

List of Figures

Figure 1.1	Structure of basic AMX_3 perovskite unit cell	2
Figure 1.2	Schematic representation of single-layer perovskite with monoammonium ($R-NH_3^+$) (a) and biammonium ($^+NH_3-R-NH_3^+$) (b), organic cations	4
Figure 1.3	Two hydrogen bonding schemes observed in $(R-NH_3)_2MX_4$ and $(NH_3-R-NH_3)MX_4$ type structures: bridging halide configuration (a) and terminal halide configuration (b)	4
Figure 2.1	Fourier Transform Infrared Spectroscopy, Perkin Elmer Spectrum RX1 FT-IR	12
Figure 2.2	Elemental Analyzer, Fisons EA1108	14
Figure 2.3	NMR spectrophotometer	16
Figure 2.4	Diagram of X-ray generation	18
Figure 2.5	Single Crystal X-Ray Diffractometer, Bruker-Axis	19
Figure 2.6	Powder X-ray Diffractometer, D8 instrument	20
Figure 2.7	TG/DTA, SII TG/DTA6300	22
Figure 2.8	DSC, Shimadzu DSC-60	23
Figure 2.9	Raman Spectrometer, HORIBA Jobin Yvon LabRAM-HR Spectrometer	25
Figure 2.10	Diagram of energy level of an electron placed in magnetic field	26
Figure 2.11	EPR spectrums as a function of strength, B , magnetic field	27
Figure 2.12	SEM, JEOL JSM-5600	29
Figure 2.13	Mercury Porosimeter, PASCAL 440	31
Figure 2.14	(a) Magnetometer unit, (b) Magnetic coil and flux transformer	32
Figure 3.1	FT-IR transmission spectra of anilinium chloride (a); 3-chloro anilinium chloride (b); 3-nitro anilinium chloride (c); benzilinium chloride (d); 4-chloro benzilinium chloride (e); (<i>R</i>)-ethyl benzilinium chloride (f); 2-amine benzothiazolinium chloride (g) and methyl ammonium chloride (h)	42

Figure 3.2	¹ H NMR spectra of anilinium chloride	46
Figure 3.3	Packing and hydrogen bonding in anilinium chloride	48
Figure 3.4	Temperature evolutions of lattice modes in anilinium chloride	49
Figure 3.5	Raman frequencies as a function of temperature	49
Figure 3.6	Raman spectra in high frequency region as a function of temperature in anilinium chloride	51
Figure 3.7	Temperature evolution of lattice modes in 4-nitro anilinium chloride (a) and 3-nitro anilinium chloride (b)	52
Figure 3.8	TG/DTA thermogram for anilinium chloride (a) and 3-chloro anilinium chloride (b)	54
Figure 3.9	TG/DTA thermogram for (<i>R</i>)-1,2-diammonium propane dichloride (a) and (<i>R</i>)-methyl benzilinium chloride (b)	54
Figure 3.10	TG/DTA thermogram of 4-nitro anilinium chloride (a) and 4-chloro benzilinium chloride (b)	54
Figure 3.11	TG/DTA thermogram for benzilinium chloride	55
Figure 3.12	DSC thermogram of anilinium chloride showing phase transition	57
Figure 3.13	DSC thermogram of 3-nitro anilinium chloride (a) and benzilinium chloride (b), showing reversible phase transition	57
Figure 3.14	DSC thermogram of (<i>R</i>)- and (<i>S</i>)-methyl benzilinium chloride (a); (b), and (<i>R</i>)- and (<i>S</i>)-ethyl benzilinium chloride (c) and (d), showing reversible phase transition	57-58
Figure 3.15	DSC thermogram of <i>n</i> -propyl ammonium chloride at LT (a) and HT (b), showing the reversible phase transition	59
Figure 3.16	DSC thermogram of 1,2-diammonium ethylene dichloride showing the reversible phase transition	59
Figure 3.17	DSC thermogram of (<i>R</i>)- and (<i>S</i>)-1,2-diammonium propane dichloride (a) and (b), showing the reversible phase transition	60
Figure 4.1	Representative FT-IR spectra of compounds 1 , 2 , 3 , 6 and 7	71
Figure 4.2	Thermo gravimetric curve for compounds 1 (a); 2 (b); 3 (c); 4 (d); 7 (e) and 10 (f)	75

