Hydrothermal synthesis of Co^{II} chiral inorganic-organic complex: Structural, thermal and catalytic evaluation

Assila Maatar Ben Salah^a, Raquel P. Herrera^b and Houcine Naili^{a*}

^a *Laboratoire Physicochimie de l'Etat Solide, Département de Chimie, Faculté des Sciences de Sfax, BP 1171, 3000 Sfax, Université de Sfax, Tunisie.*

^b *Laboratorio de Organocatálisis Asimétrica, Departamento de Química Orgánica, Instituto de Síntesis Química y Catálisis Homogénea (ISQCH), CSIC-Universidad de Zaragoza, C/ Pedro Cerbuna 12, E-50009 Zaragoza, Spain.*

*** Corresponding Author:**

E-mail: houcine_naili@yahoo.com.

Tel: +216 98 660 026; Fax: +216 74 274 437.

Abstract

By heating the cobalt chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$) with the *R* form of the organic amine α -methylbenzylamine ($\text{C}_8\text{H}_{11}\text{N}$) under hydro(solvo)thermal conditions, we have successfully generated the corresponding non-centrosymmetric homochiral hybrid tris(α -methylbenzylammonium tetrachloridocobaltate chloride $[\text{R}-(\text{C}_8\text{H}_{12}\text{N})_3][\text{CoCl}_4]\text{Cl}$ abbreviated **R(MBA)Co**. We present the growth conditions together with a characterization of the single crystals by means of X-ray single-crystal diffraction, Fourier-transform infrared, TG/TDA thermal decomposition and catalytic properties. This inorganic–organic hybrid compound crystallizes in the chiral space group $\text{P}2_1$ and exhibits a supramolecular-layered organization wherein a double layer of (*R*)-methylbenzylammonium cations and the uncoordinated chloride anions are sandwiched between anionic layers, formed by isolated tetrachloridocobaltate tetrahedra. The crystal packing is governed by a three-dimensional network of $\text{N/C}—\text{H} \cdots \text{Cl}$ hydrogen bonds between the inorganic and organic moieties and $\text{C}—\text{H} \cdots \pi$ interactions between the aromatic rings of the organic moieties themselves. Thermal analysis discloses a phase transition at the temperature 130 °C. The Co complex was also employed as suitable catalyst activating the acetal formation reaction of aldehydes using MeOH as solvent and as the unique source of acetalisation.

KEYWORDS: Chiral; non-centrosymmetric; hybrid; hydrogen bonds; phase transition; catalytic properties.

1. Introduction

By combining the characteristic features of both organic and inorganic moieties, over the past three decades, the design and synthesis of non-centrosymmetric inorganic-organic metal-halide hybrid solids formed through self-organization under mild or solvothermal conditions, have been one of the most fascinating and challenging areas due to their relevance to non-linear optical (NLO) materials, in asymmetric catalysis and stereoselective recognition [1–5]. Among the numerous metal–organic non-centrosymmetric materials, the chiral coordination compounds with non-centrosymmetric crystal structures are of special interest owing to their distinctive physical properties, such as second-harmonic generation (SHG), ferroelectricity, piezoelectricity, and pyroelectricity, which are potentially useful in electric-optical devices, information storages, nonlinear optical (NLO) devices, and light modulators [6–8]. Hence, inclusion of chirality in the molecule is a common strategy to ensure non-centrosymmetric organization in the crystal lattice [9–10] and enantiomerically pure α -methylbenzylamine and its derivatives have important applications as effective chiral adjuvants in the resolution of racemates, and as ligands in asymmetric (or dissymmetric) catalysts [11]. Currently, this amine is being used as a chiral auxiliary and as a chiral base. As an extension of our systematic work on the organic–inorganic hybrid metal halides with the chiral α -methylbenzylamine ligand under hydrothermal conditions [12], we report herein a new inorganic–organic hybrid compound, $[R-(C_8H_{12}N)_3][CoCl_4]Cl$, possessing a zero-dimensional structure. This salt crystallizes in a non-centrosymmetric space group and hence could be a good candidate for non-linear optical applications. In addition, vibrational spectrum, thermal analysis and the catalytic properties of the material have been investigated.

2. Experimental Section

2.1. Materials

Cobalt(II) chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$), hydrochloric acid (HCl ; 37%) and (*R*)-(+)- α -methylbenzylamine ($\text{C}_8\text{H}_{11}\text{N}$) were purchased from Sigma-Aldrich and used without further purification.

