N4-H group forms two hydrogen bonds, one to the O1 atom (3.17 Å) and one to the O4 atom (3.36 Å). In this structure, a pendant methyl group (C33) was found to be encapsulated within the calix[4]pyrrole cavity. The imidazolium-ring CH groups and the other pendant methyl group are involved in hydrogen-bonding interactions to adjacent anions. As above, the net effect of these multiple interactions is the formation of a structure with long-range order, in this case a hydrogen-bonded sheet (C30···O2, C29···O3, and C32···O3 separations are 3.48, 3.39, and 3.05 Å, respectively; Figure 2 c).

Preliminary studies on cesium- and imidazolium-cation inclusion in the conelike cavity of the chloride complex of **1** were conducted using ^{1}H NMR spectroscopic analysis in a variety of different solvents (for example, [D_5]nitrobenzene, [D_6]acetone/2 % D_2O, and CD_2Cl_2). Significant shifts were

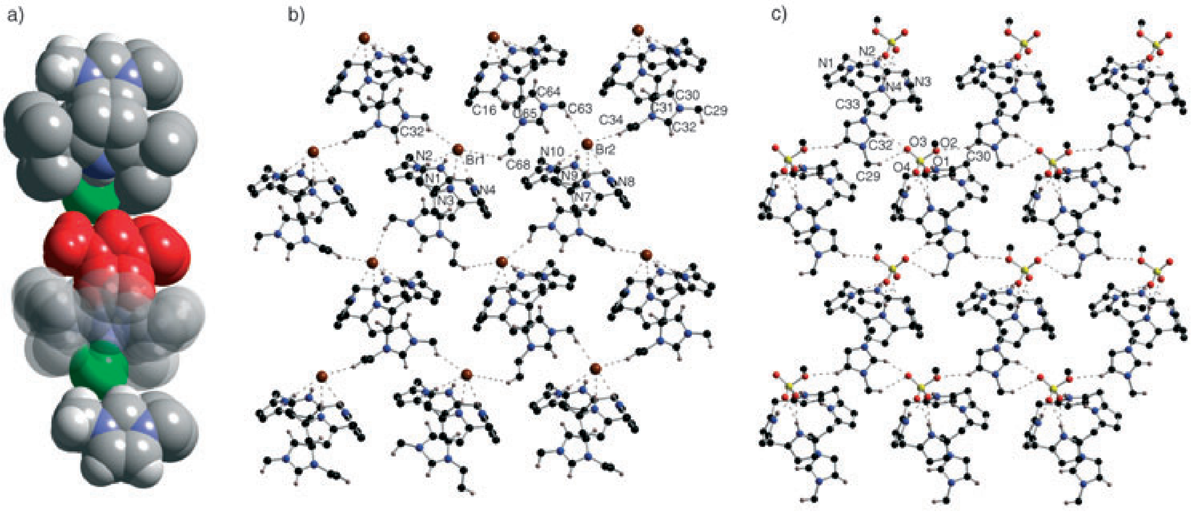


Figure 2. a) A space-filling representation of the coordination chain of **1**·**2**, which shows the imidazolium ring (4- and 5-positions) included in the calix[4]pyrrole cavity whilst the CH group at the 2-position and the pendant methyl group form a CH⋯Cl hydrogen-bonding interaction to an adjacent complex. One calix[4]pyrrole unit is rendered translucent and the included imidazolium cation is rendered red to illustrate the degree of penetration of the cation into the calix[4]pyrrole cavity. The non-acidic hydrogen atoms in the calix[4]pyrrole moiety and the solvent are omitted for clarity. Hydrogen-bonded network are formed in b) the **1**·**4** complex and c) the **1**·**5** complex (in this case, an imidazolium methyl group is included in the calix[4]pyrrole cavity). CH⋯O interactions from the imidazolium cation to the methylsulfate anion result in the formation of a two-dimensional sheet.

observed for the resonances of the pyrrole CH protons but not for the pyrrole NH protons on addition of $CsBPh_4$ or $CsClO_4$, and shielding of the imidazolium protons was also observed on addition of 1-butyl-3-methylimidazolium tetrafluoroborate to the chloride complex of **1**. These results are consistent with inclusion of the cations in the chloride/calix[4]pyrrole complex cavity in solution (see the Supporting Information). Investigations into the structure of the complexes formed in solution and quantification of the binding stoichiometry and thermodynamics under a range of experimental conditions are currently being carried out.