Figure 4.3 DSC measurement plots for compounds 3 (a); 4 (b); 7 (c); 9 (d) and 10 (e) showing the reversible transitions	77
Figure 4.4 Thermochromic behavior of single crystals for compounds 3 , 6 , 7 and 10	79
Figure 4.5 Temperature evolutions of lattice modes in compound 3	80
Figure 4.6 Representative EPR spectra for compound 10 (a) and temperature dependent of EPR line widths (b), at HT	81
Figure 4.7 The structure of compounds 2 (a); 3' (b); 8 (c) and 10' (d) showing the asymmetric units	84-85
Figure 4.8 The layered structure of CuCl_4	86
Figure 4.9 The layered structures for compounds 2 (a); 3 (b); 3' (c) and 8 (d), viewed along the crystallographic <i>b</i> -axis and <i>c</i> -axis	87-88
Figure 4.10 The “eclipsed” and “staggered” conformations of the inorganic 2-D network for compounds 2 (a); 3 (b); 3' (c) and 8 (d)	89
Figure 4.11 N-H \cdots Cl hydrogen bonding interactions for compounds 2 (a); 3 (b); 3' (c) and (d)	89-90
Figure 4.12 Powder XRD data for compound 4	92
Figure 4.13 Powder XRD data for compounds 5 (a); 6 (b) and 7 (c)	92-93
Figure 4.14 Temperature dependence χT with different applied fields for compounds 2 (a); 3 (b); 4 (c); 5 (d) and 6 (e)	94-95
Figure 4.15 The temperature dependence χ^{-1} plot for compounds 2 , 3 , 5 (a) and 4 , 6 (b) obeying the Curie-Weiss law above the 30 K	95
Figure 4.16 Temperature dependence χT with different applied fields for compounds 2 (a); 3 (b); 4 (c); 5 (d) and 6 (e)	96
Figure 4.17 Temperature dependence of the ac-susceptibility for compounds 2 (a); 3 (b); 4 (c); 5 (d) and 6 (e)	97-98
Figure 4.18 Variations of χT as function of temperature, inset with enlarge scale in the LT (a) and variation of χ as function of temperature using 500 Oe, inset shows <i>M</i> versus <i>H</i> at 1.8 K (b)	99
Figure 5A.1 FT-IR spectra of compounds 11 , 14 , 15 and 17	109

Figure 5A.2 Thermo gravimetric curve for compounds 11 (a); 13 (b); 14 (c); 15 (d) and 17 (e)	112
Figure 5A.3 DSC plot for compounds 11 (a); 13 (b); 15 at LT (c), at HT (d) and 17 (e), showing the reversible transitions	114
Figure 5A.4 Thermochromic behaviors in crystal of compounds 11 , 14 and 16 , shows complete reversible color	115
Figure 5A.5 Molecular view of compounds 11 (a); 13 (b); 15 (c) and 17 (d), at RT with labeling scheme, displacement ellipsoids are drawn at the 50 % probability level	118-120
Figure 5A.6 The monoclinic structures for compounds 11 (a) and 14 (b), viewed down along the <i>b</i> -axis, showing isolated structure of CuCl_4^{2-} and bonding scheme in the compounds	123
Figure 5A.7 The monoclinic structures for compounds 15 (a) and 15' (b), viewed down along the <i>a</i> -axis, showing isolated structure of CuCl_4^{2-} and bonding scheme in the compounds	124
Figure 5A.8 The orthorhombic structures for compound 17 viewed down along the <i>a</i> -axis, illustrate zigzag chain structure of CuCl_4^{2-} and bonding scheme in the compound	124
Figure 5B.1 FT-IR spectra of compounds 18 and 19	129
Figure 5B.2 Thermo gravimetric curves for compounds 18 (a) and 19 (b)	131
Figure 5B.3 DSC plots for compounds 18 (a) and 19 (b), at HT showing the reversible transition	132
Figure 5B.4 Thermochromic behaviors of crystals for compounds 18 and 19	132
Figure 5B.5 Molecular view of compounds 18' (a) and 19' (b), at 150 K with labeling scheme, displacement ellipsoids are drawn at the 50 % probability level	134
Figure 5B.6 View of the axially interacting CuCl_4^{2-} anions in compound 18 at RT. Except for the atoms of the central octahedron, the rest are unlabeled. Thermal ellipsoids are drawn at 50 % probability and the weak axial bonds are represented by broken bonds	135

