

Pyridine-Type Complexes of Transition-Metal Halides IX. Preparation and Characterization of 2,4- and 3,4-Dimethylpyridine Complexes of Cobalt(II) Bromide: the Crystal Structure of Dibromobis(2,4-dimethylpyridine)cobalt(II) and Bromotetrakis(3,4-dimethylpyridine)cobalt(II) Bromide

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Dibromobis(2,4-dimethylpyridine)cobalt(II) (**1**) crystallizes in an orthorhombic (pseudo-tetragonal) space group $P2_12_12_1$ and bromotetrakis(3,4-dimethylpyridine)cobalt(II) bromide (**2**) in a monoclinic space group $C2/c$. Cell parameters are obtained from Guinier–Hägg powder data: $a = 7.6742(8)$, $b = 7.6742(8)$, $c = 28.114(6)$ Å and $Z = 4$ for **1**, and $a = 14.817(4)$, $b = 13.290(5)$, $c = 14.871(4)$ Å, $\beta = 90.55(3)^\circ$ and $Z = 4$ for **2**. In **1** the cobalt(II) ion is tetrahedrally coordinated with an approximate C_{2v} symmetry, which is apparent from the infrared spectrum. In **2** the cobalt(II) ion has a rarely observed five coordination with square pyramidal geometry. The consequent spectral symmetry is C_{2v} . The thermal decomposition pattern of samples is simple: an one-step process for **1** (DTG maximum at 335°C) and a three-step process for **2**, where one, one and two ligand moles are successively released (DTG maxima at 130, 193 and 360°C).

In the last few years considerable interest has been focused on the thermal,^{1–8} spectral,^{9–18} magnetic^{8–10} and structural^{19–28} properties of pyridine type complexes of transition-metal halides. In this work 2,4- and 3,4-dimethylpyridines, also called 2,4- and 3,4-lutidines, were used as ligands. Dibromobis(2,4-dimethylpyridine)cobalt(II) (**1**) and bromotetrakis(3,4-dimethylpyridine)cobalt(II) bromide (**2**) studied in this work were prepared and characterized for the first time by Darby and Val-larino.²⁹ On the basis of the magnetic moments and electronic and infrared spectra they suggested a tetrahedral coordination for **1** and a square pyramidal geometry for **2**. Because the square pyramidal coordination is rare for the high-spin cobalt(II)³⁰ it seemed interesting to confirm the structure of this complex. In some earlier works we have described preparation and thermal and spectral characterization^{16,31,32} of some methylpyridine complexes

of transition-metal halides. This work is an extension of our previous papers concerning the structure determination of some cobalt(II) halide complexes formed with substituted pyridines.^{33–36}

Experimental

Preparation. Anhydrous cobalt bromide and the lutidine complexes were prepared as described earlier in Part VI of this series.³³ Results of elemental analysis ($\text{CoC}_{14}\text{H}_{18}\text{N}_2\text{Br}_2$: 39.12% C; 4.12% H; 6.56% N. $\text{CoC}_{28}\text{H}_{36}\text{N}_4\text{Br}_2$: 52.03% C; 5.66% H; 8.61% N) corroborated the stoichiometries.

Thermal analysis. Thermal behaviour of the complexes was investigated with a MOM OD-2 Derivatograph using the following experimental conditions: sample weight 100 mg, heating rate 5°C min^{-1} , nitrogen atmosphere, 100 mg $\alpha\text{-Al}_2\text{O}_3$ as reference material.

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Infrared spectra. Infrared spectra were recorded by a DIGILAB FTS spectrometer equipped with a 6 μm Hy-lar beam splitter. Samples were measured in KBr pellets (4000–400 cm^{-1}) and Nujol mulls in polyethylene matrix (600–40 cm^{-1}). The bands and their assignments are listed in Table 1 for **1** and **2**.

UV/VIS spectroscopy. For the rarely observed five-coordinated bromotetrakis(3,4-dimethylpyridine)cobalt(II) bromide we collected the UV/VIS spectra in the 200–250 nm region. In order to avoid ligand changing processes, solid reflectance spectra were measured using Beckman Acta MIV spectrophotometer and BaSO_4 as reference material.

X-Ray powder diffraction. Powder diffraction patterns for the complexes were obtained using a Guinier–Hägg focussing camera with $\text{CuK}\alpha_1$ radiation ($\lambda = 1.5405 \text{ \AA}$) and photographic recording. Silicon ($a = 5.430880 \text{ \AA}$) was added as internal standard and used for the correction of the 2θ scale. The film strips were measured with an automatic optical reader³⁷ which yielded relative line intensities and geometrical positions. The powder diffraction

characteristics were further evaluated with TREOR 90, a trial-and-error indexing program.^{38,39} The indexed powder diffraction peaks with observed and calculated 2θ values, d -values and relative intensities are presented in Table 2 for **1** and Table 3 for **2**.

