

knowledge, alkaline-earth 2,2'-diphenyldicarboxylate complexes have never been reported.

In this context and following our systematic studies on the alkaline-earth dicarboxylates complexes with 2,2'-diphenyldicarboxylic acid, a new barium(II) compound of formula $[\text{Ba}(\text{H}_2\text{O})_4(\text{dpdc})] \cdot 0.25 \text{ H}_2\text{O}$ has been prepared and structurally characterized by X-ray crystallography. The Barium (II) ions are nine coordinated by three oxygen atoms from two diphenato groups and six oxygen atoms from six water molecules of which five acting as bridging ligands and one as monodentate. The distances Ba – O range from 2.704(5) to 2.974(4) Å forming a slightly distorted monocapped dodecahedron. The structure of $[\text{Ba}(\text{H}_2\text{O})_4(\text{dpdc})]_n$ consists of two-dimensional layers, built up from the self-assembly of zigzag chains of face and edge-sharing $\{\text{BaO}_9\}$ polyhedra linked by bridging bidentate diphenate anions through different coordination modes of the carboxylate groups. The Ba...Ba distances across these chains are 4.3519(6) and 4.6013(5) Å. The polymer layers form a three-dimensional network via O-H...O hydrogen-bond interactions between the coordinated water molecules and the O atoms of the carboxylate groups.

- [1] J. M. Rueff, S. Pillet, N. Claiser, G. Bonaventure, M. Souhassou, P. Rabu, *Eur. J. Inorg. Chem.*, 2002, 895.
 [2] H. Kumagai, K. Inoue, M. Kurmoo, *Bull. Chem. Soc. Jpn.*, 75, 2002, 1283.
 [3] A. Thirumurugan, S. K. Pati, M. A. Green, S. Natarajan, *J. Mater. Chem.*, 13, 2003, 2937.
 [4] Y. B. Wang, X. J. Zheng, W. J. Zhuang, L. P. Jin, *Eur. J. Inorg. Chem.*, 2003, 1355.

MS13 P16

Gas sorption and binding in a nonporous single crystal
Tia Jacobs, Gareth O. Lloyd, Liliana Dobrzańska, Martin W. Bredenkamp and Leonard J. Barbour, *Department of Chemistry, University of Stellenbosch, South Africa*.
 E-mail: tj@sun.ac.za.

Keywords: gas-solid interactions; discrete metalocycles; single crystal diffraction

Recently, coordination chemistry has become an active area of research in the field of crystal engineering of porosity. The coordination-driven motif offers an easier alternative to the synthesis of discrete supramolecular units when considering the classic syntheses involved in producing covalently bonded macromolecules.^[1] Despite efforts to predict and define the parameters governing the assembly of discrete coordination compound architectures^[2], rational design of these types of molecular structures is still not possible. We are interested in molecules with this topology because, even if efficiently close-packed in the crystalline state, these structural synthons, can yield significant solvated space in the crystal.^[3] Here we report an imidazole-derived bridging ligand self-assembling with metal ions to form a series of discrete neutral metalocycles. In these solvent templated systems it is possible to remove guest solvent molecules without concomitant rearrangement of the host lattice. Such structures possess cavities of ca. 110 Å³ and have the notable feature of being structurally flexible during the gas sorption process. Since the desolvation procedure and subsequent gas sorption experiments can all occur as single-crystal to single-crystal transformations, it has been possible to study the gas-solid interactions using X-ray diffraction techniques. These studies are also

complemented by gravimetric and volumetric gas sorption experiments.

- [1] S. Leiniger, B. Olenyuk and P.J. Stang, *Chem. Rev.* 100, 853 (2000).
 [2] B. Moulton and M.J. Zaworotko, *Chem. Rev.* 101, 1629 (2001).
 [3] L. Dobrzańska, G.O. Lloyd, H.G. Raubenheimer and L.J. Barbour, *J. Am. Chem. Soc.* 127, 13134 (2005).

MS13 P17

Crystal Structure of 3,4,4-Trichloro-2-nitro-1-propylsulfanyl-1-(4-thiomorpholinyl)buta-1,3-diene
N.Gulsah Deniz^a, Cemil Ibis, ^a*Department of Chemistry, Istanbul University, Istanbul, Turkey*.
 E-mail: yurdakul@istanbul.edu.tr

Keywords: organic sulfur compounds, chemical crystallography, biologically important compounds.

