

*Editor-in-Chief*

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# **INORGANIC SYNTHESES**

**Volume XX**

**A Wiley-Interscience Publication  
JOHN WILEY & SONS**

*New York Chichester Brisbane Toronto*



**INORGANIC SYNTHESSES**

**Volume XX**



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**To  
Paolo Chini  
1928-1980**





## PREFACE

Continuing the function of *Inorganic Syntheses*, this volume contains 57 numbered sections including almost 150 individual preparations, among which are some important intermediates, covering a number of broad, currently active areas of inorganic chemistry. These areas are divided into seven chapters. First, a series of offerings, featuring the double infusion technique and crystal growth in gels, treat solid materials and techniques of crystal growth. A variety of interesting and useful stoichiometrically simple compounds are presented in Chapter 2. They include such main group element derivatives as  $\text{TeF}_4$  and  $\text{SeO}_2\text{F}_2$ , and a number of transition element derivatives (e.g., trirhenium nonahalides) the important metal chromium(III) oxides (chromites), a neat preparation for copper(I) acetate, and the simplest method yet for anhydrous  $\text{PtCl}_2$  (the third for this compound in *Inorganic Syntheses*). Chapter 3 contains an array of classic coordination compounds (ethylenediamine complexes of rhodium,  $\beta$ -diketonates of platinum(II)), and also some materials that have been of interest only in the more recent past (phosphine complexes of iron, a  $\text{CO}_2$  adduct, phosphite complexes of several metal ions). Syntheses are given for a number of rather exotic ligand complexes in Chapter 4. These include the clathrochelates of Goedken, the sepulchrates of Sargeson, the superphthalocyanine of Marks, and examples of compartmental ligands. A lengthy section is devoted to compounds of biological interest. Emphasis ranges from metal intercalation reagents, over synthetic macrocycles, corrin complexes and analogues, and porphyrins (including the  $\text{O}_2$  adduct of Collman's picket-fence porphyrin) to complexes of dinitrogen. David Dolphin contributed a large group of syntheses on the complexes of the natural macrocycles and their close relatives. Organometallic compounds are soundly represented in Chapters 6 and 7. Chapter 6 contains a number of representative element organometallic compounds (hexamethyldisilaseleneane, digermatellurane, digermoxane) and varieties of transition metal derivatives (e.g., halocyclopentadienyl complexes of manganese and rhodium, examples of the novel metalla- $\beta$ -diketone compounds). The final chapter is devoted to the timely subject of metal clusters and it includes preparations for several of Chini's rhodium clusters, some iron clusters by Volume XIX Editor D. Shriver, and  $\mu_3$ -alkylidyne (tricarbonylcobalt) compounds by Seyfreh.

I want to thank the many authors and checkers who have produced the substance of this volume. The Editorial Board has provided constant aid in evaluation and editing of original manuscripts. Special thanks go to John Bailar and

Therald Moeller in this regard. Invaluable guidance came from past Editors Durward Shriver, Bodie Douglas, George Parshall, and Aaron Wold. Warren H. Powell and Thomas E. Sloan of Chemical Abstracts Service have continued their key role in assuring the use of appropriate current nomenclature. Tom Sloan also prepared the indices. Jay Worrell, Therald Moeller, and Conard Fernelius helped with proofreading. I must add a word of sincere appreciation for my late secretary, Mrs. Denise Hughes, who provided the order and attention necessary to monitor the progress of the many manuscripts from which this volume was drawn. I have enjoyed serving as your Editor partly because I first encountered *Inorganic Syntheses* while I was in graduate school, when I was an editorial assistant, checker, and author, as well as user, and have remained an appreciative subscriber over the years.

Daryle H. Busch

*Columbus, Ohio*  
*January 1980*

## NOTICE TO CONTRIBUTORS

The *Inorganic Syntheses* series is published to provide all users of inorganic substances with detailed and foolproof procedures for the preparation of important and timely compounds. Thus the series is the concern of the entire scientific community. The Editorial Board hopes that all chemists will share in the responsibility of producing *Inorganic Syntheses* by offering their advice and assistance in both the formulation of and the laboratory evaluation of outstanding syntheses. Help of this kind will be invaluable in achieving excellence and pertinence to current scientific interests.

There is no rigid definition of what constitutes a suitable synthesis. The major criterion by which syntheses are judged is the potential value to the scientific community. An ideal synthesis is one that presents a new or revised experimental procedure applicable to a variety of related compounds, at least one of which is critically important in current research. However, syntheses of individual compounds that are of interest or importance are also acceptable. Syntheses of compounds that are available commercially at reasonable prices are not acceptable.

The Editorial Board lists the following criteria of content for submitted manuscripts. Style should conform with that of previous volumes of *Inorganic Syntheses*. The introductory section should include a concise and critical summary of the available procedures for synthesis of the product in question. It should also include an estimate of the time required for the synthesis, an indication of the importance and utility of the product, and an admonition if any potential hazards are associated with the procedure. The Procedure should present detailed and unambiguous laboratory directions and be written so that it anticipates possible mistakes and misunderstandings on the part of the person who attempts to duplicate the procedure. Any unusual equipment or procedure should be clearly described. Line drawings should be included when they can be helpful. All safety measures should be stated clearly. Sources of unusual starting materials must be given, and, if possible, minimal standards of purity of reagents and solvents should be stated. The scale should be reasonable for normal laboratory operation, and any problems involved in scaling the procedure either up or down should be discussed. The criteria for judging the purity of the final product should be delineated clearly. The section on Properties should supply and discuss those physical and chemical characteristics that are relevant to judging the purity of the product and to permitting its handling and use in an

intelligent manner. Under References, all pertinent literature citations should be listed in order. A style sheet is available from the Secretary of the Editorial Board.

The Editorial Board determines whether submitted syntheses meet the general specifications outlined above. Every synthesis must be satisfactorily reproduced in a laboratory other than the one from which it was submitted.

Each manuscript should be submitted in duplicate to the Secretary of the Editorial Board, Professor Jay H. Worrell, Department of Chemistry, University of South Florida, Tampa, FL 33620. The manuscript should be typewritten in English. Nomenclature should be consistent and should follow the recommendations presented in *Nomenclature of Inorganic Chemistry*, 2nd Ed., Butterworths & Co, London, 1970 and in *Pure Appl. Chem.*, 28, No. 1 (1971). Abbreviations should conform to those used in publications of the American Chemical Society, particularly *Inorganic Chemistry*.

