

IN THIS ISSUE

ISSN 1144-0546 CODEN NJCHES 32(5) 745–892 (2008)



Cover

See Steed *et al.*, pp. 786–789. The cover image shows two viologen-based colourimetric anion sensors that respond to different amounts of anion depending on internal competition within the molecules. They are superimposed on an image of flowers taken in Tachikawa, Japan. The colours reflect the colour changes undergone by the anion sensors. Image reproduced with permission from Jonathan W. Steed *et al.* from *New J. Chem.*, 2008, **32**, 786.



Inside Cover

See Robinson *et al.*, pp. 774–776. The cover displays the structure of a molecule containing the first unsupported group 13–hafnium bonds (pink orbs = group 13 elements; blue orb = hafnium). Two identical group 13 metals are bonded to the central hafnium atom resulting in a “V-shaped” core architecture. Image reproduced with permission from Gregory H. Robinson *et al.* from *New J. Chem.*, 2008, **32**, 774.

CHEMICAL SCIENCE

C33

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Chemical Science

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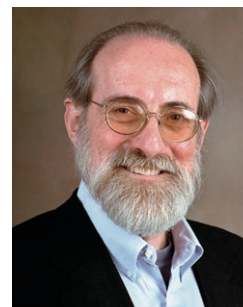
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EDITORIAL

761

Introduction to the special issue in honour of Jerry Atwood

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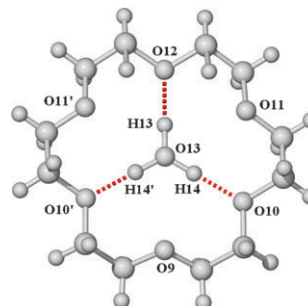
PERSPECTIVE

762

Crown ethers as stabilising ligands for oxonium ions

Peter C. Junk

Crown ethers can be used to isolate oxonium ions ($\text{H}^+ \cdot (\text{H}_2\text{O})_n$ ($n = 1, 2, 3, 4$)). The structure and oligonuclearity of the oxonium ion depends on the hydrogen bonding acceptor properties of the immediate environment.



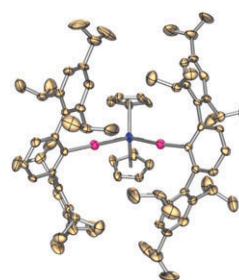
LETTERS

774

Organometallic compounds containing new Hf–Ga and Hf–In bonds: $\text{Cp}_2\text{Hf}(\text{ER})_2$ ($\text{Cp} = \text{C}_5\text{H}_5$; $\text{E} = \text{Ga}, \text{In}$; $\text{R} = -\text{C}_6\text{H}_3-2,6-(2,4,6-i\text{-Pr}_3\text{C}_6\text{H}_2)_2$)

Brandon Quillian, Yuzhong Wang, Pingrong Wei and Gregory H. Robinson*

Sodium metal reduction of RECl_2 ($\text{E} = \text{Ga}, \text{In}$; $\text{R} = -\text{C}_6\text{H}_3-2,6-(2,4,6-i\text{-Pr}_3\text{C}_6\text{H}_2)_2$) with Cp_2HfCl_2 gives $\text{Cp}_2\text{Hf}(\text{ER})_2$ compounds, which represent the first Hf–E bonds.

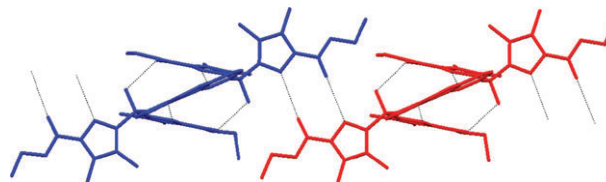


777

Oxidation-induced control of self-assembly using a bis-dipyrromethyl substituted phenanthroline building block

Patrick Plitt, Vincent M. Lynch and Jonathan L. Sessler*

Oxygenation of the *meso*-carbon atoms of the novel building block bis-dipyrromethyl substituted phenanthroline triggers a change in the hydrogen bond interactions from intramolecular to intermolecular.

