

Pyridine-Type Complexes of Transition-Metal Halides VI.[†] Preparation and Characterization of 2,6- and 3,5-Dimethylpyridine Complexes of Cobalt(II) Halides; the Crystal Structure of Di(2,6-dimethylpyridinium) Tetrachlorocobaltate(II) and Dichlorotetrakis(3,5-dimethyl- pyridine)cobalt(II)[§]

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(C₇H₁₀N)₂[CoCl₄] (**1**), Co(C₇H₉N)₄Cl₂ (**2**), Co(C₇H₉N)₄Br₂ (**3**) and Co(C₇H₉N)₄I₂ (**4**) complexes have been studied by means of thermal analysis, IR and FIR spectroscopy, and X-ray crystallography. Crystal structures for compounds **1** and **2** have been determined. They crystallize in orthorhombic space groups with cell dimensions of $a = 16.744(3)$, $b = 8.832(2)$ and $c = 13.263(3)$ Å; $a = 11.662(3)$, $b = 11.664(3)$ and $c = 10.608(3)$ Å; space groups *Pbcn* and *Pnnn*; $Z = 4$ and 2 , and R -values 4.31 and 5.91% for 1256 and 931 observed reflections for **1** and **2**, respectively. In **1** the structure consists of a tetrachlorocobaltate anion and a dimethylpyridinium cation connected by a weak N–H···Cl hydrogen bond with a N···Cl distance of $3.165(5)$ Å. The chloride ions are tetrahedrally coordinated to the cobalt ion, with two pairs of symmetry related distances of $2.259(1)$ and $2.275(1)$ Å. In **2** 3,5-dimethylpyridine is coordinated to Co and the structure is pseudo-tetragonal. Four nitrogen atoms at distances of $2.186(4)$ Å form the basal plane, and two chloride ions at the apexes with distances of $2.455(2)$ Å complete the elongated octahedral coordination around Co. Cell dimensions for **3** and **4** determined by powder diffraction are $a = b = 11.863(1)$ and $12.1327(6)$ Å; $c = 10.338(2)$ and $10.608(3)$ Å, respectively. Co–Br and Co–I distances according to Rietveld refinement are 2.63 and 2.88 Å, respectively.

The structures have also been studied by FTIR. Vibrations in FIR spectra show the difference in coordination in structures **1** and **2**. The thermal stability of the complexes in a nitrogen atmosphere has also been studied.

Since the 1960s many papers have been published in the field of transition-metal pyridine and substituted pyridine complexes.^{1–9} The most extensively studied complexes are the cobalt(II) halides and pseudo halides.^{10–16} The structure and geometry of these complexes are described

on the basis of their electronic and/or infrared spectra and magnetic moments.^{2,8–10,12,14,17,18} Very few papers have been published on the crystal structures of these compounds.^{19–28}

Transition metals with d^7 electronic configurations are known to favour octahedral and tetrahedral coordination. The formation of [CoL₄X₂][–] and [CoL₂X₂]-type compounds, where L is a sterically non-hindered ligand and X is a halide or pseudo-halide anion, was found to depend mainly on the basicity of the anion.¹² On the basis of the splitting of the absorption band ${}^4T_{1g} \rightarrow {}^4T_{2g}(F)$,

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[CoL₄X₂]-type complexes, e.g. [Co(3,5-dimethylpyridine)₄Cl₂] (**2**), were expected to have a tetragonally distorted D_{4h} environment around the cobalt(II) atom.²⁹

Mono-hindered ligands, e.g. 2-methylpyridine, tend to form compounds with a general formula of [CoL₂X₂], because of the steric repulsion between the substituent in the second position of the pyridine ring and the neighbouring anion.⁵

Relatively few papers have been published concerning the formation and properties of cobalt(II) halide and pseudo-halide complexes with doubly hindered ligands, e.g. 2,6-dimethylpyridine, which is also called 2,6-lutidine. Allan and his co-workers reported on [CoLX₂], where X is chloride or bromide, and [CoL₄I₂], where L is 2,6-lutidine.^{30,31} The existence of the latter tetrakis derivative is surprising for a doubly hindered ligand, because mono-hindered ligands form only bis-complexes with cobalt. In their excellent work, Darby and Vallarino carried out a systematic study on mono-, di- and trimethylpyridine complexes of cobalt(II) halides and thiocyanate.²⁹ In the description of the preparative work, they reported that the common procedure, i.e. the simple reaction between the metal salt and the ligand in solution, leads to a mixture of [CoX₄]²⁻ and [CoLX₃]⁻ ions in the solution and to (LH⁺)[CoLX₃]⁻ crystalline salts in the case of 2,6-lutidine and chloride and bromide. However, a (LH⁺)₂[CoX₄]²⁻ solid product was identified with iodide. This tetraiodocobaltate(II) salt was found to be stable only as a crystalline phase and in the presence of an excess of the ligand.

In this paper we report on the preparation, thermal and spectroscopic properties and crystal structures of di(2,6-dimethylpyridinium) tetrachlorocobaltate(II), as a unique example of the structure of a doubly hindered pyridine salt, and dichlorotetrakis(3,5-dimethylpyridine)cobalt(II), as a complex formed with a non-hindered ligand, to study the earlier expected tetragonal distortion of the octahedron around the central cobalt(II) atom.

On the basis of the structure of **2**, the cobalt-halogen distances were calculated from powder patterns for dibromotetrakis-(3,5-dimethylpyridine)cobalt(II) (**3**) and diiodotetrakis-(3,5-dimethylpyridine)cobalt(II) (**4**).