## TOXIC SUBSTANCES AND LABORATORY HAZARDS

The attention of the user is directed to the notices under this heading on page ix of Volume XIX and pages xv-xvii in Volume XVIII. It cannot be redundant to stress the ever-present need for the experimental chemist to evaluate procedures and anticipate and prepare for hazards. Obvious hazards associated with the preparations in this volume have been delineated, but it is impossible to foresee and discuss all possible sources of danger. Therefore the synthetic chemist should be familiar with general hazards associated with toxic, flammable, and explosive materials. In light of the primitive state of knowledge of the biological effects of chemicals, it is prudent that all the syntheses reported in this and other volumes of *Inorganic Syntheses* be conducted with rigorous care to avoid contact with all reactants, solvents, and products.



# CONTENTS

## Chapter One SOLID STATE

1. Crystal Growth in Gels . . . . .	1
A. General Experimental Considerations . . . . .	2
B. Crystals Grown by the Standard Technique . . . . .	3
C. Tartrates . . . . .	4
D. Carbonates . . . . .	4
E. Sulfides . . . . .	4
F. Other Experiments Using the Standard Technique . . . . .	5
G. The Complex-Dilution Method . . . . .	6
H. Liesegang Rings . . . . .	7
2. Crystal Growth in Gels . . . . .	9
A. Calcium Tartrate Crystals Grown by the Standard Technique . . . . .	9
B. Copper(II) Chloride Crystals Grown by the Complex-Dilution Method . . . . .	10
3. Single-Crystal Growth by a Double-Infusion Technique . . . . .	11
A. The Double-Infusion Technique . . . . .	11
B. Single Crystals of Rare Earth Transition Element Cyanides $\text{Ln}[\text{M}(\text{CN})_6 \cdot n\text{H}_2\text{O}]$ . . . . .	12
C. Silver(I) Periodate $\text{Ag}_2\text{H}_3\text{IO}_6$ and Ammonium Periodate $(\text{NH}_4)_2\text{H}_3\text{IO}_6$ . . . . .	15
4. Crystalline Silver Chloride . . . . .	18
5. The Partially Oxidized Platinum Complex Rubidium Tetracyano- platinate [Hydrogen Bis(sulfate)] (3:1:0.46): $\text{Rb}_3[\text{Pt}(\text{CN})_4](\text{SO}_4\text{-H-O}_4\text{S})_{0.46} \cdot \text{H}_2\text{O}$ . . . . .	20
6. The Rubidium-Cesium Partially Oxidized Tetracyanoplatinate (Hydrogen Difluoride)-Fluoride Systems . . . . .	23
A. Rubidium Tetracyanoplatinate (Hydrogen Difluoride) (2:1:0.29) Hydrate: $\text{Rb}_2[\text{Pt}(\text{CN})_4](\text{FHF})_{0.29} \cdot 1.67\text{H}_2\text{O}$ . . . . .	24
B. Rubidium Tetracyanoplatinate (Hydrogen Difluoride) (2:1:0.38): $\text{Rb}_2[\text{Pt}(\text{CN})_4](\text{FHF})_{0.38}$ . . . . .	25
C. Cesium Tetracyanoplatinate (Hydrogen Difluoride) (2:1:0.23): $\text{Cs}_2[\text{Pt}(\text{CN})_4](\text{FHF})_{0.23}$ . . . . .	26
D. Cesium Tetracyanoplatinate (Hydrogen Difluoride) (2:1:0.38): $\text{Cs}_2[\text{Pt}(\text{CN})_4](\text{FHF})_{0.38}$ . . . . .	28

E. Cesium Tetracyanoplatinate Fluoride (2:1:0.19): Cs <sub>2</sub> [Pt(CN) <sub>4</sub> ] F <sub>0.19</sub> .....	29
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## Chapter Two STOICHIOMETRICALLY SIMPLE COMPOUNDS

7. Tellurium Tetrafluoride .....	33
8. Sulfur Tetrafluoride Oxide .....	34
9. Selenonyl Difluoride .....	36
10. Hydrogen Pentafluorooxoselenate(VI) .....	38
11. Rhenium Pentachloride and Volatile Metal Chlorides by Direct Chlorination Using a Vertical-Tube Reactor .....	41
12. Trirhenium Nonachloride .....	44
13. Trirhenium Nonahalides .....	46
A. Tetraacetatodichlorodirhenium .....	46
B. Trirhenium Nonachloride .....	47
C. Trirhenium Nonabromide and Trirhenium Nonaiodide .....	47
14. β-Platinum(II) Chloride .....	48
15. Divalent Metal Chromium(III) Oxides (Chromites) .....	50
A. Lithium Chromium(III) Oxide, LiCrO <sub>2</sub> .....	50
B. Potassium Metal(II) Chlorides .....	51
C. Divalent Metal Chromium(III) Oxides .....	52
16. Copper(I) Acetate .....	53

## Chapter Three COORDINATION COMPOUNDS

17. Compounds Containing the <i>cis</i> -Bis(ethylenediamine)rhodium(III) Species .....	57
A. Bis(ethylenediamine) (oxalato) rhodium(III) Perchlorate .....	58
B. <i>cis</i> -Bis(ethylenediamine) Dinitrorhodium(III) Nitrate .....	59
C. <i>cis</i> -Dichlorobis(ethylenediamine)rhodium(III) Chloride Hydrate ..	60
18. Potassium Tetrahydrodioxoosmate(VI) and <i>trans</i> - Bis(ethylenediamine) dioxoosmium(VI) Chloride .....	61
A. Potassium Tetrahydrodioxoosmate(VI) .....	61
B. <i>trans</i> -Bis(ethylenediamine) dioxoosmium(VI) Chloride .....	62
19. Sodium Bis[2-ethyl-2-hydroxybutyrate(2-)] oxochromate(V) .....	63
20. The Bis(β-diketonato)platinum(II) Complexes .....	65
A. Preparation of Stock Solution .....	66
B. Bis[2,4-Pentanedionato(1-)] platinum(II) .....	66
C. Bis[1,1,1-trifluoro-2,4-pentanedionato(1-)] platinum(II) .....	67
D. Bis[1,1,1,5,5,5-Hexafluoro-2,4-pentanedionato(1-)]- platinum(II) .....	67



21. Trimethylphosphine Iron Complexes . . . . .	69
A. Dichlorobis(trimethylphosphine)iron(II) . . . . .	70
B. Tetrakis(trimethylphosphine)iron . . . . .	71
C. (Carbon dioxide-C,O)tetrakis(trimethylphosphine)iron . . . . .	73
22. Pentakis(trimethyl phosphite)complexes of the $d^8$ transition metals .	76
A. Pentakis(trimethyl phosphite)nickel(II) Bis(tetraphenylborate) .	76
B. Pentakis(trimethyl phosphite)palladium(II) Bis(tetraphenylborate) . . . . .	77
C. Pentakis(trimethyl phosphite)rhodium(I) Tetraphenylborate . . .	78
D. Pentakis(trimethyl phosphite)iron(O) . . . . .	79
E. Pentakis(trimethyl phosphite)ruthenium(O) . . . . .	80
F. Pentakis(trimethyl phosphite)cobalt(I) Tetraphenylborate . . . . .	81
23. Complexes of Aluminum Iodide with Pyridine and Related Bases . . .	82
A. Preparation of Triiodotris (pyridine) aluminum . . . . .	83