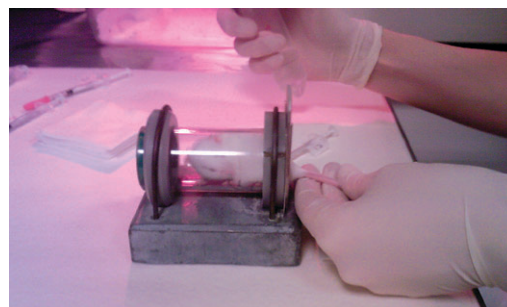


780

Toxicity and biodistribution of *para*-sulfonato-calix[4]arene in mice

Anthony W. Coleman,* Said Jebors, Sebastien Cecillon, Pascale Perret, Dominique Garin, Danièle Marti-Battle and Marcelle Moulin

In vivo testing of *para*-sulfonato-calix[4]arene in mice shows that the molecule has an acute toxicity at doses of 400 mg kg^{-1} ; the molecule is rapidly cleared from mice in urine and does not pass the blood–brain barrier.



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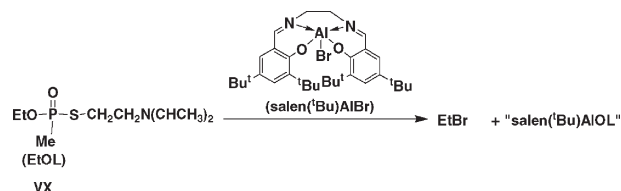
LETTERS

783

Group 13 chelates in nerve gas agent and pesticide dealkylation

Amitabha Mitra, David A. Atwood,* Jeffrey Struss, Daniel J. Williams,* Bradley J. McKinney, William R. Creasy, David J. McGarvey, H. Dupont Durst and Roderick Fry

Schiff base boron and aluminium bromides have been used to cleave organophosphate nerve agents and pesticides and their simulants.



786

Intramolecular binding site competition as a means of tuning the response of a colourimetric anion sensor

Sara Jane Dickson, Emma V. B. Wallace, Adam N. Swinburne, Martin J. Paterson, Gareth O. Lloyd, Andrew Beeby, Warwick J. Belcher and Jonathan W. Steed*

A viologen-derived double tripod receptor with pyridinium-based binding groups colourimetrically senses carboxylate ions. The number of equivalents of anion required for the onset of the colour change depends on the peripheral functional groups.

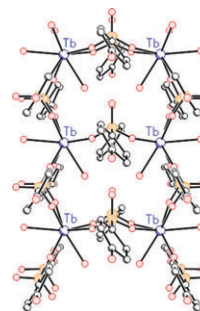


790

Synthesis and structures of luminescent ladder-like lanthanide coordination polymers of 4-hydroxybenzenesulfonate

Xiaoping Yang, Joseph H. Rivers, W. Jeffrey McCarty, Michael Wiester and Richard A. Jones*

Reaction of sodium 4-hydroxybenzenesulfonate dihydrate ($\text{NaL} \cdot 2\text{H}_2\text{O}$) with $\text{LnCl}_3 \cdot 6\text{H}_2\text{O}$ (3 : 1) in refluxing methanol gives the novel isomorphous 1-D framework compounds $[\{\text{LnL}_3(\text{H}_2\text{O})_2\} \cdot 2\text{H}_2\text{O}]_\infty$ ($\text{Ln} = \text{Tb}, \text{Er}$ and Yb) in 46–60% yields.