We believe that the present results open up a potentially new chapter in the chemistry of calix[4]pyrroles. We reported in 1996 that *meso*-octamethylcalix[4]pyrrole (**1**), a molecule known for over a century,[11] had hitherto unreported anion-complexation properties.[5] Herein, we have demonstrated that these easy-to-make macrocycles not only function as anion receptors but can act as ion-pair receptors. In particular, we have shown that in the solid state large diffuse cations, such as cesium and imidazolium ions, will occupy the electron-rich conelike cavity that is formed on anion binding to the NH portions of the calix[4]pyrrole core. These findings may inspire a range of new applications for calix[4]pyrroles, including their use as building blocks for crystal engineering and as possible receptors for anion–cation extractions. Studies of these and other possibilities are currently underway.

Experimental Section

1-CsF: $C_{28}H_{36}CsFN_4$, $M_r = 580.52$, colorless needles, $0.26 \times 0.08 \times 0.06$ mm^3, tetragonal, space group $I4mm$, $a = b = 14.044(5)$, $c = 6.452(3)$ Å, $V = 1272.6(8)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.515$ g cm^{-3}, $F_{000} = 592$, Bruker SMART APEX, $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, omega scan, $T = 173(2)$ K, $2\theta_{max} = 56.3°$, 6990 reflections collected, 894 unique ($R_{int} = 0.0258$). Final GOF = 1.105, $R1 = 0.0134$, $wR2 = 0.0330$, R indices based on 894 reflections with $I > 2\sigma(I)$, 50 parameters, 1 restraint. Lp and absorption corrections applied using SADABS, $T_{min} = 0.6987$, $T_{max} = 0.9161$, $\mu = 1.486$ mm^{-1}. Residual electron density = 0.328 e Å^3. Absolute structure parameter = 0.00(3).

1-CsCl·CH_2Cl_2: $C_{29}H_{38}N_4Cl_3Cs_1$, $M_r = 681.89$, colorless needles, $0.33 \times 0.09 \times 0.03$ mm^3, triclinic, space group $P\bar{1}$, $a = 10.669(4)$, $b = 15.300(6)$, $c = 20.543(8)$ Å, $\alpha = 110.882(7)$, $\beta = 95.529(7)$, $\gamma = 91.028(7)°$, $V = 3113(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.455$ g cm^{-3}, $F_{000} = 1384$, Bruker SMART APEX, $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, omega scan, $T = 173(2)$ K, $2\theta_{max} = 56.7°$, 35439 reflections collected, 15354 unique ($R_{int} = 0.0302$). Final GOF = 1.225, $R1 = 0.0573$, $wR2 = 0.1100$, R indices based on 13655 reflections with $I > 2\sigma(I)$, 683 parameters, 0 restraints. Lp and absorption corrections applied using SADABS, $T_{min} = 0.6424$, $T_{max} = 0.9572$, $\mu = 1.471$ mm^{-1}. Residual electron density = 1.724 e A^3.

1-CsBr·2CH_2Cl_2: $C_{30}H_{40}BrCl_4CsN_4$, $M_r = 811.28$, yellow plate, $0.31 \times 0.23 \times 0.02$ mm^3, monoclinic, space group $P2_1/n$, $a = 10.501(4)$, $b = 15.659(5)$, $c = 20.982(7)$ Å, $\beta = 97.319(6)°$, $V = 3422(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.575$ g cm^{-3}, $F_{000} = 1624$, Bruker SMART APEX, $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, omega scan, $T = 173(2)$ K, $2\theta_{max} = 56.7°$, 42059 reflections collected, 8488 unique ($R_{int} = 0.0409$). Final GOF = 1.036, $R1 = 0.0341$, $wR2 = 0.0870$, R indices based on 7009 reflections with $I > 2\sigma(I)$, 369 parameters, 0 restraints. Lp and absorption corrections applied using SADABS, $T_{min} = 0.5009$, $T_{max} = 0.9501$, $\mu = 2.588$ mm^{-1}. Residual electron density = 1.361 e Å^3.

