

# Pyridine-Type Complexes of Transition-Metal Halides V.\* Preparation, Thermal Properties, Infrared Spectra and Crystal Structure of Dibromo-bis(2-bromopyridine)cobalt(II)

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The title compound crystallizes in the triclinic space group  $P\bar{1}$  with  $a = 8.024(2)$ ,  $b = 8.696(2)$ ,  $c = 11.353(2)$  Å,  $\alpha = 84.63(1)$ ,  $\beta = 78.26(2)$ ,  $\gamma = 69.69(2)^\circ$  and  $Z = 2$ . Anisotropic refinement of Br and Co atoms and isotropic rigid group treatment of pyridine rings gave a final  $R = 0.040$  for 1504 reflections. The  $C_{2v}$  symmetry around tetracoordinated Co is slightly distorted owing to the difference in the Co–Br distances; this is also apparent from the far-infrared spectra. The structural study was extended by molecular mechanics (MM+ and MMX) and molecular orbital (SINDO1) calculations, the results from the latter method showing a remarkable agreement with the X-ray data. TG/DTA measurement showed a single-step release of all ligands around 200°C.

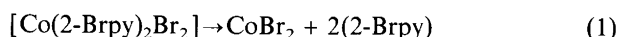
Considerable interest has been focused on studies clarifying the factors which effect the thermal and structural properties of complexes formed by cobalt(II) halides and pseudo-halides with pyridine and substituted pyridines. The symmetry and the environment around the central atom has mainly been described on the basis of spectroscopic data (electronic and/or infrared),<sup>1–9</sup> but in some cases also the accurate crystal structures are known.<sup>10–17</sup>

In the case of dibromo-bis(2-bromopyridine)cobalt(II), McWhinnie<sup>18</sup> has reported the diffuse reflectance spectra. The results of Billing and Underhill<sup>19</sup> and those by Gill and Kingdon<sup>20</sup> also support the expected tetrahedral coordination around the cobalt atom. From the electronic spectra it was suggested that the symmetry of the complex would be  $C_{2v}$  or lower.<sup>19</sup>

Relatively little attention has been paid to the far-infrared spectra of the halogenopyridine complexes of cobalt(II) halides.<sup>4,5</sup> For the  $[ML_2X_2]$  complexes eight IR-active metal–ligand modes would be expected on the basis of the  $C_{2v}$  symmetry. In addition to these bands, an extra band is observed with increasing intensity from the chloride to the iodide analogue.<sup>21</sup> This band can be as-

signed to the  $\delta(\text{Br–Co–N}) (A_2)$  mode, which is expected to be Raman-active only, and reflects a possible deviation from the ideal  $C_{2v}$  symmetry.

The thermal decomposition of the dibromo-bis(2-bromopyridine)cobalt(II) complex was found to be a single-step process:<sup>22</sup>



From calorimetric measurements Mortimer and McNaughton<sup>22</sup> calculated the mean dissociation energies of the Co–N bond for cobalt(II) chloride and bromide complexes formed with halogenopyridines. It was concluded that the substitution in the second position of the pyridine ring reduces the strength of the metal–ligand bond; however, this effect was less pronounced for the cobalt(II) bromide than for the chloride derivatives. Similar observations were made earlier by Beech *et al.*<sup>23</sup> for the 2-methyl-substituted pyridine (2-picoline) complexes. The difference between the heats of dissociation of bis-pyridine and bis-2-picoline complexes of cobalt(II) halides decreased from the chloride to the bromide analogs. The observed enthalpies for the bis-pyridine and 2-picoline complexes of cobalt(II) iodine were equal. These were explained by taking into consideration the increasing polarizability from chloride to iodide. The increasing charge

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acquired by the cobalt atom in the same order, caused by the increasing charge transfer from chloride to iodide, further reduces the affinity between the pyridine-type ligands.

In the light of the above observations we decided to determine the crystal structure of the title compound and compare it with the thermal and spectroscopic data.