#### Chapter Four COMPLEXES WITH COMPLICATED CHELATE LIGANDS

24. Caged Metal Ions: Cobalt Sepulchrates . . . . .	85
A. [Co(bicyclo[6.6.6]ane-1,3,6,8,10,13,16,19-N <sub>8</sub> )]Cl <sub>3</sub> . . . . .	86
25. Clathrochelates Formed by the Reaction of Tris(2,3-butanedione Dihydrazone)metal Complexes with Formaldehyde: [5,6,14,15,20,21- Hexamethyl-1,3,4,7,8,10,12,13,16,17,19,22-dodecaazatetracyclo- [8.8.41 <sup>3,17</sup> .1 <sup>8,12</sup> ] tetracos-4,6,13,15,19,21- hexaene-N <sup>4</sup> ,N <sup>7</sup> ,N <sup>13</sup> ,N <sup>16</sup> ,N <sup>19</sup> ,N <sup>22</sup> ] metal( $n$ ) Tetrafluoroborate . .	87
26. Compartmental Ligands . . . . .	90
A. 5,9,14,18-Tetramethyl-1,4,10,13-Tetraazacyclooctadeca- 5,8,14,17-tetraene-7,16-dione, H <sub>4</sub> daen(I) . . . . .	91
B. [5,9,14,18-Tetramethyl-1,4,10,13-tetraazacyclooctadeca- 5,8,14,17-tetraene-7,16-donato(2-),N <sup>1</sup> ,N <sup>4</sup> ,O <sup>7</sup> ,O <sup>16</sup> ] copper(II), Cu(H <sub>2</sub> daen)(II) . . . . .	92
C. [[6,6'-(Ethylenedinitrilo)bis(2,4-heptanedionato)]- (2-),N,N',O <sup>4</sup> ,O <sup>4'</sup> ] copper(II), Cu(H <sub>2</sub> daen-N <sub>2</sub> O <sub>2</sub> )(III) . . . . .	93
D. $\mu$ [[6,6'-(Ethylenedinitrilo)bis(2,4-heptanedionato)]- (4-),N,N',O <sup>4</sup> ,O <sup>4'</sup> :O <sup>2</sup> ,O <sup>2'</sup> ,O <sup>4</sup> ,O <sup>4'</sup> ] dicopper(II), Cu <sub>2</sub> (daen)(IV) .	94
E. Aqua- $\mu$ -[[6,6'-(ethylenedinitrilo)bis(2,4-heptanedionato)]- (4-),N,N',O <sup>4</sup> ,O <sup>4'</sup> :O <sup>2</sup> ,O <sup>2'</sup> ,O <sup>4</sup> ,O <sup>4'</sup> ] copper(II)oxovanadium(IV), CuVO(daaen)H <sub>2</sub> O, (V) . . . . .	95
27. [7,12:21,26-Diimino-19,14;28,33:35,5-trinitrilo-5H- pentabenzoc[ <i>c,h,m,r,w</i> ] [1,6,11,16,21] pentaazacyclopenta- cosinato(2-)]-dioxouranium(VI) (Uranyl Superphthalocyanine) . . . . .	97

## Chapter Five COMPOUNDS OF BIOLOGICAL INTEREST

28. Metallointercalation Reagents: Thiolato Complexes of (2,2':6',2''-terpyridine)platinum(II) . . . . .	101
A. Chloro(2,2':6',2''-terpyridine)platinum(II) Chloride Dihydrate, [Pt(terpy)Cl]Cl·2H <sub>2</sub> O . . . . .	102
B. (2-Mercaptoethanolato-S)(2,2':6',2''-terpyridine)platinum(II) Nitrate, [Pt(terpy)(SCH <sub>2</sub> CH <sub>2</sub> OH)]NO <sub>3</sub> . . . . .	103
C. (2-Ammonioethanethiolato-S)(2,2':6',2''-terpyridine)-platinum(II) Nitrate [Pt(terpy)(SCH <sub>2</sub> CH <sub>2</sub> NH <sub>3</sub> )](NO <sub>3</sub> ) <sub>2</sub> and other (2,2':6',2''-terpyridine)thiolatoplatinum(II) Complexes . . . . .	104
29. Saturated, Unsubstituted Tetraazamacrocyclic Ligands and Their Cobalt(III) Complexes . . . . .	105
A. 1,4,7,10-Tetraazacyclotridecane ([13]aneN <sub>4</sub> ) . . . . .	106
B. 1,4,8,12-Tetraazacyclopentadecane ([15]aneN <sub>4</sub> ) . . . . .	108
C. 1,5,9,13-Tetraazacyclohexadecane ([16]aneN <sub>4</sub> ) . . . . .	109
D. <i>trans</i> -Dichloro([13]aneN <sub>4</sub> ) cobalt(III) Chloride, (I)-and (II)- <i>trans</i> -Dichloro([15]aneN <sub>4</sub> ) cobalt(III) Chloride, (I)-and (II)- <i>trans</i> -Dichloro([16]aneN <sub>4</sub> ) cobalt(III) Perchlorate . . . . .	111
30. [7,16-Dihydro-6,8,15,17-tetramethyldibenzo[ <i>b,i</i> ] [1,4,8,11]-tetraazacyclotetradecinato(2-)] nickel(II), ([5,7,12,14-Me <sub>4</sub> -2,3:9,10-Bzo <sub>2</sub> -[14]hexaenato(2-)N <sub>4</sub> ]Ni(II) and the Neutral Macrocyclic Ligand . . . . .	115
A. [5,7,12,14-Me <sub>4</sub> -2,3:9,10-Bzo <sub>2</sub> [14]hexaenato(2-)N <sub>4</sub> ]Ni(II) . . . . .	116
B. The 5,7,12,14-Me <sub>4</sub> -2,3:9,10-Bzo[14]hexaene N <sub>4</sub> Ligand . . . . .	117
31. The Synthesis of Molybdenum and Tungsten Dinitrogen Complexes . . . . .	119
A. Bis(acetonitrile)tetrachloromolybdenum(IV), [MoCl <sub>4</sub> (CH <sub>3</sub> CN) <sub>2</sub> ] . . . . .	120
B. Tetrachlorobis(tetrahydrofuran)molybdenum(IV), [MoCl <sub>4</sub> (thf) <sub>2</sub> ] . . . . .	121
C. Trichlorotriss(tetrahydrofuran)molybdenum(III), [MoCl <sub>3</sub> (thf) <sub>3</sub> ] . . . . .	121
D. <i>trans</i> -Bis(dinitrogen)bis[ethylenebis(diphenylphosphine)]-molybdenum(0), <i>trans</i> -[Mo(N <sub>2</sub> ) <sub>2</sub> (Ph <sub>2</sub> PCH <sub>2</sub> CH <sub>2</sub> PPh <sub>2</sub> ) <sub>2</sub> ] . . . . .	122
E. Tetrachlorobis(triphenylphosphine)tungsten(IV), [WCl <sub>4</sub> (PPh <sub>3</sub> ) <sub>2</sub> ] . . . . .	124
F. Tetrachloro[ethylenebis(diphenylphosphine)]-tungsten(IV), [WCl <sub>4</sub> (Ph <sub>2</sub> PCH <sub>2</sub> CH <sub>2</sub> PPh <sub>2</sub> ) <sub>2</sub> ] . . . . .	125
G. <i>trans</i> -Bis(dinitrogen)bis[ethylenebis(diphenylphosphine)]-tungsten(0), <i>trans</i> -[W(N <sub>2</sub> ) <sub>2</sub> (Ph <sub>2</sub> PCH <sub>2</sub> CH <sub>2</sub> PPh <sub>2</sub> ) <sub>2</sub> ] . . . . .	126
32. Bis[2,3-butanedione dioximato(1-)] cobalt Complexes . . . . .	127
A. Bromobis[2,3-butanedione dioximato(1-)](dimethyl sulfide) cobalt(III) . . . . .	128