2.2. Synthesis

The synthesis was carried out in home-built Teflon-lined stainless steel pressure bombs of 120 mL maximum capacity. 1 mmol of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and 3 mmol of (*R*)- α -methylbenzylamine were dissolved together in 10 mL of water and hydrochloric acid ($\text{pH} \approx 3$). The mixture was placed in a Teflon-lined autoclave that was then sealed and heated to 120 °C for 4 days. It was then allowed to cool to room temperature in a cold water bath. Blue plate crystals with suitable dimensions for crystallographic study were collected. The crystals were washed several times with distilled water and dried in open air. They are stable for months in normal conditions of temperature and humidity.

2.3. Single-crystal data collection and structure determination

Suitable crystal was glued to a glass fiber on APEX II area detector 4-circles diffractometer. Intensity data sets were collected using Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) through the Bruker AXS APEX2 Software Suite. The crystal structure was solved in the monoclinic symmetry, space group $\text{P}2_1$, according to the automated search for space group available in Wingx [13]. Transition metal and chloride atoms were located using the direct methods with the program SIR97 [14]. C and N atoms from the amine were found from successive difference Fourier calculations using SHELXL-97 [15]. Their positions were validated from geometrical considerations as well as from the examination of possible hydrogen bonds. The absolute structure given by the structure refinement is likely correct with a Flack parameter value of 0.00(19). H atoms were positioned geometrically and allowed to ride on their parent atoms, with $\text{C-H} = 0.98 \text{ \AA}$ and $\text{N-H} = 0.89 \text{ \AA}$. The figures were made with DIAMOND program

[16]. Crystallographic data are given in Table 2. Bond distances and angles calculated from the final atomic coordinates, as well as probable hydrogen bonds, are listed in Tables 3 and 4.

2.4. Infrared Spectroscopy

Infrared measurements were recording using a Perkin Elmer 1650 FT-IR Spectrophotometer. The sample was diluted with spectroscopic grade KBr and pressed into a pellet. Scans were collected over the range of 400–4000 cm^{-1} (Table 1).

2.5. Thermal analyses

TGA–DTA measurements were performed on raw powders with a TGA/DTA 'SETSYS Evolution' (Pt crucibles, Al_2O_3 as a reference) from room temperature up to 600 °C at a constant rate of 5 °C/min under flowing air (100 ml/min).

2.6. Powder X-ray diffraction

The temperature-dependent X-ray (TDXD) was performed with a D5005 powder diffractometer (Bruker AXS) using $\text{CuK}\alpha 1$ radiation ($\lambda = 1.5406 \text{ \AA}$) selected with a diffracted-beam graphite monochromator and equipped with an Anton Paar HTK1200 high-temperature oven camera. The thermal decomposition of the compound was carried out in air with a heating rate of 7 °C h^{-1} from ambient to 600 °C. Temperature calibration was carried out with standard materials in the involved temperature range.

2.7. Catalytic study

R(MBA)Co complex (7.7 mg, 0.01292 mmol) and aldehydes **1a-l** (0.323 mmol) were dissolved in MeOH (0.25 ml) in a test tube. The resulting mixture was stirred at 40 °C during 24 h. The reactions were monitored by thin-layer chromatography. The yield of the reactions is given by ^1H NMR in Tables 6 and 7.

3. Results and discussion

3.1. Infrared spectra

Table 1 represents the major selected absorptions in the IR spectra of **R(MBA)Co** (Figure 1) with their respective assignments. The presence of α -methylbenzylammonium [17] was evidenced by the appearance of the typical absorptions bands for bending of the NH_3^+ group at $\sim 1600\text{ cm}^{-1}$, deformation of CH_3 at 1375 cm^{-1} , deformation of C–H at $\sim 700\text{ cm}^{-1}$ and stretching of the C–C ring at about 1460 cm^{-1} .