X-Ray single-crystal studies. Experimental details of crystal structure determinations including crystal data, data collection, structure determination and refinement for dibromobis(2,4-dimethylpyridine)cobalt(II) (**1**) and bromotetrakis(3,4-dimethylpyridine)cobalt(II) bromide (**2**) are listed in Table 4. The crystals were sealed in a glass capillary because they showed a tendency to decay under atmospheric conditions. Unit-cell parameters were obtained by carefully centering 25 reflections with $20 > 2\theta > 25^\circ$ using $\text{MoK}\alpha$ ($\lambda = 0.71069 \text{ \AA}$) radiation. The data were corrected for Lorentz and polarization factors and isotropic extinction. Absorption corrections were made empirically using a ψ -rotation method. Structure determinations and refinements were carried out using a SHELXTL PLUS (PC version) program package.⁴⁰ Atomic scattering factors used were those included in the program package.

Table 1. The infrared spectra of $\text{Co}(\text{C}_7\text{H}_9\text{N})_2\text{Br}_2$ (**1**) and $[\text{Co}(\text{C}_7\text{H}_9\text{N})_4\text{Br}]\text{Br}$ (**2**) (in cm^{-1}).

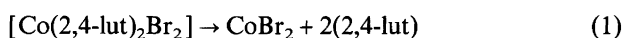
No.	2,4-lut	$[\text{Co}(2,4\text{-lut})_2\text{Br}_2]$	Assignment	No.	3,4-lut	$[\text{Co}(3,4\text{-lut})_4\text{Br}]\text{Br}$	Assignment
1	3043	3047	$\nu_1(\text{a}')$	1	3055	3042	$\nu_1(\text{a}')$
2	3007	3025	$\nu_2(\text{a}')$	2	3021	3020	$\nu_2(\text{a}')$
3	2975	2980	$\nu_{\text{as}}(\text{CH}_3)$	3	2971	2971	$\nu_{\text{as}}(\text{CH}_3)$
4	2918	2920	$\nu_{\text{s}}(\text{CH}_3)$	4	2947	2941	$\nu_{\text{as}}(\text{CH}_3)$
5	—	2364	$2 \nu \nu_{11}(\text{a}')$	5	2923	2913	$\nu_{\text{s}}(\text{CH}_3)$
6	1607	1603	$\nu_4(\text{a}')$	6	—	1654	$2 \nu \nu_{22}(\text{a}'')$
7	1565	1554	$\nu_5(\text{a}')$	7	1594	1612	$\nu_4(\text{a}')$
8	1479	1493	$\nu_6(\text{a}')$	8	1560	1560	$\nu_5(\text{a}')$
9	1449	1452	$\nu_{\text{as}}(\text{CH}_3)$	9	1493	1503	$\nu_6(\text{a}')$
10	1397	1401	$\nu_7(\text{a}')$	10	1447	1445	$\nu_{\text{as}}(\text{CH}_3)$
11	1378	1374	$\nu_{\text{s}}(\text{CH}_3)$	11	1405	1418	$\nu_7(\text{a}')$
12	1294	1305	$\nu_8(\text{a}')$	12	1384	1382	$\nu_{\text{s}}(\text{CH}_3)$
13	1273	1273	$\nu_9(\text{a}')$	13	1237	1243	$\nu_{10}(\text{a}')$
14	1236	1269	$\nu_{10}(\text{a}')$	14	1194	1202	$\nu_{11}(\text{a}')$
15	1166	1181	$\nu_{11}(\text{a}')$	15	1176	1177	$\nu_{12}(\text{a}')$
16	1037	1027	CH_3 rock.	16	1066	1083	$\nu_{13}(\text{a}')$
17	976	972	CH_3 rock.	17	1048	1028	CH_3 rock.
18	912	927	$\nu_{21}(\text{a}'')$	18	1020	1010	CH_3 rock.
19	815	811	$\nu_{22}(\text{a}'')$	19	985	974	$\nu_{20}(\text{a}'')$
20	759	754	$\nu_{15}(\text{a}')$	20	839	845	$\nu_{14}(\text{a}')$
21	560	550	$\nu_{16}(\text{a}')$	21	821	827	$\nu_{22}(\text{a}'')$
22	520	537	$\nu_{17}(\text{a}')$	22	751	749	$\nu_{15}(\text{a}')$
23	434	442	$\nu_{15}(\text{a}'')$	23	726	723	$\nu_{23}(\text{a}'')$
24	408	431	$\nu_{18}(\text{a}')$	24	604	611	$\nu_{16}(\text{a}')$
25	282	300	$\nu_{19}(\text{a}')$	25	524	534	$\nu_{17}(\text{a}')$
26	—	276	$\nu(\text{Co-Br})$	26	506	522	$\nu_{24}(\text{a}'')$
27	—	250	$\nu(\text{Co-Br})$	27	422	431	$\nu_{25}(\text{a}'')$
28	—	237	$\nu(\text{Co-N})$	28	409	409	$\nu_{18}(\text{a}')$
29	—	226	$\nu(\text{Co-N})$	29	258	276	$\nu_{19}(\text{a}')$
30	195	200	$\nu_{27}(\text{a}'')$	30	—	217	$\nu(\text{Co-Br})$
31	—	—	$\nu(\text{N-Co-N})$	31	—	203	$\nu(\text{Co-N})$
32	—	97	$\nu(\text{N-Co-Br})$	32	181	184	$\nu_{27}(\text{a}'')$
33	—	78	$\nu(\text{Br-Co-Br})$	33	—	137	$\nu(\text{N-Co-N})$
34	—	62	Lattice	34	—	101	$\nu(\text{N-Co-Br})$
35	—	42	Lattice				

