


Editorial

# Cornerstones in Contemporary Inorganic Chemistry

Duncan H. Gregory 

WestCHEM, School of Chemistry, University of Glasgow, Glasgow G12 8QQ, UK; duncan.gregory@glasgow.ac.uk

I am very happy to be able to present this Special Issue of *Inorganics*. The aim of this Special Issue, “Cornerstones in Contemporary Inorganic Chemistry”, was to assemble a collection of seminal articles representing some of the most important aspects of inorganic chemistry in the early 21st century. I am delighted to say that the response to the call for papers was overwhelming but that it has been possible to select some of the finest works for publication in this issue. Inorganic chemistry remains a broad church, and the contributions to this Special Issue reflect just that. With a healthy balance of original papers and review articles, this Special Issue is able to capture the excitement at the cutting edge of some of the most topical of research areas and to address some of the key questions that occupy inorganic chemists today. This Special Issue also collates informative and thought-provoking works that can be referred to for a long time to come by researchers at all levels.

Altogether, this Special Issue compiles 14 original research articles and 4 review papers. The original research articles are considered first, and in no particular order, several different aspects of coordination chemistry are represented within this Special Issue. As is often the case in current times with many branches of chemistry (and science, more generally), the themes can be cross-cutting. Modern coordination chemistry has often taken the researcher beyond the bounds of the traditional coordination complex or molecule into the realms of supramolecular and inorganic polymeric chemistry. In this context, Axel Klein and co-workers examined the world of copper(II) complexes formed from pyridine/pyrazine amide and amino benzamide ligands [1]. Such ligands offer a variety of hard and soft donor atoms and functional groups, offering the potential to form isolated complexes or coordination polymers. These are both the types of ligands favoured as building blocks in metal organic frameworks (MOFs) and the ones that are featured in many biological systems of interest (for example, in metalloenzymes). In this work, the authors discovered that it was the donor O atom of the amide groups that bonds preferentially to Cu(II) (as opposed to the N atom of the amide NH<sub>2</sub> group), giving axially distorted octahedral (or square pyramidal) copper environments with the remainder of the coordination sphere typically made up from pyridine/pyrazine ring N donors. The crystallography is corroborated by EPR, UV-Vis and magnetic measurements.

The theme of copper coordination polymers is continued in the paper by Housecroft et al., which elegantly demonstrated how ligand conformation can dictate the way in which coordination polymers pack, even when such packing is governed by relatively weak intermolecular interactions [2]. The ligands in question are isomers of terpyridine (4,2':6',4'' and 3,2':6',3''), and it is the positions of the N donor atoms that are crucial in determining the type of 1D chain that is observed in the resulting coordination polymers formed by reactions with Cu(hfacac)<sub>2</sub>·H<sub>2</sub>O. The zig-zag chains formed with V-shaped 4,2':6',4''-terpyridine are held together by C–F···F–C contacts, whereas chains formed with 3,2':6',3''-terpyridine are packed together through π–π stacking. The latter interactions are rendered impossible by the conformation of functional groups on the former chains.

We turn from 1D coordination polymers to Zintl phases as McGrady et al. combined experiments and calculations (density functional theory; DFT) to examine two new heterometallic clusters [3]. The two clusters, [(CO)<sub>3</sub>CrSn<sub>5</sub>Cr(CO)<sub>3</sub>]<sup>4−</sup> and [(CO)<sub>3</sub>MoSn<sub>5</sub>Mo(CO)<sub>3</sub>]<sup>4−</sup>,



**Citation:** Gregory, D.H. Cornerstones in Contemporary Inorganic Chemistry. *Inorganics* **2022**, *10*, 108. <https://doi.org/10.3390/inorganics10080108>

Received: 24 June 2022

Accepted: 4 July 2022

Published: 28 July 2022

**Publisher's Note:** MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



**Copyright:** © 2022 by the author. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

contain a similar pentagonal bipyramidal core, which can each be rationalised in terms of  $\text{Sn}_5^{4-}$  rings bridging two zero valent  $\text{M}(\text{CO})_3$  ( $\text{M} = \text{Mo}$  or  $\text{Cr}$ ) fragments. Intriguingly, their calculations revealed two types of dominant bonding: the bonds within the  $\text{Sn}_5^{4-}$  ring and *trans*-annular bonds formed between the two apical M atoms. In the case of the two synthesised compounds, the LUMO is dominated by the Sn-Sn  $\pi$ -bonding in the rings, but the balance is subtle and other isoelectronic 28 electron clusters possess LUMOs localised on the  $\text{M}_2$  apices, giving rise to the aforementioned *trans*-annular bond.