3.2. Crystal structure

Chiral (*R*)- α -methylbenzylamine or (*S*)- α -methylbenzylamine have a chiral centre which has shown tremendous scope in the synthesis of hybrid complexes [18-19]. At 100 K, the cobalt studied salt crystallizes in the chiral monoclinic space group $P2_1$ and all atoms are located in general positions. The crystal of **R(MBA)Co** contained α -methylbenzylammonium molecules with the *R*-configuration and the absolute structure parameter of 0.00(19) reflects the correct choice for the single chiral centre. As shown in Figure 2, the asymmetric unit contains three crystallographically independent chiral organic ammonium cations, a tetrahedral tetrachloridocobaltate anion and one free chloride anion. The packing of the different molecular entities is shown in Figure 3; the projection along the *b* axis reveals a supramolecular layered structure made of an alternate stacking of inorganic layers, built of discrete $[\text{CoCl}_4]^{2-}$ anions, and organic chains of $(\text{C}_8\text{H}_{12}\text{N})^+$ cations, while the free Cl^- anions are intercalated between the organic and inorganic sheets, linked together through extensive non-covalent interactions (Table 4). Within the inorganic layers, each $[\text{CoCl}_4]^{2-}$ anion exhibits a slightly distorted tetrahedral arrangement around Co with Co–Cl bonds in the range $2.2559(8)$ – $2.2929(12)\text{ \AA}$, giving a mean value of $2.744(8)\text{ \AA}$ (Table 3). The Cl–Co–Cl bond angles in the range of $105.92(3)^\circ$ – $112.55(3)^\circ$. These values compare well with those found in, for example, $(\text{C}_4\text{H}_7\text{N}_2)_2[\text{CoCl}_4]$ [20] and $(\text{C}_{10}\text{H}_{11}\text{N}_3)[\text{CoCl}_4]$ [21]. The distortion tetrahedral

coordination geometry around Co(II) atom is verified by the calculated (τ_4) parameter for **R(MBA)Co** which corresponds to 0.96 [22]. The free Cl⁻ anions play an important role in the cohesion of the structure so they are located in the gaps between the [CoCl₄]²⁻ moiety and protonated organic cations. In fact, the presence of those anions as a part of an anionic sublattice together with [CoCl₄]²⁻ leads to a total negative charge of (-3) on the framework which is balanced by the presence of three independent fully protonated (C₈H₁₂N)⁺ molecules situated in the space delimited by the anionic sublattice (CoCl₄ tetrahedra). Interestingly, the crystal structure exhibits a layered inorganic-organic structure although the 0-dimension of the inorganic backbone (isolated CoCl₄ tetrahedra as shown in Figure 3. In fact, the distance between the mean planes of two adjacent inorganic layers is remarkably high, indeed, it corresponds to the value of the c unit cell parameter, *i.e.* , 14.42 Å (see Table 2). With regard to the organic cation arrangement, the organization of methylbenzylammonium groups, not in opposition, is favourable to a non-centrosymmetric arrangement [23]. The benzene rings are nearly planar with the maximum deviation being 0.0077(19) Å for C8 in ring 1 (C8/C3–C7), 0.0098(19) Å for C12 in ring 2 (C12/C11–C13) and 0.0118(19) Å for C24 in ring 3 (C24/C19–C23). The bond lengths and angles within the organic cations are close to the usual values observed in others (*R*)- α -methylbenzylammonium salts [12,19]. To predict and control the crystal structure of such compound, one of the strategies that have been adopted in the field of crystal engineering is the identification of specific intermolecular interactions that control aggregation of molecular species, and the field of crystal supramolecularity seeks to understand intermolecular interactions by analysis of crystal packing. The compound has an extensive network of hydrogen bonding due to numerous acceptor and donor atoms. Indeed, the different organic and inorganic sublattices are stabilized and governed significantly through C/N–H $\cdots$ Cl hydrogen bonding between the inorganic and organic moieties and C–H $\cdots$ π stacking interactions between the aromatic rings of the amine molecules themselves

(Tables 4 and 5). An interesting aspect of the directional effect of the H-bonding interactions is that each organic chain has the (*R*)- α -methylbenzylammonium cations arranged radially around it with the ammonium heads pointing inwards to engage in N–H $\cdots$ Cl hydrogen bonding interactions, as shown in Figure 4. Due to the hydrogen bonds, the Co–Cl bond lengths increase, resulting in slightly deformed CoCl₄ tetrahedra. Moreover, it is worthwhile to mention that within the organic section, the protonated amines are linked together through the aromatic-aromatic C–H $\cdots$ π interactions between the benzene rings in a perpendicular arrangement to form a T-shaped configuration [24]. Indeed, the centroid to centroid distance is of 4,940(1) Å which is close enough to enable a C(7)–H(7) $\cdots$ Cg interaction to occur with a distance of 2.755(1) Å from C7. Hence, both C/N–H $\cdots$ Cl and C–H $\cdots$ π stacking interactions are the driving forces in generating a three-dimensional stable supramolecular network, as shown in Figure 5.