Experimental

Preparation. In the preparation of cobalt(II) halide hexahydrates, cobalt(II) carbonate and hydrogen bromide, hydrogen chloride and hydrogen iodide (Reanal p.a.) solutions were used. The cobalt(II) bromide and iodide hexahydrate were precipitated by suspending 0.012 mol of cobalt(II) carbonate in water, and 0.02 mol of the appropriate hydrogen halide solution was slowly added throughout intensive stirring. A small excess of the cobalt(II) carbonate was used in order to avoid detrimental acidity in the product. The remaining solid was separated in a centrifuge. The solution was filtered off, and the hexahydrates were crystallized on a water bath.

Crystals formed were collected on a glass filter and dehydrated in a drying oven.

Anhydrous cobalt(II) halides (0.005 mol) were dissolved in 20 ml of acetonitrile (Reanal p.a.). The solvent was purified previously by distillation over phosphorus pentoxide. The ligands (2,6- and 3,5-dimethylpyridine, Jansen Chimica p.a.) were dried over potassium hydroxide, and 0.05 mol of them was blended with 20 ml of acetonitrile. The dissolved dimethylpyridines (lutidines) were added to the cobalt(II) halide solutions from a dropping funnel. The mixtures were heated, kept at their boiling point for 1 h and cooled slowly. Crystals formed were collected on a glass filter and washed with a small amount of cool solvent. Products were dried over calcium chloride in a desiccator.

Analysis. The cobalt(II) content was determined by means of complexometric titration;³² carbon, hydrogen and nitrogen contents were determined by a Carlo Erba 1108 elemental analyzer obtaining the following results. Found: Co 14.15; Cl 37.56; H 4.43; C 37.19; N 6.67. Calc. for C₁₄H₂₀Cl₄CoN₂: Co 14.13; Cl 34.00; H 4.83; C 40.32; N 6.72. Found: Co 10.59; Cl 11.50; H 6.49; C 60.71; N 10.71. Calc. for C₂₈H₃₆Cl₂CoN₄: Co 10.55; Cl 12.70; H 6.50; C 60.22; N 10.03. Found: Co 10.59; Br 24.72; H, 6.49; C 60.71; N 10.71. Calc. for C₂₈H₃₆Br₂CoN₄: Co 10.55; Br 24.69; H 6.50; C 60.22; N 10.03. Found: Co 10.59; I 34.26; H 6.49; C 60.71; N 10.71. Calc. for C₂₈H₃₆I₂CoN₄: Co 10.55; I 34.24; H 6.50; C 60.22; N 10.03.

Results from thermogravimetric measurements (MOM OD-2 derivatograph; sample weight 100 mg, heating rate 5°C min⁻¹, atmosphere nitrogen, reference material 100 mg α-Al₂O₃) were used to check the stoichiometry.

IR spectra. Infrared spectra were recorded by a Digilab FTS spectrometer equipped with a 6 μm Hylar beam splitter. Samples were measured by using KBr pellets (4000–400 cm⁻¹) and Nujol mulls in polyethylene matrix (600–40 cm⁻¹).

UV/VIS spectroscopy. For di(2,6-dimethylpyridinium) tetrachlorocobaltate(II) (**1**) were collected UV/VIS spectra in the 200–2500 nm region. In order to avoid ligand-changing processes solid reflectance spectra were measured using a Beckman Acta MIV spectrophotometer and BaSO₄ as reference material.

Single-crystal X-ray structure determinations. Experimental details of crystal structure determinations including crystal data, data collection, structure determination and refinement for di(2,6-dimethylpyridinium) tetrachlorocobaltate(II) (C₇H₁₀N)₂[CoCl₄] (**1**) and dichlorotetrakis(3,5-dimethylpyridine)cobalt(II), [Co(C₇H₉N)₄Cl₂] (**2**) are listed in Table 1.

The crystals were sealed in a glass capillary. Unit-cell parameters were obtained by carefully centering 25 reflections with 20 > 2θ > 25° using Mo Kα (λ = 0.71069 Å)

Table 1. Structure determination summary for (C₇H₁₀N)₂ [CoCl₄] (1) and [Co(C₇H₉N)₄Cl₂] (2).

