

Pyridine-Type Complexes of Transition-Metal Halides X.[†] Structural Studies on the Dimethylpyridine Chloro-, Bromo- and Iodo-Complexes of Cobalt(II)

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Ternary mixed 2,4-, 2,6-, 3,4- and 3,5-dimethylpyridine complexes of cobalt(II) with chloride bromide and iodide have been prepared and analysed by X-ray powder diffraction techniques. The symmetry and cell dimensions have been calculated by means of TREOR 90, a trial-and-error indexing program.

In the last few decades there has been much interest in the factors that affect the thermal and structural properties of metal(II) halido and pseudo-halido complexes containing pyridine and substituted pyridines.^{1–16} The symmetry and the environment around the central metal(II) atom is described mainly on the basis of spectroscopic measurements (electronic and/or infrared spectra) and magnetic properties,^{2,8–10,12,14,17,18} but only few papers report on the crystal structures of complexes of this type.^{19–28}

In some earlier parts of this series we reported the unit cell parameters of the cadmium(II),^{29–31} nickel(II)^{32,33} and cobalt(II)²⁸ halide complexes formed with pyridine and methylpyridines (picolines). In the case of cobalt(II) picoline chloride and bromide complexes,^{1–28} tetragonal and monoclinic symmetry was observed for the tetrakis- and bis-complexes, respectively. The tetrakis-compounds were tetragonal in the case of the iodide analogues, but triclinic symmetry was found for the bis-complexes of cobalt(II) iodide. These results are in good agreement with the earlier determined properties of the nickel(II)^{32,33} and cadmium(II)^{29–33} analogues. The structural differences between the chloride, bromide and the iodide complexes of cobalt(II) are also reflected in different thermal decomposition mechanisms.^{16,34}

In this paper we report the structural data for the 2,4-, 2,6-, 3,4- and 3,5-dimethylpyridine (lutidine) complexes of cobalt(II) halides.

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Experimental

Preparation. Ternary mixed complexes were prepared from solution, as described in earlier parts of this series.^{16,34} The stoichiometries of the complexes were checked by elemental analysis (Table 1) and thermogravimetry.³⁵

X-Ray powder diffraction. All solid complexes were analysed in a Guinier-Hägg focusing camera with CuK_{α1} radiation. Silicon ($a = 5.430\ 880\ \text{Å}$) was always added as internal standard and used for the correction of the 2 θ scale. The film strips were measured with an automatic optical reader³⁶ yielding relative line intensities and geometrical positions. The powder diffraction characteristics were further evaluated with TREOR 90, a trial-and-error indexing program.^{37,38} The refined and indexed monophase X-ray patterns can be obtained upon request from one of the authors (G.K.) or found in the near future in the JCPDS database.

Results

In the case of the sterically double-hindered 2,6-dimethylpyridine (2,6-lutidine), the formation of the tetrachloro-complex was observed,³⁹ although no additional hydrochloric acid was used in the preparative procedure. We could not obtain the corresponding bromide and iodide analogues, although the electronic spectrum of the iodide complex has already been reported in liquid phase.⁴¹ The ligands are protonated, and weak hydrogen-bonds exist between the two chlorides of the anion and the hydrogen of the protonated ligand.³⁹ This environment around cobalt(II) is also reflected in the spectrum of the com-

Table 1. Analytical data of the complexes.

Compound	C(%)		H(%)		N(%)	
	Calcd.	Found	Calcd.	Found	Calcd.	Found
(2,6-lutH) ₂ [CoCl ₄]	40.30	37.19	4.81	4.43	6.73	6.67
[Co(2,4-lut) ₂ Cl ₂]	48.68	47.91	5.22	5.23	8.11	8.09
[Co(2,4-lut) ₂ Br ₂]	38.79	39.12	4.16	4.12	6.47	6.56
[Co(2,4-lut) ₂ I ₂]	31.88	31.51	3.42	3.50	5.31	5.33
[Co(3,4-lut) ₄ Br ₂]	51.90	52.03	5.56	5.66	8.65	8.61
[Co(3,4-lut) ₄ I ₂]	45.32	45.35	4.86	4.90	7.55	7.61
[Co(3,5-lut) ₄ Cl ₂]	60.17	60.71	6.45	6.49	10.03	10.71
[Co(3,5-lut) ₄ Br ₂]	51.90	51.86	5.56	5.51	8.65	8.63
[Co(3,5-lut) ₄ I ₂]	45.32	45.30	4.86	4.84	7.55	7.50

pound.³⁹ Relatively few lines have been observed for this complex (Table 2), although the high values of *M* and *F* indicate that the most probable space group is *Pbcn*.

