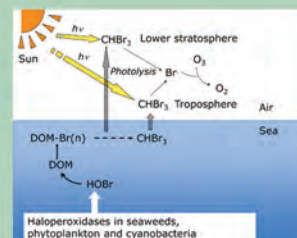
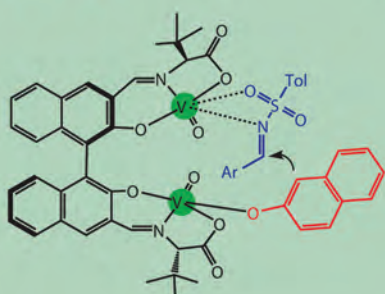
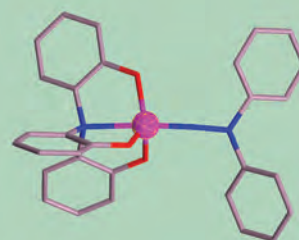
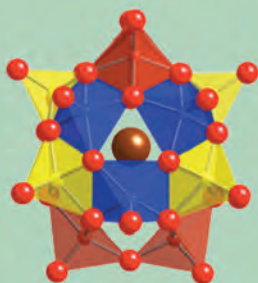
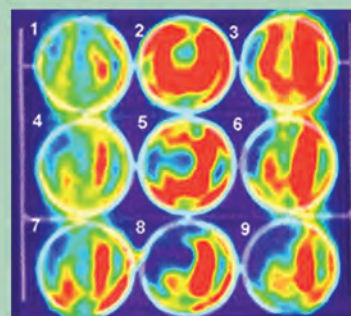
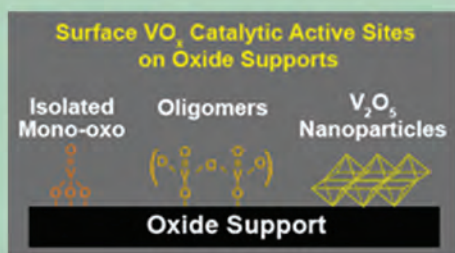


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COVER ARTICLE

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Vanadium is a fascinating trace element with a wonderful assortment of useful to spectacular properties in nature and industry. How many metal ions readily function as an anion or a cation or show the activities observed for this less-commonly-known element? As a small transition metal, vanadium exhibits more diverse chemistry than most metals, which is possible because of the small size of the metal ion combined with its orbital occupancies that support different coordination chemistries with ease. As a result, this element continues to intrigue and stimulate practitioners in the field. The colorful history of its discovery and the broad spectrum of uses of vanadium have been reviewed by numerous vanadium scientists around the world.¹ The focus of the topics covered in this issue, however, is the versatile chemistry that this metal ion is involved in and that is important for how vanadium and its complexes act in biology. Multidisciplinary interest in this redox-active transition metal has been growing of late, with an interest in many aspects of chemistry and biological chemistry, beginning in the 1970s. The variability in the oxidation state and coordination chemistry of vanadium make it an extremely interesting and diabolically challenging element to examine, a subtlety often lost on those

studying metal ions that have less diverse and more predictable chemistry. This diversity is reflected in the type of chemistry that vanadium undergoes that is reported in this issue of *Dalton Transactions*.

The 8th International Vanadium Symposium, V8, held in Washington DC, USA, in the summer of 2012 and organized by Drs Mitch Cohen, Andy Ghio and Craig McLauchlan, highlighted some of the diverse areas of vanadium science currently being investigated. The vanadium symposia have been held every two years since the first symposium in 1998 in Cancun, Mexico, organized by Alan Tracey and Debbie Crans. The conferences are hosted around the world with the next symposium, V9, to be held in 2014 in Italy, organized by Valeria Conte, and the following V10 meeting in 2016 to be held in Taiwan, organized by Biing-Jiun Uang and Chien-Tien Chen. The proceedings from previous conferences are available to interested readers in: V1 (*ACS Symposium Series*),² V2 (*J. Inorg. Biochem.*),³ V3 (*Coord. Chem. Rev.*),⁴ V4 (*Pure Appl. Chem.*),⁵ V5 (*ACS Symposium Series*),⁶ V6 (*J. Inorg. Biochem. and Pure Appl. Chem.*),⁷ and V7 (*Coord. Chem. Rev.*).⁸ The topics of the V8 symposium included coordination chemistry and structural studies, speciation and transport of vanadium salts and complexes, studies in enzymology and catalysis of systems including vanadium, therapeutic application of vanadium salts and compounds, toxicology and environmental/occupational exposures to vanadium. The scope of our conference