Crystal data		
Compound	1	2
Empirical formula	C ₁₄ H ₂₀ Cl ₄ CoN ₂	C ₂₈ H ₃₆ Cl ₂ CoN ₄
Color; Habit	Blue; Bipyramidal	Violet; Bipyramidal
Crystal size (mm)	0.21 × 0.22 × 0.25	0.26 × 0.19 × 0.31
Crystal system	Orthorhombic	Orthorhombic
Space group	<i>Pbcn</i> (No. 60)	<i>Pnnn</i> (No. 48)
Unit-cell dimensions	<i>a</i> = 16.744(3) Å <i>b</i> = 8.832(2) Å <i>c</i> = 13.263(3) Å	<i>a</i> = 11.662(3) Å <i>b</i> = 11.664(3) Å <i>c</i> = 10.608(3) Å
Volume	1961.4(10) Å ³	1443.0(7) Å ³
<i>Z</i>	4	2
Formula weight	417.0	558.4
Density (calc.)	1.412 Mg m ⁻³	1.285 Mg m ⁻³
Absorption coefficient	1.414 mm ⁻¹	0.802 mm ⁻¹
<i>F</i> (000)	852	586
Data collection		
Diffractometer used	Nicolet P3	Nicolet P3
Radiation	Mo <i>K</i> α (<i>λ</i> = 0.710 69 Å)	Mo <i>K</i> α (<i>λ</i> = 0.710 69 Å)
Temperature (K)	293	293
Monochromator	Highly oriented graphite crystal	
2θ range/°	3.0–53.0	3.0–53.0
Scan type	ω	ω
Scan speed	Variable; 1.50–29.3° min ⁻¹ in ω	
Scan range, ω/°	1.0	1.0
Background measurement	Stationary crystal and stationary counter at the beginning and end of the scan, each for 25% of total scan time.	
Standard reflections	3 measured every 100 reflections	
Index ranges	0 ≤ <i>h</i> ≤ 20 0 ≤ <i>k</i> ≤ 11 0 ≤ <i>l</i> ≤ 16	0 ≤ <i>h</i> ≤ 14 0 ≤ <i>k</i> ≤ 14 0 ≤ <i>l</i> ≤ 13
Reflections collected	2038	1524
Independent reflections	2038	1524
Observed reflections	1256 [<i>I</i> > 2.0σ(<i>I</i>)]	931 [<i>I</i> > 3.0σ(<i>I</i>)]
Absorption correction	Empirical, ψ-rotation	Empirical, ψ-rotation
Solution and refinement		
System used	Siemens SHELXTL PLUS (PC version)	
Solution	Patterson method	Direct methods
Refinement method	Full-matrix least-squares	Full-matrix least-squares
Quantity minimized	Σ <i>w</i> (<i>F</i> _o - <i>F</i> _c) ²	Σ <i>w</i> (<i>F</i> _o - <i>F</i> _c) ²
Hydrogen atoms	Riding model, fixed isotropic <i>U</i>	
Weighting scheme	<i>w</i> ⁻¹ = σ ² (<i>F</i>) + 0.0003 <i>F</i> ²	<i>w</i> ⁻¹ = σ ² (<i>F</i>) + 0.0001 <i>F</i> ²
No. of parameters refined	97	85
Formula of <i>R</i>	<i>R</i> = [Σ(<i>F</i> _o - <i>F</i> _c) / Σ <i>F</i> _o]	
Formula of weighted <i>R</i>	<i>wR</i> = [Σ <i>w</i> (<i>F</i> _o - <i>F</i> _c) ² / Σ <i>wF</i> _o ²] ^{1/2}	
Final <i>R</i> indices (obs. data)	<i>R</i> = 4.31%, <i>wR</i> = 4.57%	<i>R</i> = 5.91%, <i>wR</i> = 7.88%
Goodness-of-fit	1.43	4.36
Largest and mean Δ/σ	0.098, 0.010	0.052, 0.006
Data-to-parameter ratio	12.9:1	11.0:1
Largest difference peak/e Å ⁻³	0.31	1.50
Largest difference hole/e Å ⁻³	-0.29	-0.86

radiation. The data were corrected for Lorentz and polarization factors and for absorption empirically using a ψ-rotation method. An isotropic extinction correction was also applied, but the value for the parameter was neglectable for both compounds and was thus omitted. Structure determinations and refinements were carried out using a SHELXTL PLUS (PC version) program package.³³ Atomic scattering factors used were those included in the program package.

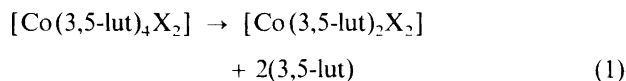
Powder diffraction. X-ray powder diffraction data of [Co(C₇H₉N)₄X₂], X = Br (3) and X = I (4) were collected at 25°C with a STOE Stadi/P powder diffractometer, using a sample mounted in a 0.5 mm rotating capillary. A symmetric focussing germanium monochromator (focal distance = 440 mm) was used to give Cu *K*α₁ radiation (*λ* = 1.5405 Å). The diffraction data were collected with a small linear position-sensitive detector (PSD) covering 7.4° in 2θ. The PSD was moved in steps of 0.2°, thus

giving an average intensity of measurements at each 2θ position. In addition, Guinier–Hägg data (Cu $K\alpha_1$) with silicon ($a = 5.430880 \text{ \AA}$) as internal standard were also collected and used for refinement of unit cell dimensions.

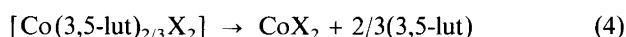
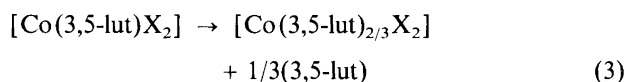
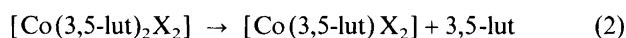
Results and discussion

Thermal analysis. The thermal decomposition pattern of the di(2,6-dimethylpyridinium) tetrachlorocobaltate(II) complex (Fig. 1) is build up from several steps; however, no intermediates corresponding to the stoichiometric composition could be identified. We suggest that in the first decomposition step 2 mol of hydrogen chloride are released, and in the following overlapping processes the remaining compound decomposes to cobalt(II) chloride. The decomposition pathway is accompanied with exothermic enthalpy effects.

The thermal decomposition of the tetrakis-3,5-dimethylpyridine complexes starts with the releasing of two ligand molecules (Fig. 2):



Afterwards the bis-intermediate phases lose one and one-third of a ligand, resulting in a mono-complex and an intermediate containing two-thirds of a mole of the ligand:



A similar decomposition pathway has been observed in the case of methylpyridine complexes.^{5,16,30} The following percentage TG weight losses were: found: 68.52, 76.63,

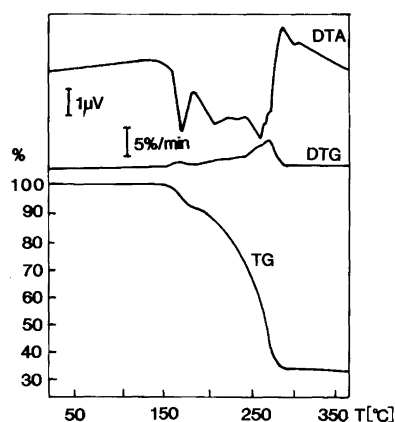


Fig. 1. Thermal decomposition of di(2,6-dimethylpyridinium) tetrachlorocobaltate(II) (1).

