

Topics in
INORGANIC AND
ORGANOMETALLIC
STEREOCHEMISTRY

Gregory Geoffroy

EDITOR

VOLUME 12 IN TOPICS IN STEREOCHEMISTRY
E.L. ELIEL AND N.L. ALLINGER, SERIES EDITORS

TOPICS IN

**INORGANIC AND
ORGANOMETALLIC
STEREOCHEMISTRY**

EDITED BY
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VOLUME 12
of
**TOPICS IN
STEREOCHEMISTRY**

Series Editors
**NORMAN L. ALLINGER
ERNEST L. ELIEL**

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VOLUME 12

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FOREWORD

This volume, devoted entirely to inorganic stereochemistry, is not a standard volume and so it does not bear our standard introduction. When Professor F. A. Cotton joined our editorial advisory board, he expressed dissatisfaction with the paucity of chapters dealing with *inorganic stereochemistry* in previous volumes of this series. He suggested that the only appropriate way to make up for past deficiencies in this area was to devote an entire volume of *Topics in Stereochemistry* to the inorganic aspects of the subject. This suggestion intrigued the editors; however, from past experience we doubted whether we would be able to put together an entire volume made up of contributions by inorganic chemists. Dr. Cotton had a suggestion in this regard: he recommended that we ask Professor Gregory Geoffroy of Pennsylvania State University to edit the proposed venture. Dr. Geoffroy was kind enough to accept our invitation, and the present volume is the result. We hope it will, in a tangible way, signal to the inorganic community the editors' awareness of stereochemistry as more than a prerogative of organic chemists and of *Topics in Stereochemistry* as a good vehicle for the dissemination of information in the area of inorganic stereochemistry. We hope that there will be many inorganic contributions in future volumes, and we encourage offerings of potential chapters in this area.

At the same time, after reading the chapters Dr. Geoffroy has acquired, we are convinced that there is much information here of considerable interest to our regular readers with organic backgrounds. Indeed, in view of the close relationship between organic and inorganic chemistry that has recently developed affecting both synthesis and mechanism, it is only appropriate that stereochemistry be included in the confluence of these two areas. We hope that our readers, including those who consider themselves organic chemists, will agree with that sentiment.

We are pleased to welcome Professor Alan R. Battersby of Cambridge, Professor Günther Snatzke of the University of Bochum, and Professor Jan Michalski of the Polish Academy of Sciences to our circle of editorial advisors, and we take this opportunity to announce that Professor Samuel H. Wilen of the City University of New York will join us as a co-editor beginning with the next volume (Volume 13).

N. L. ALLINGER
E. L. ELIEL

PREFACE

Volume 12 of Topics in Stereochemistry is devoted entirely to inorganic and organometallic stereochemical subjects.

The volume begins with a chapter by T. E. Sloan of Chemical Abstracts Service on the notation and nomenclature used to denote stereochemistry in inorganic and organometallic compounds. The need for a rational and systematic stereochemical nomenclature has become increasingly important as research interest in organometallic and asymmetric compounds has grown during the past two decades. The systematic notations that have been developed to satisfy these needs are reviewed and discussed in this chapter, with specific attention given to the use of Cahn-Ingold-Prelog ligand priority numbers for denoting complex stereochemistry.

The ubiquitous involvement of metal-carbon bonds in changes of bonding at carbon centers induced by metals, either catalytically or stoichiometrically, is well established. In Chapter 2 T. C. Flood reviews the stereochemical aspects of these reactions and importantly puts the stereochemistry into mechanistic perspective where possible. Reactions that form and disrupt metal-carbon σ bonds are discussed by reaction type: oxidative addition, reductive elimination, insertion, electrophilic cleavage, transmetalation, and addition.

An important area of current stereochemical research is the synthesis of asymmetric compounds mediated by transition metals. The incorporation of chiral ligands or the use of chiral complexes can lead to asymmetric synthesis where the chiral discrimination rivals that of enzymes. In Chapter 3 B. Bosnich and M. D. Fryzuk review the major achievements in this field. The authors attempt to give a mechanistic basis for the reactions they discuss, in spite of the notable lack of rationality and systematization in these studies.

