Chapter 6

STUDIES ON COBALT BASED ORGANIC-INORGANIC HYBRID COMPOUNDS (OIHCs): A_nCoCl_x

Abstract

In this chapter we have prepared three different OIHCs having general formula A_nCoCl_x [where A = 3-chloro anilinium (**20**), 2-adamantyl ammonium (**21**) and (*S*)-methyl benzilinium (**22**)]. These OIHCs were investigated for thermal analyses and single crystal and/or powder XRD spectroscopy. The characterizations of OIHCs have proved that by changing the OACs chlorocobaltate have been encountered into unusual formulations. DSC studies for compounds **20**, **21** and **22** conclude that it has zero, one and two reversible solid-solid phase transitions respectively. Single crystal XRD studied on these compounds revealed that compound **21** crystallized in orthorhombic space group $Pna2_1$ with cell dimensions a = 27.5293(12) Å, b = 18.8712(9) Å, c = 6.7428(3) Å, β = 90º, V = 3503.0(3) Å^3 and Z = 4. Compound **22** crystallized in monoclinic space group $P2_1$, chiral space group, with unit cell dimensions a = 16.372(8) Å, b = 7.269(4) Å, c = 18.220(9), β = 100.166(9)º, V = 2134.2(18) Å^3 and Z = 4. Indexed powder XRD patterns for compound **20** proved that it crystallizes in triclinic crystal system.

6.1 Introduction

Many compounds with A_2CuCl_4 have been extensively investigated, but very less report were found for cobalt (II). The four-coordinated complexes of cobalt (II) normally lead to a tetrahedral geometry. The distinct color of cobalt (II) complex in solid form, blue, has long known [1]. These materials frequently undergo phase transitions due to molecular motions in OIHCs which have been the subject of considerable interest [2]. The structural phase transitions in these compound have been proved using DSC [1]. In practice the colors have been attributed to the formation of different geometry, octahedral or tetrahedral around cobalt (II) ion [1,3].

Herein we describe the preparation, thermal analyses, reversible structural phase transition and single crystal XRD of cobalt (II) based OIHCs with monofunctional OACs.

6.2 Experimental

6.2.1 *Materials and Methods*

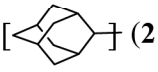
All chemicals and solvents used were of analytical grade reagents. 3-chloro aniline, 2-adamantanamidinium chloride, (*S*)-methyl benzyl amine, cobalt (II) chloride (Aldrich); conc. hydrochloric acid (qualigens) and ethyl alcohol (Baroda chemicals) were used without any further purification.

6.2.2 Syntheses of OIHCs: (A_nCoCl_x)

A general methodology of OIHCs preparation/syntheses is mentioned in scheme-II.

Scheme-II

$$R\text{-}NH_3^+\,Cl^- \xrightarrow[\text{Alcohol or Water}]{CoCl_2.2H_2O} (R\text{-}NH_3)_nCoCl_x$$

[Where, R = 3-Cl-C_6H_4- (**20**), [] (**21**) and (*R*)-$C_6H_5CH(CH_3)$- (**22**)]

In actual process, compounds (3-chloro anilinium)$_8$)[$CoCl_6$]Cl_4 (**20**), (2-adamantyl ammonium)$_3CoCl_5.H_2O$ (**21**) and [(*S*)-methyl benzilinium]$_2CoCl_4$ (**22**) were synthesized by heating 2:1 ratio of OACSs [3-chloro anilinium chloride 500.0 mg (3.048 mmol), 2-adamantyl ammonium chloride 572.0 mg (3.048 mmol) and (*S*)-methyl benzilinium chloride 481.0 mg (3.048 mmol)] and $CoCl_2.6H_2O$ 363.0 mg (1.524 mmol) in acidified distilled water for 3 hours. Evaporation of water was carried out using vacuum pump. Precipitates were washed with ether and recrystallized in ethanol by slow evaporation technique. After 2 - 4 weeks good quality crystals of compounds **20** (violet color), **21** and **22** (blue color) were obtained.

Yield: 30 - 45 %

6.3 Results and Discussions

6.3.1 General Discussion

Virgin compounds have shown structural anomalies for cobalt (II) based OIHCs at RT. Powder XRD study for the violet color compound **20** is isomorphous with (3-halo anilinium)$_8$[$CuCl_6$]Cl_4 and (3-chloro anilinium)$_8$[$NiCl_6$]Cl_4. Where copper (II) and nickel (II) have octahedral surrounding [4,5,6]. The temperature dependent single crystal study on unusual isomorphous compound shows anisotropic displacement parameters of the chloride ions involved in each of the four long Cu-Cl bonds would remain anomalously large at all temperatures [6]. While single crystal XRD studies on blue color compounds **21** and **22** have shown distorted tetrahedral geometry around the cobalt (II), which is similar with (nicotinium)$_2CoCl_4$ [3].