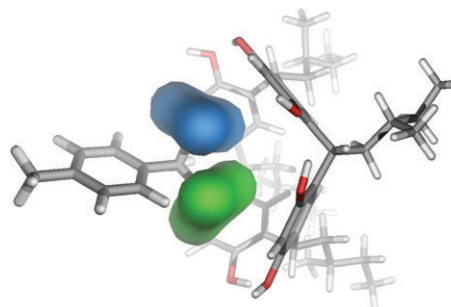


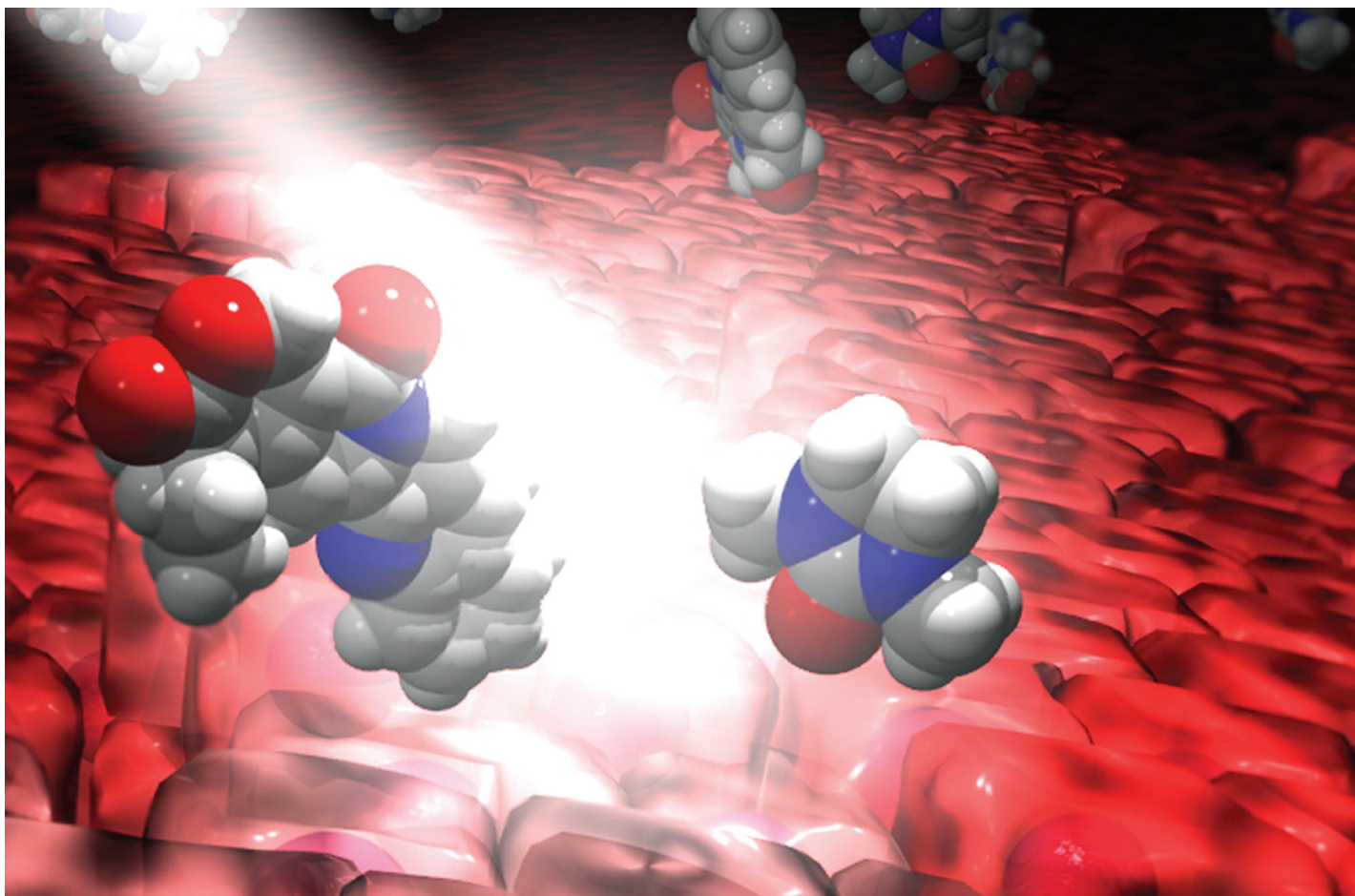
794

Effects of remote chiral centers on encapsulated molecules

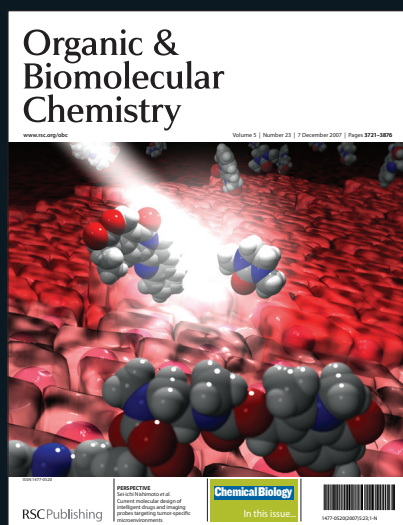
Michael P. Schramm and Julius Rebek, Jr.*

Two homotopic methyl groups become diastereotopic when encapsulated in a chiral hybrid assembly; remotely situated chiral centers at the base of the resorcinarene relay information through space, and these effects are shown to be a function of distance.





