Supramolecular Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713649759

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To cite this Article Rissanen, Kari , Huuskonen, Juhani , Windscheif, Paul-Michael and Vögtle, Fritz(1993) 'Self-assembly by co-ordination and strong hydrogen bonding. X-ray crystal structures of a dimeric trisodium complex of a new acidic complexing ligand and its dihydrate', Supramolecular Chemistry, 2: 2, 247 — 250

To link to this Article: DOI: 10.1080/10610279308038323

URL: http://dx.doi.org/10.1080/10610279308038323

SUPRAMOLECULAR CHEMISTRY, Vol. 2, pp. 247–250
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Self-assembly by co-ordination and strong hydrogen bonding. X-ray crystal structures of a dimeric trisodium complex of a new acidic complexing ligand and its dihydrate

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(Received September 1, 1992)

The new acidic complexing ligand triethanolamine-*O,O,O*-triacetic acid, 3, is synthesized by reaction of triethanolamine with chloroacetic acid in the presence of sodium tert-butoxide. The resulting Na complex, 4, and its dihydrate, 5, contain two ligand molecules, both with one Na^+ ion interaction and both co-ordinated to a third, central, Na^+ ion. In addition the acidic ligands are hydrogen bonded to each other, like carboxylic acids, and in 4, by three crystallographically symmetric hydrogen bonds, while in 5, due to the breakdown of symmetry, two normal and one crystallographically symmetrical hydrogen bond. Inside this extraordinary dimeric assembly (a pseudo-cryptate) are the three sodium ions encapsulated, like in cryptates, with a $Na^+ \cdots Na^+$ distance of 3.357(3) Å (4) and 3.325(2) Å (5). Crystal data, 4: $a = 12.198(1)$ Å, $c = 40.926(5)$ Å, $V = 5274(3)$ Å, trigonal, space group = $R\text{-}3c$ (no. 157), $d_{calc} = 1.346$ g cm^{-3}, $Z = 6$, obs. refl. $[I > \sigma I] = 396$, $R = 0.045$; 5: $a = 25.045(5)$ Å, $b = 11.373(2)$ Å, $c = 14.301(2)$ Å, $\beta = 122.38(1)°$, $V = 3440(1)$ Å^3, monoclinic, space group = $C2/c$, $d_{calc} = 1.446$ g cm^{-3}, $Z = 4$, obs. refl. $[I > 2\sigma I] = 1362$, $R = 0.041$.

INTRODUCTION

Ethylenediaminetetraacetic acid, nitrilotriacetic acid and diethylene triaminepentaacetic acid are well known as commercial complexing ligands (complexones) in complexometric analysis of various metal cations.[1] Complexones have also been studied as sequestering agents for radioisotopes, for tumour imaging and for other applications.[2] Previously this type of acidic ligand has been obtained by incorporating acidic groups into crown-type compounds.[3] Based on an earlier study on the stereology principle[4] and bipyridine-based acidic complexones,[5] we have now combined the known properties of open-chain crown compounds (podands) into a new acid ligand, 3. This type of nitrogen-containing ligand with acidic groups should allow limited zwitterion formation and should therefore show interesting solubility, complexing and selectivity features. Self-assembly of a ligand of this simplicity was previously unknown. Bipyridine-based oligomeric ligands have been shown to self-organize into helical structures when complexed with the proper metal ions.[6] A structurally quite similar linear trinuclear copper(I) lariat-ether complex, as well as the dimerization with simultaneous metal co-ordination product, and the hydrogen bonding of a few nucleotide and other natural compounds, have been reported.[7] The trinuclear copper(I) complex does not show any interaction between the ligands themselves and is therefore to be considered as a 'normal' complex. In this work we present the first example of self-assembly by co-ordination and strong hydrogen bonding of two relatively simple ligand molecules and three Na^+ ions.

RESULTS

The new ligand, 3 (TEATA, for triethanolamine-*O,O,O*-triacetic acid) is obtained by reaction of 1 mol of triethanolamine (TEA) 1 with 3 mol of chloroacetic acid 2 in the presence of Na-t-butoxide in tert-butanol. After acidification (HCl, to pH 2–2.5) of the strongly basic reaction media and recrystallization, the sodium complex 4 is formed due to simultaneous complexation with the Na^+ ions present in the reaction mixture. It is readily soluble in water and DMSO, but nearly

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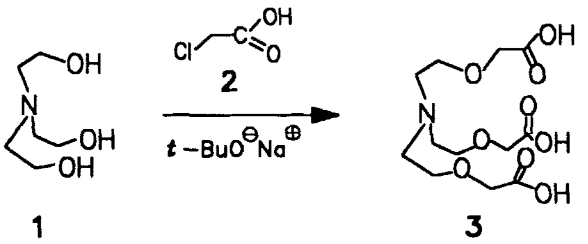
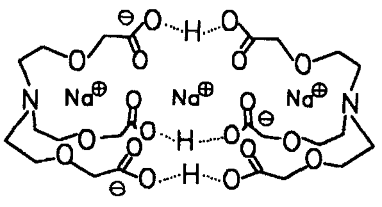