Of course, coordination complexes are not strictly the domain of d-block metals and Jones, Watts and Jones presented a study of alkali metal complexes formed with “super bulky”  $\beta$ -diketiminato (Nacnac) ligands [4]. Both lithium and potassium complexes were successfully produced, and each was shown to be highly reactive, offering the possibility of using the complexes as reagents themselves for the synthesis of new low-oxidation state metal complexes, which the ligands could stabilise kinetically. Finally, in terms of coordination chemistry, Richard Dronskowski and colleagues reported a new silver guanidine complex in their communication, which includes various aspects of its solid state chemistry [5]. In fact, the silver(I) cyanoguanidine nitrate hydrate,  $\text{Ag}(\text{C}_2\text{N}_4\text{H}_4)\text{NO}_3 \cdot 1/2\text{H}_2\text{O}$ , represents the first example of a monovalent silver complex coordinated through the inner (as opposed to terminal) nitrogen N atoms of the cyanoguanidine ligand. Given that the hydrate was an unexpected product in the intended synthesis of  $\text{Ag}(\text{C}_2\text{N}_4\text{H}_4)\text{NO}_3$ , the authors used first principles calculations to demonstrate that bonding through the inner N atom of the ligand is indeed energetically less favourable than coordinating via the terminal atoms.

This issue also contains several examples of investigations in solid-state chemistry that readily bridge into topics of materials chemistry and catalysis. Rainer Niewa and co-authors demonstrated the effectiveness of ammonothermal synthesis in the preparation of fluoroaluminate,  $\text{K}_2\text{AlF}_5$  and  $\text{Rb}_2\text{KAlF}_6$ , which contain infinite fluoroaluminate chains and isolated  $[\text{AlF}_6]^{3-}$  octahedra, respectively [6]. The former is a known compound but is shown here to exist as two new polymorphs that both crystallise in the same space group under synthesis conditions only 20 K and 2 MPa apart. One modification contains a chain with double the number of unique “links” to the other, thus doubling the unit cell in one direction.  $\text{Rb}_2\text{KAlF}_6$ , meanwhile, is a new example of a complex fluoride with the elpasolite structure, essentially a distorted double perovskite with aluminium and potassium occupying the octahedral B sites in a completely ordered arrangement. Solvothermal synthesis was also employed by Zur Loye et al. to prepare new solid-state compounds, but on this occasion, more conventionally, the solvent was water [7]. Hydrothermal synthesis leads to  $\text{K}_{1.8}\text{Na}_{1.2}[(\text{UO}_2)\text{BSi}_4\text{O}_{12}]$ —the first reported example of a uranyl borosilicate. The borosilicate forms a 3D framework from the interlinking of two different structural motifs; otherwise, isolated  $\text{UO}_6$  octahedra and infinite chains were constructed from unprecedented  $[\text{BSi}_4\text{O}_{12}]^{5-}$  anions, themselves composed of vertex-sharing  $\text{BO}_4$  and  $\text{SiO}_4$  tetrahedra. The  $\text{Na}^+$  and  $\text{K}^+$  cations then inhabit the cavities within the pseudo-3D framework. Crucially, the complex crystal chemistry and the absence of peroxy groups were established using EXAFS, thermal analysis and calculations in addition to X-ray crystallography. Ultimately, fundamental studies such as this can help us understand how nuclear waste—and actinides such as U—can be captured in glasses.

Redispersed and exsolved catalysts (such as Rh and Ni) on perovskite substrates are attracting heightened interest for a range of chemical processes, particularly in fuel cells and for steam reforming. High temperature stability and coking resistance are particularly attractive qualities. In this context, Gorte and colleagues conducted a systematic study of Ni supported on thin film perovskite substrates deposited on  $\text{MgAl}_2\text{O}_4$  by atomic layer deposition (ALD) [8]. Titanates,  $\text{ATiO}_3$  ( $\text{A} = \text{Ca}, \text{Sr}, \text{Ba}$ ), are considered, and the choice of alkaline earth metal is revealed to be crucial. Unfortunately, all the perovskite samples were less active than Ni on  $\text{MgAl}_2\text{O}_4$  alone, and Ni is more easily oxidised on the perovskite substrates. Ni interacts most strongly with  $\text{CaTiO}_3$  to the point where the catalyst is deactivated during  $\text{CO}_2$  reforming of  $\text{CH}_4$  at high  $\text{CO}_2$  pressures. Additionally,

on the topic of heterogeneous catalysis, Luo et al. used density functional theory (DFT) calculations and multivariate linear regression (MLR) to rationalise the poisoning effects in ethylene/polar monomer copolymerization catalysed by Brookhart-type catalysts [9]. Polar monomers with electron-rich functional groups such as the carbonyl, carboxyl and acyl groups demonstrated the strongest poisoning effects. Among several factors that mediate the poisoning effect, the metal-X distance in the  $\sigma$ -coordination structure was identified as important. The detailed models developed in this study should help improve copolymerization catalyst designs.