## Experimental

**Preparation of the complex.** 0.01 mol of Co(II) carbonate (Reanal p.a.) suspended in water and 0.015 mol of HBr (Reanal p.a.) were used to prepare  $\text{CoBr}_2 \cdot 6\text{H}_2\text{O}$ . The pink crystals of the hexahydrate were filtered off and dehydrated at  $300^\circ\text{C}$ , and the blue anhydrous cobalt(II) bromide obtained (0.005 mol) was dissolved in acetonitrile ( $20\text{ cm}^3$ ) and purified by distillation from  $\text{P}_2\text{O}_5$ . 2-Bromopyridine, dried over KOH, was blended with  $20\text{ cm}^3$  of acetonitrile and added to the reaction mixture under stirring from a dropping funnel. The blue solution thus formed was heated and kept at its boiling point for 1 h. Plate-shaped, blue crystals were formed during slow cooling, and they were washed with a small amount of the cooled solvent and dried over  $\text{CaCl}_2$  in a desiccator. Results from elemental analysis (C,H,N) and complexometric titration (Co) corroborated the stoichiometry.

**Thermal analysis.** Simultaneous TG/DTG/DTA measurement was made in an argon atmosphere on Seiko TG/DTA 320 equipment of the SSC 5200 series using a sample weight of 5 mg and a heating rate of  $5\text{ K min}^{-1}$ . Standard aluminium crucibles were used, and  $\alpha\text{-Al}_2\text{O}_3$  was employed as DTA reference.

The enthalpy changes were quantitatively determined by a Perkin-Elmer DSC-7 instrument with a sample weight of 5 mg and a heating rate of  $5\text{ K min}^{-1}$  in aluminium crucibles. Holes were made on the lid of the sample holder in order to avoid the increasing ligand pressure during the decomposition.

**Infrared spectra.** The far-infrared spectrum was obtained on a Digilab FTS spectrophotometer equipped by TGS detector and  $6\text{ }\mu\text{m}$  hylar beam splitter. For sample preparation, a nujol mull and polyethylene matrix were used. The observed bands together with their assignments are listed in Table 1.

**X-Ray crystallography.** A structural analysis based on single-crystal data was carried out for the title compound. Details of data collection and crystal data are summarized in Table 2. The intensities were corrected for Lorentz and polarization effects and empirically for absorption by diffraction vector rotation. Direct methods with random starting multisolution and tangent refinement were used to obtain the positions of bromine and cobalt atoms. After isotropic refinements the subsequent difference map revealed the N and O atom positions. In

Table 1. Far-infrared spectra of the title compound.

Frequency	Assignment
644(m)	ip $\delta$ -ring
469(m)	oop $\gamma$ -ring
416(vs)	Ring deformation vibrations
339(vw)	Ring deformation vibrations
308(vs)	Ring deformation vibrations
278(vw)	Ring deformation vibrations
252(vs)	$\nu(\text{Co}-\text{Br})\text{A}_1$
237(vs)	$\nu(\text{Co}-\text{Br})\text{B}_1$
219(vs)	$\nu(\text{Co}-\text{N})\text{A}_1$
202(m)	$\nu(\text{Co}-\text{N})\text{B}_1$
162(w)	$\delta(\text{Br}-\text{Co}-\text{N})\text{A}_2$
134(w)	$\delta(\text{N}-\text{Co}-\text{N})\text{A}_1$
122(w)	$\delta(\text{Br}-\text{Co}-\text{N})\text{B}_1, \text{B}_2$
97(s)	$\delta(\text{Br}-\text{Co}-\text{Br})\text{A}_1$

w=weak, m=medium, s=strong, v=very, ip  $\delta$ -ring=in-plane ring deformation, oop  $\gamma$ -ring=out-of-plane ring deformation vibrations.

the final refinements, Br and Co atoms were refined anisotropically and pyridine rings together with hydrogen atoms as rigid groups, N and C atoms with individual isotropic temperature factors, however. Hydrogen atoms were refined with a common isotropic temperature factor for each ring. All calculations were carried out with the SHELX-76 program package. The final atomic coordi-

Table 2. Summary of crystal data, intensity collection and structure refinement for  $[\text{CoBr}_2(\text{C}_5\text{H}_4\text{BrN})_2]$ .

