

PROGRESS IN INORGANIC CHEMISTRY

Edited by

KENNETH D. KARLIN

DEPARTMENT OF CHEMISTRY
JOHNS HOPKINS UNIVERSITY
BALTIMORE, MARYLAND

VOLUME 54



AN INTERSCIENCE PUBLICATION
JOHN WILEY & SONS, INC.

**Progress in
Inorganic Chemistry
Volume 54**

Advisory Board

JACQUELINE K. BARTON
CALIFORNIA INSTITUTE OF TECHNOLOGY, PASADENA, CALIFORNIA

THEODORE J. BROWN
UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS

JAMES P. COLLMAN
STANFORD UNIVERSITY, STANFORD, CALIFORNIA

F. ALBERT COTTON
TEXAS A & M UNIVERSITY, COLLEGE STATION, TEXAS

ALAN H. COWLEY
UNIVERSITY OF TEXAS, AUSTIN, TEXAS

RICHARD H. HOLM
HARVARD UNIVERSITY, CAMBRIDGE, MASSACHUSETTS

EIICHI KIMURA
HIROSHIMA UNIVERSITY, HIROSHIMA, JAPAN

NATHAN S. LEWIS
CALIFORNIA INSTITUTE OF TECHNOLOGY, PASADENA, CALIFORNIA

STEPHEN J. LIPPARD
MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE,
MASSACHUSETTS

TOBIN J. MARKS
NORTHWESTERN UNIVERSITY, EVANSTON, ILLINOIS

EDWARD I. STIEFEL
PRINCETON UNIVERSITY, PRINCETON, NEW JERSEY

KARL WIEGHARDT
MAX-PLANCK-INSTITUT, MÜLHEIM, GERMANY

PROGRESS IN INORGANIC CHEMISTRY

Edited by

KENNETH D. KARLIN

DEPARTMENT OF CHEMISTRY
JOHNS HOPKINS UNIVERSITY
BALTIMORE, MARYLAND

VOLUME 54



AN INTERSCIENCE PUBLICATION
JOHN WILEY & SONS, INC.

Cover Illustration or "a molecular ferric wheel" was adapted from Taft. K. L. and Lippard. S. J., *J. Am. Chem. Soc.*, **1990**. 112, 9629.

Copyright © 2005 by John Wiley & Sons, Inc. All rights reserved.

Published by John Wiley & Sons, Inc., Hoboken, New Jersey.

Published simultaneously in Canada.

No part of this publication may be reproduced, stored in a retrieval system, or transmitted in any form or by any means, electronic, mechanical, photocopying, recording, scanning, or otherwise, except as permitted under Section 107 or 108 of the 1976 United States Copyright Act, without either the prior written permission of the Publisher, or authorization through payment of the appropriate per-copy fee to the Copyright Clearance Center, Inc., 222 Rosewood Drive, Danvers, MA 01923, 978-750-8400, fax 978-646-8600, or on the web at www.copyright.com. Requests to the Publisher for permission should be addressed to the Permissions Department, John Wiley & Sons, Inc., 111 River Street, Hoboken, NJ 07030, (201) 748-6011, fax (201) 748-6008.

Limit of Liability/Disclaimer of Warranty: While the publisher and author have used their best efforts in preparing this book, they make no representations or warranties with respect to the accuracy or completeness of the contents of this book and specifically disclaim any implied warranties of merchantability or fitness for a particular purpose. No warranty may be created or extended by sales representatives or written sales materials. The advice and strategies contained herein may not be suitable for your situation. You should consult with a professional where appropriate. Neither the publisher nor author shall be liable for any loss of profit or any other commercial damages, including but not limited to special, incidental, consequential, or other damages.

For general information on our other products and services please contact our Customer Care Department within the U.S. at 877-762-2974, outside the U.S. at 317-572-3993 or fax 317-572-4002.

Wiley also publishes its books in a variety of electronic formats. Some content that appears in print, however, may not be available in electronic format.