Table 2. Powder diffraction characteristics of $\text{Co}(\text{C}_7\text{H}_9\text{N})_2\text{CoBr}_2$ (1).

<i>h</i>	<i>k</i>	<i>l</i>	$2\theta_{\text{obs}}/^\circ$	$2\theta_{\text{calc}}/^\circ$	<i>d</i> /Å	<i>I</i> / <i>I</i> _{max}
1	0	1	11.957	11.945	7.39	54.8
0	0	4	12.596	12.584	7.02	14.8
1	0	2	13.140	13.133	6.73	18.8
1	0	3	14.910	14.909	5.93	100.0
1	1	3	18.898	18.882	4.692	17.4
1	0	6	22.214	22.211	3.998	13.0
1	1	5	22.742	22.755	3.903	88.3
2	0	2	24.024	24.021	3.701	12.7
1	0	7	25.028	25.003	3.555	62.4
2	0	4	26.453	26.443	3.366	17.0
2	1	2	26.716	26.716	3.334	17.8
1	0	8	27.910	27.900	3.194	12.1
2	0	5	28.152	28.132	3.167	11.6
2	1	4	28.932	28.928	3.083	12.0
2	0	6	30.081	30.077	2.968	10.1
1	0	9	30.884	30.881	2.893	4.8
2	1	6	32.315	32.307	2.768	14.0
1	1	9	33.057	33.061	2.707	5.8
2	2	3	34.378	34.382	2.606	5.3
3	0	1	35.213	35.200	2.546	7.9
3	0	3	36.397	36.377	2.4665	7.0
2	0	9	37.076	37.081	2.4228	19.4
3	1	2	37.573	37.581	2.3919	5.0
2	1	9	38.942	38.955	2.3109	6.1
2	0	10	39.718	39.712	2.2675	6.2
3	0	7	41.846	41.834	2.1570	6.9
2	2	9	44.169	44.177	2.0488	5.7
3	1	8	45.392	45.379	1.9964	7.9
3	2	5	45.542	45.532	1.9902	5.0
3	2	7	48.310	48.358	1.8824	10.7
3	2	9	51.928	51.944	1.7595	5.0
4	2	3	54.312	54.304	1.6877	7.5
4	4	9	76.491	76.492	1.2444	16.4

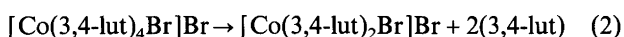
Results

Thermal studies. Thermal decomposition of the dibromobis(2,4-dimethylpyridine)cobalt(II), which immediately follows the endothermic melting (185°C), is a simple, one-step process with a DTG maximum at 335°C:



The observed weight loss (48.8%) verified the expected stoichiometry.

The thermal decomposition pathway of the bromotetrakis(3,4-dimethylpyridine)cobalt(II) bromide starts with an endothermic melting at 105°C followed by the release of 2 mol of ligands with a DTG shoulder and a peak at 102 and 130°C, respectively:

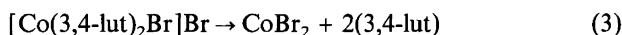


The endothermic melting could have an effect on thermal decomposition because of a local decrease of temperature. The result is slower decomposition and a shoulder on the DTG curve. This is quite obvious in the case of a large sample weight as we had in our experiment.

Table 3. Powder diffraction characteristics of $[\text{Co}(\text{C}_7\text{H}_9\text{N})_4\text{Br}] \text{Br}$ (2).

<i>h</i>	<i>k</i>	<i>l</i>	$2\theta_{\text{obs}}/^\circ$	$2\theta_{\text{calc}}/^\circ$	<i>d</i> /Å	<i>I</i> / <i>I</i> _{max}
-1	1	1	10.722	10.700	8.24	52.5
2	0	0	11.943	11.937	7.40	89.7
0	2	1	14.588	14.589	6.06	10.1
-2	0	2	16.805	16.798	5.27	11.1
2	0	2	16.959	16.963	5.22	11.4
0	2	2	17.898	17.888	4.952	100.0
-1	1	3	19.983	19.967	4.439	89.1
3	1	1	20.139	20.124	4.405	44.2
1	3	0	20.920	20.913	4.242	9.7
-2	2	2	21.498	21.495	4.130	13.2
2	2	2	21.637	21.625	4.103	17.2
0	0	4	23.927	23.917	3.716	8.8
2	2	3	25.491	25.501	3.491	8.8
-2	0	4	26.698	26.703	3.336	52.5
4	0	2	26.973	26.975	3.303	48.5
0	2	4	27.745	27.469	3.243	81.9
-2	4	1	30.023	30.036	2.974	42.7
2	4	3	34.703	34.720	2.582	14.2
-4	2	4	36.626	36.637	2.4515	13.0
-2	0	6	38.140	38.147	2.3577	13.6
6	0	2	38.488	38.494	2.3371	18.6
6	2	0	38.878	38.875	2.3146	8.5
0	4	5	40.681	40.683	2.2161	13.9
2	6	1	43.021	43.037	2.1008	9.0