There follow several original papers that focus on topical bioinorganic and organometallic chemistry. The first is a communication by Ortu, Suntharalingam and co-workers, which describes new copper complex chemotherapeutics as a potential new treatment to remove breast cancer stem cells (CSCs) [10]. The copper complexes combine tridentate (*O,N,S*)-coordinated naphthol Schiff base ligands with 1,10-phenanthroline (and PF<sub>6</sub> counter ions) to kill breast CSCs in the micromolar range, with two of the complexes more than four times more effective in this respect than the established anti CSC agent, salinomycin. Copper(II) complexes have also demonstrated anti-inflammatory properties that can be exploited in the treatment of rheumatoid arthritis. Jackson et al. explored a series of Cu(II) tripeptide complexes, in which Cu(II) was square planar and first demonstrated that the complexes have sufficiently low stability constants to allow for their release in vivo [11]. Then, using techniques including EPR, NMR, absorption spectroscopy and DFT calculations, the authors were able to develop reasonable models to describe the coordination modes for each complex. Greco, Bertini and colleagues presented studies in which Fe<sup>I</sup>Fe<sup>I</sup> Fe<sub>2</sub>(S<sub>2</sub>C<sub>3</sub>H<sub>6</sub>)(CO)<sub>6</sub>( $\mu$ -CO) (<sup>1</sup>a-CO) and its Fe<sup>I</sup>Fe<sup>II</sup> cationic species (<sup>2</sup>a<sup>+</sup>-CO) were used as a basic model for the CO-inhibited [FeFe] hydrogenase active site [12]. The site was previously shown to undergo CO photolysis but the conditions and mechanism remained unclear. Time-dependent DFT (TDDFT) analyses of the ground state and low-lying excited-state potential energy surfaces (PESs) have delivered Fe<sub>2</sub>(S<sub>2</sub>C<sub>3</sub>H<sub>6</sub>)(CO)<sub>6</sub> (<sup>1</sup>a) and [Fe<sub>2</sub>(S<sub>2</sub>C<sub>3</sub>H<sub>6</sub>)(CO)<sub>6</sub>]<sup>+</sup> (<sup>2</sup>a<sup>+</sup>) as two simple models of the catalytic site. From a calculation of free energy barriers, it should be possible for <sup>2</sup>a<sup>+</sup>-CO to be synthesized experimentally. Moreover, even when UV light is absorbed, during excited state processes, decay occurs through photo-dissociative channels involving a CO ligand, preventing irreversible enzyme photo-damage.

In one of the two more fundamental organometallic contributions, Stephen Liddle and colleagues described how alkane elimination reactions lead to two new exciting bimetallic thorium complexes [13]. These are especially notable since [Th(Tren<sup>DMBS</sup>)Re( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>] (Tren<sup>DMBS</sup> = {N(CH<sub>2</sub>CH<sub>2</sub>NSiMe<sub>2</sub>Bu<sup>t</sup>)<sub>3</sub>}<sup>3-</sup>) is the first example of a complex with a Th-Re bond that has been structurally characterised, while the [Th(Tren<sup>DMBS</sup>)Ru( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub>] complex represents only the second example of a structurally characterised analogous Th-Ru bond. The successful synthesis and isolation of these complexes has enabled a comparison to be made with uranium analogues and the Th-metal bonds were discovered to be more ionic. Finally, Louise Natrajan, David Mills and co-workers also considered f-block chemistry when they presented a study of the use of tripodal ligands to control the coordination sphere of uranium (and lanthanum) with the aim to explore the effects of the coordinatively unsaturated “steric pocket” on the activation of small molecules [14]. Two new two tris-anilido ligands with substituted aryl rings were considered for this purpose—{tacn(SiMe<sub>2</sub>Nar)<sub>3</sub>} (ar = C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>-3,5 or C<sub>6</sub>H<sub>4</sub>Me-4)—which bring enhanced flexibility to the metal environment compared with previous examples.