is broader than the manuscripts in this themed issue of *Dalton Transactions*, which are focused on the inorganic chemistry of vanadium and vanadium complexes, and only a subset of papers from the conference in the areas of bioinorganic and coordination chemistry have been selected for inclusion in this special themed issue. Other contributions will appear in, *inter alia*, a themed issue in *J. Immunotoxicology* and in other journals, such as *Metallomics*. A wide range of topics within bioinorganic and coordination chemistry were presented at the conference and the selected contributions here include the synthesis, structural characterization and reactivity of vanadium complexes and biological systems relying on vanadium for structural, for catalytic or for medicinal purposes. The contributions to vanadium science in each of the enclosed manuscripts attest to a particular aspect of vanadium chemistry presented by the participants in the V8 program.

Our themed issue begins with four Perspective articles covering different areas of vanadium chemistry.

An excellent perspective by Dieter Rehder on the Future of/for Vanadium (DOI: 10.1039/C3DT50457C) presents an overview of state-of-the-art vanadium science and looks to the future for vanadium. As an element whose study has been enriched by the biannual conferences which bring vanadium scientists together, this field have grown significantly in the past two decades. Here, Rehder points to previous victories in areas such as vanadium-containing

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haloperoxidases and nitrogenases, both with respect to the enzymes as well as vanadium compounds exhibiting such activities. The accumulation of vanadium in organisms such as *Amanita* mushrooms and sea squirts highlights the unusual metabolism involving vanadium salts and complexes. Rehder suggests the possibility that the vanadate/phosphate analogy, which has been studied extensively, may in fact have vanadate interfering with the phosphate metabolism. Studies with decavanadate have illustrated that its structure can be associated with protein or membrane interface-type structures. Indeed, Rehder suggests vanadate has a regulatory role in many organisms, including possibly human beings, which brings new areas and opportunities for vanadium coordination chemistry and bioinorganic chemistry, some of which will be represented in this volume.

The second Perspective article focuses on oxidative catalysis and vanadia catalysts, and is from Israel Wachs (DOI: 10.1039/C3DT50692D), who received the 5th Vanadis Award at the 8th International Vanadium Symposium. This Perspective describes vanadium oxide catalysts, including vanadium oxides supported on other oxides, such as Al₂O₃, SiO₂ and TiO₂. The review describes the properties of these catalytic materials, including their molecular and electronic structure, their surface chemistry and any associated structure–activity relationships. Because the surface chemistry and reactivity studies show that the vanadium sites are the catalytically active sites and vanadium is very sensitive to its environment, studies confirm that a solid oxide support for the vanadia catalysts can enhance the redox properties of the catalyst by a factor up to 1000. This finding demonstrates that the principles of coordination chemistry apply even to a more complex solid state-surface system, which has many components.