For the sterically mono-hindered 2,4-lutidine complexes, orthorhombic (pseudotetragonal) symmetry (*P*₂₁₂₁) was observed in the case of chloride and bromide ligands, and monoclinic symmetry for the iodide analogue. The most probable space group in the latter case is *P*₂₁. Although few lines have been observed and the values of *M* and *F* are relatively low for the chloride analogue, the similarity to the bromide complex⁴² further supports the expected orthorhombic symmetry. The symmetry of the iodide compound is different from those of the lighter halide analogues, which is in agreement with our earlier observation for the methylpyridine complexes.²⁸

In a plot of the calculated density vs. molecular weight of the 2,4-dimethylpyridine complexes (Fig. 1) the points fall on a straight line, which has a slightly less steep slope than that of the methylpyridine analogues.²⁸ This indicates a large distortion of the ideal tetrahedral symmetry due to the more bulky lutidine ligands.

With the sterically non-hindered 3,4-lutidine we obtained crystals of good quality only with cobalt(II) bromide and iodide. The tetrakis complex of the bromide is monoclinic (*Cc*), although the cell parameters are very close to tetragonal symmetry. The corresponding iodide analogue is tetragonal (*P*₄₂/*nmm*). The X-ray powder pattern of the bromo complex, which is just slightly

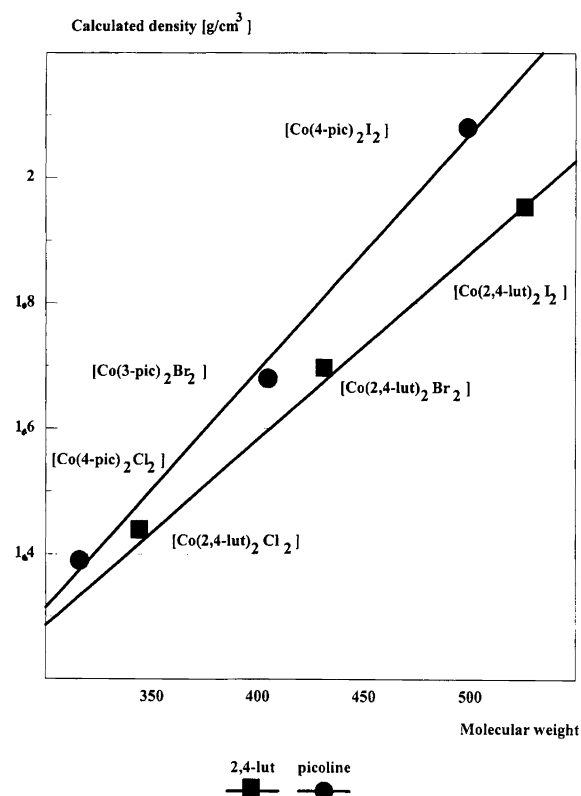


Fig. 1. Calculated density vs. molecular weight for picoline and 2,4-lutidine complexes.

Table 2. Symmetries and cell dimensions for dimethylpyridine complexes of cobalt(II) and nickel(II) halides.