The bis-intermediate melts at 193°C and decomposes in one step to the pure halide (DTG peak 360°C). The total observed weight loss was 68.2%:



Interpretation of the DTA curve is not straightforward because there is a decomposition step (2) with an endothermic enthalpy effect and recrystallization between the two meltings. The latter decomposition scheme (3) is different from the tetrakis(dimethylpyridine) analogues,⁴¹ because the process begins by melting. This may indicate a slightly different structure for this compound.

IR spectroscopy. In the infrared spectra of dibromobis(2,4-dimethylpyridine)cobalt(II) (1) (Table 1) small shifts in ligand bands can be observed due to complexation compared to free base.⁴² In addition to the cobalt(II)-bromide bands at 276 and 250 cm^{-1} , two cobalt(II)-nitrogen bands were observed (226 and 237 cm^{-1}) in agreement with the expected C_{2v} symmetry. These bands have been identified earlier²⁹ [$\nu(\text{Co}-\text{Br}) = 238, 275 \text{ cm}^{-1}$]; however, only one $\nu(\text{Co}-\text{N})$ vibration was registered at 238 cm^{-1} . We assigned the cobalt(II)-ligand deformation vibrations on the basis of infrared spectra of other halide analogues.⁴¹ Some bands were registered at low wavenumbers which can be assigned as lattice modes.

In the infrared spectra of bromotetrakis(3,4-dimethylpyridine)cobalt(II) bromide (2) one $\nu(\text{Co}-\text{N})$ and one $\nu(\text{Co}-\text{Br})$ band were observed at 203 and 217 cm^{-1} , respectively, in addition to the ligand vibrations. These metal-ligand stretching modes were assigned as one

Table 4. Structure determination summary for $\text{Co}(\text{C}_7\text{H}_9\text{N})_2\text{Br}_2$ (1) and $[\text{Co}(\text{C}_7\text{H}_9\text{N})_4\text{Br}]\text{Br}$ (2).

Crystal data		
Compound	1	2
Empirical formula	$\text{C}_{14}\text{H}_{18}\text{Br}_2\text{CoN}_2$	$\text{C}_{28}\text{H}_{36}\text{Br}_2\text{CoN}_4$
Color; habit	Blue; bipyramidal	Dark green; platelike
Crystal size (mm)	$0.22 \times 0.21 \times 0.29$	$0.20 \times 0.25 \times 0.16$
Crystal system	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$ (No. 19)	$C2/c$ (No. 15)
Unit cell dimensions	$a = 7.6742(8) \text{ \AA}$ $b = 7.6742(8) \text{ \AA}$ $c = 28.114(6) \text{ \AA}$	$a = 14.817(3) \text{ \AA}$ $b = 13.290(3) \text{ \AA}$ $c = 14.871(3) \text{ \AA}$ $\beta = 90.55(3)^\circ$
Volume	$1646.9(8) \text{ \AA}^3$	$2929.5(11) \text{ \AA}^3$
Z	4	4
Formula weight	433.1	647.36
Density (calc.)/ Mg m^{-3}	1.747	1.469
Absorption coefficient/ mm^{-1}	5.883	3.336
$F(000)$	852	1316
Data collection		
Diffractometer used	Nicolet P3	Nicolet P3
Radiation	$\text{MoK}\alpha$ ($\lambda = 0.71069 \text{ \AA}$)	$\text{MoK}\alpha$ ($\lambda = 0.71069 \text{ \AA}$)
Temperature/K	293	293
Monochromator	Highly oriented graphite	Highly oriented graphite crystal
2θ range/ $^\circ$	3.0–53.0	3.0–53.0
Scan type	ω	ω
Scan speed	Variable; 2.50 to $29.30^\circ \text{ min}^{-1}$ in ω	Variable; 2.50 to $29.30^\circ \text{ min}^{-1}$ in ω
Scan range $\omega/^\circ$	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	$0 \leq h \leq 9$ $0 \leq k \leq 9$ $0 \leq l \leq 35$	$0 \leq h \leq 18$ $0 \leq k \leq 16$ $-18 \leq l \leq 18$
Reflections collected	2027	3175
Independent reflections	2027	3055 ($R_{int} = 5.4\%$)
Observed reflections	1378 ($I^2 > 3.0\sigma(I^2)$)	1367 ($I^2 > 3.0\sigma(I^2)$)
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	$\sum w(F_o - F_c)^2$	$\sum w(F_o - F_c)^2$
Hydrogen atoms	Riding model, fixed isotropic U	
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.0082F^2$	$w^{-1} = \sigma^2(F) + 0.0090F^2$
Extinction correction	$\chi = 0.0001(3)$	$\chi = -0.00017(7)$
No. of parameters refined	174	161
Formula of R	$R = [\sum (F_o - F_c) / \sum F_o]$	
Formula of weighted R	$wR = [\sum w^2 (F_o - F_c)^2 / \sum w F_o^2]^{1/2}$	
Final R -indices (obs. data)	$R = 6.38\%$, $wR = 8.61\%$	$R = 6.02\%$, $wR = 8.08\%$
Goodness of fit	0.73	0.77
Largest and mean Δ/σ	0.010, 0.003	0.549, 0.016
Data-to-parameter ratio	6.9:1	8.5:1
Largest difference peak/ $e \text{ \AA}^{-3}$	1.34	0.76
Largest difference hole/ $e \text{ \AA}^{-3}$	-1.14	-0.77

