

Contents

List of Contributors	xy
Foreword	xvii
Preface	xix
Acknowledgements	xxiii
1 Hydrazine and Its Inorganic Derivatives	1
<i>Tanu Mimani Rattan and K. C. Patil</i>	
1.1 Introduction	1
1.1.1 Properties of Hydrazine	2
1.1.1.1 Redox Properties	3
1.1.2 Hydrazine versus Hydrazine Hydrate	6
1.1.2.1 Reducing Property of Hydrazine Hydrate	8
1.2 Inorganic Hydrazine Derivatives	10
1.2.1 Hydrazine Salts	10
1.2.1.1 Synthesis	11
1.2.1.2 Structure – Single-Crystal X-Ray Studies	12
1.2.2 Metal Hydrazines	14
1.2.2.1 Synthesis	15
1.2.2.2 Structure – Single-Crystal X-Ray Studies	16

1.2.3	Metal Hydrazine Carboxylates	17
1.2.3.1	Synthesis	20
1.2.3.2	Structure – Single-Crystal X-Ray Studies	21
1.2.4	Hydrazinium Metal Complexes	21
1.2.4.1	Synthesis	22
1.2.4.2	Structure – Single-Crystal X-Ray Studies	23
1.3	Characterization of Inorganic Hydrazine Derivatives	28
1.3.1	Analytical Techniques	28
1.3.2	Spectroscopic Methods	28
1.3.2.1	Infrared Spectroscopy	28
1.3.2.2	X-Ray Methods	30
1.3.3	Thermal Methods	30
1.4	Applications of Inorganic Hydrazine Derivatives	32
	References	33
2	Hydrazine Salts	37
	<i>Singanahally T. Aruna and K. C. Patil</i>	
2.1	Introduction	37
2.2	Salts of the Monovalent Cation (N_2H_5^+) – $\text{N}_2\text{H}_5\text{A}$	39
2.2.1	Simple Hydrazinium Salts ($\text{A}^- = \text{F}, \text{Cl}, \text{Br}, \text{I}, \text{NO}_3, \text{N}_3, \text{VO}_3, \text{HF}_2, \text{HSO}_4, \text{SCN}, \text{SO}_3\text{NH}_2, \text{COOCH}_3$)	39
2.2.1.1	Synthesis	39
2.2.1.2	Infrared Spectra	40
2.2.1.3	Thermal Properties	40
2.2.2	Hydrazinium Salts with Oxidizing Anions – $\text{N}_2\text{H}_5\text{A}$ ($\text{A}^- = \text{N}_3, \text{NO}_2, \text{NO}_3, \text{ClO}_4, \text{etc.}$)	44
2.2.2.1	Synthesis	44
2.2.2.2	Thermal Properties	45
2.3	Salts of the Divalent Cation [$(\text{N}_2\text{H}_5)_2^{2+}$ and $\text{N}_2\text{H}_6^{2+}$]	49
2.3.1	Dihydrazinium Salts $(\text{N}_2\text{H}_5)_2^{2+}$ – [$(\text{N}_2\text{H}_5)_2\text{B}$, $\text{B}^{2-} = \text{SO}_3, \text{SO}_4, \text{C}_2\text{O}_4, \text{CO}_3, \text{HPO}_4$]	50
2.3.1.1	Synthesis, Infrared Spectra, and Thermal Properties	50
2.3.2	Hydrazonium Salts $(\text{N}_2\text{H}_6^{2+})$ – $\text{N}_2\text{H}_6(\text{A})_2$ or $\text{N}_2\text{H}_6\text{B}$	52
2.3.2.1	Synthesis, Infrared Spectra, and Thermal Properties	52