B.	Bromobis[2,3-butanedione dioximato(1-)](4- <i>tert</i> -butylpyridine) cobalt(III) . . . . .	130
C.	Bis[2,3-butanedione dioximato(1-)](4- <i>tert</i> -butylpyridine)-(2-ethoxyethyl) cobalt(III) . . . . .	131
D.	Bis[2,3-butanedione dioximato(1-)](4- <i>tert</i> -butylpyridine)-(ethoxymethyl) cobalt(III) . . . . .	132
33.	Cobalamins and Cobinamides . . . . .	134
A.	Methylcobalamin . . . . .	136
B.	Hydroxocobalamin . . . . .	138
C.	(2,2-Diethoxyethyl)cobalamin[I, R = -CH <sub>2</sub> CH(OEt) <sub>2</sub> ] . . . . .	138
D.	Dicyanocobyrinic Acid Heptamethyl Ester(II, R = R' = -CN) . . . . .	139
E.	Aquacyanocobrinic Acid Heptamethyl Ester Perchlorate . . . . .	141
F.	Aquamethylcobrinic Acid Heptamethyl Ester Perchlorate . . . . .	141
34.	Metalloporphines . . . . .	143
A.	[5,10,15,20-Tetraphenyl-21 <i>H</i> ,23 <i>H</i> -porphinato(2-)] nickel(II) . . . . .	143
B.	Oxo[5,10,15,20-tetraphenyl-21 <i>H</i> ,23 <i>H</i> -porphinato(2-)]-vanadium(IV) . . . . .	144
C.	[2,3,7,8,12,13,17,18-Octaethyl-21 <i>H</i> ,23 <i>H</i> -porphinato(2-)]-magnesium(II) . . . . .	145
35.	Iron Porphines . . . . .	147
A.	Chloro[dimethyl protoporphyrinato(2-)] iron(III), chloro(dimethyl-7,12-diethenyl-3,8,13,17-tetramethyl-21 <i>H</i> ,23 <i>H</i> -porphine-2,18-dipropionato(2-)] iron(III) . . . . .	148
B.	Chloro[octaethyl-21 <i>H</i> ,23 <i>H</i> -porphinato(2-)] iron(III) . . . . .	151
C.	Chloro[mesoporphyrinato(2-)] iron(III) (mesopheemin IX), chloro[7,12-diethyl-3,8,13,17-tetramethyl-21 <i>H</i> ,23 <i>H</i> -porphine-2,18-dipropionato(2-)] iron(III) . . . . .	152
D.	The Insertion of <sup>57</sup> Fe into Porphyrins . . . . .	153
36.	Metallophthalocyanins and Benzoporphines . . . . .	155
A.	[1,4,8,11,15,18,22,25-Octamethyl-29 <i>H</i> ,31 <i>H</i> -tetrabenzo[ <i>b,g,l,q</i> ]-porphinato(2-)] cobalt(II) . . . . .	156
B.	1,4,8,11,15,18,22,25-Octamethyl-29 <i>H</i> ,31 <i>H</i> -tetrabenzo[ <i>b,g,l,q</i> ]-porphine . . . . .	158
C.	Dilithium Phthalocyanine . . . . .	159
D.	Phthalocyaninato(2-) iron(II) . . . . .	160
37.	(Dioxygen)(N-methylimidazole)[( <i>all-cis</i> )-5,10,15,20-tetrakis[2-(2,2-dimethylpropionamido)phenyl] porphyrinato(2-)-iron(II) . . . . .	161
A.	5,10,15,20-tetrakis(2-nitrophenyl)porphyrin, H <sub>2</sub> TNPP . . . . .	162
B.	5,10,15,20-Tetrakis(2-aminylphenyl)porphyrin, H <sub>2</sub> TAPP . . . . .	163
C.	Separation of <i>all-cis</i> -H <sub>2</sub> TAPP . . . . .	164
D.	( <i>all-cis</i> )-5,10,15,20-Tetrakis[2,2-dimethylpropionamido)-phenyl] porphyrin, H <sub>2</sub> TpiVPP . . . . .	165

E. Bromo {( <i>all-cis</i> )-5,10,15,20-tetrakis[2-(2,2-dimethylpropionamido)phenyl] porphyrinato(2-)} iron(III), Fe[( <i>all-cis</i> )TpivPP] Br . . . . .	166
F. Bis(N-methylimidazole)[( <i>all-cis</i> )-5,10,15,20-tetrakis[2-(2,2-dimethylpropionamido)phenyl] porphyrinato(2-)]-iron(II), Fe[( <i>all-cis</i> )TpivPP] ( <i>N</i> -MeC <sub>3</sub> H <sub>3</sub> N <sub>2</sub> ) <sub>2</sub> . . . . .	167
G. (Dioxygen)(N-methylimidazole)[( <i>all-cis</i> )-5,10,15,20-tetrakis[2-(2,2-dimethylpropionamido)phenyl] porphyrinato(2-)] iron(II), Fe[( <i>all-cis</i> )TpivPP] ( <i>N</i> -MeC <sub>3</sub> H <sub>3</sub> N <sub>2</sub> )(O <sub>2</sub> ) . . . . .	168