Thermal studies using TG/DTA on a series of cobalt (II) based OIHCs, [(C_nH_{n+1})$_2NH_3$)$_2CoCl_4$, [(CH_3)$_n NH_{3-n}$]$_2CoCl_4$, [(C_2H_5)$_n NH_{3-n}$)$_2CoCl_4$ (n = 1, 2 and 3), have shown first weight loss correspond to the two molecules of organic ammonium chloride and second weight loss correspond to the oxidation and/or hydrolysis of $CoCl_2$ to the oxide, Co_3O_4 [1]. But in our studies for compounds **20** and **21**, we have found organic amine fragment first weight loss then hydrochloride, leaving behind $CoCl_2$ up to the 773.0 K. For compound **22** we have found organic amine goes out along with organic ammonium chloride, in second weight loss one mole of hydrochloride and the final third weight loss at 984.6 K due to the $CoCl_2$.

6.3.2 FT-IR Spectra

Analytical data for the OIHCs are given below.

20: FT-IR (KBr) 3418 (m), 2999 (vs), 2876 (vs), 2566 (s), 1597 (s), 1560 (vs), 1491 (s), 1475 (vs), 1443 (m), 1410 (w), 1302 (w), 1280 (w), 1204 (w) 1164 (w), 1097 (s), 1080 (vs), 1051 (s), 1000 (m), 870 (ssh), 778 (vssh), 673 (vssh), 528 (ssh) and 434 (s) cm^{-1}.

21: FT-IR (KBr) 3346 (s), 3038 (vs), 2917 (vs), 2586 (m), 1606 (s), 1574 (s), 1550 (w), 1530 (w), 1498 (vssh), 1475 (s), 1396 (s), 1319, (w), 1292 (w), 1267 (w), 1225 (m), 1191 (w), 1108 (m), 1090 (s), 1054 (m), 1018 (m), 995 (s), 769 (s), 700 (ssh), 536 (w), 518 (w), 438 (m) and 419 (m) cm^{-1}.

22: FT-IR (KBr) 3400 (vs), 3032 (vs), 2681 (m), 2586 (w), 1611 (vs), 1552 (m), 1496 (s), 1457 (s), 1386 (s), 1316 (m), 1291 (m), 1225 (ssh), 1169 (w), 1088 (s), 1064 (s), 1029 (m), 976 (w), 918 (w), 768 (ssh), 700 (vssh), 582 (w), 536 (s) and 476 (m) cm^{-1}.

The vibrational spectra for compounds **20**, **21** and **22** were recorded in the range of 4,000 - 400 cm^{-1}. The asymmetric stretching modes of N-H (-NH_3^+ group) shifted around 3038 - 2681 cm^{-1}, (this result in broad feature) indicates breaking of continuous series of hydrogen bond. However, an intense band around 2586 cm^{-1} are corresponds to combination of N-H (-NH_3^+ group) deformation modes and N-H (-NH_3^+ group) rocking modes [7]. Specifically, the features arise from (i) a combination band comprising the anti-symmetric N-H (-NH_3^+ group) deformation around 1496 cm^{-1} and N-H (-NH_3^+ group) rocking mode around 1088 cm^{-1} plus (ii) a combination band comprising the symmetric N-H (-NH_3^+ group) deformation around 1475 cm^{-1} and a rocking mode around 1108 cm^{-1}. The vibration observed at 1080 cm^{-1} (aliphatic) and around 1316 cm^{-1} (aromatic) were due to C-N stretching. Other modes which provide vital information about the aromatic ring due to aromatic C-H out of plane deformation at 769 cm^{-1} signify three hydrogen adjacent positions and at 768 cm^{-1} and 700 cm^{-1} signify five hydrogen adjacent positions. Other band observed around the 1606 cm^{-1}, 1574 cm^{-1} and 1498 cm^{-1} indicating the aromatic carbon-carbon vibration. The FT-IR spectra of compounds **20**, **21** and **22** are shown in Figure 6.1.