Compound	Symmetry	<i>a</i> /Å	<i>b</i> /Å	<i>c</i> /Å	β /°	<i>V</i> /Å ³	<i>Z</i>	<i>D</i> _{XRD} /g cm	<i>M</i> ^a	<i>F</i> ^b
(2,6-lutH) ₂ [CoCl ₄]	Orthorhombic	16.75	8.84	13.26	—	1965	4	1.41	43(15)	57(15)
[Co(2,4-lut) ₂ Cl ₂]	Orthorhombic	7.52	7.52	27.97	—	1582	4	1.45	19(16)	14(16)
[Co(2,4-lut) ₂ Br ₂]	Orthorhombic	7.67	7.67	28.11	—	1656	4	1.75	32(20)	51(20)
[Co(2,4-lut) ₂ I ₂]	Monoclinic	12.85	18.52	7.80	104.78	1795	4	1.95	24(20)	61(20)
[Co(3,4-lut) ₄ Br ₂]	Monoclinic	14.81	13.29	14.87	90.55	2928	4	1.47	15(20)	20(20)
[Co(3,4-lut) ₄ I ₂]	Tetragonal	10.53	—	13.90	—	1540	2	1.59	36(20)	52(20)
[Co(3,5-lut) ₄ Cl ₂]	Orthorhombic	11.66	11.69	10.61	—	1448	2	1.28	25(20)	39(20)
[Co(3,5-lut) ₄ Br ₂]	Orthorhombic	11.86	11.86	10.34	—	1454	2	1.48	31(20)	48(20)
[Co(3,5-lut) ₄ I ₂]	Orthorhombic	12.13	12.13	10.21	—	1503	2	1.64	37(20)	57(20)

^aRef. 44. Numbers of lines used in the calculation are in parentheses. ^bRef. 45. Numbers of lines used in the calculation are in parentheses.

distorted from the tetragonal symmetry, can be indexed by omitting a few weak lines, in a tetragonal cell of $a = 10.49 \text{ \AA}$, $c = 13.33 \text{ \AA}$ with $D_{\text{XRD}} = 1.47 \text{ g cm}^{-3}$. The monoclinic a or c axes divided by $\sqrt{2}$ equal the tetragonal a dimension. In this way a simpler correspondence to the iodide analogue is seen.

The unit cells of the tetrakis-3,5-dimethylpyridine (3,5-lutidine) complexes are closely similar to those of the tetrakis-methylpyridine analogues, but a slight distortion from the tetragonal symmetry was observed.

While there are many reported studies on pyridine-type halogeno complexes of transition metals, the fluoro complexes have not been prepared before. In a previous paper³³ we reported some methylpyridine fluoro complexes of nickel(II). These compounds were prepared by solid-gas chemisorption. The 3,5-dimethylpyridine fluoro complex of cobalt(II) was obtained from water solution. The unit cell contains approximately two and a half molecules of water,⁴³ and is slightly different from those of the other halide analogues.

A plot of the calculated density vs. molecular weight for the tetrakis 3,5-lutidine complexes of cobalt(II) halides (Fig. 2) shows a linear relationship, indicating the previously described effect of the halide on the cell dimensions.

On the basis of the single-crystal structure of dichlorotetrakis(3,5-dimethylpyridine)cobalt(II)³⁹ we have calcu-

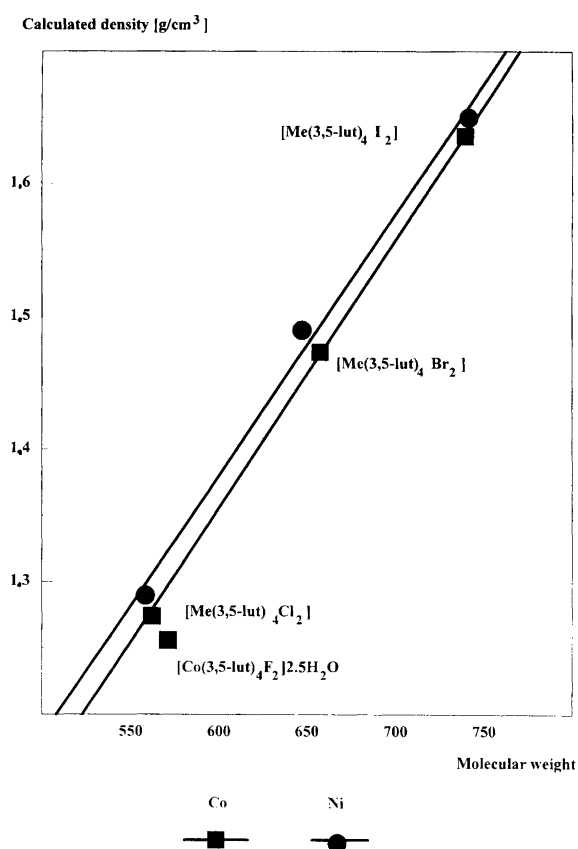


Fig. 2. Calculated density vs. molecular weight for 3,5-lutidine complexes.