Library of Congress Catalog Card Number 59-13035
ISBN 0-471-72348-7

Printed in the United States of America

10 9 8 7 6 5 4 3 2 1

Contents

Chapter 1	Atomlike Building Units of Adjustable Character: Solid-State and Solution Routes to Manipulating Hexanuclear Transition Metal Chalcogenide Clusters	1
	ERIC J. WELCH AND JEFFREY R. LONG	
Chapter 2	Doped Semiconductor Nanocrystals: Synthesis, Characterization, Physical Properties, and Applications	47
	J. DANIEL BRYAN AND DANIEL R. GAMELIN	
Chapter 3	Stereochemical Aspects of Metal Xanthate Complexes: Molecular Structures and Supramolecular Self-Assembly	127
	EDWARD R. T. TIEKINK AND IONEL HAIDUC	
Chapter 4	Trivalent Uranium: A Versatile Species for Molecular Activation	321
	ILIA KOROBKOV AND SANDRO GAMBAROTTA	
Chapter 5	Comparison of the Chemical Biology of NO and HNO: An Inorganic Perspective	349
	KATRINA M. MIRANDA, LISA RIDNOUR, MICHAEL ESPREY, DEBORAH CITRIN, DOUGLAS THOMAS, DANIELE MANCARDI, SONIA DONZELLI, DAVID A. WINK, TATSUO KATORI, CARLO G. TOCCHETTI, MARCELLA FERLITO, NAZARENO PAOLOCCI AND JON M. FUKUTO	
Chapter 6	Alterations of Nucleobase pK_a Values upon Metal Coordination: Origins and Consequences	385
	BERNHARD LIPPERT	
Chapter 7	Functionalization of Myoglobin	449
	YOSHIHITO WATANABE AND TAKASHI HAYASHI	
Subject Index		495
Cumulative Index, Volumes 1–54		519

**Progress in
Inorganic Chemistry
Volume 54**

Atomlike Building Units of Adjustable Character:
Solid-State and Solution Routes to Manipulating
Hexanuclear Transition Metal Chalcohalide Clusters

ERIC J. WELCH and JEFFREY R. LONG

*Department of Chemistry
University of California, Berkeley
Berkeley, CA 94720*

CONTENTS

I. INTRODUCTION	2
A. Cluster Geometries / 2	
B. Electronic Structures / 5	
II. SOLID-STATE SYNTHESIS	8
A. Dimensional Reduction / 12	
1. Standard Salt Incorporation / 12	
2. Core Anion Substitution / 13	
3. Heterometal Substitution / 18	
4. Interstitial Substitution / 21	
B. Low-Temperature Routes / 21	
III. SOLUTION METHODS	25
A. Cluster Excision / 25	
B. Solution-Phase Cluster Assembly / 26	

C. Ligand Substitution Reactions / 27	
1. Core Anion Exchange / 27	
2. Terminal Ligand Exchange / 28	
IV. ELECTRONIC PROPERTIES	30
A. Electrochemistry / 30	
B. Paramagnetism / 32	
C. Photochemistry / 32	
V. CLUSTERS AS BUILDING UNITS	33
A. Extended Solid Frameworks / 33	
B. Supramolecular Assemblies / 36	
VI. CONCLUDING REMARKS	38
ACKNOWLEDGMENTS	38
ABBREVIATIONS	38
REFERENCES	39

1. INTRODUCTION

Over the past two decades, considerable progress has been made in the synthesis and characterization of compounds containing discrete hexanuclear clusters (1–12). Most recently, soluble, molecular forms of these clusters have begun to see use as building units in the construction of extended solid frameworks and supramolecular assemblies. In our view, certain hexanuclear cluster cores are very much akin to a new transition metal ion, but one with a large radius, a fixed coordination geometry, and electronic properties that can be adjusted through synthesis. In particular, clusters of this type are encountered with second- and third-row transition elements of groups 4–7 in reduced oxidation states, accompanied by core halide and/or chalcogenide ligands. Herein, we review the methods available for manipulating the composition of such species, and give a brief overview of their use in solution assembly reactions.

A. Cluster Geometries

The clusters of interest here bear one of three distinct geometries, all of which are based upon a central M_6 unit exhibiting some degree of metal–metal bonding. In two of the geometries, the metal atoms are arranged in an octahedron, while in the third they form a regular trigonal prism. Importantly,