Metal nitrosyl complexes represent an important class of organometallic compounds. The nitrosyl ligand can adopt linear and bent geometries conforming to the valence-bond structures $|\text{N}\equiv\text{O}|^+$ and $\langle\text{N}=\text{O}\rangle^-$, respectively, depending on the electronic nature of the complex. This area of organometallic chemistry has grown rapidly in recent years and previous reviews are severely outdated. Thus the review of the structural aspects of nitrosyl complexes by R. D. Feltham and J. H. Enemark in Chapter 4 is timely. This review is restricted to a discussion of metal nitrosyl complexes whose structures have been determined by X-ray crystallography, neutron diffraction, electron diffraction or microwave spectroscopy, that is, of compounds whose stereochemistry is known with certainty.

The stereochemistry of compounds of germanium and tin is the subject of Chapter 5 by M. Gielen. This article nicely complements Sommer's earlier review of the stereochemical aspects of silicon chemistry (L. Sommer, *Stereochemistry, Mechanism, and Silicon*, McGraw-Hill, New York, 1965); it thus completes coverage of all the heavier group IV elements, since few stereochemical studies have been conducted with lead compounds. The optical stability of stereoisomers of germanium and tin compounds is discussed, and there is a summary of the stereochemistry of substitution reactions and intermolecular rearrangements.

In Chapter 6 B. F. G. Johnson and R. E. Benfield discuss the structures of transition metal carbonyl clusters, summarizing recent progress in this rapidly expanding area and providing a semi-quantitative rationalization of the structures for these clusters. Focus is on the bonding considerations of the central metal framework as well as the influence of the ligand envelope on the structures of such clusters.

G. L. GEOFFROY

University Park, Pennsylvania
February 1981

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THOMAS E. SLOAN

Chemical Abstracts Service, Columbus, Ohio

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I. INTRODUCTION

The synthesis of urea in 1828 by Wöhler and the founding of structural chemistry in the mid-nineteenth century by Kekulé, Pasteur, van't Hoff, and Le Bell mark the origins of stereochemistry (1). The development of structural carbon chemistry would have been difficult without the experimental clues and disclosures derived from the development of stereochemistry. It was the number of isomers of disubstituted benzene that provided the proof in distinguishing between the several possible structural formulations. The then new structural concepts and insights gained led to the rapid development of carbon (organic) chemistry and for the next 60 years overwhelmed the more traditional subjects in chemical investigations of "mineral" and "pneumatic" chemistry. The residue of this preponderance of carbon chemistry still exist in the language and notation found in today's chemical literature.

II. HISTORICAL DEVELOPMENT OF STEREOCHEMICAL NOMENCLATURE

Three of the great precepts of classical carbon chemistry: (a) the constant valency of four for the carbon atom, (b) the ability of carbon to form homogeneous chains, and (c) the tetrahedral configuration of four coordinate carbon, were so successful and pervasive that the same concepts were thought to be the basis of structural chemistry for all chemical systems. Following these precepts and preserving an ideal valency, scientists set forth the chain-type structures to explain the structures and properties of many inorganic systems. Experimental evidence that challenged these theories continued to accumulate, and finally Werner formulated and popularized the more complex and less certain bonding theory of coordination compounds.

The first nomenclature applied to isomers of inorganic compounds was derived from the colors of compounds with the same stoichiometric proportions (2). Cobalt trichloride tetraammoniate had two forms known as the cobalt *praseo* or green complex and the cobalt *violeo* or violet complex. Often within the same family of compounds the color nomenclature was able to group together molecules of similar characteristics. Since there was no agreement among inorganic chemists of the period on the constitutional structures of inorganic species, it would have been difficult to develop any type of rational nomenclature.

As the Werner-Jorgensen controversy was actively pursued (11), experimental evidence of structures accumulated, and the classification by color broke down. The color nomenclature became less meaningful. Finally, as Werner's structural postulates became widely accepted, it became possible to develop a stereo-

chemical nomenclature and notation based on the accepted and experimentally accurate structure.