2.4	Salts of Monovalent (N_2H_5^+) and Divalent [$(\text{N}_2\text{H}_5)_2^{2+}$, $\text{N}_2\text{H}_6^{2+}$] Cations	53
2.4.1	Hydrazine Fluorides – Hydrazinium Fluoride ($\text{N}_2\text{H}_5\text{F}$), Hydrazinium Bifluoride ($\text{N}_2\text{H}_5\text{HF}_2$), and Hydrazonium Fluoride ($\text{N}_2\text{H}_6\text{F}_2$)	54
	2.4.1.1 Synthesis	54
	2.4.1.2 Infrared Spectra	55
	2.4.1.3 Thermal Properties	56
2.4.2	Hydrazine Sulfates – Hydrazinium Bisulfate ($\text{N}_2\text{H}_5\text{HSO}_4$), Dihydrazinium Sulfate [$(\text{N}_2\text{H}_5)_2\text{SO}_4$], and Hydrazonium Sulfate ($\text{N}_2\text{H}_6\text{SO}_4$)	58
	2.4.2.1 Synthesis	59
	2.4.2.2 Infrared Spectra	59
	2.4.2.3 Thermal Properties	60
2.4.3	Hydrazine Oxalates – Hydrazinium Hydrogen Oxalate ($\text{N}_2\text{H}_5\text{HC}_2\text{O}_4$) and Dihydrazinium Oxalate [$(\text{N}_2\text{H}_5)_2\text{C}_2\text{O}_4$]	64
	2.4.3.1 Synthesis	64
	2.4.3.2 Thermal Properties	65
2.4.4	Hydrazine Phosphates – Monohydrazinium Phosphate ($\text{N}_2\text{H}_5\text{H}_2\text{PO}_4$) and Dihydrazinium Phosphate [$(\text{N}_2\text{H}_5)_2\text{HPO}_4$]	67
	2.4.4.1 Synthesis	67
	2.4.4.2 Thermal Properties	68
2.4.5	Hydrazine Perchlorates – Hydrazinium Perchlorate ($\text{N}_2\text{H}_5\text{ClO}_4$), Hydrazinium Perchlorate Monohydrate ($\text{N}_2\text{H}_5\text{ClO}_4 \cdot \text{H}_2\text{O}$), Hydrazinium Perchlorate Hemihydrate ($\text{N}_2\text{H}_5\text{ClO}_4 \cdot 0.5\text{H}_2\text{O}$), and Hydrazonium Perchlorate [$\text{N}_2\text{H}_6(\text{ClO}_4)_2$]	70
	2.4.5.1 Synthesis	70
	2.4.5.2 Infrared Spectra	71
	2.4.5.3 Thermal Properties	72
	2.4.5.4 Nature of Water Present in Hydrazinium Perchlorate Hydrates, $\text{N}_2\text{H}_5\text{ClO}_4 \cdot 0.5\text{H}_2\text{O}$ and $\text{N}_2\text{H}_6(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$	73
2.4.6	Hydrazine Perchlorate Ammoniates – $\text{N}_2\text{H}_5\text{ClO}_4 \cdot \text{NH}_3$ and $\text{N}_2\text{H}_6(\text{ClO}_4)_2 \cdot 2\text{NH}_3$	74
	2.4.6.1 Synthesis, Infrared Spectra, and Thermal Properties	75

2.5	Hydrazine Salts of Organic Acids	76
2.6	Summary	78
	References	80
3	Metal Hydrazines	83
	<i>Dasaratharam Gajapathy and Tanu Mimani Rattan</i>	
3.1	Introduction	83
3.2	Metal Hydrazines – $\text{MX}(\text{N}_2\text{H}_4)_n$, M = metal, X = SO_4 , SO_3 , N_3 , NCS , NO_3 , ClO_4 , RCOO , and so on, ($n = 1-3$)	84
3.2.1	Metal Isothiocyanate Hydrazines $[\text{M}(\text{NCS})_2(\text{N}_2\text{H}_4)_2]$	84
3.2.2	Metal Sulfate Hydrazines $[\text{MSO}_4 \cdot x\text{N}_2\text{H}_4]$	89
3.2.3	Metal Formate Hydrazines $[\text{M}(\text{HCOO})_2(\text{N}_2\text{H}_4)_2]$	91
3.2.4	Metal Acetate Hydrazines $[\text{M}(\text{CH}_3\text{COO})_2(\text{N}_2\text{H}_4)_2]$	93
3.2.4.1	Mixed Metal Acetate Hydrazines	96
3.2.5	Metal Oxalate Hydrazines $[\text{MC}_2\text{O}_4(\text{N}_2\text{H}_4)_2]$	97
3.2.5.1	Synthesis	98
3.2.5.2	Spectral and Thermal Analysis	99
3.2.5.3	Temperature Profile Studies	101
3.2.6	Mixed Metal Oxalate Hydrazines	103
3.2.7	Metal Sulfite Hydrazine Complexes	106
3.2.7.1	Metal Sulfite Hydrazines $[\text{MSO}_3 \cdot x\text{N}_2\text{H}_4 \cdot y\text{H}_2\text{O}]$	107
3.2.7.2	Mixed Metal Sulfite Hydrazines	108
3.2.7.3	Magnesium Bisulfite Hydrazine Hydrate	111
3.2.8	Metal Azide Hydrazines $[\text{M}(\text{N}_3)_2(\text{N}_2\text{H}_4)_2]$	112
3.2.8.1	Synthesis	112
3.2.8.2	Spectral, Structural, and Thermal Data	114
3.2.8.3	Dinitrogen Compound	116
3.2.9	Metal Nitrate Hydrazines $[\text{M}(\text{NO}_3)_2(\text{N}_2\text{H}_4)_n]$	120
3.2.9.1	Synthesis	120
3.2.10	Metal Perchlorate Hydrazines $[\text{M}(\text{ClO}_4)_2(\text{N}_2\text{H}_4)_2]$	121
3.2.10.1	Synthesis and Properties	121
3.2.11	Metal Hydrazines of Organic Acids	127
3.3	Reactivity of Metal Salt Hydrazines (from Detonation to Deflagration to Decomposition)	128
3.3.1	Precautions in Handling Explosive Materials	129
3.4	Summary	129
	References	129