Figure 5B.7 Orthorhombic structure of compounds 18 (a) and 19 (b), at 296 K viewed along the b-c plane, which showing hydrogen bonding arrangements in oriented organic-inorganic layers	136
Figure 5B.8 Orthorhombic structure of compounds 18 (a) and 19 (b), at 150 K view along b-c plane, which reveal hydrogen bonding arrangements between chlorine and -NH ₃ ⁺ group and zigzag chain layers structure of CuCl ₄ ²⁻ and their stability	137
Figure 5B.9 The temperature dependent χ and χT plots on polycrystalline compounds 18 (a) and 19 (b), at 1000 Oe, FC and ZFC susceptibility plots at 300 Oe (inset)	140
Figure 5B.10 The temperature dependence χ (above) and χT (below) plots for compounds 18 (a) and 19 (b), at different applied magnetic fields	141
Figure 5B.11 The χ^{-1} versus T plot for compounds 18 and 19 and $M-H$ plots for compound 19 measured at 2 K	142
Figure 5B.12 The temperature variation ac-susceptibility plots real (χ') (a) and imaginary (χ'') (b), for compounds 18 and 19 at 997 Hz	142
Figure 6.1 FT-IR spectra of compounds 20 , 21 and 22	150
Figure 6.2 TG/DTA thermograms for compounds 20 (a); 21 (b) and 22 (c)	151-152
Figure 6.3 DSC plots for compounds 21 (a) and 22 (b), showing the reversible transitions	153
Figure 6.4 Molecular view of compounds 21 (a) and 22 (b) with labeling scheme, thermal ellipsoids are drawn at the 50 % probability level	155
Figure 6.5 The orthorhombic structure of compound 21 (a), viewed down along c-axis and monoclinic structures for compound 22 (b), viewed down along the b -axis, showing isolated structure of CoCl ₄ ²⁻	156
Figure 6.6 The non-covalent N-H \cdots Cl and C-H \cdots Cl synthon interactions for compounds 21 (a) and 22 (b)	157
Figure 6.7 Powder XRD data for compound 20	158

Figure 7.1 FT-IR spectra of compounds 23 and 24	166
Figure 7.2 TG/DTA curves for compounds 23 (a); 23-D (b); 23-RE (c) and 24 (d)	168
Figure 7.3 DTA curves of compounds 23-RE , 23-RE-1 , 23-RE-2 (a), showing peak at constant temperature; DTA curves of compounds 23-RE , 23-RM , 23-RW , 23-RWE (b) and DTA of desorption after placing in different E/W vapor mixture (c)	169
Figure 7.4 TG/DTA curve of compounds 23-RM (a); 23-RW (b) and 23-RWE (c)	170
Figure 7.5 DSC plots for compounds 23 , 23-D and 23-RE (a); for compounds 23-RE , 23-RE-1 and 23-RE-2 (b), showing transition nearly at same temperature indicating adsorption-desorption is completed reversibly; and resolvated compounds with different vapor 23-RE , 23-RM , 23-RW and 23-RWE (c)	171-172
Figure 7.6 DSC plots of desorption after placing in different E/W vapor mixture (a) and Plot of moisture adsorption capacity in compound 23-D time versus absorbance % (b)	173
Figure 7.7 Comparison of powder XRD diagrams for compounds 23 , 23-D and 23-RE (a); and compounds 23-D , 23-RE , 23-RM and 23-RW (b), illustrate reversibility during desorption-resorption	175
Figure 7.8 Images of simple optical microscope shows shiny transparent crystals of compound 23 , becomes opaque on desolvation, compound 23-D (a); and SEM images comparison of porous materials for compounds 23 , 23-D and 23-RE (b), indicate completely reversible adsorption-desorption	176
Figure 7.9 The structure of compound 24 showing the asymmetric units	177
Figure 7.10 Stereo view that illustrates the packing of ions in the unit cell for compound 24	179