Crystal data	
Formula	$\text{C}_{10}\text{H}_8\text{Br}_4\text{CoN}_2$
Mol. wt./g mol <sup>-1</sup>	534.8
Crystal system	Triclinic
Space group	<i>P</i> 1
<i>a</i> /Å	8.024(2)
<i>b</i> /Å	8.696(2)
<i>c</i> /Å	11.353(2)
$\alpha/^\circ$	84.63(1)
$\beta/^\circ$	78.26(2)
$\gamma/^\circ$	69.69(2)
<i>V</i> /Å <sup>3</sup>	727.1(3)
<i>Z</i>	2
<i>d</i> <sub>calc</sub> /g cm <sup>-3</sup>	2.434
Radiation	MoK $\alpha$ ( $\lambda = 0.71069\text{ Å}$ )
$\mu(\text{MoK}\alpha)/\text{mm}^{-1}$	12.05
Crystal size/mm <sup>3</sup>	0.2 × 0.2 × 0.5
Crystal description	Blue plates
Data collection and structure refinement	
Data collection	$\omega$ -Scan
Scan speed/ $^\circ\text{ min}^{-1}$	10
No. of data collected	1918
No of data with $I_{\text{obs}} > 2\sigma(I_{\text{obs}})$	1514
Solution	Direct methods
Absorption correction	Empirical
No. of variables	73
Weighting scheme	$w = [\sigma^2(F_o)]^{-1}$
$R = \sum \ F_o -  F_c \ ^2 / \sum  F_o $	0.0532
$R_w(R_w = [\sum w( F_o -  F_c  )^2 / \sum wF_o^2]^{1/2})$	0.0402
Max/min peaks in difference map/e <sup>-</sup> Å <sup>-3</sup>	0.87/-0.76

nates of nonhydrogen atoms are presented in Table 3. Table 4 lists selected intramolecular distances and angles.

**Molecular geometry calculations.** The conformation of the complex was also studied by molecular mechanics and molecular orbital calculations. MM+<sup>24</sup> and MMX<sup>25</sup> force fields as well as SINDO1<sup>26,27</sup> semiempirical methods were used in an IBM 80486 PC and on IBM RISC 6000 system, respectively. MM+ molecular mechanics calculations were carried out using Hyperchem computational package.<sup>28</sup>

## Results and discussion

**Thermal analysis.** TG/DTA curves showed a simple, one-step endothermic decomposition [eqn. (1)] with a DTG maximum at 201 °C. Simultaneous release of both ligands indicates a similar bond strength. The enthalpy of the reaction as determined from the DSC curve (188.1 J g<sup>-1</sup>) is significantly lower than that found by Mortimer and McNaughton (241.7 J g<sup>-1</sup>).<sup>22</sup>

**Far-infrared spectra.** On the basis of the C<sub>2v</sub> symmetry several metal–ligand vibrations are expected, but only the Co–Br and Co–N stretching frequencies appearing above 200 cm<sup>-1</sup> have been described previously.<sup>18</sup> The spectrum below 200 cm<sup>-1</sup> is complicated (Table 1). Our assignments are based on the shifts due to the change of

Table 3. Atomic positional parameters and isotropic temperature factors for CoBr(C<sub>5</sub>H<sub>10</sub>NBr)<sub>2</sub>.