Thiomorpholine analogues have found applications in medicine and agriculture [1]. Substituted thiomorpholino, morpholino and piperidino compounds enhanced the activity against Gram-positive bacteria, but reduced the activity against Gram-negative bacteria [2]. The aim of this study was to determine the conformation of the title compound [3]. In the title compound, C₁₁H₁₅Cl₃N₂O₂S₂, the structure contains the expected N,S-substituted butadienyl skeleton, an alkylsulfanyl chain and a thiomorpholine ring. The thiomorpholine ring adopts a chair conformation and the butadiene has a conformation closer to cisoid than to transoid. The C—C bond lengths within the butadiene unit are similar to those in related compounds [4]. The thiomorpholine ring adopts a chair conformation, as shown by the puckering angles of $\varphi = 1(3)^\circ$ and $\theta = 10.2(4)^\circ$ [5].

- [1] Barbacyn, M. R., Hutchinson, D. K., Brickner, S. J., Cynamon, M. H., Kilburn, J. O., Klemens, S. P., Glickman, S. E., Grega, K. C., Hedges, S. K., Toops, D. S., Ford, C. W. & Zurenko, G. E. *J. Med. Chem.*, 1996, 6802.
 [2] Taguchi, M., Kondo, H., Inoue, Y., Kawahata, Y., Jinbo, Y., Sakamoto, F. & Tsukamoto, G. *J. Med. Chem.*, 1992, 35, 94.
 [3] Ibis, C., Deniz, N.G., *Acta. Cryst.*, 2006, E62, o5373.
 [4] Ibis, C., Deniz, N.G., *Acta. Cryst.*, 2007, E63, o1091.
 [5] Cremer, D., Pople, J. A., *J. Am. Chem. Soc.*, 1975, 97, 1354.

MS13 P18

Metal-Organic Frameworks using pyridyldiynes ligands
Leigh Loots, Martin W. Bredenkamp and Leonard J. Barbour, *Department of Chemistry, University of Stellenbosch*. E-mail: leighl@sun.ac.za

Keywords: metal-organic frameworks, gas sorption, porosity

The ability to predict and thus control the assembly of networks is an ongoing challenge. It has been proposed that thin, rigid ligands will behave in a more predictable manner, than other, more flexible versions. The assembly of molecular frameworks and network polymers using bidentate ligands such as 4,4'-bipyridyldiynes has been of considerable interest. Their rod-like structures, owing to the alkynyl spacers as well as their conjugated systems that are of a rigid nature, are of specific interest.⁰ 4,4'-Bipyridine has previously been used to assemble a variety of crystalline designs such as chains, ladders, squares, diamondoids, etc. as well as a few innovative coordination polymer networks exhibiting a measure of porosity.⁰ In

recent years these ligands have been studied for their capacity as conductors and in optical applications.⁰ Our objective is to use these previously reported ligands as well as novel ligands and coordinate them to various transition metals in order to prepare unique metal-organic frameworks (MOFs). Coordination of the ligand 1,4-bis(4'-pyridyl)butadiyne, with CuNO₃ has been shown to form square-grid architectures with the inclusion of methylene chloride solvent. This supramolecular material and other related examples have been investigated for their gas sorption abilities.

[1] N.R. Champness, A.N. Khlobystov, A.G. Majuga, M. Schröder and N.V. Zyk, *Tetrahedron Letters*, 1999, 40, 5413.

[2] J. Gonzalo Rodríguez, R. Martín-Villamil, F.H. Cano and I. Fonseca, *J. Chem. Soc., Perkin Trans. 1*, 1997, 709.

[3] Md. B. Zaman, M.D. Smith, and H.C. Zur Loye, *Chem. Mater.*, 2001, 13, 3534

MS13 P19

A gating mechanism accounts for gas transport through calixarene crystals. Charl G. Marais, Jan A. Gertenbach, Leonard J Barbour and Catharine Esterhuysen. *Department of Chemistry, University of Stellenbosch, South Africa.* E-mail: charl@sun.ac.za

Keywords: calixarene, gate-opening, storage

Porous solids have attracted considerable attention owing to their unusual physico-chemical properties [1] and are of particular economic interest with regard to their potential applications in gas storage [2], separation and sensing [3]. Commercially, alternative safe storage mechanisms for acetylene, a highly reactive and dangerous gas, should be investigated as it plays a crucial part as a starting material in several chemical products and electronic materials [1,4]. Since it is important to purify acetylene for the manufacture of these materials, it is necessary to devise systems to separate acetylene from gas mixtures that also contain carbon dioxide and other impurities.