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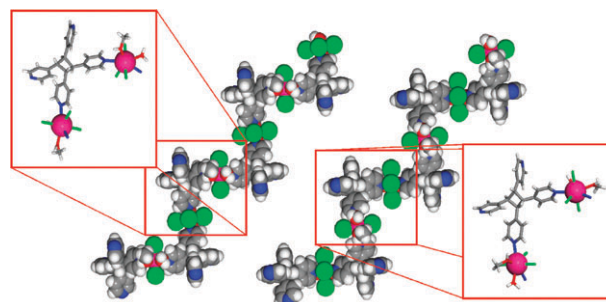
LETTERS

797

A lanthanide-based helicate coordination polymer derived from a rigid monodentate organic bridge synthesized in the solid state

Dejan-Krešimir Bučar, Giannis S. Papaefstathiou, Tamara D. Hamilton and Leonard R. MacGillivray*

A molecule synthesized in the organic solid state is shown to serve as a rigid and angular building block of a metallosupramolecular architecture, with a structure that conforms to a helicate.



PAPERS

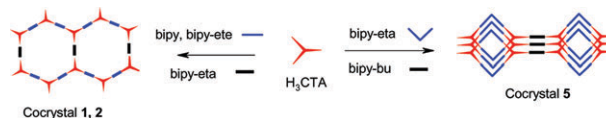
800

Ternary and quaternary co-crystals of 1,3-*cis*,5-*cis*-cyclohexanetricarboxylic acid and 4,4'-bipyridines

Balakrishna R. Bhogala and Ashwini Nangia*

Co-crystals of 1,3,5-cyclohexanetricarboxylic acid · 4,4'-bipyridine1 · bipyridine2 have hexagonal or square supramolecular network depending on the nature of methylene/ethene tether between the bipy groups.

A self-assembly model to explain the formation of different network architectures from similar node and connector building blocks is proposed.

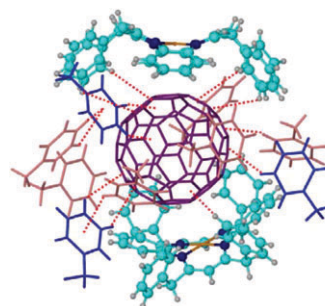


808

Controlling the confinement of fullerene C₆₀ molecules using a saddle shape Ni(II) macrocycle

Marck Norret, Mohamed Makha, Alexandre N. Sobolev and Colin L. Raston*

Synthesis of a novel saddle-shaped Ni-macrocycle (NiTBTA) and solid-state inclusion structure with fullerene C₆₀: interaction of sterically demanding ligand with fullerene C₆₀ effect dispersion of the fullerene in an overall hexagonal array.

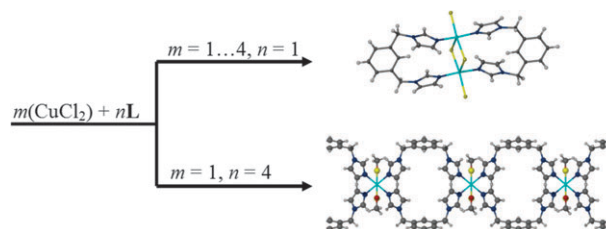


813

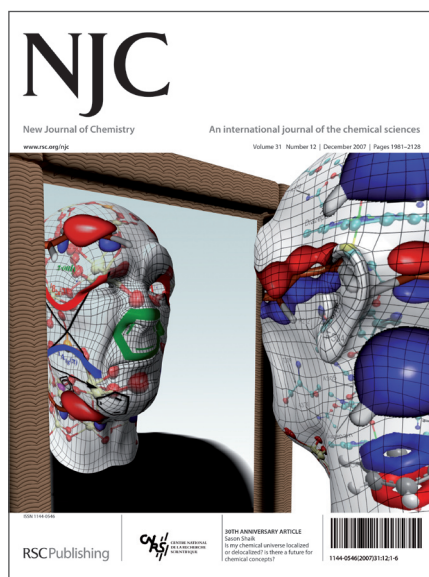
Influence of the metal-to-ligand ratio on the formation of metal organic complexes