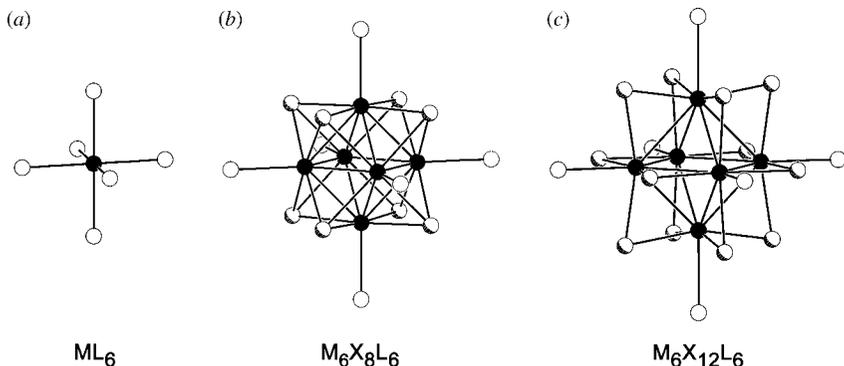


Figure 1. Idealized structures of an octahedral ML_6 complex (a), a face-capped octahedral $M_6X_8L_6$ cluster (b), and an edge-bridged octahedral $M_6X_{12}L_6$ cluster (c). Black, shaded, and white spheres represent metal atoms M, inner-ligands X, and terminal-ligands L, respectively. Each structure conforms to O_h symmetry.

each metal center bears one radially extending terminal ligand L, such that, overall, the outer coordination sphere is analogous to that of an octahedral or trigonal-prismatic metal complex.

For the metals of Groups 6 and 7, the $M_6X_8L_6$ geometry displayed in the middle of Fig. 1 is predominant. Here, the cluster core consists of a perfect octahedron of metal atoms with each face capped by a halide or chalcogenide anion X. The eight core anions form a cube, with the metal atoms positioned approximately within the plane and near the center of each cube face. Thus, each metal center has local C_{4v} symmetry, with a ligand set comprised of an axial ligand L, a square of four equatorial X anions, and a lower, staggered square of four metal atoms. Typical mean M–M bond distances range from 2.601(4) Å in $[Re_6S_8Cl_6]^{4-}$ (13) to 2.681(3) Å in $[Re_6Te_8(CN)_6]^{4-}$ (14), while mean M–X distances range from 2.403(9) Å in $[Re_6S_8Cl_6]^{4-}$ to 2.792(7) Å in $[W_6I_{14}]^{2-}$ (15). Based upon comparisons with analogous ML_6 complexes, the clusters exhibit a core radius of ~ 2.8 Å, which of course is much larger than the radius of any single transition metal ion. The M_6X_8 core geometry is perhaps most notably observed in the Chevrel phases of the type $A_xMo_6X_8$ (X = S, Se), which have long been of interest for their superconducting and magnetic properties (16–19). This geometry generally does not appear to support the presence of an interstitial atom at the center of the octahedron, with an exception arising in the electron-deficient clusters of Nb_6HI_{11} (20, 21).

Clusters containing metals from groups 4 and 5 show a strong preference for structures based upon the $M_6X_{12}L_6$ geometry shown in Figure 1(c). In this case, the core consists of an octahedron of metal atoms with each edge bridged by a halide or chalcogenide anion X. The 12 core anions form a regular cuboctahedron, with the metal atoms positioned near the center but slightly below the plane

of each square face. Accordingly, each metal center has local C_{4v} symmetry, with a ligand set comprised of an axial ligand L, a square of four equatorial X anions, and a lower, eclipsed square of four metal atoms. Typical mean M–M bond distances range from 2.803 Å in Nb_6F_{15} (22) to 3.018(2) Å in $[\text{Nb}_6\text{Cl}_{18}]^{2-}$ (23), while mean M–X distances range from 2.049 Å in Nb_6F_{15} to 2.797(5) Å in Ta_6I_{14} (24). Note that these clusters tend to be slightly larger than face-capped octahedral clusters, with a core radius of ~ 3.2 Å, based upon comparisons with analogous ML_6 complexes. The edge-bridged octahedral geometry has also been observed for a single binary group 6 halide: W_6Cl_{18} (25, 26). Importantly, for group 4 metals, this geometry typically occurs with an interstitial main group or transition metal atom situated at the center of the octahedron, giving rise to clusters of generic formula $\text{M}_6\text{ZX}_{12}\text{L}_6$. Clusters of this type are also apparent in numerous reduced rare earth halide phases, although generally only within the confines of a highly condensed framework (1, 5, 6, 10, 27). These interesting rare earth clusters will not be further discussed here, since methods for bringing them into solution have not yet been developed.