Werner recognized geometric similarities of disubstituted platinum(II) planar compounds and disubstituted cobalt(III) octahedral compounds to the geometric isomerism of ethylene compounds and used the terms "cis" and "trans" to describe the adjacent and opposite or corner and axial isomeric forms of these compounds (3). Werner also developed the first stereochemical numbering for the ligand positions on the octahedral chromium and cobalt complexes (Fig. 1). The cis compounds were designated 1,2 and the trans compounds 1,6.

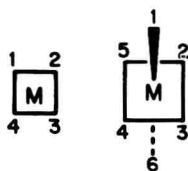


Fig. 1. Werner numbering for square planar and octahedral structures.

Stereochemical nomenclature did not change appreciably in the next 50 years. The Report of the Committee for the Reform of Inorganic Chemical Nomenclature (1940) does not mention stereochemical nomenclature (4). A comprehensive review of coordination compound nomenclature by Fernelius reaffirms the use of the terms "cis" and "trans", recognizes a standard numbering for the square planar structure, gives the Werner numbering of the octahedral structure, and proposes standard numbering practices for binuclear structures of the fused square planar and fused tetrahedral types (5). This review also notes the well-established use of the (+), (−), or, alternatively, *d* or *l* to indicate the sign of rotation for optical isomers.

The numbers and complexities of isomeric inorganic compounds increased rapidly following the renewed interest in inorganic and coordination chemistry fostered by the development of the atomic bomb during World War II. Stereochemical research had focused predominantly on coordination numbers 4 and 6. The cis and trans terminology was found to be inadequate for the relatively well-studied six-coordinate octahedral compounds (Fig. 2). In structure I of Figure 2, "cis" describes the adjacent relationship of the tricarbonyl and the trichloro ligands, and the trans isomer is the only other structure possible. However in structure II of Figure 2 the tricarbonyl ligands are mutually opposite or trans, but the chlorine ligand is adjacent or cis to the phosphine and pyridine ligands. The terms "fac" and "mer" have been used to describe the facial and meridional distributions of ligands in trisubstituted octahedral complexes. Although commonly used, these terms are not adequate because there are four possible geometric arrangements, one mer and three fac isomer for octahedral $[\text{Ma}_3\text{bcd}]$

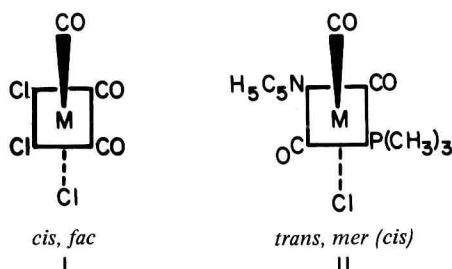


Fig. 2. Stereochemical terms for tris monodentate octahedral complexes.

compounds. Similarly, there are 15 geometric isomers of the octahedral $[\text{Mabcdef}]$ compounds, and numerous isomers for multidentate chelating ligands such as the octahedral structure with the quadridentate ligands in Figure 3, which exists in three geometric forms. Structures I and II are commonly designated α -*cis* and β -*cis*, respectively, and structure III as *trans*.

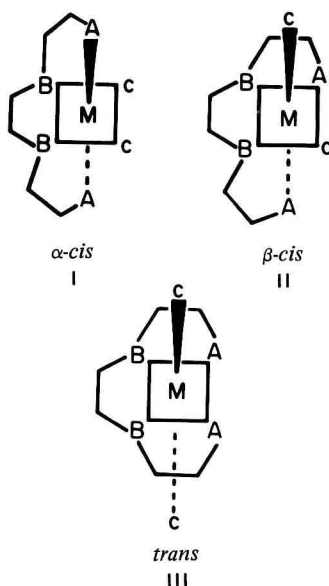


Fig. 3. Geometric isomers of octahedral complexes with linear tetradentate ligands.

