



## Synthesis, Spectral, Structural and Thermal Characterization of Inorganic Crystal: Phenyl Trimethylammonium Tetrachlorocobaltate

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Phenyl trimethylammonium tetrachlorocobaltate, crystals were grown by slow evaporation technique. The crystal was bright, transparent. The three dimensional structure of the phenyl trimethylammonium tetrachlorocobaltate was obtained from single crystal X-ray diffraction studies. The molecule belongs to monoclinic crystal system with C2/c space group. The presence of functional groups and modes of vibrations were identified by FT-IR spectroscopy. <sup>1</sup>H NMR spectroscopy was also used to characterise the compound and the thermal stability of the crystal was established by TGA/DT analysis. This work undergoes phase transition which makes the study interesting.

**Keywords:** Phenyl trimethylammonium tetrachlorocobaltate, Crystal growth, Alkyl halometallates, Thermal stability.

### INTRODUCTION

Presently, the region of coordination polymers has undergone much development, for the purpose of designing new materials with remarkable physical properties. Many one-, two- and three-dimensional structures have been synthesized and characterized [1-3]. The amine salts of halogen complexes were prepared and these compounds are interesting because they exhibit phase transitions related to motion of the ammonium cations. Recently, investigation on organic-inorganic polar crystals has become very important, because of its quadratic nonlinear optical properties [4,5]. Metal complexes find position in the fields of biological catalysis and functions, such as in metabolism [6,7]. Phenylammonium chloride is an organic monomer salt which on exposure to  $\gamma$ -radiation polymerize to polyaniline [8-10]. It was formerly used as dosimeter for detection of  $\gamma$ -radiation. Phenylammonium chloride has been used in poly(vinyl alcohol) as host films. The prepared films were irradiated with dose 10-50 kGy and showed that absorbance at 790 nm increased exponentially with dose [11]. Cobalt is an essential and integral component of vitamin B<sub>12</sub>, therefore it is physiolo-

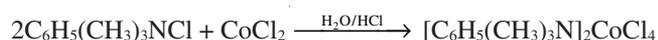
gically found in most tissues. Complexes of cobalt are useful for nutritional supplementation to deliver cobalt in a form, which effectively raises the bioavailability, for instance, vitamin B<sub>12</sub> by microorganisms present in the gut. Mixed ligands cobalt complexes find potential applications in the fields of anti-tumour, antibacterial, antimicrobial, radio-sensitization and cytotoxicity activities [12-15].

The growth of crystals containing two or more components plays an important role in several modern industrial applications [16]. The art of growing crystals has always been fascinating and challenging. Modern technology employing semiconductors, magnetic garnets, ultraviolet and infrared solid state lasers, requires materials in good crystalline form. Solid state electronics has become the key to modern technology and its importance is likely to keep growing [17]. Extensive studies have been carried out on the preparation, growth and characterization of A<sub>2</sub>BX<sub>4</sub> type compounds, where A = univalent cations like Na<sup>+</sup>, K<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, Rb<sup>+</sup> and its alkyl derivatives; B = divalent transition metal cations like Fe<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Mn<sup>2+</sup>, etc. and X = halogen (Cl, Br and I). A<sub>2</sub>BX<sub>4</sub> compounds represent the largest known groups of insulating crystals with structurally

in commensurate phases. In their normal parent phase, they are orthorhombic and pseudo hexagonal, with space group  $pcmn$  and have the structure of  $\beta$ - $K_2SeO_4$  type [18]. Typically on decreasing temperature they undergo a second order phase transition at  $T_i$  (in commensurate transition temperature) to a one dimensionally modulated incommensurate (IC) phase with the incommensurate wave vector directed along the pseudo hexagonal 'a' axis. The occurrence of incommensurate phases in these crystals was interesting. As the temperature is lowered a variety of phase transitions are observed. A comprehensive list of the relevant  $A_2BX_4$  materials and a review of their properties has been reported by Cummins [19]. In this view, we have prepared PTMATCL-Co(II) compound and characterized through elemental analysis, FTIR, TG-DTA, DSC and  $^1H$  NMR spectroscopy.