Atom	x	y	z	B <sub>iso</sub> <sup>a</sup>
Br(1)	0.7868(4)	-0.9334(2)	0.7935(2)	5.03
Br(2)	0.7429(3)	0.4669(2)	0.6459(2)	4.01
Br(3)	0.2755(3)	0.1306(2)	0.8833(2)	4.24
Br(4)	0.2569(3)	0.4953(2)	0.6671(2)	3.92
Co	0.4606(4)	0.2618(3)	0.7535(2)	3.17
C(1)	0.6047(13)	0.1644(10)	0.5007(9)	3.48
C(2)	0.7037(13)	0.0632(10)	0.4048(9)	4.03
C(3)	0.8304(13)	-0.0887(10)	0.4257(9)	3.97
C(4)	0.8581(13)	-0.1394(10)	0.5225(9)	3.42
C(5)	0.7579(13)	-0.0382(10)	0.6384(9)	3.38
N(1)	0.6324(13)	0.1137(10)	0.6175(9)	2.94
H(1)	0.5067(19)	0.2820(10)	0.4845(9)	11.53
H(2)	0.6822(13)	0.1025(10)	0.3144(9)	11.53
H(3)	0.9070(13)	-0.1670(10)	0.3515(9)	11.53
H(4)	0.9562(13)	-0.2569(10)	0.5587(9)	11.53
C(6)	0.5983(14)	0.2738(12)	0.9755(8)	3.52
C(7)	0.6996(14)	0.3127(12)	1.0471(8)	4.89
C(8)	0.8152(14)	0.3997(12)	0.9974(8)	4.58
C(9)	0.8295(14)	0.4476(12)	0.8762(8)	4.07
C(10)	0.7282(14)	0.4086(12)	0.8046(8)	3.33
N(2)	0.6126(14)	0.3217(12)	0.8542(8)	2.55
H(6)	0.5087(14)	0.2065(12)	1.0139(8)	11.90
H(7)	0.6885(14)	0.2756(12)	1.1409(8)	11.90
H(8)	0.8937(14)	0.4298(12)	1.0528(8)	11.90
H(9)	0.9191(14)	0.5149(12)	0.8378(8)	11.90

<sup>a</sup> The isotropic temperature factors were calculated here from the mean-square displacements:  $B = 8\pi^2\mu^{-2}$ .

Table 4. Selected intramolecular bond lengths (in Å) and angles (in °).<sup>a</sup>

Bond lengths			
Co–Br(3)	2.379(3)	Co–N(1)	2.061(10)
Co–Br(4)	2.396(3)	Co–N(2)	2.045(10)
Bond angles			
N(1)–Co–Br(3)	112.6(3)	N(2)–Co–Br(4)	113.3(3)
N(1)–Co–N(2)	108.4(4)	Br(3)–Co–Br(4)	105.7(1)
N(1)–Co–Br(4)	108.9(2)	Co–N(1)–C(1)	116.5(2)
N(2)–Co–Br(3)	107.9(2)	Co–N(1)–C(5)	123.1(2)

<sup>a</sup> The rigid refinement of pyridine ring C–H and C–C/C–N distances gave 1.080 and 1.395 Å, respectively. The angles within the ring were fixed at 120°.

substituent in the second position of the pyridine ring and on the fact that the halide ligands are bound directly to the metal.<sup>21</sup> The observed δ(Br–Co–N) (A<sub>2</sub>) mode in the IR spectra indicates a distortion from C<sub>2v</sub> symmetry.

**Crystal structure.** In the tetracoordinated cobalt(II) complex, the environment around the central atom is slightly distorted (Fig. 1). The Co–N bond lengths are equal within the standard deviation (Table 4); thus the bromopyridine ligands are bound with the same energy, explaining the one-step thermal decomposition pattern. On the other hand, the Co–Br(3) and Co–Br(4) distances are slightly different, which leads to a distorted C<sub>2v</sub> symmetry. The angles formed by Br(3)–Co–Br(4), N(1)–Co–Br(4), N(2)–Co–Br(3) and N(2)–Co–N(2) are somewhat smaller, while N(1)–Co–Br(3) and N(2)–Co–Br(4) are significantly larger compared with those in an ideal tetrahedron (Table 4). This arrangement leads to large distances between the bromide atoms substituted in the pyridine rings and those bound directly to the metal. The distortion can also be explained by the electronic repul-