3.3. Thermal analyses

The simultaneous (TG-DTA) curves of **R(MBA)Co**, carried out with a heating rate of 5 °C/min from 25 to 600 °C, are depicted in Figure 6. Figure 7 shows the successive powder patterns obtained during the thermal decomposition. According to the TG curve, this compound seems to be stable up to about 200 °C; however, the TDA curve depicts a strong endothermic peak at 130 °C which is assigned to a phase transition confirmed by the significant modification of the powder patterns shown on the TDXD plot at ~ 130 °C. The only weight loss observed between 200 and 350 °C, is due to the loss of the organic moiety, Cl₂ molecule and the free Cl[–] anion, thus leading to the formation of CoCl₂ moiety. While the experimental weight loss as observed in the TG curve is 78.26%, the theoretical weight loss as the suggested pattern is 79.25%. This decomposition process is accompanied by two endothermic peaks on the DTA curve at 262 and 273 °C. The final transformation corresponds to the formation of Cobalt oxide, Co₃O₄, which crystallises immediately after

CoCl₂ starts to decompose between 300 and 550 °C as shown on the TDXD plot (PDF N° 00-042-1467).

3.4. Catalytic properties

The acetalisation process is one of the most straightforward strategies for protecting carbonyl groups [25]. Proof of that is the huge amount of bibliography treating this organic process [26-33], which in spite of their wide development still presents some disadvantages. Therefore, the design of new effective and simple catalyst is of interest in this area of research as demonstrated by the recent publications [34-37]. It is worth mention that despite the great number of reports concerning this synthetic protocol, to the best of our knowledge the use of Co-based catalysts to perform this reaction has been almost disregarded in the literature so far [38,39]. Hence, the development of new Co catalysed examples using mild reaction conditions is still interesting in this field.

As a part of our ongoing project to discover new catalysts and based on our previous experience in the acetalisation reaction [40,41], we explored the effectiveness of **R(MBA)Co** in this model process.

The catalytic activity of **R(MBA)Co** was initially tested in the acetalisation reaction described in Table 6 between aldehyde **1a** and MeOH as the unique source of acetalisation, and in sharp contrast with the commonly used CH(OMe)₃.

Based on the results reported in Table 6, the best values were achieved at 40 °C, using only 4 mol% of catalyst and 0.25 mL of MeOH (entry 5). Interestingly, the reaction also worked with only 2 mol% (entry 1) although with lower yield. The dilution (entry 4) or the concentration (entry 6) of the reaction mixture had a slight negative effect over the reactivity of the process. It is interesting that the reaction worked well using MeOH as solvent and as the unique source of acetalisation without the necessity of an additional source. Moreover, the

use of MeOH as a source of acetalisation, in the absence of the commonly used trimethyl orthoformate, is highly desirable due to its major availability.

With the best reaction conditions in hand, different substituted aldehydes **1** were explored in order to show the scope of our reaction (Table 7).

The reaction crudes are very clean and the desired products **2** are obtained in all cases from moderate to excellent yields. Therefore, this straightforward method was successfully applied to all aldehydes examined **1a–l**. It is remarkable that no special conditions to carry out the reactions were needed, such as inert atmosphere or dry conditions. Interestingly, the process does not have background since the reactions did not work in the absence of catalyst, which support the role played by our catalyst promoting the process. In general, it seems that the activated aldehydes, bearing electron-withdrawing groups in their structure, afforded better yields in comparison with non-activated ones (compare entries 1-5 with entries 6-8). The protocol also worked with aliphatic aldehydes, although in the case of aldehyde **1l** the steric effect could be the responsible of the lowest reactivity observed in comparison with **1j** and **1k**. The mechanism of this process could be envisioned as that proposed previously by us [40,41], where the Cobalt would act as a Lewis acid promoting the activation of the carbonyl group. Interestingly, during the exploration of the screening of the reaction (Table 6) we observed by NMR the hemiacetal intermediate of this process (<5%), which supports our mechanism. It is also expected that in the course of the reaction the intermediate was consumed giving rise to the final acetal **2**.