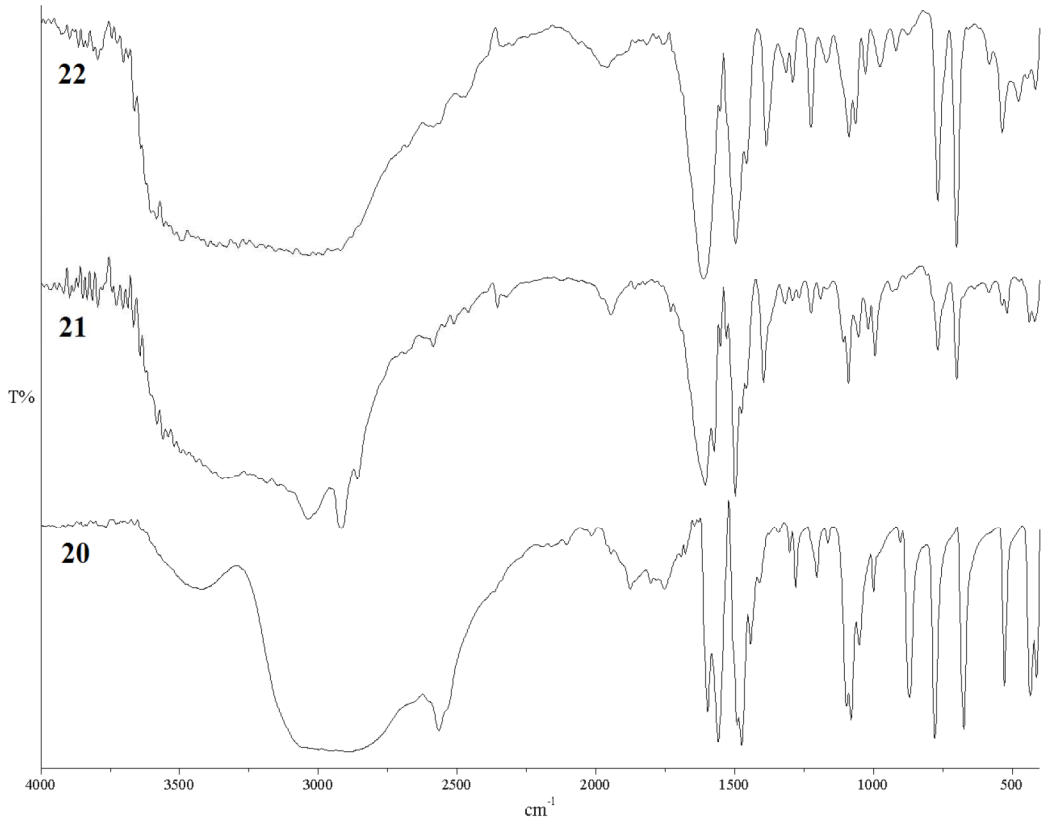


Figure 6.1 FT-IR spectra of compounds **20**, **21** and **22**.

6.3.3 Elemental Analyses

The elemental analyses were consistent with the formulae A_nCoCl_x. *Anal.* Ref. sulfanilamide: Found (calc.) %; C, 41.85 (41.81); H, 4.68 (4.65); N, 15.26 (16.25). (3-Cl-$C_6H_4NH_3)_8[CoCl_6]Cl_4$ (**20**)**:** Found (calc.) %; C, 39.59 (39.94); H, 3.90 (3.88); N, 7.52 (7.77). (2-$C_{10}H_{18}NH_3)_3CoCl_5.H_2O$ (**21**)**:** Found (calc.) %; C, 49.75 (50.64); H, 7.08 (7.88); N, 5.85 (5.91). [(*S*)-$C_6H_5CH(CH_3)NH_3]_2CoCl_4$ (**22**)**:** Found (calc.) %; C, 43.65 (43.14); H, 5.30 (5.39); N, 6.27 (6.29).

6.3.4 Thermal Analyses

6.3.4.1 Thermo Gravimetry/Differential Thermal Analysis (TG/DTA)

TG/DTA of cobalt base OIHCs were performed on the powdered sample. Figure 6.2 show the thermal analyses of compounds **20**, **21** and **22**. Compounds **20** and **21** follow similar degradation pathways as compared to compound **22**, as tabulated below.

$[(3\text{-Cl-}C_6H_4NH_3)_8CoCl_6]Cl_4$

Temp. 457.5 K ↓ $8(3\text{-Cl-}C_6H_4NH_2)$
Loss = 70.76 % (theory)
Loss = 62.42 % (found)

$(H)_8CoCl_{10}$

Temp. 485.8 K ↓ 8HCl
Loss = 20.24 % (theory)
Loss = 27.04 % (found)

$CoCl_2$

9.00 % (theory)

10.52 % (found)

$(2\text{-Adamantyl-}NH_3)_3CoCl_5.H_2O$

Temp. 360.0 K ↓ H_2O
Loss = 2.53 % (theory)
Loss = 2.24 % (found)

$(2\text{-Adamantyl-}NH_3)_3CoCl_5$

Temp. 584.1 K ↓ $3(2\text{-Adamantyl-}NH_2)$
Loss = 63.81 % (theory)
Loss = 55.07 % (found)

$(H)_3CoCl_5$

Temp. 609.5 K ↓ 3HCl
Loss = 15.39 % (theory)
Loss = 24.23 % (found)

$CoCl_2$

18.26 % (theory)

18.44 % (found)

$[(S)\text{-}C_6H_5CH(CH_3)NH_3]_2CoCl_4$

Temp. 549.2 K ↓ $(S)\text{-}C_6H_5CH(CH_3)NH_2 + (S)\text{-}C_6H_5CH(CH_3)NH_2HCl$
Loss = 62.71 % (theory)
Loss = 55.77 % (found)

$(H)CoCl_3$

Temp. 596.2 K ↓ HCl
Loss = 8.19 % (theory)
Loss = 12.80 % (found)

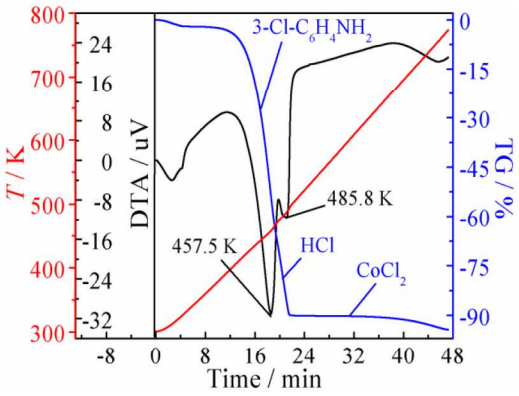
$CoCl_2$

29.17 % (theory)