Liliana Dobrzańska, Dewald J. Kleinhans and Leonard J. Barbour*

Three Cu(II) salts with Cl⁻, Br⁻ or NO₃⁻ counterions in combination with the ditopic ligand 1,3-bis(imidazol-1-ylmethyl)benzene (L) were used to study the influence of the metal to ligand molar ratio on the formation of the final product. Single-crystal X-ray analysis revealed structural diversity of the products formed, ranging from discrete species to extended 1D and 2D coordination polymers.



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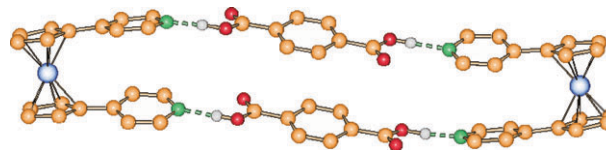
PAPERS

820

Mechanochemical assembly of hybrid organic–organometallic materials. Solid–solid reactions of 1,1'-di-pyridyl-ferrocene with organic acids

Dario Braga,* Stefano Luca Gialfreda, Fabrizia Grepioni,* Giuseppe Palladino and Marco Polito

Manual kneading of the organometallic complex $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{-C}_5\text{H}_4\text{N})_2]$ with solid fumaric, succinic, tridecanedioic, terephthalic, trimesic and thiophene-2,5-dicarboxylic acids generated the corresponding adducts, whether salts or molecular complexes.

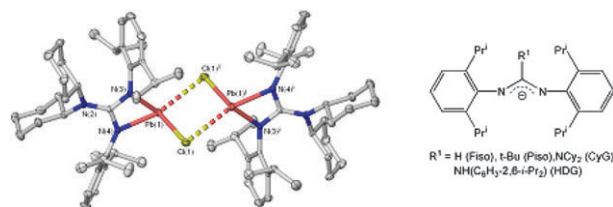


829

Thermally stable lead(II) amidinates and guanidates

Andreas Stasch, Craig M. Forsyth, Cameron Jones and Peter C. Junk*

Synthetically discriminating, bulky amidinate and guanidinate ligands (A) provide stable lead(II) complexes $[\text{Pb}(\text{L})_2]$ (L = Fiso) or $[\text{Pb}(\text{L})\text{Cl}]_2$ (L = Piso, CyG, HDG), the latter existing as loosely associated dimers in the solid state.

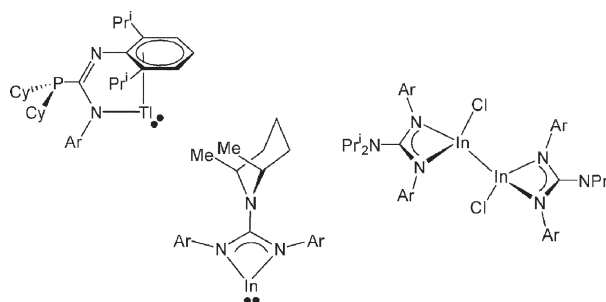


835

Group 13 metal(I) and (II) guanidinate complexes: effect of ligand backbone on metal oxidation state and coordination sphere

Guoxia Jin, Cameron Jones,* Peter C. Junk, Andreas Stasch and William D. Woodul

Reactions of guanidinate and phosphaguanidinate salts with group 13 metal(I) halides are reported. These have given a variety of metal(I) and (II) complexes that reveal how subtle changes to the sterics and electronics of the backbone substituents of the ligands can have a significant effect on the product obtained.