## Chapter Six ORGANOMETALLIC COMPOUNDS

38. Silyl and Germyl Selenides and Tellurides . . . . .	171
A. Hexamethyldisilaselene and Hexamethyldisilatellurane-[Bis(trimethylsilyl) selenide and Bis(trimethylsilyl telluride)] . . . . .	173
B. Digermaselenane and Digermatellurane(Digermyl selenide and Digermyl telluride) . . . . .	175
39. Digermoxane and 1,3-Dimethyl-, 1,1,3,3-Tetramethyl-, and Hexamethyldigermoxane . . . . .	176
A. Digermoxane . . . . .	178
B. 1,3-Dimethyl-, 1,1,3,3-Tetramethyl-, and Hexamethyl Digermoxane . . . . .	179
40. Di- $\mu$ -chloro-dichlorobis(ethylene)diplatinum(II), Di- $\mu$ -chloro-dichlorobis(styrene)diplatinum(II), and Di- $\mu$ -chloro-dichlorobis(1-dodecene)diplatinum(II) . . . . .	181
A. <i>trans</i> -Dichloro(ethylene)(pyridine)platinum(II) . . . . .	181
B. Di- $\mu$ -chloro-dichlorobis(ethylene)diplatinum(II) . . . . .	182
C. Di- $\mu$ -chloro-dichlorobis(styrene)diplatinum(II) . . . . .	182
D. Di- $\mu$ -chloro-dichlorobis(1-dodecene)diplatinum(II) . . . . .	183
41. Dibromomethylplatinum(IV) and Dihydroxodimethylplatinum(IV) Sesquihydrate . . . . .	185
A. Dibromodimethylplatinum(IV) . . . . .	185
B. Dihydroxodimethylplatinum(IV) Sesquihydrate . . . . .	186
42. Halocyclopentadienyl Complexes of Manganese and Rhodium . . . . .	188
A. Tetrachloro-5-diazo-1,3-cyclopentadiene . . . . .	189
1. Procedures for Tetrachloro-2,4-cyclopentadiene-1-one Hydrazone, C <sub>5</sub> Cl <sub>4</sub> NNH <sub>2</sub> . . . . .	190
2. Procedures for Tetrachloro-5-diazo-1,3-cyclopentadiene, C <sub>5</sub> Cl <sub>4</sub> N <sub>2</sub> . . . . .	190
B. 5-Diazo-1,3-Cyclopentadiene, C <sub>5</sub> H <sub>4</sub> N <sub>2</sub> . . . . .	191
C. (Chlorotetraphenyl- $\eta^5$ -cyclopentadienyl)( $\eta^4$ -1,5-cyclooctadiene)-rhodium, Rh( $\eta^5$ -C <sub>5</sub> Ph <sub>4</sub> Cl)(cod) . . . . .	191
D. (Bromotetraphenyl- $\eta^5$ -cyclopentadienyl)( $\eta^4$ -1,5-cyclooctadiene)	

	rhodium, $\text{Rh}(\eta\text{-C}_5\text{Ph}_4\text{Br})(\text{cod})$ and dicarbonyl (chlorotetraphenyl- $\eta^5$ -cyclopentadienyl) rhodium, $\text{Rh}(\eta^5\text{-C}_5\text{Ph}_4\text{Cl})(\text{CO})_2$ . . . . .	192
E.	(Chloro- $\eta^5$ -cyclopentadienyl)( $\eta^4$ -1,5-cyclooctadiene) rhodium, $\text{Rh}(\eta^5\text{-C}_5\text{H}_4\text{Cl})(\text{cod})$ . . . . .	192
F.	(Tricarbonyl(chloro- $\eta^5$ -cyclopentadienyl)-manganese, $\text{Mn}(\eta^5\text{-C}_5\text{H}_4\text{Cl})(\text{CO})_3$ . . . . .	192
G.	(Bromo- $\eta^5$ -cyclopentadienyl)tricarbonyl-manganese, $\text{Mn}(\eta^5\text{-C}_5\text{H}_4\text{Br})(\text{CO})_3$ . . . . .	193
H.	Tricarbonyl(iodo- $\eta^5$ -cyclopentadienyl)manganese, $\text{Mn}(\eta^5\text{-C}_5\text{H}_4\text{I})(\text{CO})_3$ . . . . .	193
I.	Pentacarbonyl(pentachloro- $\eta^1$ -cyclopentadienyl)manganese, $\text{Mn}(\eta^1\text{-C}_5\text{Cl}_5)(\text{CO})_5$ . . . . .	193
J.	(Bromotetrachloro- $\eta^1$ -cyclopentadienyl)pentacarbonylmanganese, $\text{Mn}(\eta^1\text{-C}_5\text{Cl}_4\text{Br})(\text{CO})_5$ . . . . .	194
K.	( $\eta^4$ -1,5-cyclooctadiene)(pentachloro- $\eta^5$ -cyclopentadienyl)- rhodium, $\text{Rh}(\eta^5\text{-C}_5\text{Cl}_5)(\text{cod})$ . . . . .	194
L.	Tricarbonyl(pentachloro- $\eta^5$ -cyclopentadienyl)manganese, $\text{Mn}(\eta^5\text{-C}_5\text{Cl}_5)(\text{CO})_3$ . . . . .	194
M.	(Bromotetrachloro- $\eta^5$ -cyclopentadienyl)tricarbonylmanganese, $\text{Mn}(\eta^5\text{-C}_5\text{Cl}_4\text{Br})(\text{CO})_3$ . . . . .	195
43.	( $\eta^6$ -Benzene)( $\eta^5$ -cyclopentadienyl)molybdenum and ( $\eta^6$ -Benzene)- ( $\eta^5$ -cyclopentadienyl)molybdenum Derivatives . . . . .	196
A.	( $\eta^6$ -Benzene)( $\eta^5$ -cyclopentadienyl)molybdenum . . . . .	197
B.	( $\eta^6$ -Benzene)chloro( $\eta^5$ -cyclopentadienyl)molybdenum . . . . .	198
C.	( $\eta^6$ -Benzene)bromo( $\eta^5$ -cyclopentadienyl)molybdenum . . . . .	199
D.	( $\eta^6$ -Benzene)( $\eta^5$ -cyclopentadienyl)iodomolybdenum . . . . .	199
44.	<i>cis</i> -[Acetyltetracarbonyl(1-hydroxyethylidene)rhenium] ( <i>cis</i> -Diacetyltetracarbonylrhenium hydrogen) . . . . .	200
A.	Acetylpentacarbonylrhenium . . . . .	201
B.	<i>cis</i> -[Acetyltetracarbonyl-(1-hydroxyethylidene)rhenium ( <i>cis</i> -Diacetyltetracarbonylrhenium hydrogen) . . . . .	202
45.	<i>cis</i> -[Acetyl(1-aminoethylidene)tetracarbonylrhenium]- [ <i>cis</i> -(Acetimidoyl)(acetyl)tetracarbonylrhenium hydrogen)] . . . . .	204
46.	Hyrido Complexes of Cobalt with Bis(phosphines) . . . . .	206
A.	Hydridobis [ <i>cis</i> -vinylenebis(diphenylphosphine)] cobalt (I) . . . . .	207
B.	Hydridobis [ethylenebis(diphenylphosphine)] cobalt (I) . . . . .	208