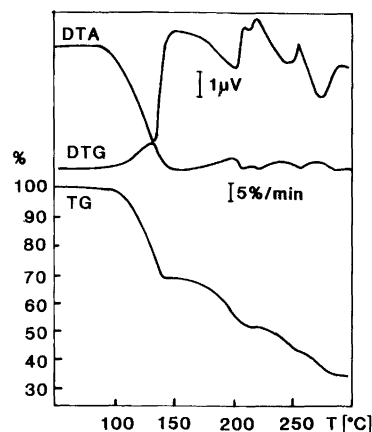


Fig. 2. Thermal decomposition of dichlorotetrakis(3,5-dimethylpyridine)cobalt(II) (2).

66.09 and 57.69; calc. 68.87, 76.70, 66.21 and 57.82 for 1–4, respectively.

IR spectroscopy. The protonation of the nitrogen atom in the lutidine ring is apparent from the IR spectra (Table 2) for compound 1. The $\nu_{\text{as}}(\text{NH})$ and $\nu_{\text{s}}(\text{NH})$ bands appear at 3285 and 3196 cm^{-1} , respectively.³⁴ In the 2900–1600 cm^{-1} region some new additional vibrations occur owing to the complexation. These bands have rather small intensities. In the spectra of the 3,5-lutidine complex the $\nu_{\text{s}}(\text{CH}_3)$ band disappeared and the wavenumber of the $\nu_{\text{as}}(\text{CH}_3)$ vibration is decreased on going from the chloride to iodide analogues, indicating a possible effect of the anion. The observed $\nu_{21}(\text{b}_2)$ bands decrease in the same order.

The far-infrared spectrum (Table 2) of the di(2,6-dimethylpyridinium) tetrachlorocobaltate(II) complex contains some weak Co–Cl vibrations due to the coordination, which have not been reported before. Four main cobalt–halogen bands were observed; however, the triply (F_2) and doubly (E) degenerate vibrations split into three and two bands, respectively. These facts indicate that in the inner coordination sphere there are only chloride ions, and the structure is slightly distorted from T_d symmetry owing to the C_{2v} point group.

The far-infrared spectra of the 3,5-dimethylpyridine complexes also contain some vibrations which have not been reported before. They also occur as a result of the formation of the coordination compound. Bands in the far-infrared region can be assigned on the assumption of D_{4h} symmetry; however, some vibrations were registered at low wavenumbers which can be assigned as lattice modes. The observed results are in good agreement with the earlier work of Darby and Vallarino,²⁹ although the bands under 200 cm^{-1} are described for the first time in the present work.

UV/VIS spectroscopy. In the spectrum of di(2,6-dimethylpyridinium) tetrachlorocobaltate(II) (1) two main

Table 2. Infrared spectra of the complexes (cm^{-1}).