An alternative $\text{M}_6\text{ZX}_{12}\text{L}_6$ cluster geometry of relevance here has been encountered in a few compounds. As shown at the right in Fig. 2, the metal atoms in this geometry surround the interstitial atom Z to form a trigonal prism instead of an octahedron. Twelve edge-bridging anions X complete the cluster core, with two bridging each of the longer edges of the trigonal prism, and one bridging each of the shorter edges. Here again, a single terminal ligand L extends from

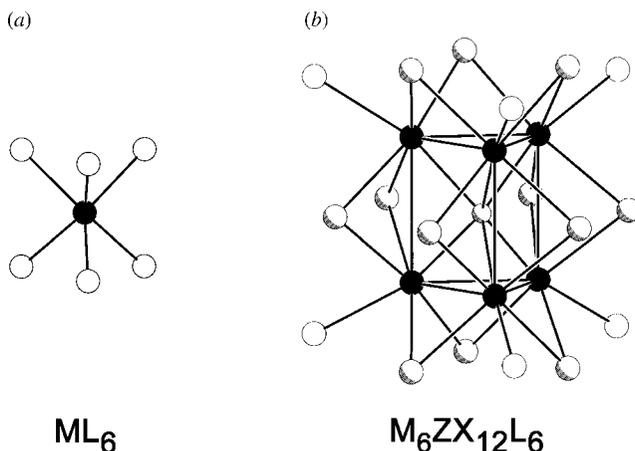


Figure 2. Idealized structures of a trigonal prismatic ML_6 complex (a) and a centered edge-bridged trigonal-prismatic $\text{M}_6\text{ZX}_{12}\text{L}_6$ cluster (b). Black, small shaded, large shaded, and white spheres represent metal atoms M, interstitial atom Z, inner ligands X, and terminal ligands L, respectively. Each structure conforms to D_{3h} symmetry.

each metal vertex, now resulting in an outer ligand set akin to that of a trigonal prismatic ML_6 complex. Note that the nonmetal atoms of the cluster are arranged in a hexagonal closest packing, whereas those of the centered, edge-bridged octahedral geometry are arranged in a cubic closest packing. Trigonal-prismatic clusters of this type were first observed within the one-dimensional (1D) compounds $A_3Nb_6SBr_{17}$ ($A = K, Rb, Cs, Tl$) (28, 29). Very recently, they have also been observed in the two-dimensional (2D) solid W_6CCl_{16} and as the molecular species $[W_6CCl_{18}]^{n-}$ ($n = 0-3$) and $[W_6NCl_{18}]^{n-}$ ($n = 1-3$) (30-32). Taking $[W_6CCl_{18}]^{2-}$ as a prototype, it is worth noting that mean $Cl^a \cdots C \cdots Cl^a$ angles of 71.7° and 89.2° deviate somewhat from the analogous $S-Mo-S$ angles of 78.7° and 84.0° in MoS_2 (33, 34). While trigonal-prismatic technetium and rhenium halide clusters are known without interstitial atoms, these have multiple-bond character along three parallel edges, leading to an outer ligand arrangement that is unlike that of any simple metal complex (34).

B. Electronic Structures

The electronic structures for many hexanuclear clusters adopting the basic geometries displayed in Figs. 1 and 2 have been investigated using a variety of computational methods (30, 35-47). We will therefore only briefly summarize the results obtained from DFT calculations performed—by methods described in detail elsewhere (30, 44, 45)—on a few representative examples.

The frontier orbitals calculated for the face-capped octahedral cluster $[Re_6Se_8Cl_6]^{4-}$ consist of a pair of e_g highest occupied molecular orbitals (HOMOs) and an a_{2g} lowest unoccupied molecular orbitals (LUMO), as shown in the middle of Fig. 3. The former are primarily rhenium-rhenium bonding in character, with some rhenium-selenium antibonding contributions, while the latter is almost exclusively rhenium-rhenium antibonding in character. The 10 orbitals (three triply degenerate orbital sets and an a_{1g} orbital) directly lower in energy than the HOMO are principally rhenium-rhenium bonding in character. This result is quite analogous to that obtained previously for the face-capped octahedral Mo_6S_8 units of the Chevrel phases (38). Filling 12 rhenium-rhenium bonding orbitals with 24 electrons gives the equivalent of a single two-center, two-electron bond per $Re-Re$ edge of the Re_6 octahedron; thus, the cluster is electron precise. Consistent with the expectation that all of these bonding orbitals should be filled, the cluster formally contains $Re(III)$, affording a count of $6 \times 4 = 24$ metal-based valence electrons. While the majority of the face-capped octahedral clusters have this preferred electron count of 24, counts as low as 19 and as high as 25 have been established within Nb_6I_{11} and $[Re_4Os_2Se_8(CN)_6]^{3-}$, respectively (20, 45). Since the HOMO for $[Re_6Se_8Cl_6]^{4-}$ is doubly degenerate, one would expect the one-electron oxidized (23-electron) cluster to undergo a first-order Jahn-Teller distortion. Indeed, careful examination of