## Chapter Seven METAL CLUSTER COMPLEXES

47.	Tri- $\mu$ -carbonyl-nonacarbonyltetrahodium, $\text{Rh}_4(\text{CO})_9(\mu\text{-CO})_3$ . . . . .	209
48.	Dipotassium $\mu_6$ -Carbido-nona- $\mu$ -carbonyl-hexacarbonylhexarhodate- (2-), $\text{K}_2[\text{Rh}_6(\text{CO})_6(\mu\text{-CO})_9(\mu_6\text{-C})]$ . . . . .	212

xx Contents

49.	Disodium Di- $\mu$ -carbonyl-octa- $\mu_3$ -carbonyl-icosacarbonyldodecarhodate(2-), $\text{Na}_2 [\text{Rh}_{12}(\text{CO})_{20}(\mu\text{-CO})_2(\mu_3\text{-CO})_8]$ . . . . .	215
50.	$\mu$ -Nitrido bis(triphenylphosphorus)(1+) Undecacarbonylhydridotriferrate(1-), $[(\text{Ph}_3\text{P})_2\text{N}] [\text{Fe}_3\text{H}(\text{CO})_{11}]$ . . . . .	218
51.	Bis[ $\mu$ -nitrido-bis(triphenylphosphorus)(1+)] Undecacarbonyltriferrate, $[(\text{Ph}_3\text{P})_2\text{N}]_2 [\text{Fe}_3(\text{CO})_{11}]$ . . . . .	222
52.	$\mu_3$ -Alkylidyne-tris(tricarbonylcobalt) Compounds: Organocobalt Cluster Complexes . . . . .	224
53.	$\mu_3$ -Methylidyne- and $\mu_3$ -Benzylidyne-tris(tricarbonylcobalt) . . . . .	226
	A. $\mu_3$ -Methylidyne-tris(tricarbonylcobalt) . . . . .	227
	B. $\mu_3$ -Benzylidyne-tris(tricarbonylcobalt) . . . . .	228
54.	$\mu_3$ [(Ethoxycarbonyl)methylidyne]- and $\mu_3$ -{[(Methylamino)carbonyl]methylidyne}-tris(tricarbonylcobalt) . . . . .	230
	A. $\mu_3$ -[(Ethoxycarbonyl)methylidyne]-tris(tricarbonylcobalt) . . . . .	230
	B. $\mu_3$ -{[(Methylamino)carbonyl]methylidyne}-tris(tricarbonylcobalt) . . . . .	232
55.	$\mu_3$ -(Chloromethylidyne)-and $\mu_3$ -[ <i>tert</i> -butoxycarbonyl]methylidyne]-tris(tricarbonylcobalt) . . . . .	234
	A. $\mu_3$ -(Chloromethylidyne)-tris(tricarbonylcobalt) . . . . .	234
	B. $\mu_3$ -[( <i>tert</i> -Butoxycarbonyl)methylidyne]-tris(tricarbonylcobalt) . . . . .	235
56.	Tetracarbonyl bis- $\mu$ -(2-methyl-2-propane thiolato)diiridium(I) . . . . .	237
57.	Decacarbonyl- $\mu$ -[diborane(6)]- $\mu$ -hydrido-trimanganese . . . . .	240
	<i>Correction</i> . . . . .	243
	<i>Index of Contributors</i> . . . . .	245
	<i>Subject Index</i> . . . . .	249
	<i>Formula Index</i> . . . . .	281

**INORGANIC SYNTHESSES**

**Volume XX**





# Chapter One

## SOLID STATE

### 1. CRYSTAL GROWTH IN GELS

Submitted by A. F. ARMINGTON\* and J. J. O'CONNOR\*

The growth of crystals in gel media is a relatively old method of crystal growth that gained some prominence about 60 years ago. Much of the earlier work on the subject has been reviewed by Holmes.<sup>1</sup> After this initial interest the subject remained nearly dormant, except as a curiosity, until a paper by Hensch et al.<sup>2</sup> revived interest in this type of crystal growth. Since then, approximately 100 papers have been published on the subject.

Gel growth is the easiest and least expensive of all crystal-growth techniques in that it consists merely of allowing two materials to react in a gel medium, forming a product that crystallizes in the gel. The simplest arrangement consists of mixing one reactant with the gel and then allowing the gel to set in a test tube that it partially fills. An aqueous solution of the second reactant is added above the set gel in the tube. The reactants diffuse through the gel until they come into contact; they then form an insoluble product that precipitates in crystalline form. In the second common method, a U-tube is partially filled with neutral gel and allowed to set. In this context, neutral means no reactants are added to the gel. The two reactants are placed above the set gel on the opposite sides of the U-tube, and the reaction again proceeds by diffusion. The quality and size of the crystals are similar for the two methods.

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## 2 Solid State

The most commonly used medium is silica gel. Numerous other gels have been used but with limited success, apparently because of the structural differences in the gels. A more detailed description of the various gels is given by Henisch.<sup>3</sup>

There are several chemical requirements that must be fulfilled to grow crystals by this method. First, the reactants employed must be soluble in the solvent (usually water), and the product must be relatively insoluble in the same solvent. Some solubility of the product crystal is required to grow crystals of appreciable size. While it is believed that this is related to supersaturation of the product, the exact mechanism is not yet understood. A second requirement is that the gel must remain stable in the presence of the reacting solutions and must not react with these solutions or the product formed. Silica gels are most stable in acid solutions and tend to dissolve at pH values much greater than 8. This can create problems with chelating agents, since these agents are most useful in highly basic solutions where the gel is unstable. If the pH is only slightly higher than 8 (up to 10) some crystals may still form, but the gel near the alkaline solution-gel interface will start to decompose and sometimes one must race with time to get the crystals grown and out of the gel before the gel itself dissolves.

The influence of the gel in crystal growth is not fully understood. It appears that the main effect of the gel is to slow down the rate of diffusion, which allows the crystal to grow at a slower rate. It is generally believed that the gel does not actually react with the solutions involved, but there is a possibility that it may have some effect on the degree of saturation that is attainable in the solution. The role the gel plays on the nucleation process is also unknown, but some observations on nucleation have been made by Henisch<sup>3</sup> and Armington et al.<sup>4</sup>

The sizes of the crystals grown in a simple experiment are rather small. With the exception of tartrates, which can be grown at least 2 cm long, most experiments yield crystals less than 5 mm along their major axes. Somewhat larger crystals have been grown by using more exotic equipment,<sup>5</sup> or in some cases by using larger tubes and allowing more time for growth to occur.<sup>6</sup> For most purposes, 50-mL test tubes are adequate.