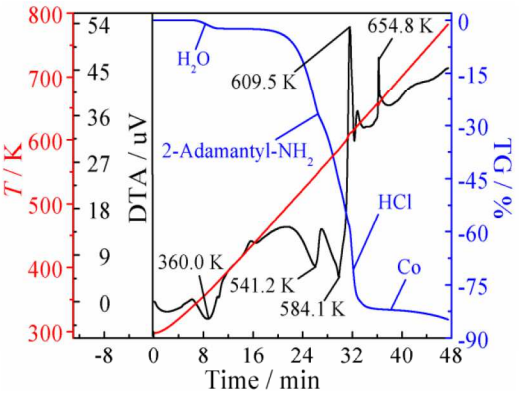
31.42 % (found)

Temp. 984.6 K ↓

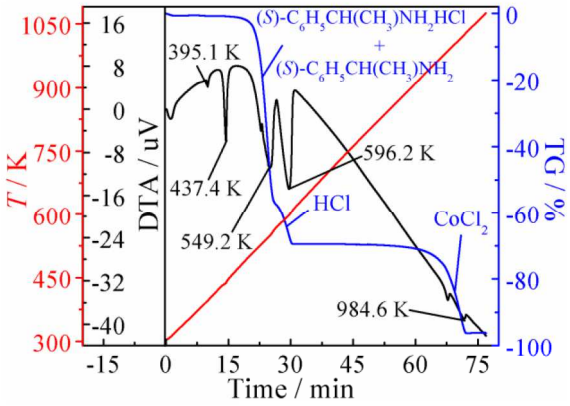
Complete loss



(a)



(b)



(c)

Figure 6.2 TG/DTA thermograms for compounds **20** (a); **21** (b) and **22** (c).

DTA of compound **20** shows endothermic peaks at 457.5 K and 485.8 K due to thermal decomposition. At these temperatures it loses eight moles of 3-chloro aniline and eight moles of hydrochloride. Calculations of first weight loss come very close to the evaporation of eight moles of 3-chloro aniline per formula unit. After loses of 3-chloro aniline $(H)_8CoCl_{10}$ is left. It again loses hydrochloride molecule above 457.5 K, with $CoCl_2$ at the bottom. Calculation of second weight loss comes very near to the evaporation of eight moles of hydrochloride molecule per formula unit. The decomposition pathway of compound **20** is very similar to compound **21**. The first small weight loss in compound **21** at 360.0 K is due to the liberation of one mole of water molecule from formula unit. The thermal decomposition pathway of compound **22** is different. DTA of compound **22** shows five endothermic peaks at 395.1 K, 437.4 K, 549.2 K, 596.2 K and 984.6 K the former two peaks 395.1 K and 437.4 K before the decomposition are characteristic for solid-solid phase transitions. Later three peaks are due to thermal decomposition. At 549.2 K one mole of (*S*)-methyl benzyl amine goes out along with (*S*)-methyl benzilinium chloride. Calculations of weight loss at this temperature come close to the evaporation of one mole of (*S*)-methyl benzyl amine and (*S*)-methyl benzilinium chloride per formula unit. After the weight loss of (*S*)-methyl benzyl amine and (*S*)-methyl benzilinium chloride, $(H)CoCl_3$ left behind. Above 550.0 K loss of one mole of hydrochloride form $CoCl_2$, which remains stable up to the 885.0 K. With increasing temperature $CoCl_2$ 'sublimes' with complete weight loss above 984.6 K. Calculation of second weight loss comes very close to the evaporation of one mole of hydrochloride per formula unit. The degradation pathways and solid-liquid phase transitions are shown in Figure 6.2.

6.3.4.2 Differential Scanning Calorimetry (DSC)

DSC studies on **20** have not shown any signature of solid-solid phase transition. On the other hand, compound **21** has shown one endothermic peak at 404.28 K (-2.52 J g^{-1}) while heating and one exothermic peak at 387.90 K (0.99 J g^{-1}) while cooling, due to solid-solid phase transition. DSC studies on compound **22** have two endothermic peaks at 403.80 K (-0.54 J g^{-1}) and 422.51 K (-15.08 J g^{-1}) while heating and two exothermic peaks at 379.52 K (0.85 J g^{-1}) and 398.08 K (17.13 J g^{-1}) while cooling which are characteristics for solid-solid phase transitions. OACSs of **20** and **21** are devoid of any phase transition, while (*S*)-methyl benzilinium chloride shows one solid-solid phase transition. These transitions are reversible in nature and can be repeated over many cycles without any observable change in peak position (Figure 6.3). To understand this solid-solid phase transition, we heated the compounds, up to their transition temperature, in open atmosphere using heating plate. We observed compound **22** showing change in color from light-blue ↔ dark-blue while other compounds do not undergo any observable change.