## EXPERIMENTAL

**Preparation and crystal growth:** Crystals of phenyl trimethylammonium pentachlorocobaltate(II)-alkyl halometallate were grown by slow evaporation method at room temperature (Scheme-I). Aqueous solutions of Analar grade (E. Merck) phenyl trimethylammonium chloride and cobaltous chloride were prepared separately in 2:1 molar ratio using triple distilled water. The two solutions were mixed thoroughly. In order to maintain acidic medium and to avoid hydrolysis 1 mL of HCl is added. The resulting solution was filtered and the collected filtrate in the beaker was covered by filter paper with minute pores for growing crystals. Care was taken to minimize the temperature gradient and mechanical shock. The PTMATCL-Co(II) crystals obtained by slow evaporation method at room temperature after 15 days were bright, blue colour and transparent (Fig. 1). The grown crystals of phenyl trimethylammonium-pentachlorocobaltate(II) were characterized through elemental analysis, NMR spectroscopy, powder X-ray diffraction and thermal analysis.



**Scheme-I:** Reaction of phenyl trimethylammonium tetrachlorocobaltate

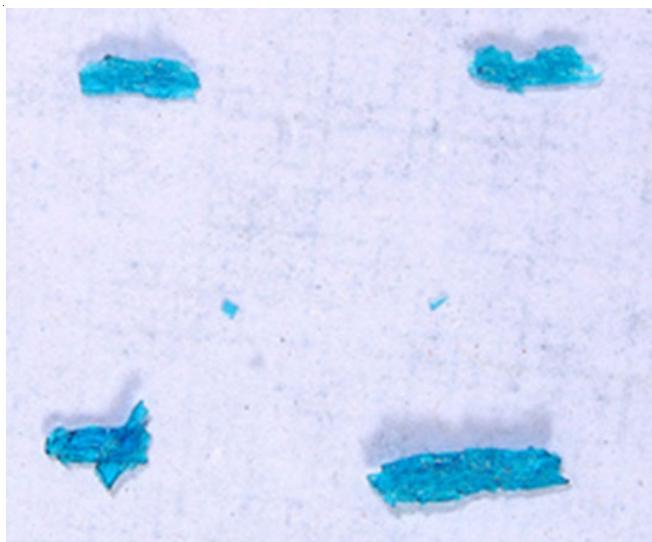


Fig. 1. Crystal photo of PTMATCL-Co(II)

## RESULTS AND DISCUSSION

**Elemental analysis:** The results of elemental analysis (C, H and N) of phenyl trimethylammonium pentachlorocobaltate (II) crystals is shown in Table-1. The experimental values of carbon, hydrogen and nitrogen are very close to the theoretical values based on  $A_2BX_4$  formula. The elemental analysis thus confirmed the stoichiometry of [PTMATCL-Co(II)] compound.

TABLE-1  
ELEMENTAL ANALYSIS (%) OF PTMATCL-Co(II)

Carbon		Hydrogen		Nitrogen	
Exp.	Theo.	Exp.	Theo.	Exp.	Theo.
41.76	45.64	9.14	5.91	5.37	5.91

**FT-IR studies:** Various absorption frequencies and the assignments of PTMATCL-Co(II) are presented in Table-2. The peak is observed at  $3386.04\text{ cm}^{-1}$  due to N-H stretching of ammonium ion is confirmed. The peak at  $3030.36\text{ cm}^{-1}$  is due to Ar-H stretching vibrations of phenyl group. Bending deformation mode of methyl scissoring is seen at  $1491.20\text{ cm}^{-1}$ . Peak at  $1465.56\text{ cm}^{-1}$  is due to bending deformation mode of methyl group. The peak at  $998.69\text{ cm}^{-1}$  is due to C-H out of plane bending vibration. The peak at  $844.74\text{ cm}^{-1}$  is due to C-H deformation out of plane vibration. The peak at  $767.59\text{ cm}^{-1}$  is due to methyl in-plane bending vibration, mono-substituted aromatic ring stretching, C-N-C and C-C-N deformation modes, disubstituted *meta* C-H deformation are seen at  $690.84\text{ cm}^{-1}$ . The peak is observed at  $552.90\text{ cm}^{-1}$  is due to greater electronegativity in C-Cl atom.