Vanadium in oxidation state V exists mainly in anionic forms. At neutral and physiological pH, vanadium(v) exists as vanadate, and because this simple salt can take on several forms, researchers use ⁵¹V NMR spectroscopy to characterize

the form in a particular system. The effects of aqueous vanadium(v) chemistry are represented in a Perspective focusing on studies with the compact multinuclear anion decavanadate, with a minus 6 charge at neutral pH (V₁₀O₂₈^{6−}). Aureliano and co-workers (DOI: 10.1039/C3DT50462J) review the concept of decavanadate targeting ion pumps. This review describes how the pump works and focuses on the proposed modes of action of decavanadate, oligomeric vanadates and other vanadium compounds. For example, the binding sites of known ion pump inhibitors are discussed, with a particular emphasis on the E1 and E2 conformations of Ca²⁺-ATPase. Decavanadate is known to bind to all forms of the protein, whereas the monomeric vanadium ion, *i.e.* vanadate (VO₄^{3−}), is found to only bind to the E2 conformation. However, the interaction of decavanadate with the sarcoplasmic reticulum Ca²⁺-ATPase may lead to the reduction of vanadium and explain the potent inhibition found with this anion.

Ronald Wever and his coworker Michael van der Horst (DOI: 10.1039/C3DT50525A) provide a Perspective on the enzyme responsible for the biosynthesis of halogenated hydrocarbons. This review describes the synthesis of bromoform and dibromomethane catalyzed by haloperoxidases and how these enzymes work. This group of enzymes is able to catalyze a non-trivial halogenation process under very mild conditions. These enzymes have caught the interest of biological and synthetic chemists since their discovery by Hans Vilter in the mid 1980s in part because of their vanadium(v) content. Several groups have worked on this area, including the Butler⁹ and Pecoraro¹⁰ groups as well as the Conte, Pessoa and Hartung groups (see contributions in this volume), but the Wever group has been focusing particularly on the genetic and evolutionary aspects. In addition, enzyme-catalyzed processes have been of keen interest and attempts have been made to make protein-catalyzed reactions for commercial use. This review compiles the available research on the reactions specifically forming brominated compounds that will react according to the

haloform reaction and ultimately form bromoform and dibromomethane. The materials form in huge amounts and it is concluded that seaweeds, phytoplankton and cyanobacteria triggered by light or stress release HOBr in seawater. The authors conclude that these processes are likely to undergo a catalytic cycle, which will result in the depletion of ozone.

The next three original research contributions focus on describing the catalytic effects that vanadium complexes exhibit. In their communication, Sasai and co-workers (DOI: 10.1039/C2DT32202A) report the enantioselective Friedel–Crafts-type reaction of imines using a chiral dinuclear vanadium complex. The dinuclear vanadium complexes are elaborate complexes with the ligand formed from condensation products of 2-imines with 2-naphthols or indoles. This ligand contains two binding sites which each formed a vanadium complex and the combination supported the enantioselective catalysis. These complexes catalyzed the C–H bond activation and thus describe intriguing new oxidation reactions.

The following paper by Pombeiro, Shul'pin and co-workers (DOI: 10.1039/C3DT50584G) describes a novel binuclear oxovanadium(v) complex. The complex is synthesized from the condensation of a pyrazinecarboxylic acid co-catalyst that catalyzes the oxidation catalysis of alkanes. These complexes were able to generate alkyl hydroperoxides with an initial turnover of 3300 h^{−1} per molecule of the vanadium complex. The mechanism of the reaction was investigated and hydroxyl radicals are implicated.

Hayashi and co-workers (DOI: 10.1039/c3dt50398d) introduce two novel polynuclear oxovanadates, specifically hexadecavanadates. These complexes form from the reaction of decavanadate with *p*-toluenesulfonic acid in the presence of excess bromide anions, which act as both a template anion and as a reducing reagent. These complexes have a wide range of properties depending on the nuclearity, redox state and structure, and this V₁₆ cluster showed a series of stepwise reversible redox processes that

the authors attribute to the reduction of the vanadium in the spherical polyoxo-vanadate framework. The bromination reactions of aromatic substrates were also investigated and found to be catalyzed by the hexadecavanadates under mild aerobic conditions.

