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The central role of the d-block metals in the periodic table

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The d-block metals are central within the periodic table and are at the core of numerous branches of inorganic chemistry, including materials chemistry, applied biological and analytical sciences, and catalysis. The term 'transition metal' is still much used but this strictly excludes the group 10 metals (Zn, Cd, and Hg) since IUPAC defines a transition metal as an 'element whose atom has an incomplete d sub-shell, or which can give rise to cations with an incomplete d sub-shell'. The traditional picture of the d-block is of ten triads or three rows of metallic elements. The fourth row (Ac, Rf–Cn) is often ignored by those of us who teach inorganic chemistry courses, largely because of the paucity of data and chemistry of the elements from rutherfordium (Rf, $Z = 104$) onwards. And, of course, categorization of group 3 (Sc, Y, La and Ac) is ambiguous because of the insertion of the f-block elements after lanthanum and actinium. The latter metals are therefore typically grouped with the f-block, rather than the d-block, elements. Definitions aside, there is no question that the d-block elements at the centre of the periodic table play a central role in the field of inorganic chemistry.

Where would we be without the d-block metals? Among the d-block metals, copper emerges as having had a particularly significant impact on mankind, so we provide a brief historical perspective on copper to highlight the pivotal technological role that such d-block metals have played. Few transition metals occur as the native elements in the Earth's crust, and many extraction processes to recover metals from their ores belong to relatively recent history. The ancient world most commonly utilized copper, silver and gold, and a timeline for copper[1,2] shows the metal being hard-worked into tools and ornaments as early as 8700 BCE. The use of copper in tools and domestic utensils became more prevalent by 4000 BCE, notably in ancient Egypt, when it was discovered that native copper could be melted and cast. In the period 4000–2000 BCE, the first copper mining began in Asia Minor (Anatolia) and China. The name 'copper' derives from Cyprus, celebrating the importance of the island for its rich copper reserves first worked in the 4000–2500 BCE era. Bronze (an alloy of copper and tin) emerged in this same era, heralding the start of the Bronze Age. Between 0 and 200 CE (0–200 AD), brass (an alloy of copper and zinc) was developed. A long delay appears before the next epoch of note for copper: copper mining in Michigan, US, in the 19th century greatly boosted the availability of the metal. It was also during this period that the importance of copper in biological systems was first recognized: chlorosis (a form of anaemia) was found to be effectively treated using a combination of copper and iron; in contrast, iron supplements alone were ineffective.[3] The early 1900s saw the landmark discovery of the electrical conductivity of copper and many new applications followed; with the exception of silver, copper remains the best electrically conducting d-block metal. From 1960 onwards, the worldwide production of copper increased dramatically; more recent data reveal a growth from 9 Mt in 1990 to 21 Mt in 2018.[4] Coupled with this has been a rising importance in copper recycling so that in the US, for example, copper recycled from scrap metal contributed about 35% of the US copper supply chain in 2018. In the Earth's crust, the principal copper ore is $CuFeS_2$ (chalcopyrite), but conventional extraction processes generate large amounts of SO_2. Bioleaching using naturally occurring *Acidithiobacillus thiooxidans* is an environmentally preferred extraction technology that now works alongside the leach–solvent extraction–electrowinning (SX/EW) process to extract copper from ores such as azurite and malachite. This brief look at copper highlights not only its significance in the development of mankind, but also the manner in which the modern world must react to provide a sustainable future for generations to come.

Because of the vast array of inorganic materials and coordination compounds

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containing d-block metals, we decided to focus on four specific themes to gain some homogeneity among the articles in this themed issue on d-block elements: Education, Sustainable Energy, Catalysis, and Diagnostics and Medical Applications. *Education* is very much a part of the goals of the *International Year of the Periodic Table*, and this theme is represented by two reviews entitled 'Evolution and Understanding of the d-Block Elements in the Periodic Table' (Constable, DOI: 10.1039/C9DT00765B) and 'The Past, Present, and Future in the Nomenclature and Structure Representation of Inorganic Compounds' (Hartshorn, DOI: 10.1039/C9DT00352E).

The last few decades have witnessed a substantial growth in the development of d-block inorganic materials for environmental and energy applications as we strive for accessible and cost-efficient, renewable energy and for ways in which to reduce greenhouse gas emissions. Against this backdrop, we selected *Sustainable Energy* as the second theme of this issue. The development of solid-state lighting is one area that is critical for energy saving. Contributions on the theme of *Sustainable Energy* include perspectives on periodic trends of transition metal catalysts for electrocatalytic CO_2 reduction (Machan, DOI: 10.1039/C9DT00491B), and on perovskites with d-block metals for solar energy applications (Stergiopoulous, DOI: 10.1039/C9DT01485C) and studies on the emission properties of iridium(III) complexes (Ortí, DOI: 10.1039/C9DT00412B, Zysman-Colman, DOI: 10.1039/C9DT00423H, Duan, DOI: 10.1039/C9DT00495E, Zheng, DOI: 10.1039/C9DT00298G, and Park, Lee and Kang, DOI: 10.1039/C9DT00596J), luminescent properties of platinum(II) dimers (Slinker, DOI: 10.1039/C9DT00795D), photoluminescent silver(I) and copper(I) complexes (Costa, Viciano-Chumillas and Cano, DOI: 10.1039/C9DT00772E), polymeric electrochromic materials embedded in a metal–organic framework (MOF) (Navalon and Horcajada, DOI: 10.1039/C9DT00917E), copper(I) complexes for dye-sensitized solar cells (Colombo, DOI: 10.1039/C9DT00790C, Dragonetti, DOI: 10.1039/C9DT01448A), copper(II) porphyrins for flexible solid-state supercapacitors (Huang and Zhao, DOI: 10.1039/C8DT05069D), first row transition metal photocatalysts for CO_2 reduction (Robert and Lau, DOI: 10.1039/C9DT00425D) and cobalt-based molecular electrocatalysis of nitrile reduction (Fielden, DOI: 10.1039/C9DT00773C).