TABLE-2  
FOURIER TRANSFORM INFRARED SPECTROSCOPIC  
(FTIR) STUDIES OF PTMATCL-Co(II)

Frequency ( $\text{cm}^{-1}$ )	Assignment
3386.04	N-H stretching due to ammonium ion
3030.36	Ar-H stretching vibrations of phenyl group
1627.00	C-N bending mode
1491.20	C-H in-plane asymmetric bending due to methyl group
1465.56	Bending deformation mode of methyl group
998.69	C-H out of plane bending vibration
844.74	C-H deformation out of plane vibration
767.59	Aromatic in-plane bending vibration, meta di-substituted aromatic ring stretching
690.84	C-N-C and C-C-N deformation modes, di-substituted meta C-H deformation

**$^1H$  NMR studies:**  $^1H$  NMR spectrum of PTMATCL-Co(II) is shown in Fig. 2. In this spectrum, two signals are observed at different  $\delta$  values for methyl and Ar-H groups present in the compound. All the methyl and Ar-H groups are in the same environment. The expected  $\delta$  values for methyl and aromatic protons are 1.2 to 1.4 ppm and 7.5 to 7.8 ppm, respectively. In this spectrum higher  $\delta$  value is obtained. This is due to the deshielding effect which confirms the presence of positive charge on nitrogen containing three methyl groups and Ar-H groups. The signal at  $3.4\delta$  is due to the presence of methyl group protons. The intensity of the peak is higher due to methyl proton. Peak at  $7.5\delta$  is due to Ar-H protons. The higher  $\delta$  value is due to deshielding effect because of electropositive nitrogen adjacent



compound is shown in Fig. 4 and the displacement ellipsoids were drawn at 50 % probability level. The molecule composes of two anilinium moiety and a tetrachlorocobaltate moiety. The cell parameters were  $a = 15.5329(4)$  Å,  $b = 9.5793(4)$  Å,  $c = 30.8443(8)$  Å and  $\beta = 95.450(2)^\circ$  belongs to monoclinic crystal system with  $C2/c$  space group. The crystal data of PTMATCL-Co(II) molecule is presented in Table-3. Table-4 depicted the atomic coordinates and its equivalent isotropic displacement parameters for non-hydrogen atoms of PTMATCL-Co(II).

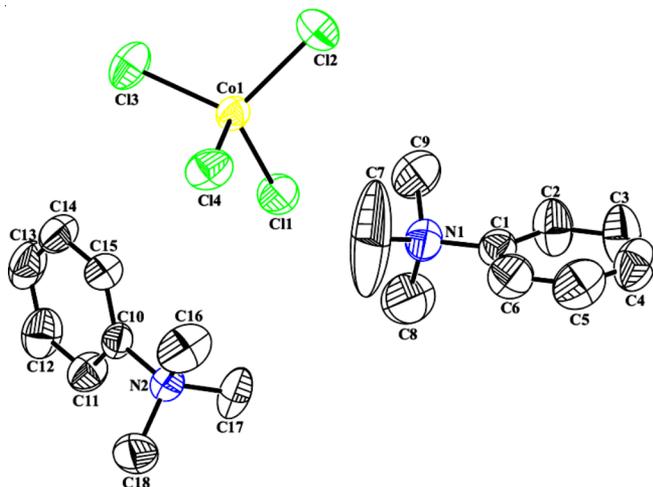


Fig. 4. ORTEP diagram for PTMATCL-Co(II) compound

TABLE-3  
CRYSTAL DATA FOR PTMATCL-Co(II)