In spite of some difficulties, the gel method has two distinct advantages. First, since the crystals are grown at or near room temperature, thermal strains are absent. Thus gel-grown crystals should be better for some purposes than are crystals grown at higher temperatures. Second, the method is simple and inexpensive.

### A. GENERAL EXPERIMENTAL CONSIDERATIONS

Silica gels are formed in two ways. The most used method is that of mixing commercial waterglass (sp gr 1.06) with an equal amount of 1 *N* acid, usually hydro-

chloric or acetic acid, and allowing the gel to set for 2 days. A better reagent than waterglass<sup>3</sup> is a laboratory stock solution of 500 mL of water mixed with 244 g of  $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ , since the composition and purity of the commercial solution does vary. The authors prefer a variation of this method<sup>7</sup> in which the acid solution is titrated with sodium metasilicate solution to produce a specific pH. The pH has two effects on the gel.<sup>8</sup> First, the gelling rate is strongly affected by pH. Gels with a pH above 5 tend to set in a few minutes, while gels with a pH of 3 can require several days of setting time. Second, a gel with a pH of 3 will never set as firmly as one with a slightly higher pH. As a general rule, the firmness (or pH) does not significantly alter growth results. There are exceptions to this, however, notable in the growth of tartrate crystals.<sup>3</sup> It should be noted that gels that are formed too rapidly are often brittle. Gel aging, allowing the gel to set for a time before adding the reactant solution, has been investigated,<sup>9</sup> but not with conclusive results.

The purity of most crystals produced by this method is quite high; crystals generally contain only a few parts per million (atomic) of impurity except when doped. The sodium ion, which is present in the solutions, does not tend to enter the growing crystal. Some workers remove the sodium prior to the reaction by allowing it to diffuse into distilled water above the solution, but this is not necessary. The authors filter all solutions<sup>7</sup> through  $0.45\text{-}\mu$  "millipore" filters to eliminate larger particles that might serve as nucleation sites, but there is no evidence that this greatly affects the results.

One final caution concerns adding the solution above the gel when initiating the reaction. The gel is very fragile, particularly if it is formed at low pH. It is best to add the top solution with a pipette. In this way one can first add a few drops to cover the gel, which tends to protect its surface, and then slowly add the rest of the solution.

Three types of reactions that have been performed in gels are covered in the following sections: (1) standard growth, (2) the complex dilution method, and (3) reduction to form metallic crystals or dendrites.

## B. CRYSTALS GROWN BY THE STANDARD TECHNIQUE

The preceding comments apply to this technique and it is by far the most used. The experiments can be done in a test tube, where one of the reactants is added to the gel before setting, or in a U-tube using a neutral gel to separate the reactants. The technique giving the better result varies from case to case. The tartrates, for example, produce better results in a test tube.

### C. TARTRATES

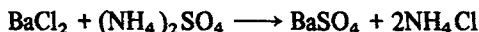
While calcium tartrate has been chosen to illustrate the standard technique (see following synthesis), a host of other tartrates have been studied in the past few years with varying degrees of success.<sup>3,8</sup> The growth of iron, copper, and zinc tartrates has been reported by Kachi,<sup>8</sup> who essentially followed the procedure for calcium tartrate outlined here. These experiments have been performed at room temperature using the same molarities as the calcium tartrate. Crystals of about centimeter size are produced, but the time of reaction is unknown. This work is a follow-up of work previously reported by Henisch,<sup>3</sup> who also mentions cobalt, strontium, and the ammonium ion as possible reagents for tartrate crystal growth. Small crystals of lead tartrate have been obtained<sup>10</sup> using the same concentrations at room temperature.

### D. CARBONATES

Several workers have reported on the growth of carbonates. Most attention has been given to calcium carbonate<sup>11-13</sup>; other carbonates have been reported<sup>13</sup> to produce only very small crystals. The growth of the calcite modification of calcium carbonate is well documented. The most satisfactory method involves the use of a U-tube at room temperature. A neutral gel is formed by titrating 0.5 *M* sodium metasilicate with 1 *M* acetic acid. The pH must be fairly high (6-8) to prevent the formation of calcium silicate. Crystals form during the first week and reach their maximum size in about 6 weeks. The crystals grow and remain clear until they reach a size of about 2 mm. Thereafter they tend to become cloudy (but still essentially single crystal) because of inclusion of the silica gel. During the growth, a few spherulites of aragonite and vaterite (calcium carbonate modifications) appear dispersed in the gel. The formation of aragonite is favored at high temperatures (70°).

### E. SULFATES

The growth of both barium and strontium sulfate has been reported by Barta, et al.<sup>12</sup> and substantiated in other work.<sup>14-18</sup> The reaction is:



The experiment is generally conducted in a U-tube, and several variations have been reported. Strong acid may be used to titrate the metasilicate, or a strongly

acid cation exchange resin may be used. Crystals of potassium-rare earth sulfates have also been reported.<sup>18</sup>

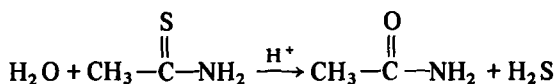
## F. OTHER EXPERIMENTS USING THE STANDARD TECHNIQUE

Numerous other materials have been grown by the standard gel technique. The procedures are generally quite similar to those outlined and illustrated in later sections. Experiments with iodates often lead to interesting and unexpected results. Armington and O'Connor<sup>19</sup> attempted to grow potassium, rubidium, and cesium iodates in gel. No crystals resulted in the potassium iodate experiments and only microcrystalline platelets were produced in the cesium iodate experiments. One-centimeter crystals have been produced in the rubidium experiments along with several smaller ones. These have been identified as  $\text{RbIO}_3 \cdot 2\text{HIO}_3$ . Arend and Perison<sup>20</sup> grew 2-mm  $\text{Ag}_2\text{H}_3\text{IO}_6$  crystals in test tubes at room temperature and a pH of 4.1. The pH varies as a function of depth in the gel as a result of the release of acid by the reaction:  $2\text{AgNO}_3 + \text{H}_5\text{IO}_6 \rightarrow \text{Ag}_2\text{H}_3\text{IO}_6 + 2\text{HNO}_3$ . This causes three iodates to form in the gel:  $\text{Ag}_3\text{IO}_5$  which forms as a brown layer near the surface, rings of red-brown  $\text{Ag}_2\text{HIO}_5$ , and the 2-mm  $\text{Ag}_2\text{H}_3\text{IO}_6$  yellow crystals at the lower end of the gel. The red-brown rings are Liesegang rings and are discussed at the end of this chapter.