Figure 8.1 Hair-like crystal growth of anilinium nitrate-I from gel after 8 hours	184
Figure 8.2 FT-IR spectra of anilinium nitrate-I (a); 3-fluoro anilinium nitrate-I (b); 4-chloro anilinium nitrate-I (c); 4-bromo anilinium nitrate-I (d); 4-methyl anilinium nitrate-I (e); (<i>S</i>)-methyl benzilinium nitrate-I (f); 2-amino pyridinium nitrate-I (g) and phenyl hydrazinium nitrate-I (h)	189
Figure 8.3 ¹ H NMR spectra of anilinium nitrate-I (a) and anilinium nitrate-II (b)	194-195
Figure 8.4 ²⁷ Al NMR spectra of rosette shaped alumina, recorded at MAS frequency of 10 kHz	196
Figure 8.5 TG/DTA thermograms of anilinium nitrate-I (a) and benzilinium nitrate-II (b)	200
Figure 8.6 TG/DTA thermograms of 4-methyl anilinium nitrate-II (a) and 3-amino pyridinium nitrate-II (b)	200
Figure 8.7 TG/DTA thermograms of 4-fluoro anilinium nitrate-I (a) and 4-chloro anilinium nitrate-I (b)	201
Figure 8.8 DSC Thermogram of anilinium nitrate (I and II) (a) and anilinium nitrate-I repeated heating and cooling cycle (b)	202
Figure 8.9 DSC Thermogram of (<i>R</i>)- and (<i>S</i>)-methyl benzilinium nitrate-I (a) and (b)	202
Figure 8.10 DSC Thermogram of benzilinium nitrate-I (a) and 4-methyl anilinium nitrate (I and II) (b)	204
Figure 8.11 DSC Thermogram of ammonium nitrate-II at HT	205
Figure 8.12 Molecular views of Anilinium nitrate-II at 293 K (a); 4-methyl anilinium nitrate-II at 150 K (b) and benzilinium nitrate-II at 298 K (c), with labeling scheme, displacement ellipsoids are drawn at the 50 % probability level	207-208
Figure 8.13 A view of crystal packing of anilinium nitrate-II (a); benzilinium nitrate-II (b) and 4-methyl anilinium nitrate-II (c), N-H···O hydrogen bonds are shown as dashed lines	209-210
Figure 8.14 N-H···O interactions in the crystal structure of anilinium nitrate-II at 293 K (a); benzilinium nitrate-II at 296 K (b); 4-	

<p>methyl anilinium nitrate-II at 296 K (c), at 100 K (d); ammonium nitrate phase II at 357 K (e), phase III at 318 K (f), phase IV at 300 K (g), phase V at 233 K (h) and methyl ammonium nitrate at 300 K (i)</p>	211-212
<p>Figure 8.15 Powder XRD data for Anilinium nitrate-I (a); Anilinium nitrate-II (b) and Anilinium nitrate-III (c)</p>	214-215
<p>Figure 8.16 Powder XRD data for Anilinium nitrate-I collected at RT, after heated at 383 K (a) and after reheated at 383 K (b)</p>	216
<p>Figure 8.17 Powder XRD pattern on white powder, obtained after drying the washed hard cocoon shaped materials in methanol at 343 K</p>	217
<p>Figure 8.18 SEM photograph showing hair-like crystal structure for anilinium nitrate-I (a), and rosette shaped porous alumina left before wash right after washed with methanol (b)</p>	218