overlapping band at 220 cm^{-1} .²⁹ Two deformation vibrations occur at low wavenumbers.

UV/VIS spectroscopy. In the spectrum of bromotetraakis(3,4-dimethylpyridine)cobalt(II) bromide five main absorption bands were observed, which was in good agreement with the energy level diagram for a d^7 ion in a square

pyramidal crystal field⁴² and the earlier described electronic spectra.²⁹ The first transition was assigned to ${}^4A_2(\text{F}) \rightarrow {}^4A_2(\text{P})$ at 21978 cm^{-1} (21834 cm^{-1} in Ref. 29). The doubly degenerate ${}^4A_2(\text{F}) \rightarrow {}^4E_2(\text{P})$ was split into two bands at 17921 and 16806 cm^{-1} . This transition was reported²⁹ as a single band at 17361 cm^{-1} . The ${}^4A_2(\text{F}) \rightarrow {}^4B_1$ band was observed at 15625 cm^{-1} (13495 cm^{-1}

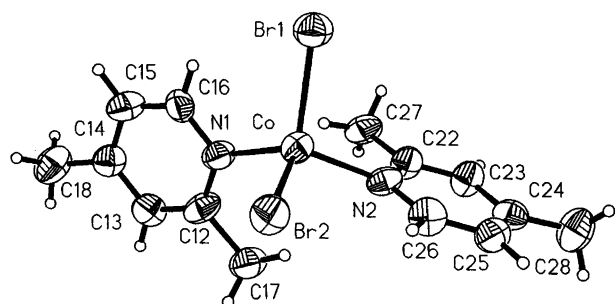


Fig. 1. The structure of dibromobis(2,4-dimethylpyridine)cobalt(III) (**1**) with atomic labelling. Thermal ellipsoids are drawn at 50% probability level.

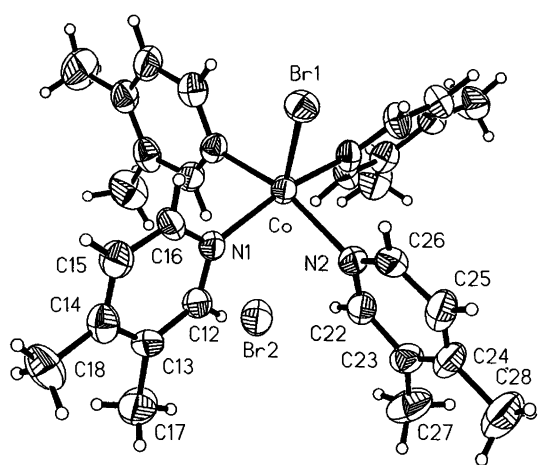


Fig. 2. The structure of bromotetrakis(3,4-dimethylpyridine)cobalt(III) bromide (**2**) with atomic labelling. Thermal ellipsoids are drawn at 50% probability level.

in Ref. 29). Splitting was also observed for the other degenerate band [${}^4A_2(F) \rightarrow {}^4E_1(F)$] with maxima at 8196 and 7246 cm^{-1} . This transition was reported by Darby and Vallarino as a single band at 8000 cm^{-1} .²⁹ The last band, ${}^4A_2(F) \rightarrow {}^4B_2$, was observed at 5814 cm^{-1} (5882 cm^{-1} in Ref. 29). The splitting indicates a distortion from the ideal square-pyramidal geometry.