4 Metal Hydrazine Carboxylates	133
<i>K. C. Patil and Tanu Mimani Rattan</i>	
4.1 Introduction	133
4.2 Metal Hydrazine Carboxylates – $M(N_2H_3COO)_2$	134
4.3 Metal Hydrazine Carboxylate Hydrates – $M(N_2H_3COO)_n \cdot xH_2O$; $n = 2, 3$	136
4.3.1 Lead Hydroxy Metal Hydrazine Carboxylate Hydrates – $[PbMO(OH)_2(N_2H_3COO)_2 \cdot xH_2O]$	142
4.3.2 Rare Earth Metal Hydrazine Carboxylate Hydrates – $Ln(N_2H_3COO)_3 \cdot 3H_2O$	144
4.3.3 Metal Ion Doped Metal Hydrazine Carboxylate Hydrates – $M^{x+}/M(N_2H_3COO)_2 \cdot xH_2O$	147
4.3.3.1 Manganese-Substituted Calcium Hydrazine Carboxylate Hydrate	148
4.3.3.2 Praseodymium-Substituted Cerium Hydrazine Carboxylate Hydrate	148
4.3.3.3 Europium-Substituted Yttrium Hydrazine Carboxylate Hydrate	150
4.4 Metal Hydrazine Carboxylate Hydrazines – $M(N_2H_3COO)_2 \cdot (N_2H_4)_2$	152
4.5 Hydrazinium Metal Hydrazine Carboxylate Hydrates – $N_2H_5M(N_2H_3COO)_3 \cdot H_2O$	155
4.5.1 Cobalt-Substituted Hydrazinium Iron Hydrazine Carboxylate Hydrate	158
4.5.2 Manganese-Substituted Hydrazinium Zinc Hydrazine Carboxylate Hydrate	159
4.6 Solid Solutions of Hydrazinium Metal Hydrazine Carboxylate Hydrates – $N_2H_5 M_{1-x} (Co/Fe/Mn)_x (N_2H_3COO)_3 \cdot H_2O$	160
4.6.1 Synthesis	161
4.6.2 XRD Data	162
4.6.3 Thermal Properties	164
4.7 Summary	168
References	168
5 Hydrazinium Metal Complexes	171
<i>Subbiah Govindrajan and Singanahally T. Aruna</i>	
5.1 Introduction	171
5.2 Hydrazinium Metal Sulfates	172
5.2.1 Hydrazinium Metal Sulfates – $(N_2H_5)_2M(SO_4)_2$	172