Parameters	PTMATCL-Co(II)
CCDC number	1029779
Empirical formula	$C_{18}H_{28}N_2Cl_4Co$
Formula weight	473.15
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$C2/c$
Unit cell dimensions	
a (Å)	15.5329(4)
b (Å)	9.5793(4)
c (Å)	30.8443(8)
$\beta$ (°)	95.450(2)
Volume (Å <sup>3</sup> )	4568.7(3)
Z	8
Calculated density (Mg/m <sup>3</sup> )	1.376
Absorption coefficient (mm <sup>-1</sup> )	1.223
F(000)	1960
Crystal size (mm)	0.10 × 0.20 × 0.20
$\theta$ -range for data collection (°)	1.33 to 26.53
Limiting indices	-19 ≤ h ≤ 19; -11 ≤ k ≤ 12; -36 ≤ l ≤ 38
Reflections collected/unique	32141/4750 [R(int) = 0.0341]
Completeness to $\theta = 25.00$ (%)	100 %
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data/restraints/parameters	4750/0/227
Goodness-of-fit on F <sup>2</sup>	1.075
Final R indices [I > 2 $\sigma$ (I)]	R1 = 0.0387, wR2 = 0.1000
R indices (all data)	R1 = 0.0471, wR2 = 0.1056
Largest diff. peak and hole (e Å <sup>-3</sup> )	0.364 and -0.311

TABLE-4  
ATOMIC COORDINATES ( $\times 10^4$ ) AND EQUIVALENT ISOTROPIC DISPLACEMENT PARAMETERS ( $\text{Å}^2 \times 10^3$ ) FOR THE NON-HYDROGEN ATOMS OF PTMATCL-Co(II)

Atoms	PTMATCL-Co(II)			*U(eq)
	x	y	z	
C1	61(2)	-2659(3)	5209(1)	54(1)
C2	-98(2)	-2653(4)	4768(1)	82(1)
C3	555(3)	-3008(5)	4513(1)	95(1)
C4	1346(2)	-3353(4)	4698(1)	84(1)
C5	1490(2)	-3375(4)	5138(1)	88(1)
C6	859(2)	-3028(4)	5396(1)	73(1)
C7	-520(5)	-2765(11)	5918(2)	246(5)
C8	-701(3)	-692(5)	5484(2)	157(3)
C9	-1497(3)	-2739(6)	5280(2)	130(2)
C10	2015(2)	-3065(3)	6931(1)	44(1)
C11	1605(2)	-1792(3)	6937(1)	59(1)
C12	725(2)	-1756(4)	6970(1)	73(1)
C13	266(2)	-2965(4)	6989(1)	76(1)
C14	676(2)	-4229(4)	6974(1)	75(1)
C15	1557(2)	-4287(3)	6945(1)	60(1)
C16	3358(2)	-4488(4)	6972(1)	85(1)
C17	3109(2)	-2645(4)	6435(1)	73(1)
C18	3434(2)	-2096(4)	7210(1)	74(1)
N1	-646(2)	-2233(3)	5476(1)	68(1)
N2	2970(1)	-3077(2)	6890(1)	45(1)
Co1	3232(1)	-3061(1)	8692(1)	44(1)
Cl1	2992(1)	-1023(1)	9042(1)	67(1)
Cl2	3225(1)	-4801(1)	9192(1)	68(1)
Cl3	4494(1)	-3023(1)	8377(1)	74(1)
Cl4	2145(1)	-3342(1)	8156(1)	68(1)

$$*U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

The phenyl rings of both anilinium group were existing in the planar geometry. The C-C distances among the benzene ring of both phenyl trimethylammonium moiety is in agreement with the literature values [26] (Table-5). The dihedral angle between two phenyl trimethyl ammonium moieties was found to be  $89.49(16)^\circ$ . The hydrogen bond lengths were in the range of 0.9300 Å to 0.9600 Å. The sum of bond angles around N1[ $328.6(12)^\circ$ ] and N2[ $330.7(6)^\circ$ ] of two phenyl trimethylammonium moieties was in accordance with  $sp^3$  hybridization [27]. The torsion angles of PTMATCL-Co(II) compound are given in Table-6. The tetrachlorocobaltate group exhibited distorted tetrahedral geometry with Co(II) ion surrounded by four Cl atoms, Cl-Co-Cl angles ranging from  $107.16(3)^\circ$  and  $112.12(3)^\circ$ . The Co-Cl bond lengths are in the range of 2.2653(7) Å and 2.2798(8) Å, which were close to those observed in related literature [28]. In general, metal-halogen bonds are weaker and they have higher bond lengths [29]. The Co-Cl bond lengths are larger, when matched with C-N and C-C bond lengths (Table-5).