These deficiencies in stereochemical terminology were compounded by the synthesis of compounds having coordination numbers 2 through 9 with many different geometries. The inadequacy of stereochemical nomenclature was recognized by several investigators. In a review of compounds forming higher

coordination number polyhedra and molecular clusters, Muetterties and Wright proposed rules for numbering polyhedra and produced a table of numbered polyhedra with 5 to 20 vertices, representing 29 different geometries (6). The numbering rules were developed from the symmetry properties of the polyhedra. They define a principal or preferred axis, number a position on this axis, and number positions in belts or planes perpendicular to the preferred axis, in a clockwise direction. This generates the Werner numbering of the octahedron and is very similar to the numbering of closo polyhedral boranes adopted by IUPAC (7).

In developing a linear notation for coordination compounds, McDonnell and Pasternack proposed a ligand locant designator notation that follows the numbering pattern proposed by Muetterties (8). The McDonnell locant designators substitute lowercase Roman characters to designate the ligand positions. This was done to eliminate any confusion that would occur between the substitution numbering within a ligand and the numbering of the ligand position. Another innovation in the McDonnell notation is the class symbol (Arabic number, capital Roman letter) to indicate the coordination geometry about the central atom (Fig. 4).

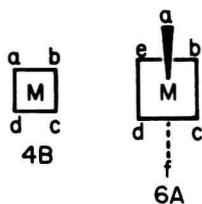
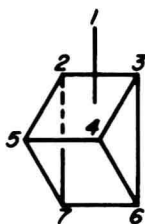


Fig. 4. McDonnell locant designators and class symbols for square planar and octahedral structures.

The traditional stereochemical descriptors *cis*, *trans*, *fac*, and *mer*, along with the McDonnell locant designators, were codified in the *IUPAC Nomenclature of Inorganic Chemistry, 1970* (9). The IUPAC nomenclature elaborates extensively on the McDonnell notation to allow for chelating ligands, develops ligating atom priorities to eliminate ambiguities, and extends the notation to polynuclear compounds.

A method for unambiguous, structurally exact stereochemical nomenclature is provided by specific ligand numbering or locant designators. These have been employed very sparingly in the chemical literature, however, perhaps because of the rather complicated rules for the unambiguous application of locants to the complicated structures for which they are most useful. Also, in the case of directionally specific locants, it is difficult to distinguish enantiomeric pairs of compounds (Table 1). A further notation or symbol is required when the geo-

Table 1
Chiral $(\text{NbCl}_2\text{F}_5)^{2-}$ Compounds.



Muetterties-Wright Numbering

- 1,2-dichloro-3,4,5,6,7-pentafluoroniobate(2-) I
 1,3-dichloro-2,4,5,6,7-pentafluoroniobate(2-) I
 2,4-dichloro-1,3,5,6,7-pentafluoroniobate(2-) VII
 2,6-dichloro-1,3,4,5,7-pentafluoroniobate(2-) VIII
 2,7-dichloro-1,3,4,5,6-pentafluoroniobate(2-) IV
 3,5-dichloro-1,2,4,6,7-pentafluoroniobate(2-) VII
 3,6-dichloro-1,2,4,5,7-pentafluoroniobate(2-) IV
 3,7-dichloro-1,2,4,5,6-pentafluoroniobate(2-) VIII

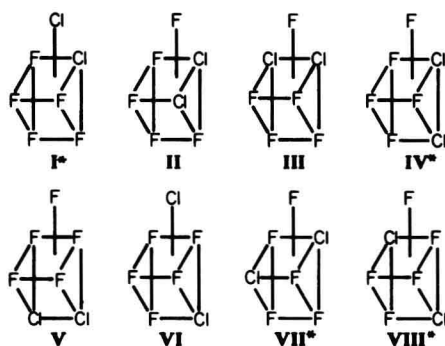


Fig. 5. Isomers of $[\text{NbCl}_2\text{F}_5]^{2-}$ (chiral structures indicated by asterisk).

metric configuration of an asymmetric compound is known, but not the absolute configuration, since it is not possible to draw and number such a structure ambiguously (structure IV, Fig. 5).

The stereochemical nomenclature for optically active compounds has also abounded with attempts to provide rational and exact notation. The sign of optical rotation, + or -, was first used to indicate an optically pure or nearly