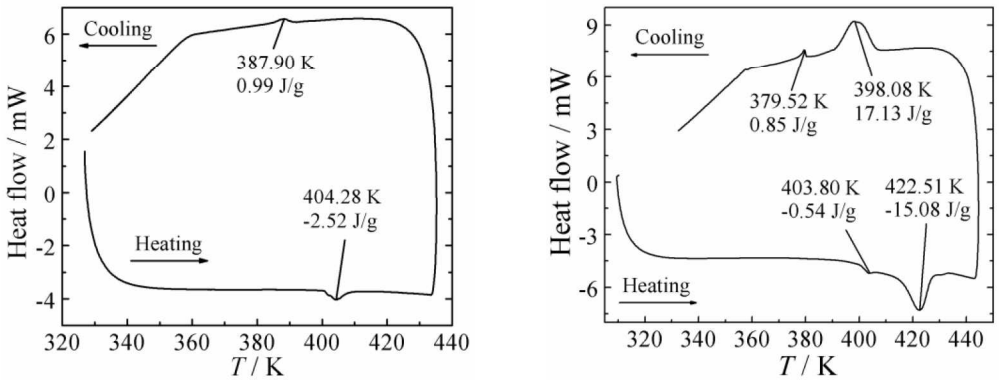


Figure 6.3 DSC plots for compounds **21** (a) and **22** (b), showing the reversible transitions.

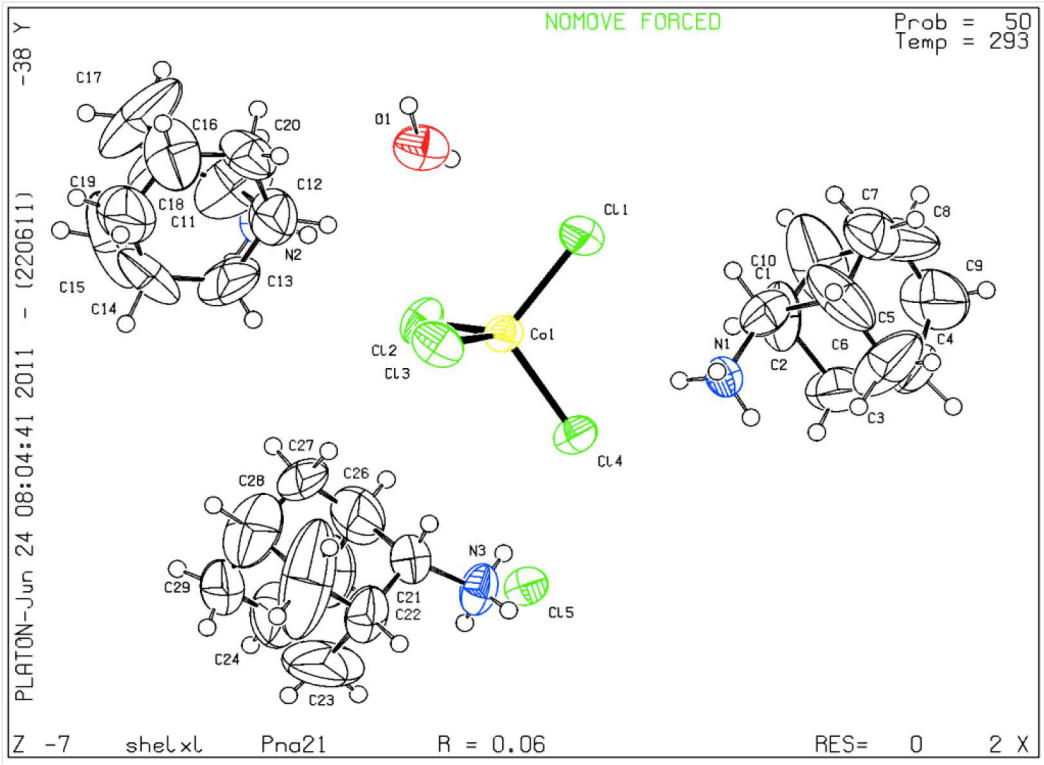
6.3.5 Crystal Structure

6.3.5.1 Single Crystal X-ray Diffraction

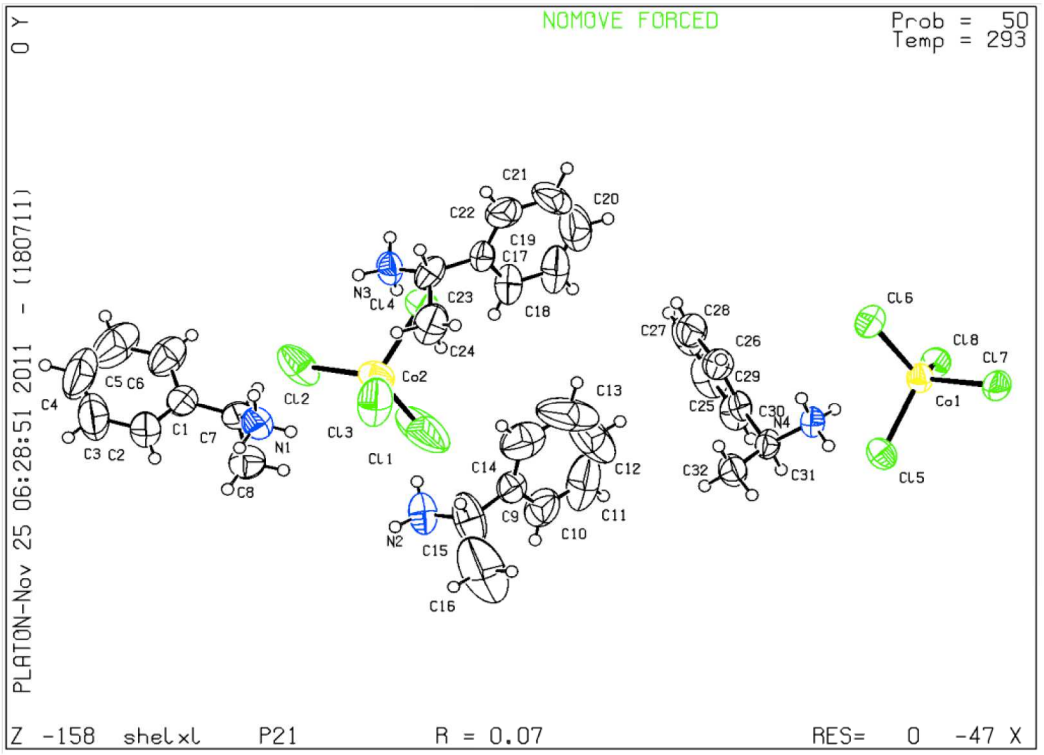
A summary of crystallographic data and structure solutions for compounds **21** and **22** are given in Table 6.1. Figure 6.4 shows the asymmetric unit consisting of compounds **21** and **22**.