No	2,6-lut	(2,6-lut) ₂ [CoCl ₄]	3,5-lut	[Co(3,5-lut) ₄ Cl ₂]	[Co(3,5-lut) ₄ Br ₂]	[Co(3,5-lut) ₄ I ₂]	Assignment
1	—	3285 m	—	—	—	—	$\nu_{\text{as}}(\text{NH})$
2	—	3196 m	—	—	—	—	$\nu_{\text{s}}(\text{NH})$
3	3064 m	3075 s	3047 m	3074 m	3074 m	3065 m	$\nu_1(a_1)$
4	3018 s	3032 s	3029 s	3012 m	—	3010 s	$\nu_{19}(b_2)$
5	2985 m	2980 vs	2985 m	2947 s	2943 m	2933 m	$\nu_{\text{as}}(\text{CH}_3)$
	2957 m	2934 vs	2971 m	—	—	—	$\nu_{\text{s}}(\text{CH}_3)$
6	1920 m	2906 vs	2930 m	2911 s	2911 m	2909 m	
	—	—	—	2864 s	2862 m	2857 m	
	—	2849 w	—	2835 m	—	—	
	—	2774 w	—	2744 m	2742 m	2737 m	
	—	2631 vw	—	2631 w	2631 w	2628 w	
	—	—	—	2493 vw	2495 w	2496 vw	$2 \times \nu_{23}(b_2)$
	—	2363 vw	—	2364 vw	2363 vw	2365 vw	$2 \times \nu_{24}(b_2)$
	—	2339 vw	—	2338 vw	2338 vw	2339 vw	
	—	—	—	2103 vw	—	2100 vw	
7	1600 s	—	1591 s	1598 s	1598 s	1596 s	$\nu_3(a_1)$
8	1578 s	—	1581 m	—	1577 w	—	$\nu_{20}(b_2)$
9	1470 s	1472 w	1426 vs	1445 s	1437 s	1429 s	$\nu_{21}(b_2)$
10	1451 vs	1440 w	1463 s	1458 s	1459 s	1459 s	$\delta_{\text{as}}(\text{CH}_3)$
11	1411 m	1401 w	1463 s	1458 s	1459 s	1459 s	$\nu_4(a_1)$
12	1369 m	1379 w	1380 m	1384 w	1382 w	1382 w	$\delta_{\text{s}}(\text{CH}_3)$
13	1326 vw	—	1320 vw	1321 vw	1322 vw	1324 vw	$\nu_{22}(b_2)$
14	1222 vw	—	1232 w	1246 w	1247 w	1246 w	$\nu_{23}(b_2)$
15	1153 m	1180 w	1164 s	1179 m	1179 m	1178 m	$\nu_{24}(b_2)$
16	1094 w	—	1139 m	1153 vs	1153 vs	1151 vs	$\nu_6(a_1)$
17	1028 m	1042 m	1043 m	1034 m	1035 m	1034 m	CH_3 rock.
	969 w	986 vw	—	—	—	—	3
18	905 m	905 m	929 vw	—	—	—	$\nu_{14}(b_1)$
19	888 w	—	1011 m	1120 m	—	—	$\nu_{25}(b_2)$
20	772 s	796 vs	857 vs	866 s	866 s	867 s	$\nu_{15}(b_1)$
21	728 w	748 s	716 m	712 w	725 w	725 w	$\nu(a_1)$
22	719 s	—	710 m	703 vs	703 vs	703 vs	$\nu_{16}(b_1)$
23	554 w	559 m	538 m	534 m	536 m	537 m	$\nu_9(a_1)$
24	537 w	533 vw	532 m	534 m	536 m	537 m	$\nu_{26}(b_2)$
25	417 m	417 s	438 w	415 m	417 m	429 m	$\nu_{17}(b_1)$
26	—	309 vx	—	—	—	—	$\nu(\text{Co-Cl})(b_2)$
27	—	300 vs	—	—	—	—	$\nu(\text{Co-Cl})(b_1)$
28	—	278 vx	—	—	—	—	$\nu(\text{Co-Cl})(a_1)$
29	289 w	289 sh	274 w	286 w	287 w	284 w	$\nu_{10}(a_1)$
30	—	217 w	—	—	—	—	$\nu(\text{Co-Cl})(a_1)$
31	—	185 s	—	—	—	—	wagg. (Co-Cl)(b ₂)
32	—	143 sh	—	—	—	—	rock. (Co-Cl)(b ₂)
33	—	125 s	—	—	—	—	$\delta(\text{Cl-Co-Cl})(a_2)$
34	—	92 s	—	—	—	—	$\delta(\text{Cl-Co-Cl})(a_2)$
35	—	59 m	—	—	—	—	twist. (Cl-Co-Cl)(a ₂)
36	—	—	233 w	239 m	—	—	$\nu_{13}(a_2)$
37	—	—	—	206 vs	206 vs	206 vs	$\nu(\text{Co-N})$
38	—	—	—	211 sh	184 vs	181 vs	$\nu(\text{Co-X})$
39	—	—	—	178 sh	184 vs	181 vs	$\delta(\text{N-Co-N})$
40	—	—	—	143 s	137 s	122 m	$\delta(\text{N-Co-X})$
41	—	—	—	118 vs	100 m	90 m	$\delta(\text{X-Co-X})$
42	—	—	—	—	84 m	79 m	Lattice
43	—	—	—	65 m	66 m	59 m	Lattice
44	—	—	—	45 s	47 s	44 m	Lattice
45	—	—	—	—	—	—	Lattice

absorption bands were observed in addition to the charge-transfer band at 37736 cm^{-1} . In the $4500\text{--}6100 \text{ cm}^{-1}$ region the first band, assigned as ${}^4A_2(\text{F}) \rightarrow {}^4T_1(\text{F})$, was split into three bands at 4784, 5494 and 6097 cm^{-1} . The 4A_2 , 4B_2 and 4B_1 terms derived from the triply degenerated ${}^4T_1(\text{F})$ term subsequently indicate the C_{2v} symmetry. Splitting was also observed in the

other band [${}^4A_2(\text{F}) \rightarrow {}^4T_1(\text{P})$] having maxima at 14326 and 15625 cm^{-1} . This type of splitting has been observed in other $[\text{CoX}_4]^{2-}$ complexes as a result of the Jahn-Teller effect.³⁵ The observed wavenumbers are significantly different from those reported for the 2,6-dimethylpyridinium (2,6-dimethylpyridinetrichloro)cobaltate(II) $\{(\text{2,6-lutH})[\text{Co}(\text{2,6-lut})\text{Cl}_3]\}^{29}$ viz. 5050 and 6897 cm^{-1}

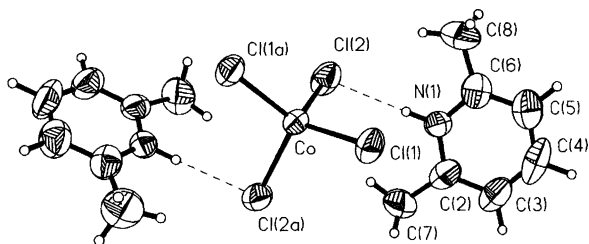


Fig. 3. The structure of bis(2,6-dimethylpyridinium) tetrachlorocobaltate(II) (**1**) showing atomic labelling and hydrogen bonding. Thermal displacement ellipsoids are drawn at the 50% level. For the symmetry code see Table 6.

for ${}^4A_2(F) \rightarrow {}^4T_1(F)$ and 15837 cm^{-1} for ${}^4A_2(F) \rightarrow {}^4T_1(P)$. The calculated crystal field strength ($10Dq = 3680\text{ cm}^{-1}$), Racah parameter ($B = 635\text{ cm}^{-1}$) and nephelauxetic parameter ($\beta = 0.66$) were obtained for **1** using the weighted average of the ${}^4A_2(F) \rightarrow {}^4T_1(F)$ ³⁶ and the average value of the ${}^4A_2(F) \rightarrow {}^4T_1(P)$ transitions. The values of the parameters are smaller than those observed for $[\text{Co}(\text{L})_2\text{X}_2]$ type compounds³⁷ and are close to those reported for $[\text{CoX}_4]^{2-}$ complexes.³⁸