The next four original research contributions focusing on the coordination chemistry of vanadium can be categorized according to the type of coordination complex, which correlate with the type of coordinating ligand. Many coordination complexes containing vanadium are known and depending on the ancillary ligand, can support different coordination geometries. The coordination chemistry in these first contributions centers around the synthesis and structure of the vanadium compounds, representing several classes of coordination complexes and very different reactivity patterns. The coordination sphere of several vanadium complexes was investigated in detail by Plass and co-workers (DOI: 10.1039/C3DT50890K). The complexes with 2-aminoglucose Schiff base ligands contained both O and N donor ligands, forming several chiral vanadium(v) complexes. These complexes were characterized using X-ray crystallography and in solution, and in the process, detailed structural information was obtained for this series of complexes. They examined the effect of methanol solvent coordination on the complex's geometry and investigated the possibility of the inter-conversion of diastereomers by undertaking density functional calculations on the species involved. These studies showed the ease by which this class of vanadium complexes can isomerize and the role of methanol as a proton donor in the process.

Moriuchi, Ikeuchi and Hirao (DOI: 10.1039/C3DT50533B) characterize the formation of vanadium(v) complexed to O, O, O and N coordination functionalities. The work seeks to determine the impact of the coordination of an apical N-ligand to the vanadium center and how much the V–N multiple bond was weakened. In these complexes, the electronic properties of the ancillary ligand is critical and as a consequence, it is

possible to fine-tune the electronic properties of the vanadium. These authors find that small substitutions on the ancillary ligand are critical for the stability of the vanadium–nitrogen adducts and their subsequent hydrolysis. Specifically, in a O,O,O,N-based ancillary ligand, the electronic properties of the coordinating phenol in the 3-position has a particularly high influence on the electronic properties of a coordinating vanadium atom, which will have implications for the design for molecular nitrogen activation.

Drouza, Vlasίου, and Keramidas (DOI: 10.1039/C3DT50619C) continue to probe the properties of vanadium complexes to catechols and in this work present the characterization of dinuclear vanadium catecholate complexes containing one five-coordinate and one six-coordinate vanadium. The new complexes are particularly unique because of their structural and electronic properties. Two complexes exist, one is the major species at low temperature and the other at higher temperature. The diamagnetic species is stable at higher temperature but at lower temperature the electronic structure changes as one electron is transferred from the catechol to the two vanadium atoms. Because the complexes are characterized in detail, the reader can appreciate the diversity of the reactivity of these systems as the molecular design becomes more complex. The properties of the complexes are very sensitive to the specific orientation of the ligand, which can change the electronic nature of the complex. The dinuclear vanadium-*p*-dioxolene complex investigated is able to show an intramolecular electron transfer reaction and the simultaneous coordination sphere change as the solvent molecules coordinate to the vanadium.

Illustrating how effectively coordination chemistry and bioinorganic chemistry work together toward understanding how vanadium compounds exert their action, Avecilla, Costa Pessoa and co-workers (DOI: 10.1039/C3DT50553G) discuss the formation of a new vanadyl complex with a pyrimidinone and its solution speciation. These complexes are related to the anti-

diabetic compounds that were in clinical trials,^{11–14} and these studies detail how subtle ligand changes affect speciation. Such studies are important because the administration of these vanadium complexes brings the vanadium compounds into circulation in the blood, and understanding how the species behave and how they interact with the major complexes that are present in the blood stream is of fundamental importance. This work characterizes the species present and studies the subsequent binding with human serum transferrin. Indeed, how vanadium binds to transferrin has been controversial¹¹ and studies have demonstrated that although the vanadium separated from the ligand in pharmacokinetic studies,¹² vanadium complexes are now known to interact not only with transferrin but also with other serum proteins. Importantly, such interactions extend the life-time and action of the complexes. This work describes complexes with a new pyrimidinone ligand that bind to transferrin, providing spectroscopic evidence that the vanadium(IV) complex binds to the Fe(III) site on the transferrin.