4. Conclusions

In summary, promising non-centrosymmetric optical single crystals of $[R-(C_8H_{12}N)_3][CoCl_4]Cl$ have been successfully synthesized and structurally characterized. Crystallographic studies have illustrated that the studied compound crystallizes in the chiral

non-centrosymmetric space group $P2_1$, confirmed by the absolute structure parameter. Despite the 0-inorganic backbone dimensionality, this hybrid material exhibits a layered inorganic-organic structure stabilized and governed significantly through extensive C/N–H $\cdots$ Cl hydrogen bonding between the inorganic and organic moieties and C–H $\cdots$ π interactions between the aromatic rings of the amine molecules themselves. Furthermore, thermal analyses reveal that the title compound undergoes one phase transition around 130 °C, confirmed by the three-dimensional representation of the powder diffraction patterns (TDXD). Moreover, we disclosed the study of **R(MBA)Co** complex as catalyst in the acetalisation reaction of different aldehydes under very mild conditions in the presence of MeOH, as the solvent of the process and, more interesting, as the unique source of acetalisation.

Supplementary materials

Crystallographic data (excluding structure factors) for the structure reported in this article have been deposited with the Cambridge Crystallographic Data Center as supplementary publication No CCDC-1478232 via www.ccdc.cam.ac.uk/data_request/cif.

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Table 1. Assignments of the Bands of the Infrared Absorption Spectrum for [R-(C₈H₁₂N)₃][CoCl₄]Cl

[R-(C ₈ H ₁₂ N) ₃][CoCl ₄]Cl	vibrational mode assignement
691.11	C–H out of plane deformation mode
761.11	
917	CH ₂ rocking mode
975	C–C stretching mode
1096	in plan C–H deformation mode
1166	
1228	CH ₃ deformation mode
1350	NH ₃ ⁺ rocking mode

1375	CH ₃ symmetric deformation mode
1455	C–C ring stretching
1507	
1612	NH ₃ ⁺ symmetric bending mode
2923	antisymmetric CH ₂ stretch
3040	aromatic CH
3417	

Table 2. Crystal data and structure refinement details for [R-(C₈H₁₂N)₃][CoCl₄]Cl

Chemical formula	[R-(C ₈ H ₁₂ N) ₃][CoCl ₄]Cl
Compound weight (g mol ⁻¹)	602.74
Temperature (K)	100 (2)
Crystal system	Monoclinic
Space group	P2 ₁
a(Å)	13.9553(4)
b (Å)	7.5120(2)
c (Å)	14.4210(4)
β (°)	98.4830(10)
V (Å ³)	1495.25(7)
Z	2
ρ _{cal} (g cm ⁻³)	1.339
Crystal dimension, mm ³	0.37×0.3×0.25
Habit- colour	Prismatic blue
μ (mm ⁻¹)	1.04
θ range (deg)	θ _{min} = 2.9 θ _{max} = 27.5
index ranges	-18 ≤ h ≤ 17 -9 ≤ k ≤ 9 -18 ≤ l ≤ 18
Unique data	5905
Observed data [I > 2σ(I)]	4979
F(000)	626
R ₁	0.041
wR ₂	0.132
GooF	0.91
No. param	299
Transmission factors	T _{min} = 0.688, T _{max} = 0.995
Largest difference map hole (e Å ⁻³)	Δρ _{min} = -0.63 Δρ _{max} = 0.53

Table 3. Selected bond distances (Å) and angles (°) for [R-(C₈H₁₂N)₃][CoCl₄]Cl

<i>Within the [CoCl₄]²⁻ tetrahedra</i>		<i>Within the (C₈H₁₂N)⁺ cation</i>	
Co—Cl1	2.2559 (8)	N2—C10	1.491 (6)
Co—Cl3	2.2694 (10)	N1—C2	1.508 (5)
Co—Cl2	2.2923 (10)	N3—C18	1.513 (5)
Co—Cl4	2.2929 (12)	C3—C8	1.389 (6)
Cl1—Co—Cl3	110.90 (5)	C3—C4	1.392 (6)