Table 6.1 Crystallographic data and structure refinements for compounds **21** and **22**

Compounds	**21**	**22**
Empirical formula	$C_{30}H_{56}Cl_5CoN_3O$	$C_{16}H_{24}Cl_4CoN_2$
Formula weight	710.906	445.10
T (K)	293	293
Wavelength (Å)	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic
Space group	$Pna2_1$	$P2_1$
a (Å)	27.5293(12)	16.372(8)
b (Å)	18.8712(9)	7.269(4)
c (Å)	6.7428(3)	18.220(9)
β (°)	90.00	100.166(9)
V (Å^3)	3503.0(3)	2134.2(18)
Z	4	4
D_{calc} (Mg/m^3)	1.348	1.385
Crystal size (mm^3)	0.25×0.21×0.18	0.22×0.16×0.10
F(000)	1508	916
2θ range (°)	3.10 - 29.22	1.14 - 25.96
Index ranges	-20 ≤ h ≤ 37, -23 ≤ k ≤ 25, -9 ≤ l ≤ 4	-20 ≤ h ≤ 19, -8 ≤ k ≤ 8, -22 ≤ l ≤ 22
Reflections collected	11517	11009
Independent reflections	5830 [R_{int} = 0.0289]	6699 [R_{int} = 0.0367]
Completeness to θ = 25.00°	96.3 %	98.9 %
Goodness-of-fit on F^2	0.997	1.029
Data / restraints / parameters	5830 / 1 / 369	6699 / 1 / 415
Final R indices [I>2σ(I)]	$R1$ = 0.0648, w$R2$ = 0.1555	$R1$ = 0.0686, w$R2$ = 0.1362
R indices (all data)	$R1$ = 0.0956, w$R2$ = 0.1779	$R1$ = 0.0964, w$R2$ = 0.1502



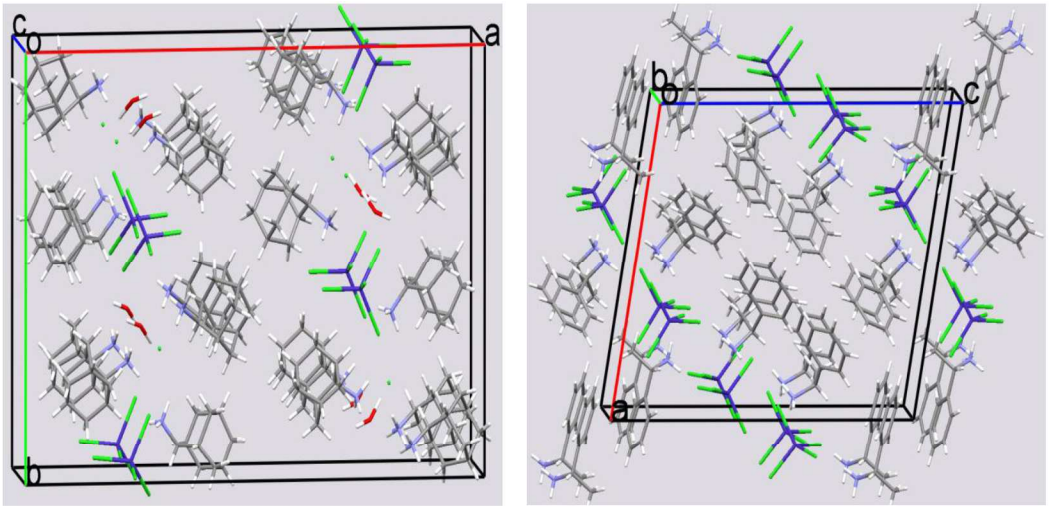
(a)



(b)

Figure 6.4 Molecular view of compounds **21** (a) and **22** (b) with labeling scheme, thermal ellipsoids are drawn at the 50 % probability level.