X-Ray powder diffraction. The X-ray powder pattern of **1** was indexed within an orthorhombic space group based on the single-crystal results with cell dimensions of $a = 7.6742(8)$, $b = 7.6742(8)$ and $c = 28.114(6)$ Å, $Z = 4$, $V = 1655.77$ Å³, and $D = 1.75$ g cm^{-3} . The results of the calculation were supported with $M(20) = 32$ and $F(20) = 51$. The complex is isostructural with the chloride analogue but different from the iodide derivative.³⁵ Compound **2** crystallizes in a monoclinic space group also based on the single-crystal study, with $a = 14.817(4)$, $b = 13.290(5)$ and $c = 14.871(4)$ Å and $\beta = 90.55(3)^\circ$, $Z = 4$, $V = 2928.27$ Å³, $D = 1.47$ Mg m^{-3} [$M(20) = 15$, $F(20) = 20$]. The symmetry deviates only slightly from tet-

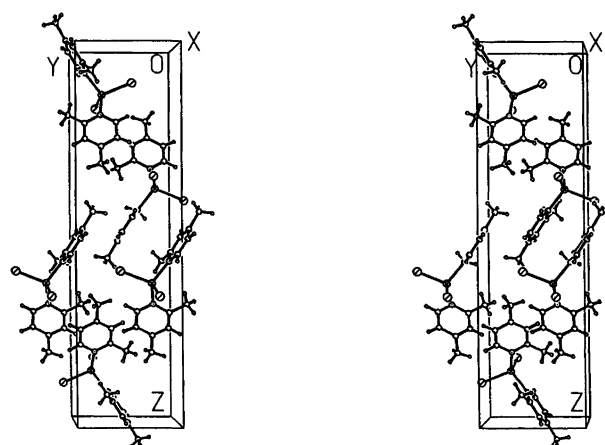


Fig. 3. Unit cell packing of dibromobis(2,4-dimethylpyridine)cobalt(III) (**1**) seen down the *a*-axis.

ragonal, which is common for the tetrakis complexes of this type.³⁵

Single-crystal structure determinations. Cell dimensions obtained with four-circle diffractometer for compounds **1** and **2** deviated within 1σ from those obtained by powder diffraction, and the latter, more accurate, cell dimensions were used in single-crystal structure calculations. The structures of **1** and **2** are shown in Figs. 1 and 2, respectively, with atom labelling and thermal ellipsoids at 50% probability level. Unit-cell packing is seen in Figs. 3 and 4. Non-hydrogen atom positional parameters with equivalent isotropic thermal parameters are given in Tables 5 and 6, bond lengths and angles are listed in Tables 7 and 8 for non-hydrogen atoms for **1** and **2**, respectively.

In **1** the coordination sphere of Co is a tetrahedron with two bromide ions at the distances of 2.395(3) and 2.392(3) Å and two nitrogen atoms of two 2,4-lutidine molecules at distances of 2.062(13) and 2.024(13) Å. The N–Co–N angle is 117.7(5)° and the Br–Co–Br angle is 112.8(1)°, indicating sterical hindrance of the methyl groups in lutidines.

To check the enantiomorph, Roger's parameter η , with values of 1.08(10) and $-1.08(10)$, was calculated for the given enantiomorph and its inversion, respectively. This indicates that the given enantiomorph is probably correct.

Least-square planes 1 and 2 are defined by atoms N1, C12, C13, C14, C15 and C16 and atoms N2, C22, C23, C24, C25 and C26, respectively. Atoms C17 and C18 deviate 0.075(2) and 0.060(2) Å from plane 1 and atoms C27 and C28 deviate 0.062(2) and $-0.035(2)$ Å from

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

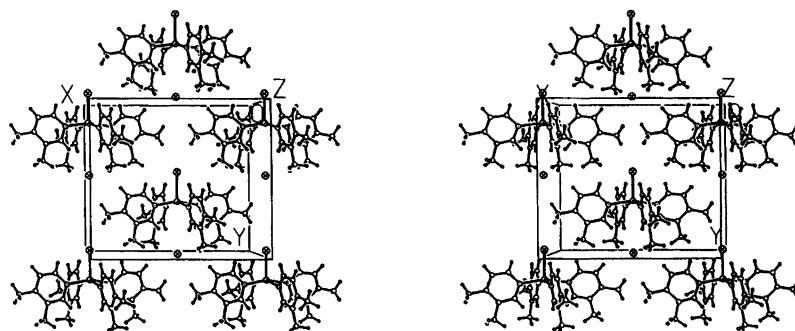


Fig. 4. Unit cell packing of bromotetrakis(3,4-dimethylpyridine)cobalt(II) bromide (**2**) seen down the *c*-axis.

Table 5. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{\AA}^2 \times 10^3$) for $\text{Co}(\text{C}_7\text{H}_9\text{N})_2\text{Br}_2$ (**1**) with e.s.d.s in parentheses.