In PTMATCL-Co(II) compound, C-H...Cl type of hydrogen bonding plays an important role in creating the molecular association. Here, two chlorine atoms Cl1 and Cl3 acts as acceptors of C-H...Cl H-bonds. The remaining chlorine atoms Cl2 and Cl4 do not contribute in hydrogen bonding network with the van der Waals forces. The deviation from the perfect tetrahedral arrangement around Co(II) in PTMATCL-Co(II) molecule can be described by participation of chlorine ions in the hydrogen bonding. The Cl1 atom behaves as an acceptor for the methyl group hydrogen's from the neighbouring molecule *via*

TABLE-5  
SELECTED BOND LENGTHS (Å) AND  
BOND ANGLES (°) OF PTMATCL-Co(II)

Atoms	Length	Atoms	Angles
C1-C2	1.359(4)	C2-C1-C6	119.7(3)
C1-C6	1.364(4)	C2-C1-N1	118.6(2)
C1-N1	1.491(4)	C6-C1-N1	121.6(3)
C2-C3	1.381(5)	C1-C2-C3	119.7(3)
C3-C4	1.347(5)	C4-C3-C2	120.6(3)
C4-C5	1.353(5)	C3-C4-C5	119.0(3)
C5-C6	1.361(5)	C4-C5-C6	121.5(3)
C7-N1	1.453(6)	C5-C6-C1	119.4(3)
C8-N1	1.479(5)	C15-C10-C11	120.9(2)
C9-N1	1.481(5)	C15-C10-N2	121.0(2)
C10-C15	1.373(4)	C11-C10-N2	118.1(2)
C10-C11	1.377(4)	C10-C11-C12	119.1(3)
C10-N2	1.501(3)	C13-C12-C11	120.4(3)
C11-C12	1.381(4)	C12-C13-C14	120.2(3)
C12-C13	1.363(5)	C13-C14-C15	120.3(3)
C13-C14	1.371(5)	C10-C15-C14	119.1(3)
C14-C15	1.380(4)	C7-N1-C8	109.7(5)
C16-N2	1.492(4)	C7-N1-C9	107.7(5)
C17-N2	1.496(3)	C8-N1-C9	106.4(4)
C18-N2	1.497(4)	C7-N1-C1	112.5(3)
Co1-C14	2.2653(7)	C8-N1-C1	109.2(3)
Co1-Cl3	2.2678(7)	C9-N1-C1	111.1(3)
Co1-C12	2.2713(8)	C16-N2-C17	108.5(2)
Co1-C11	2.2798(8)	C16-N2-C18	107.1(2)
		C17-N2-C18	109.9(2)
		C16-N2-C10	112.3(2)
		C17-N2-C10	108.01(19)
		C18-N2-C10	110.9(2)
		C14-Co1-Cl3	107.72(3)
		C14-Co1-C12	110.88(3)
		C13-Co1-C12	111.28(3)
		C14-Co1-C11	107.66(3)
		C13-Co1-C11	112.12(3)
		C12-Co1-C11	107.16(3)

TABLE-6  
TORSION ANGLES (°) OF PTMATCL-Co(II)

Atoms	Angles
C6-C1-C2-C3	-0.6(6)
N1-C1-C2-C3	178.3(4)
C1-C2-C3-C4	-0.4(7)
C2-C3-C4-C5	1.4(7)
C3-C4-C5-C6	-1.4(6)
C4-C5-C6-C1	0.5(6)
C2-C1-C6-C5	0.5(5)
N1-C1-C6-C5	-178.3(3)
C15-C10-C11-C12	1.8(4)
N2-C10-C11-C12	179.3(2)
C10-C11-C12-C13	-1.2(5)
C11-C12-C13-C14	-0.1(5)
C12-C13-C14-C15	0.7(5)
C11-C10-C15-C14	-1.2(4)
N2-C10-C15-C14	-178.6(2)
C13-C14-C15-C10	-0.1(4)
C2-C1-N1-C7	158.4(5)
C6-C1-N1-C7	-22.7(6)
C2-C1-N1-C8	-79.5(4)
C6-C1-N1-C8	99.3(4)
C2-C1-N1-C9	37.6(5)
C6-C1-N1-C9	-143.5(4)
C15-C10-N2-C16	-13.4(3)
C11-C10-N2-C16	169.0(3)
C15-C10-N2-C17	106.2(3)
C11-C10-N2-C17	-71.3(3)
C15-C10-N2-C18	-133.3(3)
C11-C10-N2-C18	49.2(3)