Cl1—Co—Cl2	106.22 (5)	C3—C2	1.500 (6)
Cl3—Co—Cl2	111.14 (4)	C10—C11	1.508 (5)
Cl1—Co—Cl4	112.55 (5)	C10—C9	1.523 (5)
Cl3—Co—Cl4	109.96 (4)	C19—C20	1.383 (7)
Cl2—Co—Cl4	105.92 (4)	C19—C24	1.397 (6)
		C19—C18	1.508 (6)
		C11—C12	1.384 (7)
		C11—C16	1.384 (7)
		C2—C1	1.513 (7)
		C4—C5	1.385 (7)
		C24—C23	1.391 (7)
		C6—C5	1.371 (7)
		C6—C7	1.384 (7)
		C12—C13	1.415 (7)
		C23—C22	1.378 (7)
		C22—C21	1.374 (7)
		C13—C14	1.364 (9)
		C15—C14	1.379 (10)
		C16—C15	1.391 (7)
		C20—C21	1.386 (7)
		C18—C17	1.520 (7)
		C8—C7	1.396 (7)
		C8—C3—C4	117.9 (4)
		C8—C3—C2	121.6 (4)
		C23—C24—C19	119.8 (4)
		C5—C6—C7	119.9 (5)
		C11—C12—C13	118.9 (5)
		C22—C23—C24	121.2 (4)
		C21—C22—C23	118.7 (5)
		C4—C3—C2	120.6 (4)
		N2—C10—C11	112.0 (4)
		N2—C10—C9	108.0 (3)
		C11—C10—C9	112.9 (3)
		C6—C7—C8	120.1 (4)
		C6—C5—C4	120.0 (4)
		C20—C19—C24	118.6 (4)
		C20—C19—C18	120.8 (4)
		C24—C19—C18	120.6 (4)
		C12—C11—C16	119.7 (4)
		C12—C11—C10	122.9 (4)
		C16—C11—C10	117.3 (4)
		C3—C2—N1	109.5 (4)
		C3—C2—C1	113.8 (3)
		N1—C2—C1	108.2 (3)
		C6—C5—C4	120.0 (4)
		C5—C4—C3	121.6 (4)
		C19—C18—N3	109.7 (3)

C19—C18—C17	114.0 (4)
N3—C18—C17	108.8 (4)
C14—C13—C12	121.0 (6)
C19—C20—C21	120.6 (4)
C11—C16—C15	120.5 (6)
C14—C15—C16	120.1 (6)
C22—C21—C20	121.1 (5)
C3—C8—C7	120.6 (4)
C13—C14—C15	119.7 (4)

Table 4. Hydrogen-bonding geometry (Å, °) for [R-(C₈H₁₂N)₃][CoCl₄]Cl

D—H···A (Å)	d (D—H) (Å)	d (H···A) (Å)	d (D···A) (Å)	D—H···A (°)
N2—HN2B···Cl5 ⁱ	0.89	2.30	3.096 (3)	149
N2—HN2A···Cl5	0.89	2.26	3.131 (4)	167
N2—HN2C···Cl4 ⁱⁱ	0.89	2.30	3.176 (3)	168
N1—HN1A···Cl4 ⁱⁱⁱ	0.89	2.47	3.299 (4)	155
N1—HN1B···Cl5	0.89	2.36	3.195 (4)	156
N1—HN1C···Cl2 ^{iv}	0.89	2.39	3.234 (4)	160
N3—HN3A···Cl4 ⁱⁱ	0.89	2.45	3.270 (4)	154
N3—HN3B···Cl2 ^v	0.89	2.32	3.183 (3)	162
N3—HN3C···Cl3	0.89	2.56	3.319 (4)	144
N3—HN3C···Cl1	0.89	2.71	3.319 (4)	126
C10—H10···Cl1	0.98	2.97	3.815 (4)	145
C1—H1B···Cl2 ⁱⁱⁱ	0.96	2.80	3.741 (5)	168
N2—HN2B···Cl5 ⁱ	0.89	2.30	3.096 (3)	149
N2—HN2A···Cl5	0.89	2.26	3.131 (4)	167
N2—HN2C···Cl4 ⁱⁱ	0.89	2.30	3.176 (3)	168
N1—HN1A···Cl4 ⁱⁱⁱ	0.89	2.47	3.299 (4)	155
N1—HN1B···Cl5	0.89	2.36	3.195 (4)	156
N1—HN1C···Cl2 ^{iv}	0.89	2.39	3.234 (4)	160
N3—HN3A···Cl4 ⁱⁱ	0.89	2.45	3.270 (4)	154
N3—HN3B···Cl2 ^v	0.89	2.32	3.183 (3)	162
N3—HN3C···Cl3	0.89	2.56	3.319 (4)	144
N3—HN3C···Cl1	0.89	2.71	3.319 (4)	126
C1—H1B···Cl2 ⁱⁱⁱ	0.96	2.80	3.741 (5)	168
N1—HN1B···Cl5	0.89	2.36	3.195 (4)	156
N1—HN1C···Cl2 ^{iv}	0.89	2.39	3.234 (4)	160
N3—HN3A···Cl4 ⁱⁱ	0.89	2.45	3.270 (4)	154
N3—HN3B···Cl2 ^v	0.89	2.32	3.183 (3)	162
N3—HN3C···Cl3	0.89	2.56	3.319 (4)	144
N3—HN3C···Cl1	0.89	2.71	3.319 (4)	126
C1—H1B···Cl2 ⁱⁱⁱ	0.96	2.80	3.741 (5)	168