1$_2$-Cs_2CO_3·4CH_2Cl_2: $C_{61}H_{80}Cl_8Cs_2N_8O_3$, $M_r = 1522.75$, colorless plates, $0.34 \times 0.23 \times 0.04$ mm^3, monoclinic, space group $P2_1/n$, $a = 15.273(7)$, $b = 20.942(10)$, $c = 22.787(11)$ Å, $\beta = 105.769(9)°$, $V = 7014(6)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.442$ g cm^{-3}, $F_{000} = 3088$, Bruker SMART APEX, $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, omega scan, $T = 173(2)$ K, $2\theta_{max} = 56.8°$, 86226 reflections collected, 17469 unique ($R_{int} = 0.0566$). Final GOF = 1.054, $R1 = 0.0595$, $wR2 = 0.1596$, R indices based on 13173 reflections with $I > 2\sigma$(I), 755 parameters, 0 restraints. Lp and absorption corrections applied using SADABS, $T_{min} = 0.6492$, $T_{max} = 0.9465$, $\mu = 1.391$ mm^{-1}. Residual electron density = 3.524 e Å^3.

1-CsEtOCO$_2$·0.5EtOH: $C_{64}H_{88}N_8O_7Cs_2$, $M_r = 1347.24$, colorless plates, $0.20 \times 0.19 \times 0.03$ mm^3, triclinic, space group $P\bar{1}$, $a = 10.606(5)$, $b = 15.618(7)$, $c = 20.147(9)$ Å, $\alpha = 95.107(8)$, $\beta = 98.914(8)$, $\gamma =$

101.189(8)°, $V = 3210(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.394$ g cm^{-3}, $F_{000} = 1388$, Bruker SMART APEX, Mo$_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, omega scan, $T = 173(2)$ K, $2\theta_{max} = 56.7°$, 40329 reflections collected, 15892 unique ($R_{int} = 0.0339$). Final GOF = 1.048, $R1 = 0.0459$, $wR2 = 0.1284$, R indices based on 12142 reflections with $I > 2\sigma(I)$, 742 parameters, 0 restraints. Lp and absorption corrections applied using SADABS, $T_{min} = 0.7964$, $T_{max} = 0.9651$, $\mu = 1.192$ mm^{-1}. Residual electron density = 1.747 e Å^3.

1·**2**·CH_2Cl_2·2 H_2O: $C_{37}H_{57}N_6O_2Cl_3$, $M_r = 724.24$, pale-red prisms, $0.2 \times 0.2 \times 0.2$ mm^3, triclinic, space group $P\bar{1}$, $a = 10.4222(14)$, $b = 10.7682(11)$, $c = 17.993(2)$ Å, $\alpha = 74.664(11)$, $\beta = 81.603(13)$, $\gamma = 84.951(10)°$, $V = 1923.9(4)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.250$ g cm^{-3}, $F_{000} = 776$, Bruker Nonius KappaCCD, Mo$_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, phi and omega scans, $T = 120(2)$ K, $2\theta_{max} = 55.34°$, 41654 reflections collected, 8681 unique ($R_{int} = 0.0566$). Final GOF = 1.070, $R1 = 0.0519$, $wR2 = 0.1186$, R indices based on 8681 reflections with $I > 2\sigma(I)$, 484 parameters, 12 restraints. Lp and absorption corrections applied using TWINABS, $T_{min}/T_{max} = 0.763$, $\mu = 0.278$ mm^{-1}. Residual electron density = 1.288 e Å^{-3}.

1·**3**·CH_2Cl_2·2 H_2O: $C_{37}H_{57}N_6O_2Cl_2Br$, $M_r = 768.70$, colorless rods, $0.18 \times 0.05 \times 0.05$ mm^3, triclinic, space group $P\bar{1}$, $a = 10.5710(14)$, $b = 10.7800(11)$, $c = 18.082(2)$ Å, $\alpha = 74.528(11)$, $\beta = 81.155(13)$, $\gamma = 84.715(10)°$, $V = 1959.4(4)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.303$ g cm^{-3}, $F_{000} = 812$, Bruker Nonius KappaCCD, Mo$_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, phi and omega scans, $T = 120(2)$ K, $2\theta_{max} = 50.6°$, 21008 reflections collected, 6576 unique ($R_{int} = 0.1857$). Final GOF = 1.088, $R1 = 0.1113$, $wR2 = 0.2789$, R indices based on 6576 reflections with $I > 2\sigma(I)$, 467 parameters, 30 restraints. Lp and absorption corrections applied using TWINABS, $T_{min}/T_{max} = 0.563$, $\mu = 1.225$ mm^{-1}. Residual electron density = 1.208 e Å^{-3}.