In addition to the impressive collection of original papers above, this Special Issue contains four review articles covering solid-state materials chemistry, coordination chemistry, metal organic frameworks and catalysis. Richard Walton and colleagues provided a comprehensive overview of how solvothermal methods can be exploited to produce cerium dioxide, CeO<sub>2</sub> and a whole host of substituted ceria materials [15]. Substituents from transition metals through lanthanides to main group metals (both p- and s-block) can be introduced via this technique. Equally, nitrogen can be doped into the system and

multiple cation substitutions can be performed. Perhaps almost as important, however, is the power of the technique in manipulating morphology and nanostructure, including allowing the synthetic chemist to deposit materials as structured layers. In an entirely different vein, Kótai et al. presented a timely review of pyridine complexes formed with silver perchlorate, permanganate and perrhenate ( $X = \text{Cl}, \text{Mn}, \text{Rh}$ , respectively) [16]. Given the excellent solubility of the  $\text{AgXO}_4$  salts, it is not surprising that examples have been known for over a century and that their oxidative properties are well known and well utilised. Nevertheless, the literature contains some apparently contradictory information and a compilation of details on their synthesis, composition, structure and redox properties is overdue. Contrasts between reducing pyridine and oxidizing  $\text{XO}_4^-$  can lead to quasi-intramolecular redox reactions, and the hydrogen bonds between the acidic C–H and polarized X–O bonds were discussed.

Single molecule magnets (SMMs) have been known now for several decades but are still generating considerable interest and excitement with prospects of high-density information storage and quantum computing. Lanthanide SMMs with Schiff base ligands form a most promising subset given their combination of magnetic ordering, anisotropy and relaxation pathways. Linnert, Thomas et al. presented an extensive review of these SMMs with a consideration of synthesis techniques through an evaluation of their structures to an in-depth exploration of their magnetic properties [17]. Among some of the highlights, the authors picked out dysprosium as a likely metal of choice; they considered salicylaldehyde derivatives in terms of useful Schiff base ligands and they concentrated on ways in which ligand and SMM design can be exploited to afford slow magnetic relaxation. Just as SMMs have been one of the revelations of inorganic chemistry over recent decades, so have MOFs. The review by Alessia Tombesi and Claudio Pettinari considered the role of MOFs specifically in the context of heterogeneous catalysts in olefin epoxidation and carbon dioxide cycloaddition [18]. The authors related the catalytic performance to specific building blocks such as organic linkers and metal nodes/clusters and considered the influence of mixed-metal species and nanocomposites. That article not only considered the relative merits of a large cross section of MOF materials but also delineated the major challenges that remain to be addressed. In common with many of the articles in this excellent Special Issue, that review should encourage researchers to devise new strategies to meet these future challenges.

Before I conclude, I thank all of the authors who have contributed to this Special Issue and fashioned it into the outstanding collection that it is. I also thank all my editorial and publishing colleagues who have enabled this issue to come into being.

**Conflicts of Interest:** The author declares no conflict of interest.

## References

1. Wackerbarth, I.; Widhyadnyani, N.; Schmitz, S.; Stirnat, K.; Butsch, K.; Pantenburg, I.; Meyer, G.; Klein, A.  $\text{Cu}^{\text{II}}$  Complexes and Coordination Polymers with Pyridine or Pyrazine Amides and Amino Benzamides—Structures and EPR Patterns. *Inorganics* **2020**, *8*, 65. [[CrossRef](#)]
2. Manfroni, G.; Capomolla, S.; Prescimone, A.; Constable, E.; Housecroft, C. Isomeric 4,2':6',4''- and 3,2':6',3''-Terpyridines with Isomeric 4'-Trifluoromethylphenyl Substituents: Effects on the Assembly of Coordination Polymers with  $[\text{Cu}(\text{hfacac})_2]$  ( $\text{Hhfacac} = \text{Hexafluoropentane-2,4-dione}$ ). *Inorganics* **2021**, *9*, 54. [[CrossRef](#)]
3. Mondal, S.; Chen, W.; Sun, Z.; McGrady, J. Synthesis, Structure and Bonding in Pentagonal Bipyramidal Cluster Compounds Containing a cyclo-Sn<sub>5</sub> Ring,  $[(\text{CO})_3\text{MSn}_5\text{M}(\text{CO})_3]^{4-}$ ; ( $\text{M} = \text{Cr}, \text{Mo}$ ). *Inorganics* **2022**, *10*, 75. [[CrossRef](#)]
4. Jones, D.; Watts, S.; Jones, C. Synthesis and Characterization of Super Bulky  $\beta$ -Diketiminato Group 1 Metal Complexes. *Inorganics* **2021**, *9*, 72. [[CrossRef](#)]
5. Qiao, X.; Corkett, A.; Luo, D.; Dronskowski, R. Silver Cyanoguanidine Nitrate Hydrate:  $\text{Ag}(\text{C}_2\text{N}_4\text{H}_4)\text{NO}_3 \cdot 1/2 \text{H}_2\text{O}$ , a Cyanoguanidine Compound Coordinating by an Inner Nitrogen Atom. *Inorganics* **2020**, *8*, 64. [[CrossRef](#)]
6. Bäucker, C.; Becker, P.; Morell, K.; Niewa, R. Novel Fluoridoaluminates from Ammonothermal Synthesis: Two Modifications of  $\text{K}_2\text{AlF}_5$  and the Elpasolite  $\text{Rb}_2\text{KAlF}_6$ . *Inorganics* **2022**, *10*, 7. [[CrossRef](#)]
7. Pace, K.; Klepov, V.; Smith, M.; Williams, T.; Morrison, G.; Lauterbach, J.; Misture, S.; zur Loye, H. Hydrothermal Synthesis and Structural Investigation of a Crystalline Uranyl Borosilicate. *Inorganics* **2021**, *9*, 25. [[CrossRef](#)]