Several of the latter contributions bridge the themes of *Sustainable Energy* and *Catalysis*. Catalysis is, of course, a huge field and invited contributions focus on resource sustainability, highlighting advances in the production of other value-added products as well as the use of more abundant metals in place of precious metal catalysts. The topics covered span a broad field and include homoleptic arenemetalates of the first row d-block metal-superoxo complexes (reviewed by Ellis, DOI: 10.1039/C8DT05029E, Fukuzumi, Lee and Nam, DOI: 10.1039/C9DT01402K), first row early transition metal complexes of amino triphenolate ligands (Lee and Son, DOI: 10.1039/C9DT00456D), studies of binding modes of amine-boranes to silver(I) and rhodium(I) (Weller and Macgregor, DOI: 10.1039/C9DT00971J), rhodium complexes with P,N-chelating carborane ligands for applications in catalytic dehydrogenation of amine boranes (Hey-Hawkins, DOI: 10.1039/C9DT00628A), cobalt(I)-mediated $C(sp^3)$–H bond activation reactions (Deng, DOI: 10.1039/C9DT00731H), first row transition metal-catalyzed hydrosilative amide reduction (Sydora, Stradiotto and Turculet, DOI: 10.1039/C8DT04221G), tri-iron and tri-zinc complexes supported by cyclophane ligands (Murray, DOI: 10.1039/C9DT00799G), a fundamental study of the donor/acceptor properties of cyclic fluorophosphites when bound to molybdenum(0), platinum(0), and rhodium(I) (Pringle, DOI: 10.1039/C9DT00893D), titanium complexes with tridentate Schiff base and phosphoramidate ligands with applications in catalytic hydroamination reactions (Johnson, DOI: 10.1039/C8DT05156A, Schafer, DOI: 10.1039/C9DT00911F), palladium pincer ligand complexes that feature redox-active carbene functionalities (Iluc, DOI: 10.1039/C9DT00585D) and hemi-labile donor arms (Bourissou and Martin-Vaca, DOI: 10.1039/C9DT00898E), and catalytically active palladium pincer complexes incorporated into MOFs (Wade, DOI: 10.1039/C8DT03801E).

Finally, the crucial role that d-block metal ions play in therapeutics is celebrated by the theme of *Diagnostics and Medical Applications*. Invited papers reflect recent advances in the development of metallodrugs and metal-based responsive probes, highlighting the impact of chemistry on human health. A timely overview of the role of iron in biosynthesis, translocation, and signal transduction of NO (Lu, DOI: 10.1039/C9DT00777F) is accompanied by articles dealing with the influence of copper on azole antifungal activity (Franz, DOI: 10.1039/C9DT00642G), iron nanomineralization (Wang, DOI: 10.1039/C9DT00459A, Sadler and Danaie, DOI: 10.1039/C9DT00514E), the cytotoxicity and applications of iridium(III) complexes as biological sensors (Lo, DOI: 10.1039/C9DT00793H), platinum anticancer agents (Berners-Price, DOI: 10.1039/C9DT00753A), the metal coordination design in the apo-ferritin cage (Ueno, DOI: 10.1039/C9DT00609E), the activity and inhibition of dicopper azacryptands in azide–alkyne cycloaddition reactions under biologically relevant conditions (Do, DOI: 10.1039/C9DT00724E), and the development of an oligonucleotide-based microfluidic device (Ma, DOI: 10.1039/C9DT00427K).

We hope that this issue appropriately celebrates the central role of the d-block metals in the periodic table, and inspires further development of their chemistry and applications.

Note: Two papers which were accepted for this special issue were inadvertently published in regular issues of the journal:

C. L. Rock and R. J. Trovitch, *Dalton Trans.*, 2019, **48**, 461–467.

F. Brunner, A. Babaei, A. Pertegás, J. M. Junquera-Hernández, A. Prescimone, E. C. Constable, a H. J. Bolink, M. Sessolo, E. Ortí and C. E. Housecroft, *Dalton Trans.*, 2019, **48**, 446–460.

References

1 R. R. Conry and K. D. Karlin, in *Encyclopedia of Inorganic Chemistry*, ed. R. B. King, Wiley, Chichester, 1994, vol. 2, p. 829.

2 https://www.copper.org/education/history/timeline/timeline.html (accessed 3 May 2019).

3 M. Solioz, *Metallomics*, 2016, 8, 824 and references therein.

4 https://www.usgs.gov/centers/nmic/copper-statistics-and-information (accessed 3 May 2019).