Single crystal XRD interpretation on compounds **21** and **22** proved that compound **21** crystallized in orthorhombic space group $Pna2_1$ with unit cell dimension a = 27.5293(12) Å, b = 18.8712(9) Å, c = 6.7428(3) Å, β = 90.00º, V = 3503.0(3) Å^3 and Z = 4. Compound **22** crystallized in monoclinic space group $P2_1$ (chiral space group) with unit cell dimension a = 16.372(8) Å, b = 7.269(4) Å, c = 18.220(9) Å, β = 100.166(9)º, V = 2134.2(18) Å^3 and Z = 4. These crystal structures consisted of isolated near tetrahedral geometry around $CoCl_4^{2-}$ anion. The dianions of compounds **21** and **22** exhibit isolated near tetrahedral geometry with average Cl-Co-Cl trans angles in the range of 105º - 116º see Figure 6.5. These dianions are intercalated by OACs and stabilized by weak force (van der Waals) and hydrogen bonding interaction. The two ions (cations and anions) are held together by N-H···Cl interaction and angles are close to 110º - 173º with the N-H···Cl distance 3.052(8) Å - 3.300(7) Å. The data summarizing these contacts are listed in Table 6.2. As expected these structures shows two non-covalent interactions, N-H···Cl and C-H···Cl (Figure 6.6). Here we observed two N-H···Cl distances, of 3.052(8) Å and 3.275(7) Å, with angles 162.8(5)º and 173.2(4)º respectively. Similar interactions are observed for (2-bromopyridinium)$_2$CuBr$_4$ and (4-bromopyridinium)$_2$CuCl$_4$ [8].

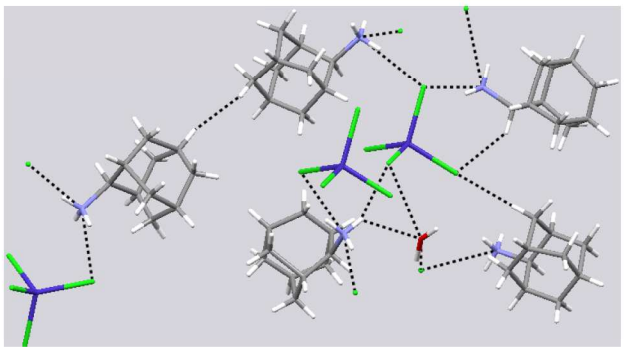


(a) (b)

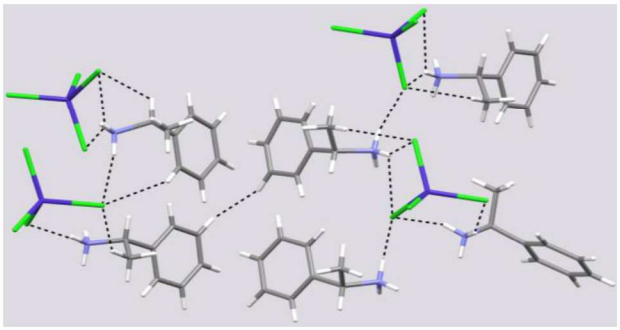
Figure 6.5 The orthorhombic structure of compound **21** (a), viewed down along c-axis and monoclinic structures for compound **22** (b), viewed down along the *b*-axis, showing isolated structure of $CoCl_4^{2-}$.

Table 6.2 Crystal parameter for compounds **21** and **22**

Compounds	Co-Cl Dist. [Å]	Co-Co Dist. [Å] Inter	Co-Co Dist. [Å] Intra	Cl-Co-Cl Angle[°]	N-H···Cl Dist. [Å]	N-H···Cl Angle[°]	C-H···Cl Dist. [Å]	C-H···Cl Angle[°]
21	2.2588(19)	13.063(1)	6.743(1)	112.69(8)	3.180(5)	136.2(3)	3.86(2)	166.1(1)
	2.2812(19)			111.87(8)	3.275(6)	159.1(3)	3.60(1)	132.7(6)
	2.2501(19)			109.40(8)	3.165(6)	142.3(3)		
	2.2876(17)			108.74(8)	3.276(6)	156.4(3)		
				107.58(7)	3.230(6)	162.5(3)		
				106.34(8)	3.300(7)	139.6(4)		
					3.131(6)	110.6(4)		
22	2.240(2)	14.361(5)	5.738(2)	115.39(9)	3.27(1)	150.0(5)	3.73(1)	150.2(6)
	2.255(2)			114.28(11)	3.052(8)	162.8(5)	3.64(1)	140.0(7)
	2.266(2)			110.62(11)	3.294(8)	163.0(5)	3.649(8)	137.0(5)
	2.273(2)			110.14(9)	3.220(6)	123.9(4)	3.499(8)	119.1(5)
	2.222(3)			109.92(9)	3.260(7)	152.6(4)	3.53(2)	144(1)
	2.224(4)			109.0(2)	3.286(7)	128.5(4)		
	2.260(2)			108.60(9)	3.275(7)	173.2(4)		
	2.265(3)			106.69(13)	3.242(7)	167.6(4)		
				105.60(9)	3.266(6)	146.3(4)		
				105.27(13)	3.173(5)	166.0(4)		
					3.258(6)	128.8(4)		



(a)



(b)

Figure 6.6 The non-covalent N-H···Cl and C-H···Cl synthon interactions for compounds **21** (a) and **22** (b).