Single-crystal X-ray structure. The structures, showing anisotropic thermal ellipsoids at the 50% probability level and atomic labelling for non-hydrogen atoms, are illustrated in Figs. 3 and 4 for **1** and **2**, respectively. Molecular packing is shown in Figs. 5 and 6 for **1** and **2**, respectively. All non-hydrogen atom positions are based on Fourier synthesis. For most of hydrogens in the atom positions were also found by the difference-Fourier method, but the positions were roughly close to the calculated positions where they were placed by a riding model. Non-hydrogen atom positions and anisotropic displacement parameters were refined using a full-matrix least-squares method. Atomic fractional coordinates and equivalent isotropic thermal parameters are listed in Tables 3 and 4 for **1** and **2**, respectively. Interatomic dis-

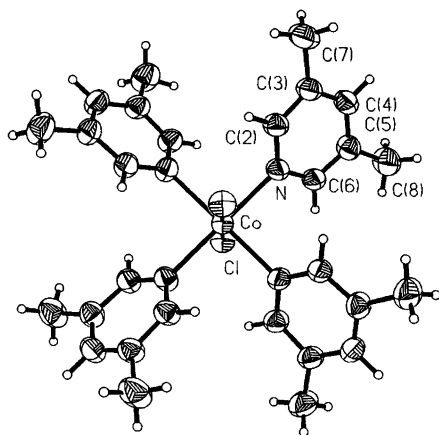


Fig. 4. Molecular packing of bis(2,6-dimethylpyridinium) tetrachlorocobaltate(II) (**1**).

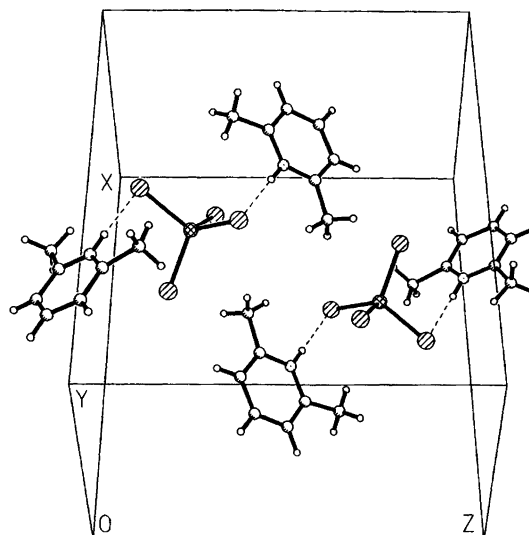


Fig. 5. The structure of dichlorotetrakis(3,5-dimethylpyridine)cobalt(II) (**2**) showing atomic labelling. Thermal displacement ellipsoids are drawn at 50% level. For the symmetry codes see Table 6.

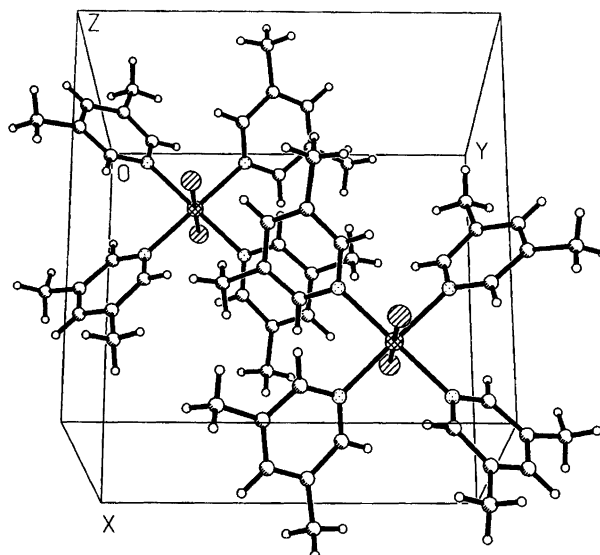


Fig. 6. Molecular packing of dichlorotetrakis(3,5-dimethylpyridine)cobalt(II) (**2**).

tances in Table 5 and angles between bonds in Table 6 are also presented for both **1** and **2**.*

In these two complexes of differently substituted dimethylpyridines (lutidines) with cobalt(II) chloride, two totally different coordination spheres were found. In **1** the steric hindrance of the methyl groups in 2 and 6 positions prevents nitrogen atom coordination to the cobalt ion. Additionally, being the strongest base among differently

* Lists of observed and calculated structure factors, anisotropic positional displacement parameters for non-hydrogen atoms and hydrogen atom coordinates are obtainable from one of the authors (J.K.).

Table 3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{\AA}^2 \times 10^3$) for $(\text{C}_7\text{H}_{10}\text{N})_2[\text{CoCl}_4]$ (**1**) with e.s.d.s in parentheses.

	x/a	y/b	z/c	U_{eq}^a
Co	0	2220(1)	2500	46(1)
Cl1	1045(1)	853(1)	1923(1)	63(1)
Cl2	433(1)	3738(2)	3774(1)	74(1)
N1	1230(2)	3480(4)	78(3)	53(1)
C2	1875(3)	4170(5)	471(3)	60(2)
C3	2586(3)	3961(7)	-26(4)	85(2)
C4	2594(4)	3092(7)	-891(5)	96(2)
C5	1928(4)	2420(6)	-1251(4)	86(2)
C6	1230(3)	2615(5)	-759(4)	66(2)
C7	1761(3)	5105(7)	1386(4)	91(2)
C8	451(3)	1926(7)	-1050(4)	100(2)

^a Equivalent isotropic U is of the form $U_{\text{eq}} = 1/3(\sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j)$.