1·**4**: $C_{34}H_{47}N_6Br$, $M_r = 619.69$, colorless blocks, $0.2 \times 0.05 \times 0.04$ mm^3, monoclinic, space group $P2_1/c$, $a = 21.238(3)$, $b = 17.043(4)$, $c = 18.287(4)$ Å, $\beta = 108.477(14)°$, $V = 6278(2)$ Å^3, $Z = 8$ (2 molecules), $\rho_{calcd} = 1.311$ g cm^{-3}, $F_{000} = 2624$, Bruker Nonius KappaCCD, Mo$_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, phi and omega scans, $T = 120(2)$ K, $2\theta_{max} = 50.06°$, 54773 reflections collected, 11067 unique ($R_{int} = 0.1162$). Final GOF = 1.052, $R1 = 0.0885$, $wR2 = 0.2409$, R indices based on 11067 reflections with $I > 2\sigma(I)$, 749 parameters, 60 restraints. Lp and absorption corrections applied using SADABS, $T_{min}/T_{max} = 0.765$, $\mu = 1.343$ mm^{-1}. Residual electron density = 1.382 e Å^{-3}.

1·**5**: $C_{36}H_{52}N_6O_4Cl_4S$, $M_r = 806.70$, colorless plates, $0.4 \times 0.3 \times 0.05$ mm^3, monoclinic, space group $P2_1$, $a = 10.611(5)$, $b = 18.193(6)$, $c = 10.803(3)$ Å, $\beta = 106.36(2)°$, $V = 2001.0(12)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.339$ g cm^{-3}, $F_{000} = 852$, Bruker Nonius KappaCCD, Mo$_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, phi and omega scans, $T = 120(2)$ K, $2\theta_{max} = 55.54°$, 17479 reflections collected, non-merohedral twinned data—not merged. Final GOF = 1.173, $R1 = 0.1005$, $wR2 = 0.1831$, R indices based on 17479 reflections with $I > 2\sigma(I)$, 467 parameters, 5 restraints. Lp and absorption corrections applied using TWINABS, $T_{min}/T_{max} = 0.663$, $\mu = 0.394$ mm^{-1}. Residual electron density = 1.461 e Å^{-3}. Absolute structure parameters were not reliably determined because of twinning. All structures were solved with direct methods by using SHELXS 97, and refined on F^2 by using SHELXL 97.[12] Non-hydrogen atoms were refined anisotropically. H atoms were calculated and placed in idealized position by using a riding model. CCDC-257828–257832 and -258077–258080 contain the supplementary crystallographic data for **1**-CsF, **1**-CsCl·CH_2Cl_2, **1**-CsBr·2 CH_2Cl_2, $\mathbf{1}_2$-Cs_2CO_3·4 CH_2Cl_2, **1**-CsEtOCO$_2$·0.5 EtOH, **1**·**3**·CH_2Cl_2·2 H_2O **1**·**2**·CH_2Cl_2·2 H_2O, **1**·**4**, and **1**·**5**, respectively. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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dimension as a result of complexation by **1**. This arrangement leads to the shorter intermolecular contact distances observed in the **1**-CsX structures. Although these latter distances may appear short, they are, however, a simple consequence of crystal packing within one-dimensional coordination polymers. The binding of ion pairs within appropriate ditopic receptors can also lead to a shortening of the interionic distance relative to that seen in pure M^+X^- salts. For a particularly cogent example of this latter effect, see: J. M. Mahoney, R. A. Marshall, A. M. Beatty, B. D. Smith, S. Camiolo, P. A. Gale, *J. Supramol. Chem.* **2001**, *1*, 289–292, in which an NaCl ion pair is bound by an ion-pair receptor with a shorter interionic distance than that found in the NaCl crystalline lattice.

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