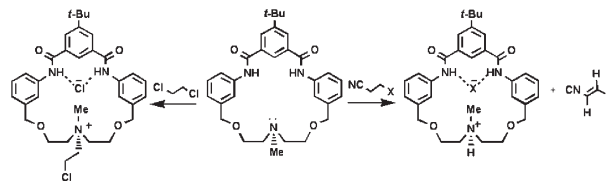


843

Crossing the threshold from accelerated substitution to elimination with a bifunctional macrocycle

Jeremiah J. Gassensmith, Jung-Jae Lee, Bruce C. Noll and Bradley D. Smith*

A macrocyclic amine with anion binding amide residues undergoes a highly accelerated substitution reaction with 1,2-dichloroethane but the outcome with 3-halopropionitriles is accelerated substitution.



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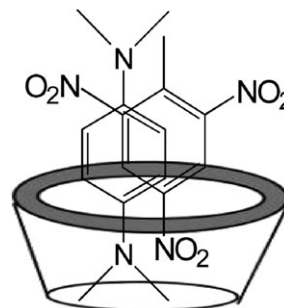
PAPERS

848

Pattern recognition based identification of nitrated explosives

Aravindan Ponnu, Nicola Y. Edwards and Eric V. Anslyn*

We report an effective approach for the identification of nitro explosives by the reaction of an electron-acceptor with an electron-donor with and without the addition of γ -cyclodextrin (γ -CD). Pattern recognition analysis was applied to analyze the data collected and it showed successful discrimination of the nitro explosives. This work represents the simplest colorimetric chemical sensor technique to be used in monitoring the range of common nitro explosives.

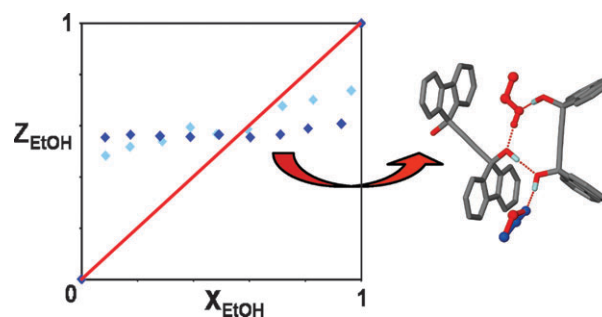


856

Selectivity and structure of mixed guest clathrates

Tanya le Roex,* Luigi R. Nassimbeni and Edwin Weber

Crystal structure analyses of mixed guest clathrates are correlated to their selectivity profiles giving surprising results.

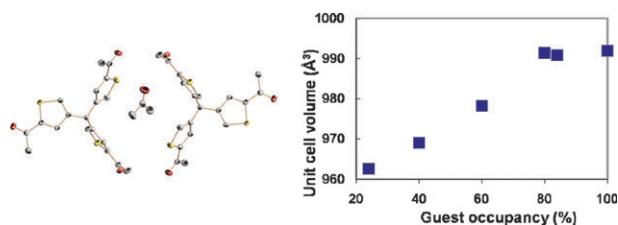


864

Guest capture, storage and removal in the TATM host framework: a single-crystal study

Tara J. Burchell, Gary D. Enright and John A. Ripmeester*

Herein we examine the effects of guest removal on the crystallographic parameters of TATM host–guest inclusion compounds and the degree to which simple organic guest molecules can be removed from the inclusion before framework collapse.

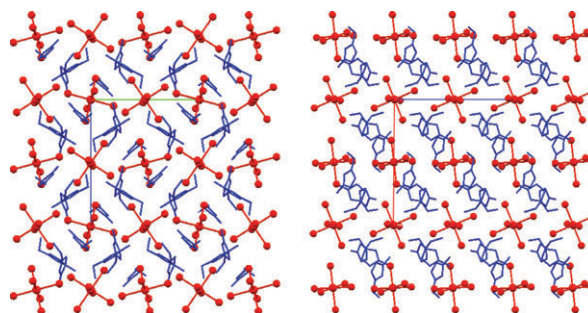


872

Flexible coordination environments of lanthanide complexes grown from chloride-based ionic liquids

C. Corey Hines, David B. Cordes, Scott T. Griffin, Savannah I. Watts, Violina A. Cocalia and Robin D. Rogers*

Hydrated lanthanide(III) chlorides readily dissolve in the low melting ionic liquid 1-ethyl-3-methylimidazolium chloride in an open vessel at 110 °C, and upon cooling crystallize as the anhydrous $[\text{C}_2\text{mim}]_3[\text{LnCl}_6]$.