Table 4. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{\AA}^2 \times 10^3$) for $[\text{Co}(\text{C}_7\text{H}_9\text{N})_4\text{Cl}_2]$ (**2**) with e.s.d.s in parentheses.

	x/a	y/b	z/c	U_{eq}^a
Co	2500	2500	2500	42(1)
Cl	2500	2500	4814(2)	52(1)
N1	3833(3)	3818(4)	2504(5)	46(1)
C2	4733(4)	3767(5)	1732(5)	47(2)
C6	3762(4)	4739(5)	3265(5)	49(2)
C3	5606(4)	4567(5)	1711(5)	50(2)
C5	4569(5)	5608(5)	3291(5)	50(2)
C4	5505(4)	5504(5)	2500(7)	54(2)
C7	6617(5)	4424(6)	843(7)	73(2)
C8	4422(6)	6612(5)	4157(7)	72(2)

^a Equivalent isotropic U is of the form $U_{\text{eq}} = 1/3(\sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j)$.

Table 5. Bond lengths (in \AA) for $(\text{C}_7\text{H}_{10}\text{N})_2[\text{CoCl}_4]$ (**1**) and $[\text{Co}(\text{C}_7\text{H}_9\text{N})_4\text{Cl}_2]$ (**2**) with e.s.d.s in parentheses.

$(\text{C}_7\text{H}_{10}\text{N})_2[\text{CoCl}_4]$		$[\text{Co}(\text{C}_7\text{H}_9\text{N})_4\text{Cl}_2]$	
Co–Cl1	2.259(1)	Co–Cl	2.455(2)
Co–Cl2	2.275(1)	Co–N1	2.186(4)
N1–C2	1.346(6)	N1–C2	1.333(7)
N1–C6	1.347(6)	N1–C6	1.345(7)
C2–C3	1.372(7)	C2–C3	1.381(7)
C2–C7	1.480(7)	C6–C5	1.384(8)
C3–C4	1.380(9)	C3–C4	1.381(8)
C4–C5	1.352(9)	C3–C7	1.505(9)
C5–C6	1.350(8)	C5–C4	1.382(8)
C6–C8	1.490(7)	C5–C8	1.499(9)

substituted lutidines, the nitrogen atom is protonated, and two of these lutidinium ions are hydrogen-bonded to chloride ions of a tetrachlorocobaltate(II) anion, with a $\text{Cl2}\cdots\text{H1}$ distance of 2.27(2) and a $\text{Cl2}\cdots\text{N1}$ distance of 3.182(5) \AA . A similar bonding feature between a substituted pyridinium ion and a tetrachloro transition-metal anion has been found in bis(2,6-diamino-3,5-dichloropyridinium) tetrachlorocuprate(II),³⁹ where the Cl–N distances are 3.077(5) and 3.125(5) \AA and in bis(2-amino-5-methylpyridinium) tetrachlorocuprate(II),⁴⁰ where the

Table 6. Bond angles (in $^\circ$) for $(\text{C}_7\text{H}_{10}\text{N})_2[\text{CoCl}_4]$ (**1**) and $[\text{Co}(\text{C}_7\text{H}_9\text{N})_4\text{Cl}_2]$ (**2**) with e.s.d.s in parentheses.

$(\text{C}_7\text{H}_{10}\text{N})_2[\text{CoCl}_4]^a$		$[\text{Co}(\text{C}_7\text{H}_9\text{N})_4\text{Cl}_2]^b$	
Cl1–Co–Cl2	108.6(1)	Cl–Co–N1	89.9(1)
Cl1–Co–Cl1(a)	115.4(1)	Cl–Co–Cl(a)	180.0(1)
Cl2–Co–Cl1(a)	108.1(1)	N1–Co–Cl(a)	90.1(1)
Cl1–Co–Cl2(a)	108.1(1)	Cl–Co–N1(a)	89.9(1)
Cl2–Co–Cl2(a)	107.8(1)	N1–Co–N1(a)	179.8(2)
Cl1(a)–Co–Cl2(a)	108.6(1)	Cl(a)–Co–N1(a)	90.1(1)
C2–N1–C6	125.1(4)	Cl–Co–N1(b)	90.1(1)
N1–C2–C3	116.7(4)	N1–Co–N1(b)	90.6(2)
N1–C2–C7	117.8(4)	Cl(a)–Co–N1(b)	89.9(1)
C3–C2–C7	125.5(4)	N1(a)–Co–N1(b)	89.4(2)
C2–C3–C4	118.9(5)	Cl–Co–N1(c)	90.1(1)
C3–C4–C5	122.0(6)	N1–Co–N1(c)	89.4(2)
C4–C5–C6	119.2(5)	Cl(a)–Co–N1(c)	89.9(1)
N1–C6–C5	118.1(5)	N1(a)–Co–N1(c)	90.6(2)
N1–C6–C8	116.4(4)	N1(b)–Co–N1(c)	179.8(2)
C5–C6–C8	125.5(5)	Co–N1–C2	121.8(4)
		Co–N1–C6	121.3(3)
		C2–N1–C6	116.9(4)
		N1–C2–C3	124.1(5)
		N1–C6–C5	123.7(5)
		C2–C3–C4	117.5(5)
		C2–C3–C7	120.8(5)
		C4–C3–C7	121.7(5)
		C6–C5–C4	117.4(5)
		C6–C5–C8	120.5(5)
		C4–C5–C8	122.1(5)
		C3–C4–C5	120.3(5)

^a Symmetry code refers to symmetry operation: (a) $-x, y, 1/2-z$. ^b Symmetry codes refer to symmetry operations: (a) $1/2-x, 1/2-y, z$, (b) $1/2-x, y, 1/2-z$ and (c) $x, 1/2-y, -1/2-z$.