The interface between chemistry and biological–medicinal chemistry, respectively, illustrates the multi-disciplinary nature of current vanadium science. In the following subsection, five manuscripts are presented on a range of different complexes describing the compound preparation and characterization as well as testing the effects of these compounds on a range of different biological systems.

Makinen and co-workers (DOI: 10.1039/C3DT50549A) combined state-of-the-art spectroscopic studies with biomedical studies, probing the mode of action of anti-diabetic vanadium compounds. These studies describe a study of vanadium(IV) complexes with human breast cancer cells. The well-known organic vanadyl (VO²⁺) chelates that facilitate increased uptake of glucose *in vitro* as insulin-enhancing reagents are found to also enhance the uptake of 2-(fluorine-18)-2-deoxy-D-glucose (FDG) by cultured human breast cancer cells. The results point to a link between anti-diabetic agents and anti-cancer

activities, an important observation that has also been previously noted by the Willsky¹⁴ and Yang¹⁵ groups.

Etcheverry and co-workers (DOI: 10.1039/C3DT50524C) report on the anti-tumor activities of a vanadyl complex with chrysin on human osteosarcoma cells. These studies extend previous explorations of some flavonoids compounds, which represent coordination complexes with all-oxygen donors. Despite the anticipated active redox chemistry of these compounds, these studies show very beneficial effects *in vitro* in the MG-63 osteosarcoma cell line. The compounds' action was attributed to oxidative stress which triggered cytotoxicity, genotoxicity and apoptosis. Specifically, the authors suggest that the complex between vanadium(IV) and chrysin is a death modulator and has potential in the treatment of cancer.

Holder and co-workers (DOI: 10.1039/C3DT50547B) report the preparation and characterization of a mixed Ru(II)–V(IV) complex. The supporting ligands are previously known to form coordination complexes with vanadium and thus, the unique properties of these novel complexes originate from the formation of the dinuclear complex with Ru(II). Although a range of dinuclear complexes exist, mixed systems are less common and the exploration of these systems in a biological context as potential photodynamic phototherapeutic agents is novel. These complexes were tested on a range of cells including human epidermoid carcinoma cells, human amelanotic malignant melanoma cells and HFF, non-cancerous human skin fibroblast cells, for comparison. The anti-cancer properties of the compounds were observed upon exposure to light in the cancer cells whereas no effect was observed in the non-cancerous skin fibroblast cells.

Gambino and co-workers have generated a series of ten ternary vanadyl complexes with salicylaldehyde semicarbazone derivatives and phenanthroline derivatives as possible inhibitors of *Trypanosoma cruzi*, the parasite causing Chagas disease (DOI: 10.1039/C3DT50512). The compounds were characterized in the solid state and in

solution before being subjected to testing and analysis. The lipophilicity of the compounds allowed for their analysis using quantitative structure activity relationships, and the correlations pointed to the important role of the co-ligand in the ternary complexes. The investigators examined the excreted metabolites from the parasite using ¹H NMR spectroscopy and suggested that the target for these drugs is the mitochondrion. It is important to note that all the compounds tested were more potent than the drug currently in use for the treatment of this disease, Nifurtimox.

In a study by the Roess/Crans team (DOI: 10.1039/c3dt50398d), decavanadate is used as a structural model for vanadium oxides or more specifically, V₂O₅. Decavanadate is also a hydrolysis product when V₂O₅ is placed in aqueous environments. Because vanadium oxides have been identified as low molecular weight sensitizing agents associated with asthma and compromised pulmonary immunocompetence, how they exert their mode of action was investigated using the decavanadate system as a probe. Specifically, the possibility of whether decavanadate was able to initiate plasma membrane events associated with the activation of Type I Fcε receptors (FcεRI) was evaluated. Three lines of evidence were obtained, namely, decavanadate was found to increase degranulation of RBL-2H3 cells, increase lipid packing as measured by a fluorescent probe, ANEPDHDQ, in cells and in Langmuir monolayers of dipalmitoylphosphatidylcholine (DPPC). These results are consistent with decavanadate altering the lipid packing both in model systems and in cells and may be a mode of action.