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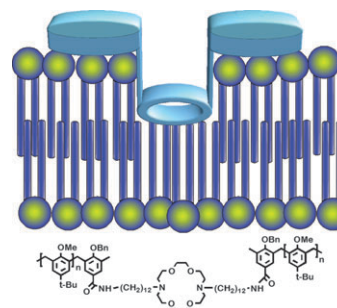
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Synthetic cation transporters incorporating crown ethers and calixarenes as headgroups and central relays: a comparison of sodium and chloride selectivity

José Carlos Iglesias-Sánchez, Wei Wang, Riccardo Ferdani, Pilar Prados, Javier de Mendoza and George W. Gokel*

Calixarenes, explored as headgroups and central relay elements in synthetic hydrophile-like ion channels, afforded poor transporters but amide elements incorporated as central relay controls showed chloride over sodium selectivity.



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AUTHOR INDEX

- Anslyn, Eric V., 848
 Atwood, David A., 783
 Barbour, Leonard J., 813
 Beeby, Andrew, 786
 Belcher, Warwick J., 786
 Bhogala, Balakrishna R., 800
 Braga, Dario, 820
 Bučar, Dejan-Krešimir, 797
 Burchell, Tara J., 864
 Cecillon, Sebastien, 780
 Cocalia, Violina A., 872
 Coleman, Anthony W., 780
 Cordes, David B., 872
 Creasy, William R., 783
 de Mendoza, Javier, 878
 Dickson, Sara Jane, 786
 Dobrzańska, Liliana, 813
 Durst, H. Dupont, 783
 Edwards, Nicola Y., 848
 Enright, Gary D., 864
 Ferdani, Riccardo, 878
 Forsyth, Craig M., 829
 Fry, Roderick, 783
 Garin, Dominique, 780
 Gassensmith, Jeremiah J., 843
 Giaffreda, Stefano Luca, 820
 Gokel, George W., 878
 Grepioni, Fabrizia, 820
 Griffin, Scott T., 872
 Hamilton, Tamara D., 797
 Hines, C. Corey, 872
 Iglesias-Sánchez, José Carlos, 878
 Jebors, Said, 780
 Jin, Guoxia, 835
 Jones, Cameron, 829, 835
 Jones, Richard A., 790
 Junk, Peter C., 762, 829, 835
 Kleinhans, Dewald J., 813
 le Roex, Tanya, 856
 Lee, Jung-Jae, 843
 Lloyd, Gareth O., 786
 Lynch, Vincent M., 777
 MacGillivray, Leonard R., 797
 Makha, Mohamed, 808
 Marti-Battle, Danièle, 780
 McCarty, W. Jeffrey, 790
 McGarvey, David J., 783
 McKinney, Bradley J., 783
 Mitra, Amitabha, 783
 Moulin, Marcelle, 780
 Nangia, Ashwini, 800
 Nassimbeni, Luigi R., 856
 Noll, Bruce C., 843
 Norret, Marck, 808
 Palladino, Giuseppe, 820
 Papaefstathiou, Giannis S., 797
 Paterson, Martin J., 786
 Perret, Pascale, 780
 Plitt, Patrick, 777
 Polito, Marco, 820
 Ponnu, Aravindan, 848
 Prados, Pilar, 878
 Quillian, Brandon, 774
 Raston, Colin L., 808
 Rebek, Jr., Julius, 794
 Ripmeester, John A., 864
 Rivers, Joseph H., 790
 Robinson, Gregory H., 774
 Rogers, Robin D., 872
 Schramm, Michael P., 794
 Sessler, Jonathan L., 777
 Smith, Bradley D., 843
 Sobolev, Alexandre N., 808
 Stasch, Andreas, 829, 835
 Steed, Jonathan W., 786
 Struss, Jeffrey, 783
 Swinburne, Adam N., 786
 Wallace, Emma V. B., 786
 Wang, Wei, 878
 Wang, Yuzhong, 774
 Watts, Savannah I., 872
 Weber, Edwin, 856
 Wei, Pingrong, 774
 Wiester, Michael, 790
 Williams, Daniel J., 783
 Woodul, William D., 835
 Yang, Xiaoping, 790

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