CCDC No. 882753 and 882754 contains the crystallographic data for the compounds **21** and **22**. This data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

6.3.5.2 Powder X-ray Diffraction

Figure 6.7 illustrate powder XRD pattern for compound **20** at 296 K. Powder pattern of compound **20** was indexed using powder X5 software. These powder patterns were indexed in triclinic lattice type *P* with unit cell a = 8.694(4) Å, b = 13.424(4) Å, c = 14.423(2) Å, α = 81.63(3)º, β = 72.61(5)º, γ = 79.95(3)º, V = 1578.595(3) Å^3, R factor = 0.002 with 2θ error 0.17 Table 6.3. Close examination of the powder XRD on compound **20** revealed its resemblance to the (3-Cl-$C_6H_4NH_3)_8[NiCl_6]Cl_4$ [6].

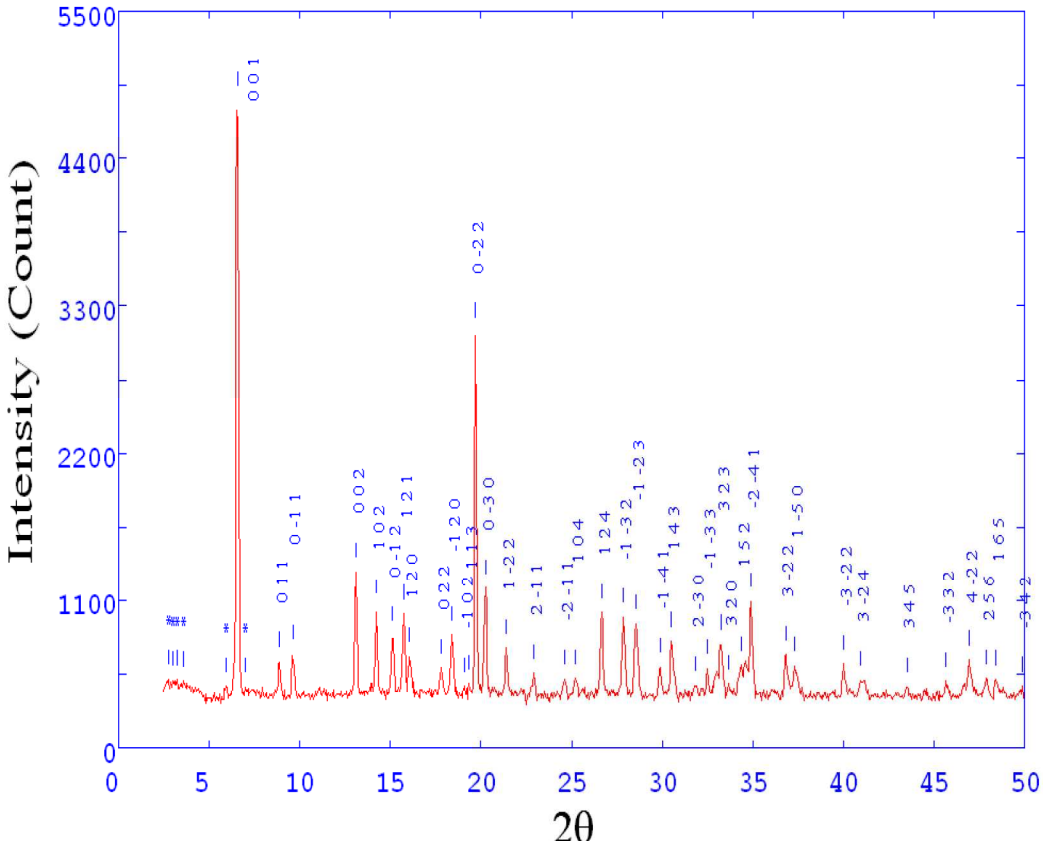


Figure 6.7 Powder XRD data for compound **20**.

Table 6.3 Crystal data and structure index parameters for compound **20**

Formula	$(3\text{-Cl-}C_6H_4NH_3)_8[CoCl_6]Cl_4$	α (°)	81.63(3)
Molecular weight	1578.6(4)	β (°)	72.61(5)
Temperature K	296	γ (°)	79.95(3)
Crystal system	Triclinic	V Å^3	1578.595(3)
Lattice Type	P	Radiation (λ)	1.54184
a Å	8.694(4)	2θ range (°)	2.5 - 50
b Å	13.424(4)	N. reflections	951
c Å	14.423(2)	R factor	0.002

6.4 Conclusion

- We have synthesized three new cobalt based OIHCs having general formula A_nCoCl_x.
- TG/DTA results on these OIHCs explain compounds **20** and **21** have a similar degradation pathway (loses organic amine initial) as compared to compound **22** (loses organic amine along with organic ammonium chloride initial).
- DSC studies have shown zero, one and two reversible solid-solid phase transitions for compounds **20**, **21** and **22**.
- Single crystal XRD pattern showed compound **21** crystallized in orthorhombic space group $Pna2_1$ and compound **22** crystallized in monoclinic space group $P2_1$. The isolated $CoCl_4^{2-}$ has distorted tetrahedral geometry for compounds **21** and **22**.
- The structural study shows two important non-covalent interactions N-H···Cl, C-H···Cl play a significant role in forming the structures of OIHCs.
- Powder XRD pattern indexed for compound **20** shows that it crystallizes in triclinic, isomorphous with $(3\text{-Cl-}C_6H_4NH_3)_8[MnCl_6]Cl_4$.

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