Scheme 1



4

Scheme 2

insoluble in cold methanol. It was therefore recrystallized from hot methanol. The IR spectrum shows an asymmetric C=O stretching band at $v = 1700\,\text{cm}^{-1}$, δ_{oop} (OH···H) deformation at $v = 870\,\text{cm}^{-1}$ and a weak band for O—H at $v = 3450\,\text{cm}^{-1}$ for strong hydrogen bonding. ^{13}C-NMR (D_2O) shows four signals with normal chemical shifts and ^{1}H-NMR (DMSO-d_6), two triplets and one singlet for the six protons (the hydrogen-bonded proton could not be seen). Due to the poor solubility in hot methanol, crystals suitable for X-ray analysis were obtained by slow cooling of a hot DMF solution resulting in small colourless prismatic crystals.

X-ray diffraction analysis* shows an extraordinary self-organization of two ligand molecules of **3** and three Na^+ cations to form the highly symmetric (only 1/16 of the molecule has to be defined), five-component supramolecular complex, **4**. Due to the resemblance of this assembly to cryptates, we call it a pseudo-cryptate.

The formation route of this surprising complex, **4**, is yet unknown but it presumably proceeds via a TEATA monomer complex with one Na^+ ion followed by additional complexation with the third Na^+ ion coupled with spontaneous self-organization of strong hydrogen bonds into the dimeric pseudo-cryptate. This pseudo-cryptate structure of **4** is closed and reinforced by three very strong, crystallographically symmetrical[8] hydrogen bonds [O···O distance 2.421(7) Å; Fig 1].

The recrystallization vessel of **4** was left standing at room temperature (DMF slowly evaporating) for a few days and after 24 h new and differently shaped crystals began to crystallize from the solution. These new crystals were also colourless but were octahedral shaped. The unit cell analysis showed a lower crystal symmetry (monoclinic; for **4** it was trigonal) but the structure analysis showed the same overall pseudo-cryptate structure with the three Na^+ ions inside as in **4**, but now with two water molecules hydrogen bonded to two of the carbonyl oxygens (Fig 2). The crystallization with the two water molecules breaks down the extraordinarily high symmetry of the unhydrated complex **4** and also produces slight changes in bond distances and angles. In addition to the change in the overall symmetry, a change in the extraordinary hydrogen bonding pattern was found. The three crystallographically symmetrical hydrogen bonds present in **4** are changed to two 'normal' hydrogen bonds (due to the hydrogen bond with the water molecule) and one crystallographically symmetrical hydrogen bond. The O···O distances are nearly the same as in **4**, being 2.466(4) Å for the 'normal' hydrogen bond and 2.419(6) Å for the crystallographically symmetrical hydrogen bond.

The Na^+ ions are co-ordinated to all oxygens and nitrogens, except for those associated with hydrogen bond formation (Figs 1 and 2). The bond distances around the central Na^+ ions are 2.439(4) Å (**4**) and 2.357(3)–2.517(3) Å (**5**). For the side Na^+ ions the bond distances are 2.390(4)–2.438(4), 2.643(7) Å (**4**) and 2.389(3)–2.446(3), 2.620(4) Å (**5**) for oxygen and nitrogen atoms, respectively. The co-ordination of the Na^+ ions is the same in both compounds. The co-ordination sphere of the central sodium is a slightly twisted trigonal prism (6 co-ordinate), while the side sodium ions have a slightly twisted mono-capped trigonal prismatic co-ordination (7 co-ordinate). The distance between the Na^+ ions inside the pseudo-cryptate is 3.357(3) Å in **4** and 3.325(2) Å in **5**, quite normal values for an oxygen-bridged Na···Na distance. The assembly shows, considered as a pseudo-cryptate, an *endo-endo* conformation with an N···N distance of 9.90(1) Å. A structurally similar three metal-ion-containing true cryptate, the Ag^{I}_3 complex of a tris-bipyridine cryptand, has earlier been studied by our group in co-operation with Lehn and de Mendoza.[9] The Ag^{I}_3–tris-bipyridine cryptate, which was the first example of a cryptand with three encapsulated silver ions, shows an *endo-endo* conformation with an N···N distance of 14.66 Å.

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*Supplementary material on the X-ray analyses of **4** and **5** is available from the authors and contains details of structure analysis, experimental data, fractional co-ordinates and equivalent isotropic thermal parameters for all atoms, bond distances and angles, anisotropic thermal parameters for non-H atoms and observed and calculated structure factors.