An investigation of gas transport and storage mechanisms in *t*-butylcalix[4/8/9]arenes using standard crystallographic and computational molecular force field techniques was conducted with a view to gaining greater insight into solid-gas interactions and solid-state dynamics. Furthermore, X-ray structural studies have also been undertaken in order to identify the active site within the guest-accessible voids.

Results from computational calculations were used to predict a mechanism for gas transport and storage. These findings are correlated with the crystallographic and sorption data. The investigation suggests that a gating mechanism is the driving force for gas transport and sequestration in the calixarene crystals.

[1] Kitagawa, S *et al.* Highly controlled acetylene accommodation in a metal-organic microporous material. *Nature* 436, 238-241 (2005).

[2] Zhao, X. *et al.* Hysteretic adsorption and desorption of hydrogen by nanoporous metal-organic frameworks. *Science* 306, 1012–1015 (2004).

[3] Bradshaw, D., Prior, T. J., Cussen, E. J., Claridge, J. B. & Rosseinsky, M. J. Permanent microporosity and enantioselective sorption in a chiral open framework. *J. Am. Chem. Soc.* 126, 6106–6114 (2004).

[4] Stang, P. J. & Diederich, F. *Modern Acetylene Chemistry* (VCH, New York, 1995).

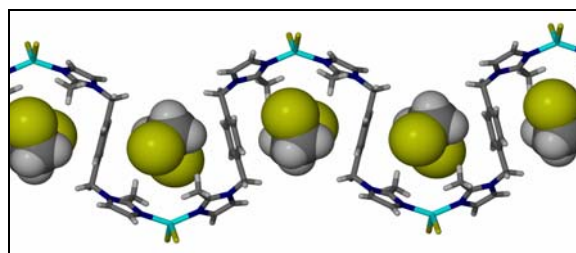
MS13 P20

Porosity studies of wave-like, one-dimensional coordination polymers. Storm Potts, Liliana Dobrzańska, Martin W. Bredenkamp and Leonard J Barbour. *Department of Chemistry, University of Stellenbosch, South Africa.* E-mail: storm@sun.ac.za

Keywords: porous materials, coordination compounds, gas-solid interactions

The formation of porous crystalline materials is a central theme of our research efforts. Our approach is to design and prepare solvent-templated host-guest systems consisting of simple coordination compounds grown from common solvents. In general, the solvent molecules can be removed as single-crystal to single-crystal processes to afford porous or seemingly nonporous systems that are still permeable to various gases.

A range of such compounds have been characterised by X-ray diffraction methods with supporting data obtained using thermogravimetry, sorption isotherms and modeling studies. Although we are primarily interested in forming discrete dinuclear complexes, we have also obtained interesting new results using wave-like one-dimensional coordination polymeric systems. These are obtained from the crystallization of CuCl₂·L from 1,2-dichloroethane. We find that that the polymeric waves stack one over the other to form guest-accessible pockets of approximately 143 Å³. We will present X-ray structural data as well as the results of gas sorption studies.



[1] L. Dobrzańska, G.O. Lloyd, H.G. Raubenheimer and L.J. Barbour, *J. Am. Chem. Soc.* 127, 13134 (2005).

MS13 P21

Crystal Structures and Properties of [M(NH₃)₅Cl]₂[Re₆S₈(CN)₆]·3H₂O Kirill Yusenko^a, Elena Shusharina^b, Iraida Baidina^a, Sergey Gromilov^a ^a*Nikolaev Institute of Inorganic Chemistry, Novosibirsk, Russia.* ^b*Faculty of Natural Science, Novosibirsk State University, Russia.* E-mail: yusenko@che.nsk.su

Keywords: clusters in coordination complexes, platinum group, rhenium

Using an inert [M(NH₃)₅Cl]²⁺ (M = Rh, Ir, Ru) cations upon crystallisation of the salt with the [Re₆S₈(CN)₆]⁴⁻ anion makes possible the preparation of compounds with the island crystal structures containing the isolated cations and large cyanide anions. The compounds [M(NH₃)₅Cl]₂[Re₆S₈(CN)₆]·3H₂O (M = Rh (1); Ir (2); Ru (3)) have been synthesized by crystallization from aqueous solutions. The compounds are isostructural. They crystallize in the triclinic space group P-1 with the cell parameters for 1: a = 10.7574(7), b = 13.9423(9), c = 14.7975(9) Å, α = 92.031(2)°, β = 110.137(2)°, γ = 109.976(2)°, V = 1928.7(2) Å³.