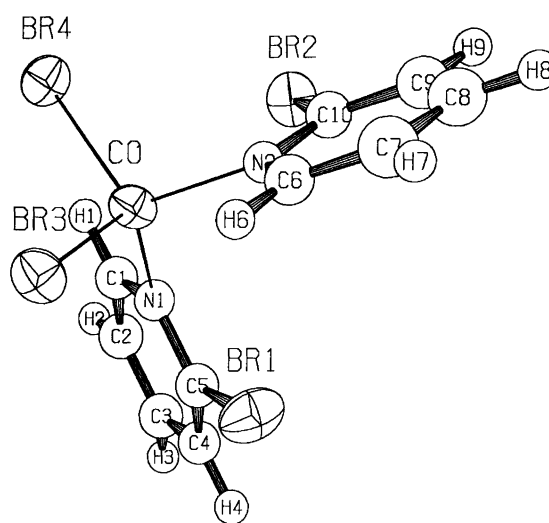


Fig. 1. A perspective view of the coordination around the cobalt(II) ion showing the atomic numbering scheme.

sive effect between the bromide ligands Br(3) and Br(4) and the pyridine rings having high electron densities. The high charge around the Br(3) and Br(4) is reduced by charge transfer from the halides to the cobalt(II) atom. This process could become more effective when the charge around the central cobalt(II) atom is lowered by back-donation of electrons to the non-bonding  $\pi$ -orbital of the nitrogen in the pyridine rings. The charge transfer along the Co–N  $\sigma$ -bond is small because of the relatively low electron density on the nitrogen atoms ( $pK_a = 0.71$ )<sup>29</sup> as compared to the 2-substituted alkyl and amino analogs, and thus the polarization of the Co–Br bonds can become more dominant. The effects combined lead to the small Br(3)–Co–Br(4) angle.

Judging from the long Br(1)–H(6) distance (2.92 Å), it appears that hydrogen bonds of significant strength are not present in the structure. Nevertheless, the N(1)–C(5)–Br(1) angle is slightly smaller compared to the Br(1)–C(5)–C(9) angle (118.2 and 121.8°, respectively), indicating possible interactions involving the hydrogen atoms.

*Calculations on molecular geometry.* The geometry optimization was started from the X-ray geometry. MM+ molecular mechanics calculations yielded bond lengths which deviated from the X-ray values, but calculated bond angles for bonds involving the cobalt atom were in agreement with the experimental values (Table 5). Geometry optimization on MMX force field resulted in metal bond lengths which could be correlated with experimental values, but here the corresponding bond angles were significantly different. Our results suggest that the MMX transition-metal bond-stretching parameters are better than in MM+. Calculation of the bending energy with MM+ angle bending parameters gave more accurate results than the MMX calculation.

In order to get more reliable results semiempirical calculations were carried out on SINDO1 level, which has recently been extended to transition-metal compounds.<sup>30</sup> SINDO1 has proven to be accurate for molecular geometry calculation of transition-metal complexes; the results

Table 5. Comparison of the bond lengths (in Å) and bond angles (in °) for dibromo-bis(2-bromopyridine)cobalt(II) obtained from X-ray analysis and geometry optimization by MMX and MM+ molecular mechanics and SINDO1 semiempirical calculation.

Bonds/Angles	MM+	MMX	SINDO1	X-ray
Co–N1	1.79	2.05	2.05	2.06
Co–N2	1.78	2.02	2.05	2.04
Co–Br1	2.71	2.30	2.37	2.38
Co–Br2	2.70	2.30	2.41	2.40
N1–Co–Br1	112.0	106.5	112.4	112.6
N1–Co–Br2	109.3	107.4	108.5	108.9
N2–Co–Br1	113.3	109.6	112.9	113.3
N2–Co–Br2	108.4	106.4	107.5	107.9
N1–Co–N2	110.5	115.6	108.7	108.4
Br1–Co–Br2	106.7	107.1	105.3	105.7

are comparable to the 3-21 *ab initio* method.<sup>31</sup> The geometry of title compound was optimized by INDO ROHF method starting from the X-ray geometry. Updated Hessian geometry optimization was carried out using Givens matrix diagonalization; convergence was improved by variable weighting method.