8. Lin, C.; Foucher, A.; Stach, E.; Gorte, R. A Thermodynamic Investigation of Ni on Thin-Film Titanates (ATiO<sub>3</sub>). *Inorganics* **2020**, *8*, 69. [[CrossRef](#)]
9. Zhao, W.; Liu, Z.; Zhao, Y.; Luo, Y.; He, S. Multivariate Linear Regression Models to Predict Monomer Poisoning Effect in Ethylene/Polar Monomer Copolymerization Catalyzed by Late Transition Metals. *Inorganics* **2022**, *10*, 26. [[CrossRef](#)]
10. Northcote-Smith, J.; Johnson, A.; Singh, K.; Ortu, F.; Suntharalingam, K. Breast Cancer Stem Cell Active Copper(II) Complexes with Naphthol Schiff Base and Polypyridyl Ligands. *Inorganics* **2021**, *9*, 5. [[CrossRef](#)]
11. Vicatos, G.; Hammouda, A.; Alnajjar, R.; Bonomo, R.; Valora, G.; Bourne, S.; Jackson, G. Aqueous Solution Equilibria and Spectral Features of Copper Complexes with Tripeptides Containing Glycine or Sarcosine and Leucine or Phenylalanine. *Inorganics* **2022**, *10*, 8. [[CrossRef](#)]
12. Arrigoni, F.; Zampella, G.; De Gioia, L.; Greco, C.; Bertini, L. The Photochemistry of Fe<sub>2</sub>(S<sub>2</sub>C<sub>3</sub>H<sub>6</sub>)(CO)<sub>6</sub>(μ-CO) and Its Oxidized Form, Two Simple [FeFe]-Hydrogenase CO-Inhibited Models. A DFT and TDDFT Investigation. *Inorganics* **2021**, *9*, 16. [[CrossRef](#)]
13. Ostrowski, J.; Wooles, A.; Liddle, S. Synthesis and Characterisation of Molecular Polarised-Covalent Thorium-Rhenium and -Ruthenium Bonds. *Inorganics* **2021**, *9*, 30. [[CrossRef](#)]
14. Formanuik, A.; Ortu, F.; Vitorica-Yrezabal, I.; Tuna, F.; McInnes, E.; Natrajan, L.; Mills, D. Functionalized Tris (anilido)triazacyclononanes as Hexadentate Ligands for the Encapsulation of U(III), U(IV) and La(III) Cations. *Inorganics* **2021**, *9*, 86. [[CrossRef](#)]
15. Annis, J.; Fisher, J.; Thompsett, D.; Walton, R. Solvothermal Synthesis Routes to Substituted Cerium Dioxide Materials. *Inorganics* **2021**, *9*, 40. [[CrossRef](#)]
16. Franguelli, F.; Béres, K.; Kótai, L. Pyridinesilver Tetraoxometallate Complexes: Overview of the Synthesis, Structure, and Properties of Pyridine Complexed AgXO<sub>4</sub> (X = Cl, Mn, Re) Compounds. *Inorganics* **2021**, *9*, 79. [[CrossRef](#)]
17. Gebreziabher, M.; Bayeh, Y.; Gebretsadik, T.; Gebresslassie, G.; Elemo, F.; Thomas, M.; Linert, W. Lanthanide-Based Single-Molecule Magnets Derived from Schiff Base Ligands of Salicylaldehyde Derivatives. *Inorganics* **2020**, *8*, 66. [[CrossRef](#)]
18. Tombesi, A.; Pettinari, C. Metal Organic Frameworks as Heterogeneous Catalysts in Olefin Epoxidation and Carbon Dioxide Cycloaddition. *Inorganics* **2021**, *9*, 81. [[CrossRef](#)]