Vanadium is a co-factor for several enzymes, including haloperoxidases and vanabins, and in the following four manuscripts, the enzyme reactions are studied using the enzyme reaction or model compounds.

Ueki and co-workers (DOI: 10.1039/C3DT50404B) report a study probing the potential role of Vanabin2, the vanadium binding protein from tunicates, also referred to as sea squirts or

ascidians. Vanabins are a new group of vanadium binding proteins and are structurally distinct from others with regard to their coordination chemistry, which in this case is based on vanadium–sulfur chemistry. The recent discovery that Vanabin2 has reductase activity was investigated by a series of enzyme studies testing a range of other cations as potential substrates for the protein. They also determined the reduction potential of Vanabin2, for transition metals other than vanadium(V). The fact that only vanadium(V) was an effective substrate for the enzyme led the authors to propose that this selectivity may be at least partially responsible for the unusual accumulation of vanadium by tunicates. A range of other reductases exist and future research will document the relationship between these and Vanabin2.

As noted previously, the halogenation reaction catalyzed by haloperoxidases is an important biological and technological reaction in biological chemistry.^{9,10} In the manuscript by Hartung and co-workers (DOI: 10.1039/C3DT51582F), the details for the formation of carbon–bromine bonds catalyzed by the two different bromoperoxidase enzymes from the brown alga *Ascophyllum nodosum* were investigated. Because these enzymes are very different, one being a dimer (V_{Br}PO(AnI)) and the other a hexamer (V_{Br}PO(AnII)), the details of the substrate binding and mechanism of reaction are explored. Specifically, a frontier molecular orbital (FMO)-analysis was undertaken and the experimentally observed reactant was found to correlate with the π-type HOMO of an alkene and the σ*_{Br,X}-type LUMO of the bromination reagent. This analysis allows for the prediction of reactions catalyzed by vanadate-dependent bromoperoxidases, as demonstrated in the analysis of the synthesis of bromopyrroles, which occur naturally in marine sponges.

Chemically modeling the reaction catalyzed by haloperoxidases is an important area that has received much interest from a number of groups worldwide since the discovery of the enzyme,^{9,10} and a couple of such contributions are presented in this themed

issue in addition to the Perspective described above by the Wever group. The team of Maurya, Costa Pessoa and co-workers (DOI: 10.1039/C3DT50469G) prepared a series of Schiff base complexes with VO^{2+} , VO^{3+} and VO_2^+ cores and characterized them in the solid state and in solution. They characterized both the vanadium(IV) and (V) forms of these methoxy and methanol adducts of the Schiff base complexes. X-ray characterization of two of the vanadium(V) complexes shows that the ligand is coordinated through the ONO^{2-} enolate tautomeric form and one of the hydrazide moieties remained free (that is non-coordinated). These vanadium(V) complexes are capable of catalyzing oxidative bromination of styrene, which demonstrates that they are functional mimics of bromoperoxidase.

Exploring a different approach to halogenation reactions, Conte and co-workers (DOI: 10.1039/C3DT50907A) use a two-phase system to catalyze the bromination of toluene. The aqueous phase was adjusted to pH 1, H_2O_2 and KBr were added and then it was combined with the organic phase consisting of CH_2Cl_2 or CH_3Cl containing toluene. The reaction was shown to be effective under mild conditions with potential for recycling of the catalytic phase.

This themed issue describes a diverse sampling of vanadium chemistry and the reader is encouraged to continue to enjoy the chemistry of the versatile vanadium. We thank the authors for their contributions, and those that have participated at the meeting and continue to make the International Vanadium Symposium a success. This thematic issue provides an important role of documenting the progress of the field and introducing several new emerging areas.

The quality of the work presented suggests a new and bright future for the field and a stimulating upcoming meeting in 2014.

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