OBITUARY

Malcolm H. Chisholm

David L. Clark¹

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Malcolm H. Chisholm, Distinguished University Professor at The Ohio State University, and one of the world's leading inorganic chemists, passed away on Friday November 20 at the age of 70. Born in Bombay India, raised in Scotland and England, he earned his doctorate working with Don Bradley at Queen Mary College, London. After a postdoctoral appointment at the University of Western Ontario with Howard Clark, he accepted a faculty position at Princeton in (1972–1978), followed by 22 years at Indiana University (1978–2000), and 15 years at Ohio State University (2000–2015).

David L. Clark dlclark@lanl.gov

¹ Los Alamos National Laboratory, Los Alamos, USA

The author of over 650 publications, he was a member of the National Academy of Sciences, and a Fellow of the Royal Society of Chemistry (London). He was a Fellow of the American Academy of Arts and Sciences, the American Association for the Advancement of Science, the American Chemical Society, the Royal Society of Edinburgh, and Die Deutsche Akademie der Naturforscher—Leopoldina. He was the recipient of numerous awards from the American Chemical Society, including ACS Awards in Inorganic Chemistry, Distinguished Service in the Advancement of Inorganic Chemistry, the Nobel Laureate Signature Award, the Basolo Medal and the Bailar Medal. He was the recipient of the Nyholm prize of the Royal Society of Chemistry.

Chisholm was immersed in the study of structure, bonding, spectroscopy and chemical reactivity of multiple bonds between metal atoms. He showed early in his career how π -donor ligands could stabilize low coordination numbers, and how π -bonding models could explain chemical behaviors. It was the consideration of how a d³ center like Mo(NMe₂)₃ could be diamagnetic that led Chisholm to the discovery of ethane-like dimers M₂(NMe₂)₆ of Mo and W, with d³-d³ M-M triple bonds of $\sigma^2 \pi^4$ electronic configuration in analogy to the triple bond in acetylene. He was fascinated by the analogy of M-M multiple bonds to the C-C multiple bonds in organic chemistry.

From his efforts to systematize the chemistry of the M_2X_6 triple bond, he found a vast array of chemical reactivity at the dinuclear center that included ligand substitution, oxidative addition, and reductive elimination. The stepwise changes in M–M bond order brought about by oxidative-addition and reductive elimination reactions have a parallel in the organic chemistry of C–C bonds. Moreover, he showed that the dinuclear center could be a redox active template for activation of small molecules and unsaturated organic groups illustrated by carbene-like additions across $M \equiv M$ bonds by groups like $C \equiv O$ and $C \equiv NR$. He showed that covalently linked assemblies of redox active M_2 units can exist in more than one metastable state. These systems can be electronically tuned to show signaling and switching behavior and electro-, thermo- and solvatochromism, or they can be introduced into organic polymers and liquid crystals with the intent of making new "smart" materials.

Chisholm showed that M–M multiple bonds are synthetically useful as "inorganic functional groups" and can be used in selective organic transformations, e.g., as templates for carbon–carbon, carbon–hydrogen, and carbon–oxygen bond cleavage and formation, and as the building blocks for cluster forming reactions. For example, $M_2(OR)_6$ complexes can dimerize to $M_4(OR)_{12}$, with fascinating cluster dynamics, including reversible equilibria between M_2 and M_4 molecules. Here again, Chisholm found analogy with organic chemistry and the comparison of the electronic structure of $M_4(OR)_{12}$ and C_4H_4 , where both compounds avoid a D_{4h} square structure due to second-order Jahn–Teller instabilities. He showed that many of the alkoxide supported small clusters of Mo and W bear a striking similarity to carbonyl clusters of the later transition elements, e.g. $W_3(OR)_9(\mu_3$ -CR) and $Co_3(CO)_9(\mu_3$ -CR), traced to an isolobal analogy between ML₃ fragments [W(OR)₃ vs. Co(CO)₃] containing π -donor OR or π -acceptor CO ligands. The molecular alkoxide clusters provided templates for developing organometallic chemistry that

may model the heterogeneous reactions of the lower-valent metal oxides. Many fascinating reactions involving small, unsaturated molecules such as carbon monoxide, ethylene, and acetylene provided model studies for surface reactions.

Chisholm was a remarkable mentor and teacher who was respected for his generosity and graciousness as a person. He was an exceedingly influential and supportive father, husband, friend, and colleague for all who knew him. For his students, postdocs, and colleagues, he was a remarkable role model, as a mentor and teacher, and as a person. He had a wonderful sense of humor, and he cared deeply and genuinely about everyone around him.