Cl–N distance is 3.25(1) \AA . The interplanar angle between the dimethylpyridine rings in **1** is 107.95(3) $^\circ$.

Two pairs of different Co–Cl distances are observed in the tetrachlorocobaltate anion. The Co–Cl distances involving the hydrogen bonded chlorides are 0.014 \AA longer than those to the chlorides not participating in hydrogen bonding. The Cl–Co–Cl angles differ pairwise as well, the angles between non-hydrogen-bonded chlorines Cl1–Co–Cl1($-x, y, 1/2-z$) of 115.4(1) $^\circ$ being 7.6(1) $^\circ$ larger than the angle Cl2–Co–Cl2($-x, y, 1/2-z$) of 107.8(1) $^\circ$.

In **2** the coordination sphere around Co consists of a plane of four nitrogens of the 3,5-dimethylpyridines with Co–N distances of 2.186(4) \AA , and the elongated octahedron is completed with two chloride ions at distances of 2.455(2) \AA . The program XPREP, included in SHELXTL-Plus, gave several possibilities for tetragonal and orthorhombic space groups, but the $Pnmm$ group had overwhelmingly best form. Also some tetragonal space groups were tested based on the cell dimensions. It was possible to solve the structure either in a tetragonal space group $P4(2)/n$ or an orthorhombic space group $Pnmm$, but refinement of a disordered model in the tetragonal space group did not converge well. This is also obvious, when $Z = 2$; the point symmetry of the site $(1/4, 1/4, 1/4)$ is $\bar{4}$ and 222 in space groups $P4(2)/n$ and $Pnmm$, respectively. In $P4(2)/n$ the positions of N1 and C4 atoms obtain values

whose symmetry-related positions are ca. 0.2 Å apart from each other, but setting an occupancy factor equal to 0.5 for each position, the atomic parameters were correlated strongly. The angles N1–Co–N1($1/2 - x, y, 1/2 - z$) and N1–Co–N1($x, 1/2 - y, -1/2 - z$) are 90.4(2) and 89.6(2)°, respectively, also showing deviation from tetragonal symmetry.

The coordination plane consisting of four nitrogen atoms forms an angle of 44.90(3)° with the lutidine rings, which again form angles of 89.79(4)° with each other. The interatomic distances and angles within the lutidine rings in both compounds are normal.

Powder diffraction study. The compounds [Co(C₇H₉N)₄X₂], X = Br (3) and X = I (4), which were supposed to be isostructural with 2, were studied by X-ray powder diffraction. The cell dimensions obtained for 3 are $a = b = 11.863(1)$ Å, $c = 10.338(2)$ Å and for 4 $a = b = 12.1327(6)$ Å and $c = 10.211(1)$ Å. Rietveld profile refinements were performed with the program DBW3.2 by Wiles *et al.*⁴¹ Only one positional coordinate, z for a

halogen atom, was allowed to vary. All other positional coordinates were fixed at the values reported in Table 4. Although it was impossible to refine the light-atom positions, both refinements converged at a structure factor R -value of 10.3%. Final Rietveld plots are shown in Fig. 7.

From the z -coordinates found, $-0.0046(4)$ for Br and $-0.0320(2)$ for I, and the length of the corresponding c -axis, the Co–X distances were calculated to be 2.63 and 2.88 Å for X = Br and I, respectively. The calculated bond distances must be judged with caution, but it is notable that the bond lengths are very close to the sum of the ionic radii of cobalt(II) and the appropriate halide. The difference between the observed bond lengths and the sum of the ionic radii decreases from the chloride to the iodide.

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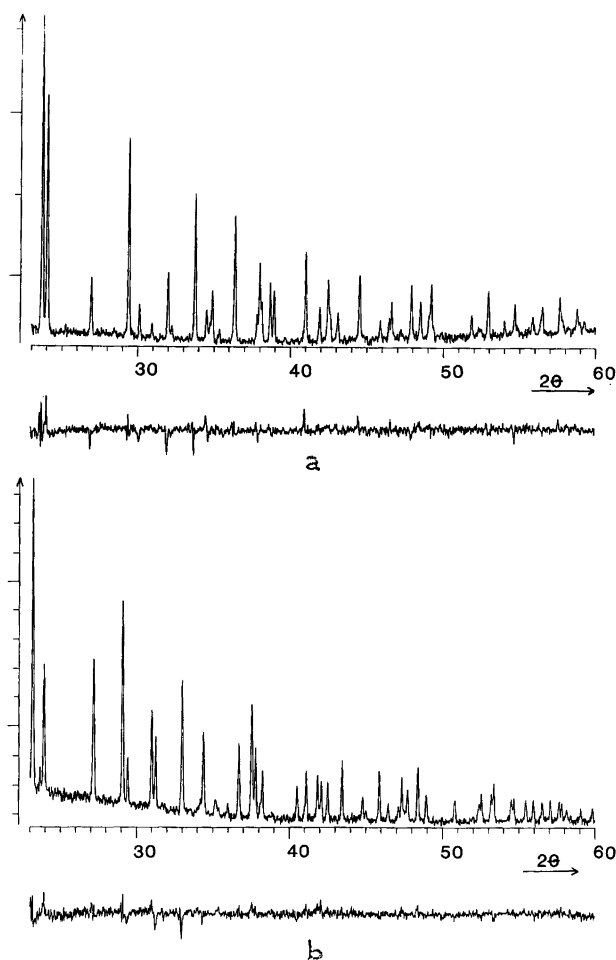


Fig. 7. Final Rietveld plots for [Co(C₇H₉N)₄X₂]. The upper curves illustrate the observed data, while the lower curves are the differences between observed and calculated data. (a) X = Br (3) (b) X = I (4).

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