lated the cobalt(II)-halogen distances for the bromide and iodide analogues from good quality powder diffraction patterns. The calculated bond lengths (Table 3) increase from the fluoro to the iodo complex, and they 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 sums of the ionic radii of cobalt(II) and the appropriate halide thus decreases from the fluoride to the iodide (Fig. 3). This is probably due to the increasing polarisation in the same order. Pyridine-type complexes are stabilized by back donation [Co $d\pi \rightarrow p\pi N(py)$]. These electrons may be localized on the second, fourth and sixth positions of the pyridine ring. With increasing polarisability of the anions, the

Table 3. The cobalt-halogen bond lengths for dihalogenotetrakis(3,5-dimethylpyridine)cobalt(II).

Compound	Co=X bond lengths/ \AA	Sum of the ionic radii of the Co ^{II} and the halogen/ \AA
[Co(3,5-lut) ₄ F ₂]·2H ₂ O	2.02 ^a	2.10
[Co(3,5-lut) ₄ Cl ₂]	2.45 ^b	2.55
[Co(3,5-lut) ₄ Br ₂]	2.63	2.69
[Co(3,5-lut) ₄ I ₂]	2.88	2.90

^a Obtained from single-crystal measurements.⁴⁴ ^b Obtained from single-crystal measurements.³⁹

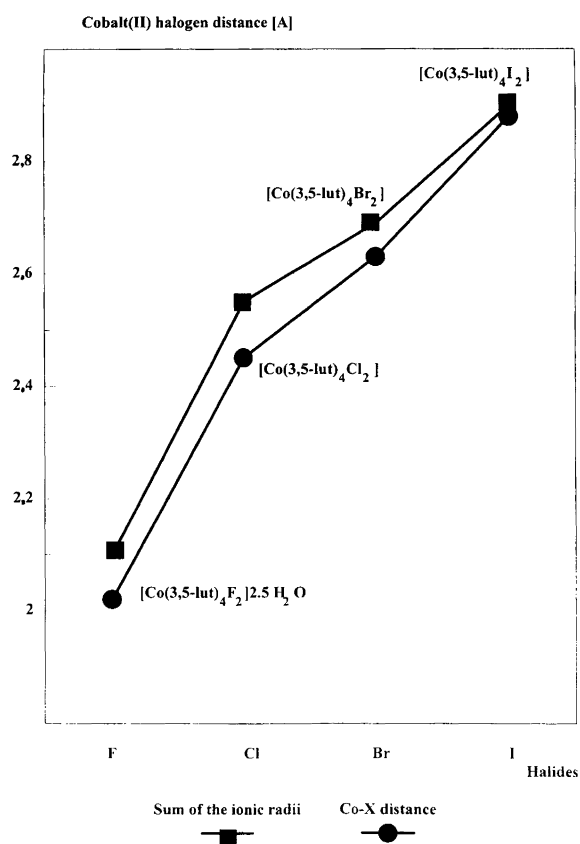


Fig. 3. Cobalt(II)-halogen distances and the sum of the ionic radii for 3,5-lutidine complexes.

high charge acquired by the central Co ion can be reduced via back donation. Although the observed cobalt–halogen distances increase from chloride to iodide, as expected, the *c* cell parameters falling into the cobalt–halogen bond direction decrease in the same order. This is probably due to molecular packing effects or halogen–halogen intermolecular interactions. There are two molecules in the unit cell, occupying approximately two quarters of the cell. The shortest intermolecular halogen–halogen distances are approximately half of the *c* parameters, which are slightly longer than 5 Å. Owing to these relatively long intermolecular halogen–halogen distances we suggest that the molecular packing effect plays a major role in the observed change of the *c* parameters.

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