The calculated bond lengths and bond angles were in extremely good agreement with corresponding experimental data (cf. Table 5); the geometry optimization gave more reliable results than molecular mechanics calculations. Results demonstrate that SINDO1 appears to be a most powerful tool for the calculation of molecular geometry of cobalt complexes. The calculated electronic structure will be further discussed in a forthcoming paper.<sup>32</sup>

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## References

- Gill, N. S., Nuttall, R. H., Sceife, D. E. and Sharp, D. W. A. *J. Inorg. Nucl. Chem.* 18 (1969) 79.
- Gill, N. S., Nyholm, R. S., Barclay, G. A., Christy, T. I. and Pauling, P. J. *J. Inorg. Nucl. Chem.* 18 (1961) 88.
- Allan, J. R., Brown, D. H., Nuttall, R. H. and Sharp, D. W. A. *J. Inorg. Nucl. Chem.* 26 (1964) 1895.
- Clark, R. J. H. and Williams, C. S. *Inorg. Chem.* 4 (1965) 350.
- Allan, J. R., Brown, D. H., Nuttall, R. H. and Sharp, D. W. A. *J. Inorg. Nucl. Chem.* 27 (1965) 1305.
- Allan, J. R. and Baillie, G. M. *J. Therm. Anal.* 14 (1978) 291.
- Darby, E. W. L. and Vallarino, L. M. *Inorg. Chim. Acta* 48 (1981) 215.
- Allan, J. R. and Weitch, P. M. *J. Therm. Anal.* 27 (1983) 3.
- Thornton, D. A. *Coord. Chem. Rev.* 104 (1990) 251.
- Admiraal, L. J. and Gafner, G. *Chem. Commun.* (1968) 1221.
- Goldstein, M. and Unsworth, G. W. *Inorg. Chim. Acta* 4 (1970) 342.
- Cameron, A. F., Taylor, D. W. and Nuttall, R. H. *J. Chem. Soc., Dalton Trans.* (1972) 1603.
- Andreetti, G. D. and Sgarabotto, P. *Cryst. Struct. Commun.* 1 (1972) 55.
- Laing, M. and Carr, G. *Acta Crystallogr., Sect. B* 31 (1975) 2683.
- Hartl, H. and Steidl, S. *Acta Crystallogr., Sect. B* 36 (1980) 65.
- Hartl, H. and Brudgam, I. *Acta Crystallogr., Sect. B* 36 (1980) 162.
- Kenessey, G., Parkanyi, L., Werner, P.-E., Wadsten, T., Bihatsi, L. and Liptay, G. *Struct. Chem. In press.*
- McWhinnie, W. R. *J. Inorg. Nucl. Chem.* 25 (1965) 2573.
- Billing, D. E. and Underhill, A. E. *J. Chem. Soc. A* (1968) 29.
- Gill, N. S. and Kingdon, H. J. *Austral. J. Chem.* 19 (1966) 2197.

21. Kenessey, G., Mink, J. and Liptay, G. *Unpublished results*.
22. Mortimer, C. and McNaughton, J. L. *Thermochim. Acta* 10 (1974) 207.
23. Beech, G., Mortimer, C. T. and Tyler, E. G. *J. Chem. Soc. A* (1967) 925.
24. MM+ molecular mechanics force field from Hyperchem computation package.
25. MMX is a generalized version of Allinger's MM2, extended by W. C. Still and adapted to Microsoft FORTRAN by G. Gajewski and K. Gilbert.
26. Nanda, D. N. and Jug, K. *Theor. Chim. Acta* 57 (1980) 95.
27. Jug, K., Iffert, R. and Schultz, J. *Int. J. Quantum Chem.* 32 (1987) 265.
28. Hyperchem from Autodesk Inc. (1992) 2320 Marinship Way, Sausalito, CA 94965, USA. The program used was an authorized copy of Prof. N  ray-Szab  .
29. Perrin, P. P. *Dissociation Constants of Organic Bases in Aqueous Solutions*, Academic Press, London 1965.
30. Li, J., Correa, P. and Jug, K. *J. Comput. Chem.* 13 (1992) 85.
31. Li, J. and Jug, K. *J. Comput. Chem.* 13 (1992) 93.
32. Keser  , G. M., Hajnal, Z. and Kenessey, G. *Theochem., J. Mol. Struct.* (1994). *In press*.

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