C16-H16B...C11 and C17-H17C...C11 interactions, forming a loop (Fig. 5, Table-7). The trifurcation of chlorine atom C11 was done at  $(-x, y, -z+3/2)$  via C9-H9B...C11 hydrogen bond. The C17-H17A...Cl3 intermolecular interaction also contributes to the crystal packing, which forms zig-zag chains along *a*-axis.

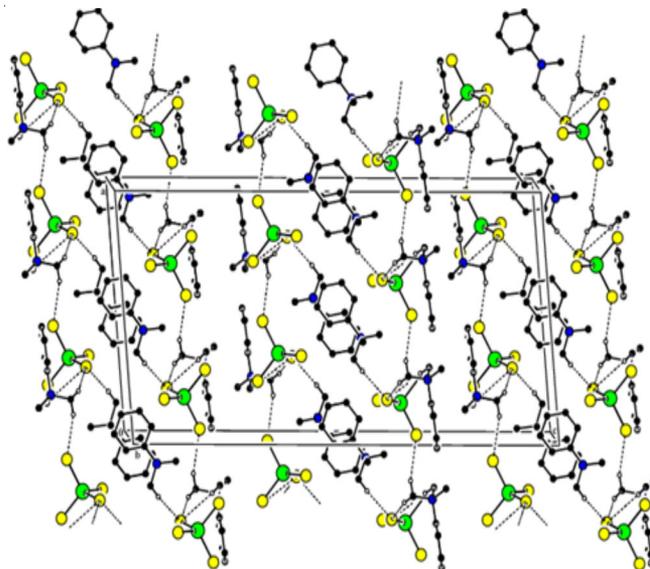


Fig. 6. Packing diagram for PTMATCL-Co(II) compound along *a*-axis

TABLE-7  
HYDROGEN BONDING GEOMETRY  
(Å AND °) FOR PTMATCL-Co(II)

D-H...A	d(D-H)	d(H...A)	d(D...A)	∠(DHA)
C17-H17A...Cl3 <sup>1</sup>	0.96	2.82	3.731(3)	158.5
C17-H17C...Cl1 <sup>2</sup>	0.96	2.99	3.884(4)	154.8
C16-H16B...Cl1 <sup>2</sup>	0.96	2.99	3.886(4)	155.8
C9-H9B...Cl1 <sup>3</sup>	0.96	2.71	3.659(5)	168.3

Symmetry codes: (1)  $-x+1, y, -z+3/2$  (2)  $-x+1/2, y-1/2, -z+3/2$  (3)  $-x, y, -z+3/2$

## Conclusion

Alkyl halometallate crystals of phenyl trimethyl ammonium pentachlorocobaltate(II) [PTMATCL-Co(II)] was grown by slow evaporation method at room temperature. The spectral studies of FTIR, <sup>1</sup>H spectra and the elemental analysis to confirm the stoichiometry of the compound were obtained which is in agreement with the three dimensional crystal structure derived from the single crystal X-ray studies. The crystal data and cell parameters evidently showed that the compound belongs to monoclinic crystal system with *C2/c* space group. In thermal studies, the mass change of the system is measured as the function of temperature which shows PTMATCL-Co(II) molecule with stands up to 200 °C elucidating its good melting point. Overall, the compound phenyl trimethylammonium pentachlorocobaltate(II) was synthesized and crystallized to progress the modern industrial applications of alkyl halometallates with its good thermal stability.

## CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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