Symmetry codes: (i) $-x+2, y+1/2, -z+2$; (ii) $x, y-1, z$; (iii) $-x+2, y-3/2, -z+2$; (iv) $-x+2, y-1/2, -z+2$; (v) $-x+1, y-1/2, -z+2$.

Table 5. Details of C–H...Cg interactions for R(MBA)Co

D–H...Cg	D–H (Å)	H...Cg (Å)	Cg...Cg (Å)	∠ D–H...Cg (°)	Symmetry transformations
C7–H7...Cg1	0.93(1)	2.755(1)	4.9409(1)	154.819(3)	-1+x, y, z
C14–H14...Cg2	0.93(1)	3.5483(1)	5.015(1)	119.296(2)	1-x, 1/2+y, 1-z

Table 6. Screening of the acetalisation reaction using R(MBA)Co as catalyst.

Entry	R(MBA)Co (mol %)	MeOH (mL)	Temp (°C)	Yield (%) ^a
1	2	0.25 mL	r.t.	60
2	4	0.25 mL	r.t.	72
3	6	0.25 mL	r.t.	64
4	4	0.50 mL	r.t.	62
5	4	0.25 mL	40	89
6	4	0.10 mL	40	77

^a Yields of **2a** [42] determined by ¹H-NMR spectroscopy.

Table 7. Scope of the acetalisation reaction using R(MBA)Co as catalyst.

Entry	R	Product	Yield (%) ^a
1	4-ClPh, 1b	2b [43]	87
2	3-ClPh, 1c	2c [43]	80
3	4-BrPh, 1d	2d [43]	80
4	4-NO ₂ Ph, 1e	2e [43]	82
5	4-CNPh, 1f	2f [44]	92
6	4-PhPh, 1g	2g [45]	49
7	Ph, 1h	2h [43]	55
8	1-Naphthyl, 1i	2i [43]	70
9	PhCH ₂ CH ₂ , 1j	2j [43]	>95
10	CH(CH ₃)CH ₂ CH ₂ , 1k	2k [46]	>95
11	<i>t</i> Bu, 1l	2l [47]	75

^a Yields determined by ¹H-NMR spectroscopy.

Figures

Fig.1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Figures captions

Figure 1: The infrared absorption spectra of **R(MBA)Co**, dispersed in a KBr pellet.

Figure 2: A view of the asymmetric unit cell of **R(MBA)Co**. Displacement ellipsoids for non-H atoms are presented at the 50 % probability level.

Figure 3: Packing diagram of **R(MBA)Co**, showing the lamellar character and the stacking along the *c* axis.

Figure 4: Packing diagram view along the *b* axis, showing hydrogen bonding interactions between the chloride atoms and the hydrogen atoms on the organic cation in **R(MBA)Co**.

Figure 5: Crystal packing arrangement showing the C/N–H···Cl hydrogen bonding between the inorganic and organic moieties (dashed purple lines) and the C...H– π interaction between the cations (dashed blue lines)

Figure 6: Simultaneous TG-DTA curves for the decomposition of **R(MBA)Co**, under flowing nitrogen (5 °C/min from 25 to 600 °C).

Figure 7: TDXD plot for the decomposition of **R(MBA)Co** in air (7 °C h⁻¹ from 20 to 600 °C).