5.2.1.1	Synthesis, Spectra, and Thermal Analysis	172
5.2.1.2	Single-Crystal Structures of (N ₂ H ₅) ₂ M(SO ₄) ₂ , M = Transition Metal	178
5.2.2	Hydrazinium Rare Earth Metal Sulfate Hydrates – N ₂ H ₅ Ln(SO ₄) ₂ ·H ₂ O	179
5.2.2.1	Synthesis, Spectra, and Thermal Analysis	179
5.2.2.2	Single-Crystal Structure of N ₂ H ₅ Nd(SO ₄) ₂ ·H ₂ O	181
5.3	Hydrazinium Metal Oxalates	182
5.3.1	Hydrazinium Metal Oxalates – (N ₂ H ₅) ₂ M (C ₂ O ₄) ₂ ·nH ₂ O, M = Co, Ni, Cu, and so on	183
5.3.1.1	Synthesis, Spectra, and Thermal Analysis	183
5.3.1.2	Single-Crystal Structure of (N ₂ H ₅) ₂ Cu (C ₂ O ₄) ₂ ·nH ₂ O	187
5.3.2	Hydrazinium Uranyl Oxalates	190
5.3.2.1	Synthesis, Spectra, and Thermal Analysis	191
5.3.2.2	Single-Crystal Structures of {(N ₂ H ₅) ₆ [(UO ₂) ₂ (C ₂ O ₄) ₅]·2H ₂ O and (N ₂ H ₅) ₂ (UO ₂)(C ₂ O ₄) ₂ ·H ₂ O	193
5.4	Hydrazinium Metal Halides	195
5.4.1	Hydrazinium Metal Chloride Hydrates – (N ₂ H ₅) ₂ MCl ₄ ·2H ₂ O, M = Transition Metal	195
5.4.1.1	Synthesis, Spectra, and Thermal Analysis	195
5.4.1.2	Single-Crystal Structures of (N ₂ H ₅) ₂ FeCl ₄ ·2H ₂ O and (N ₂ H ₅) ₂ PtCl ₄ ·2H ₂ O	198
5.4.2	Hydrazinium Metal Bromide Hydrates – (N ₂ H ₅) ₂ MBr ₄ ·4H ₂ O, M = Transition Metal	201
5.4.2.1	Synthesis, Spectra, and Thermal Analysis	201
5.4.3	Anhydrous Hydrazinium Metal Chlorides – N ₂ H ₅ CuCl ₃ , (N ₂ H ₅) ₂ ZnCl ₄ , (N ₂ H ₅) ₃ MnCl ₅ , and (N ₂ H ₅) ₄ FeCl ₆	202
5.4.3.1	Synthesis, Spectra, and Thermal Analysis	202
5.4.3.2	Single-Crystal Structure of (N ₂ H ₅) ₃ MnCl ₅	207
5.5	Hydrazinium Metal Thiocyanates – (N ₂ H ₅) ₂ M(NCS) ₄ ·2H ₂ O, M = Co and Ni	208
5.5.1	Synthesis, Spectra, and Thermal Analysis	209
5.5.2	Single-Crystal Structure of (N ₂ H ₅) ₂ Co (NCS) ₄ ·2H ₂ O	212

5.6	Recent Studies on Hydrazinium Metal Complexes	214
5.7	Summary	216
	References	216
6	Applications of Inorganic Hydrazine Derivatives	219
	<i>K. C. Patil and Tanu Mimani Rattan</i>	
6.1	Introduction	219
6.2	Applications of Hydrazine Salts	220
6.2.1	Synthesis of Hydrazinium Metal Complexes	220
6.2.2	Solid-State Synthesis of Ammonium Vanadyl Complex	220
6.2.3	Synthesis of 4-Amino-3,5-dimethyl-1,2,4-triazole	222
6.2.4	Hydrazinium Phosphates as Flame Retardants	223
6.2.5	Hydrazinium Thiocyanate as Analytical Reagent for the Quantitative Estimation of Copper	228
6.3	Energetic Materials	229
6.3.1	Explosives and Initiators	230
6.3.2	Energetic Oxidizers for Solid Propellants	231
6.3.2.1	Metal Perchlorate Hydrazines	231
6.3.2.2	Magnesium-Doped $N_2H_5ClO_4 \cdot 0.5H_2O$	232
6.4	Combustible Metal Hydrazine Complexes	234
6.4.1	Synthesis of γ - Fe_2O_3 – Recording Material	234
6.4.2	Synthesis of Nano-Copper Chromite ($CuCr_2O_4$) Catalyst	235
6.4.3	Synthesis of Lithium Metal Oxide ($LiMO_2$) – Battery Material	236
6.4.4	Synthesis of Nano-Titania – Photocatalyst	236
6.4.5	Metal Ion Substituted Oxide Materials	238
6.4.6	Synthesis of Nano-Cobaltites, -Ferrites, -Chromites, and -Manganites	239
6.4.7	Synthesis of Nano-Metal Powders as Catalysts	244
6.5	Miscellaneous Applications	245
6.5.1	Reducing Agents	245
6.5.2	Antibacterial Agents	246
6.5.2.1	Antibacterial Activity Testing	246
6.5.3	Synthesis of 1D and 2D Nanostructures	246
	References	249
	Index	253