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	U_{eq}^a
Co	5438(3)	2061(3)	3750(1)	44(1)
Br(1)	8311(2)	2485(3)	3438(1)	58(1)
Br(2)	5015(3)	-806(2)	4063(1)	58(1)
N(1)	5135(18)	3724(18)	4320(5)	47(4)
N(2)	3789(17)	2342(16)	3193(5)	44(4)
C(12)	3606(21)	4051(23)	4548(7)	52(5)
C(13)	3550(26)	4999(22)	4959(6)	53(5)
C(14)	5070(24)	5634(20)	5157(5)	48(4)
C(15)	6611(24)	5312(26)	4915(7)	59(6)
C(16)	6576(24)	4352(23)	4512(5)	51(5)
C(17)	1960(23)	3367(27)	4319(7)	62(6)
C(18)	4971(26)	6612(26)	5619(7)	70(6)
C(22)	3494(24)	3891(19)	2962(6)	46(5)
C(23)	2534(26)	3924(22)	2543(6)	51(5)
C(24)	1835(21)	2445(23)	2344(5)	50(5)
C(25)	2156(24)	863(25)	2571(6)	54(5)
C(26)	3121(25)	894(20)	2994(6)	53(5)
C(27)	4133(23)	5525(20)	3189(7)	53(5)
C(28)	837(28)	2485(27)	1883(7)	72(6)

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

Table 6. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{\AA}^2 \times 10^3$) for $[\text{Co}(\text{C}_7\text{H}_9\text{N})_4\text{Br}]$ (**2**) with e.s.d.s in parentheses.

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	U_{eq}^a
Co	5000	6435(2)	7500	36(1)
Br(1)	5000	4555(1)	7500	44(1)
Br(2)	5000	9779(1)	7500	64(1)
N(1)	3688(5)	6669(6)	6972(5)	39(2)
N(2)	5530(5)	6749(6)	6231(5)	40(3)
C(12)	3430(6)	7568(8)	6662(7)	42(3)
C(13)	2581(7)	7782(8)	6330(7)	48(3)
C(14)	1917(7)	7024(8)	6358(7)	48(3)
C(15)	2181(7)	6108(9)	6714(7)	52(4)
C(16)	3048(7)	5966(8)	7006(7)	44(3)
C(17)	2380(9)	8834(9)	5996(10)	78(5)
C(18)	983(8)	7207(10)	6040(9)	70(4)
C(22)	5716(7)	7693(8)	5991(7)	47(3)
C(23)	6085(8)	7980(9)	5159(8)	53(4)
C(24)	6265(7)	7201(9)	4548(7)	53(4)
C(25)	6046(8)	6226(9)	4784(7)	56(4)
C(26)	5691(7)	6039(9)	5620(7)	47(3)
C(27)	6249(10)	9063(10)	4975(9)	80(5)
C(28)	6650(11)	7436(13)	3628(8)	93(6)

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

plane 2. Co deviates 0.251(2) and -0.272(2) Å from planes 1 and 2, respectively. The interplanar angle between the lutidine molecules and planes 1 and 2 is 85.79(3)°. The square-pyramidal coordination sphere of Co in **2** is rarely met. The basal plane is formed by four nitrogens of four 3,4-lutidines with two different Co-N distances of 2.113(7) and 2.093(7) Å. The bromide ion is at the apex at a distance of 2.498(2) Å. The other bromide ion lies at the opposite side of Co at a distance of

4.442(2) Å. Co deviates 0.371(1) Å towards the coordinated bromide ion from the least-squares plane formed by the four nitrogen atoms. The interplanar angles between the least-squares planes formed by the lutidine ring atoms and the coordination plane are 72.40(3) and 95.90(3)° and the angles between the opposite lutidines are 11.81(3) and 35.21(3).

Bond lengths and angles within the lutidine molecules are normal in both compounds.

Table 7. Bond lengths (in Å) for $\text{Co}(\text{C}_7\text{H}_9\text{N})_2\text{Br}_2$ (1) and $[\text{Co}(\text{C}_7\text{H}_9\text{N})_4\text{Br}]^+\text{Br}^-$ (2) with e.s.d.s in parentheses.

$\text{Co}(\text{C}_7\text{H}_9\text{N})_2\text{Br}_2$		$[\text{Co}(\text{C}_7\text{H}_9\text{N})_4\text{Br}]^+\text{Br}^-$	
Co—Br(1)	2.395(3)	Co—Br(1)	2.498(2)
Co—Br(2)	2.392(3)	Co—N(1)	2.113(7)
Co—N(1)	2.062(13)	Co—N(2)	2.093(7)
Co—N(2)	2.024(13)	Co—N(1A) ^a	2.113(7)
N(1)—C(12)	1.361(22)	Co—N(2A)	2.093(7)
N(1)—C(16)	1.322(22)	N(1)—C(12)	1.335(13)
N(2)—C(22)	1.373(20)	N(1)—C(16)	1.333(13)
N(2)—C(26)	1.346(21)	N(2)—C(22)	1.333(13)
C(12)—C(13)	1.365(25)	N(2)—C(26)	1.333(13)
C(12)—C(17)	1.512(25)	C(12)—C(13)	1.376(14)
C(13)—C(14)	1.381(26)	C(13)—C(14)	1.409(15)
C(14)—C(15)	1.386(25)	C(13)—C(17)	1.514(16)
C(14)—C(18)	1.503(25)	C(14)—C(15)	1.382(15)
C(15)—C(16)	1.350(25)	C(14)—C(18)	1.478(16)
C(22)—C(23)	1.389(24)	C(15)—C(16)	1.366(14)
C(22)—C(27)	1.491(23)	C(22)—C(23)	1.411(15)
C(23)—C(24)	1.374(24)	C(23)—C(24)	1.404(16)
C(24)—C(25)	1.393(26)	C(23)—C(27)	1.485(18)
C(24)—C(28)	1.507(25)	C(24)—C(25)	1.383(17)
C(25)—C(26)	1.401(25)	C(24)—C(28)	1.520(17)
		C(25)—C(26)	1.377(15)