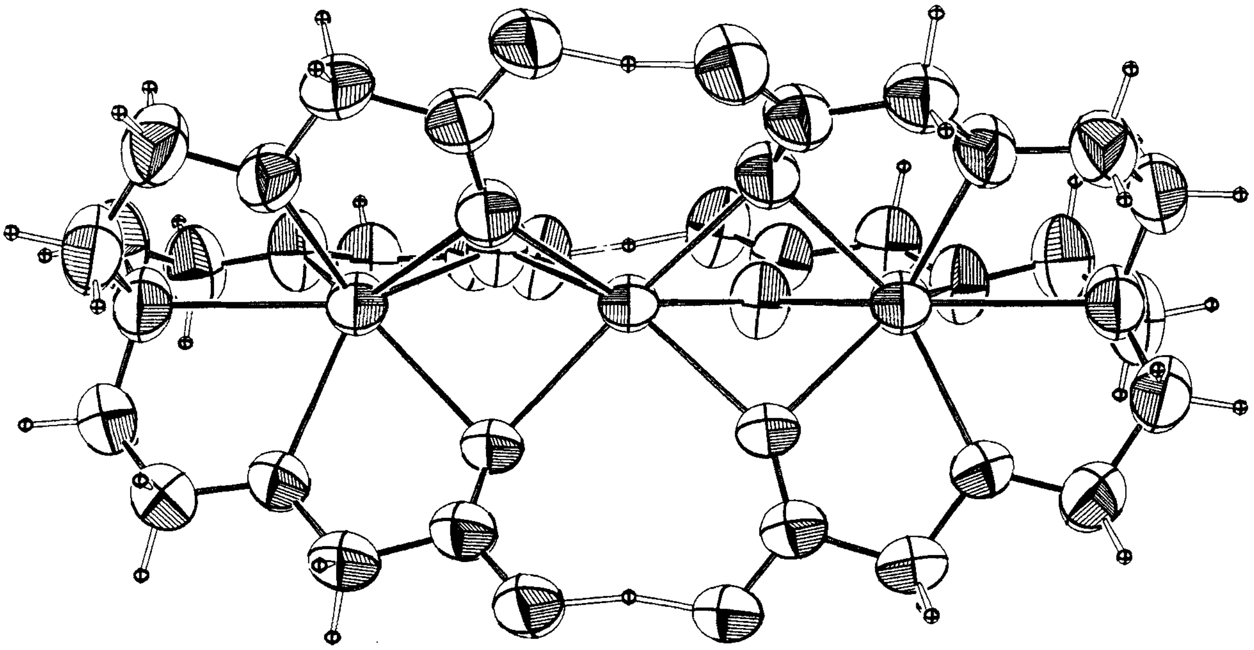

Figure 1 An ORTEP[11] plot for compound 4. The thermal ellipsoids are shown at the 40% probability level.