Nassau et al.,<sup>21</sup> using an elaborate U-tube arrangement, experimented with copper iodate and found six different forms of copper iodate in different locations in the gel. The largest of these were  $\text{Cu}(\text{IO}_3)_2 \cdot 2\text{H}_2\text{O}$ , which grew to 2 mm.

Brushite,  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ , has been grown in test tubes<sup>22</sup> at room temperature and up to 60°, with best results with the pH between 4 and 6. The crystals grew to 2 mm in about 4 weeks. Crystals of other phosphates, that is,  $\text{KH}_2\text{PO}_4$ ,<sup>23</sup>  $\text{PbHPO}_4$  and  $\text{Pb}_4(\text{NO}_3)_2(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ ,<sup>24</sup> have been reported to grow in organic gels, but apparently not in silica gels because of the high solubilities of the compounds in water.

Lead and zinc sulfides have been produced by the standard technique in gels. The lead compounds are toxic and should be handled with care. For lead sulfide,<sup>25,26</sup> the gel is prepared by mixing sodium metasilicate (sp gr 1.05) with 2.26 N HCl to reach a pH of 6. A few drops of lead acetate or chloride solution are added to the gel before it is allowed to set. Setting requires about 1 week. The solution is then covered with a 1 M solution of thioacetamide. The thioacetamide slowly releases hydrogen sulfide into the solution according to the reaction:



The sulfide ion then reacts with the lead ion in the gel to precipitate lead sulfide. Crystals up to a millimeter in length can be produced in 2 weeks. Temperatures range from room temperature to 35°, with best results reported at the higher temperature. The same sulfide source is used for the growth of zinc sulfide crystals.<sup>25,27</sup> The crystals grow to a size of 3–4 mm in 2 months. It should be mentioned that a modified U-tube system has been used to produce this size crystal and it is expected that smaller crystals will be produced if a simple U-tube is employed.

Lead iodide and lead hydroxide iodide<sup>3,28,29</sup> are popular experimental systems. The lead iodide is best prepared at 45°, but room temperature can also be used. Thin hexagonal platelets of  $\text{PbI}_2$  up to 8 mm in diameter have been grown in 3 weeks at 45°. Lower temperatures produce smaller, but thicker, crystals. Lead hydroxide iodide ( $\text{PbIOH}$ ) is formed in a basic gel in a test tube.<sup>30</sup> If the gel is not alkaline, some  $\text{PbI}_2$  crystals are also formed.

Other crystals grown by this technique include lead molybdate,<sup>31</sup> barium and strontium tungstate,<sup>32</sup> silver acetate,<sup>33</sup> potassium perchlorate,<sup>34</sup> and copper(I) iodide.<sup>35</sup>

## G. THE COMPLEX DILUTION METHOD

This technique differs from the standard technique in that the crystals are formed by dilution of a solution containing a complex that is stable only at higher concentrations of a common ion. The example used here (following synthesis) is copper(I) chloride, which is soluble only with high concentrations of chloride ion.<sup>36</sup> The role of the gel in this case is dilution of the complexed solution as it diffuses through the gel. This causes slow decomposition of the complex in the gel resulting in precipitation of the desired material. While copper(I) chloride has been the most successful system for application of this technique, some success has been noted with other systems, including copper(I) bromide and copper(I) iodide.<sup>37</sup> Silver iodide crystals have been produced by the diffusion of an  $\text{AgI-HI}$  complex into an acid (HI) gel.<sup>2,3,38</sup> Other silver halides have been grown in the same manner.<sup>39,40</sup> These experiments should be run in the dark. The growth of  $\text{HgS}$  (cinnabar) also has been reported<sup>39</sup> using this technique. The experiments are carried out at room temperature in a test tube using a complex of  $\text{Na}_2\text{S-HgS}$ . Crystals of black metacinnabar appear after 1 day, but on standing several days, these crystals convert to the red cinnabar.

Silver phosphate ( $\text{Ag}_3\text{PO}_4$ ) has also been grown in silica gel<sup>41</sup> (0.5 *M* sodium metasilicate plus 1 *M* acetic acid). The experiments are performed at room temperature, in the dark, using test tubes. The solution above the gel contains  $\text{Ag}_3\text{PO}_4$  and nitric acid which is added to keep the phosphate in solution. As

the growth proceeds, the nitric acid diffuses more rapidly into the gel and the silver phosphate precipitates in the regions of lower acidity. Well-formed dodecahedra are produced (1.5 mm).

Small crystals or dendrites of metals can be formed in a similar way by reducing a metal salt contained in a gel. Lead dendrites are formed rapidly when metallic zinc is used as the reducing agent.<sup>42,43</sup> Similarly, small copper tetrahedra<sup>1</sup> and gold platelets<sup>3,44</sup> can be formed by reduction in gels.

## H. LIESEGANG RINGS

No discussion of gel growth could be complete without a passing reference to the phenomenon of Liesegang rings, which were observed even before crystal growth was found in gels. The rings are named after the German chemist<sup>3</sup> who first observed them in 1896. Liesegang observed that concentric rings of silver dichromate are formed (in the gel) after silver nitrate solution is dropped on a gel containing potassium dichromate. The same result occurs when a gel containing potassium dichromate in a test tube is covered with a solution of silver nitrate. The rings appear periodically, usually with no evidence of crystallization between them. In the older work, agar or gelatin was used most often. The same phenomena can be observed in silica gels, however.<sup>42</sup> The true conditions causing these rings are not known, but they have led to much speculation. Liesegang ring formation is generally attributed to the diffusion process in a gel and probably has some relation to the solubility of the product that forms microcrystals in the rings. Using gelatin gels, Hatschek<sup>45</sup> found these rings when producing calcium sulfate, calcium carbonate, barium carbonate, barium oxalate, lead sulfate, lead chloride, and silver chromate. Holmes<sup>42</sup> gives details of several cases using silica gel. Perhaps the most impressive banding was observed by Holmes,<sup>1</sup> with gold as the product. In these experiments, silica gel was formed by mixing sodium metasilicate (sp gr 1.16) with an equal amount of 3 *N* H<sub>2</sub>SO<sub>4</sub>. One milliliter of a 1% solution of AuCl<sub>3</sub> was added to 25 mL of the mixture before the gel was allowed to set. An 8% oxalic acid solution was added above the gel. The upper bands in the gel consisted of a red layer on top, a blue layer in the middle, and a green layer on the bottom. A dozen or more bands were produced within the test tube. Small golden crystals were also present throughout the gel. A recent description of Liesegang rings has been presented by Strong.<sup>46</sup>

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