^aSymmetry code refers to symmetry operation: (A) $-x, y, 1/2-z$.

Table 8. Bond angles (in °) for $\text{Co}(\text{C}_7\text{H}_9\text{N})_2\text{Br}_2$ (1) and $[\text{Co}(\text{C}_7\text{H}_9\text{N})_4\text{Br}]^+\text{Br}^-$ (2) with e.s.d.s in parentheses.

$\text{Co}(\text{C}_7\text{H}_9\text{N})_2\text{Br}_2$		$[\text{Co}(\text{C}_7\text{H}_9\text{N})_4\text{Br}]^+\text{Br}^-$	
Br(1)—Co—Br(2)	112.6(1)	Br(1)—Co—N(1)	98.5(2)
Br(1)—Co—N(1)	107.8(4)	Br(1)—Co—N(2)	101.5(2)
Br(2)—Co—N(1)	105.6(4)	N(1)—Co—N(2)	89.3(3)
Br(1)—Co—N(2)	106.1(4)	Br(1)—Co—N(1A) ^a	98.5(2)
Br(2)—Co—N(2)	107.3(4)	N(1)—Co—N(1A)	163.0(4)
N(1)—Co—N(2)	117.7(5)	N(2)—Co—N(1A)	87.3(3)
Co—N(1)—C(12)	125.3(11)	Br(1)—Co—N(2A)	101.5(2)
Co—N(1)—C(16)	116.7(11)	N(1)—Co—N(2A)	87.3(3)
C(12)—N(1)—C(16)	117.4(14)	N(2)—Co—N(2A)	157.0(5)
Co—N(2)—C(22)	124.2(11)	N(1A)—Co—N(2A)	89.3(3)
Co—N(2)—C(26)	118.1(11)	Co—N(1)—C(12)	121.3(6)
C(22)—N(2)—C(26)	117.1(14)	Co—N(1)—C(16)	122.3(6)
N(1)—C(12)—C(13)	121.6(16)	C(12)—N(1)—C(16)	116.0(8)
N(1)—C(12)—C(17)	117.1(15)	Co—N(2)—C(22)	120.6(7)
C(13)—C(12)—C(17)	121.3(16)	Co—N(2)—C(26)	123.0(7)
C(12)—C(13)—C(14)	120.1(17)	C(22)—N(2)—C(26)	116.4(8)
C(13)—C(14)—C(15)	117.4(15)	N(1)—C(12)—C(13)	124.5(9)
C(13)—C(14)—C(18)	118.8(16)	C(12)—C(13)—C(14)	118.6(10)
C(15)—C(14)—C(18)	123.8(16)	C(12)—C(13)—C(17)	119.0(10)
C(14)—C(15)—C(16)	119.4(17)	C(14)—C(13)—C(17)	122.3(10)
N(1)—C(16)—C(15)	123.9(17)	C(13)—C(14)—C(15)	116.5(10)
N(2)—C(22)—C(23)	120.3(14)	C(13)—C(14)—C(18)	121.6(10)
N(2)—C(22)—C(27)	118.1(14)	C(15)—C(14)—C(18)	121.9(10)
C(23)—C(22)—C(27)	121.5(14)	C(14)—C(15)—C(16)	120.4(10)
C(22)—C(23)—C(24)	122.5(15)	N(1)—C(16)—C(15)	124.0(10)
C(23)—C(24)—C(25)	117.7(15)	N(2)—C(22)—C(23)	124.9(10)
C(23)—C(24)—C(28)	122.2(16)	C(22)—C(23)—C(24)	116.4(10)
C(25)—C(24)—C(28)	120.1(16)	C(22)—C(23)—C(27)	119.3(10)
C(24)—C(25)—C(26)	117.9(16)	C(24)—C(23)—C(27)	124.2(11)
N(2)—C(26)—C(25)	124.6(15)	C(23)—C(24)—C(25)	118.7(10)
		C(23)—C(24)—C(28)	120.4(11)
		C(25)—C(24)—C(28)	120.8(11)
		C(24)—C(25)—C(26)	119.4(10)
		N(2)—C(26)—C(25)	124.0(10)

^aSymmetry code refers to symmetry operation: (A) $-x, y, 1/2-z$.

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