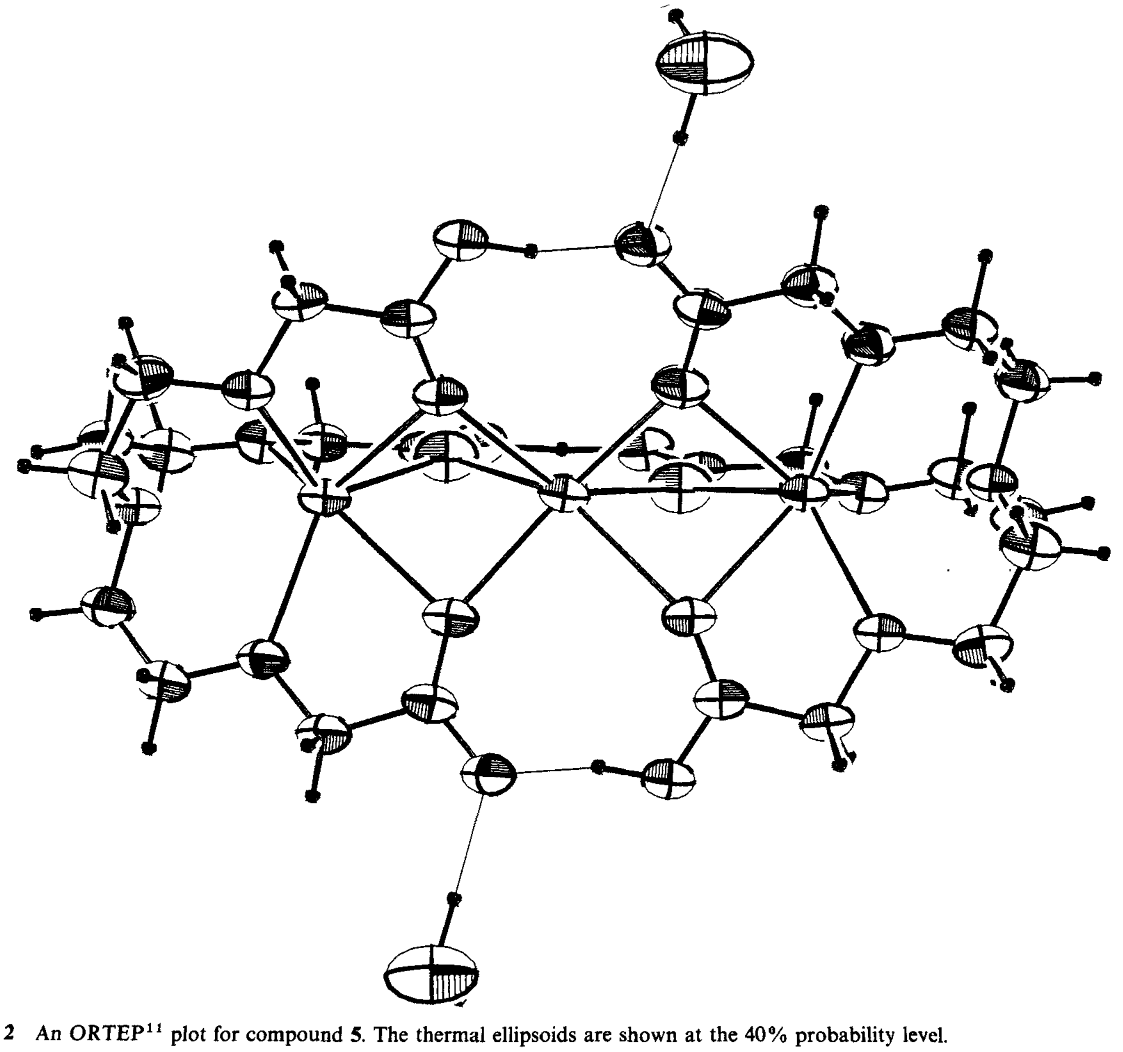

Figure 2 An ORTEP[11] plot for compound 5. The thermal ellipsoids are shown at the 40% probability level.

DISCUSSION

The discovery that self-assembly by co-ordination can be simultaneously enhanced by intermolecular hydrogen bonding combines self-organization via complexation[6] and supramolecular niche and pincer compounds[2b] in a new and exciting fashion. The possibility that spatially compatible counterparts may interact in this fashion opens up a new field of research in structural supramolecular chemistry. The spatial flexibility of TEATA and its complexing abilities make it a promising example of a new family of compounds which could be used in complexometric analytical chemistry and serves as an example of a new type of self-assembly in supramolecular chemistry comprising the novel features of podands, cryptands, dendrimers and nanoscale structures.[10]

EXPERIMENTAL

Synthesis of 3 and 4

In 300 ml of dry tert-butanol (Merck, no. 987) metallic sodium (6 g, 0.26 mol) was dissolved. In this solution TEA (6 g, 0.040 mol, Merck, no. 8377) was added and the mixture was refluxed with stirring for 30 min. A solution of chloroacetic acid (11.4 g, 0.12 mol, BDH, no. 10075) in 100 ml of dry tert-butanol was added during 45 min and refluxed with stirring for 15 h. The reaction mixture was poured into ice/water, the tert-butanol removed in vacuo, and the remaining solution extracted with chloroform. The aqueous phase, acidified with concentracted hydrochloric acid (to pH = 2.0–2.5), was evaporated to dryness. White powder, yield, as for **4**, 200 mg (1%). The compounds was dissolved into hot methanol and recrystallized upon cooling as a sodium complex, **4**.

Physical and spectroscopic data for 4

M.p. > 300°C; ^{1}H-NMR (Jeol GSX, 270 MHz, DMSO, 90°C): δ 2.76 (t, 6H, NCH_2), 3.68 (t, 6H, OCH_2), 4.00 (s, 6H, OCH_2CO); ^{13}C-NMR (Jeol GSX, 67.9 MHz, D_2O, 30°C): δ 48.66 (OCH_2COO), 59.67 (NCH_2), 64.59 (OCH_2), 172.39 (COOH); IR (Perkin-Elmer 283, KBr wafer): v (cm^{-1}) 1700 (C=O), 870 (OH$\cdots$H), 3450 (O—H).

X-ray crystal structure analysis of 4 and 5

Crystals suitable for X-ray analysis were grown from hot DMF by cooling for compound **4** and by evaporating the recrystallization solution of **4** for compound 5. Further information can be found in supplementary material available from the authors.

ACKNOWLEDGEMENT

This work has been supported by the Finnish Academy (project no. 1031137) and includes a postgrduate grant for J.H.

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