Acta Chemica Scandinavica A 30 (1976) 475—484

Short Communications

The Crystal Structure of Bromidobis(ethylenediamine)pyridinecobalt(III) Nitrate, $[CoBr(en)_2py](NO_3)_2$

OLLE BÖRTIN

Department of Inorganic Chemistry, University of Göteborg and Chalmers University of Technology, P.O. Box, S-402 20 Göteborg 5, Sweden

The crystal structure of bromidobis(ethylenediamine)pyridinecobalt(III) nitrate has been determined. The cell dimensions were obtained from powder diffraction photographs taken with a Guinier focusing camera using lead nitrate ($a = 7.8566$ Å)[1] as an internal standard and refined by the method of least squares using the program POWDER. Bromidobis(ethylenediamine)pyridinecobalt(III) nitrate was found to be monoclinic with $a = 13.141(3)$ Å, $b = 14.982(5)$ Å, $c = 9.075(3)$ Å, $\beta = 94.27(2)°$, $V = 1781$ Å^3, $Z = 4$, space group $P2_1/n$.

The positions of the cobalt and bromine atoms were obtained from Patterson calculations and the other atoms from successive electron density calculations. The structure was refined by least squares using the program BLOCK. The atomic scattering factors used were those calculated by Cromer and Waber.[2] The structure factors were weighted according to Cruickshank[3] with $a = 60.0$ and $c = 0.01$. Anisotropic thermal parameters of the atoms were introduced in the last cycles and the reliability index $R = \sum||F_o| - |F_c||/\sum|F_o|$ finally converged to 0.11. Some of the light atoms, however, were not positive definite. The resulting parameters are given in Table 1. A list of observed and calculated structure factors is available on request. The distances and angles were calculated with the program DISTAN and are listed in Tables 2 and 3.

Table 1. Final atomic parameters for $[CoBr(en)_2py](NO_3)_2$ (standard deviations in parentheses).

Atom	x	y	z
Co	0.0643(4)	0.2725(4)	0.3174(5)
Br	0.0109(4)	0.1648(5)	0.1266(5)
N(1)	0.1145(18)	0.3600(19)	0.4626(26)
C(1)	0.2200(32)	0.3871(31)	0.4363(38)
C(2)	0.2771(32)	0.3086(34)	0.3733(48)
N(2)	0.2081(19)	0.2565(24)	0.2624(29)
N(3)	0.0385(16)	0.3641(18)	0.1707(26)
C(3)	-0.0735(28)	0.3885(43)	0.1452(41)
C(4)	-0.1217(29)	0.3721(37)	0.2957(48)
N(4)	-0.0775(17)	0.2895(23)	0.3599(27)
N(5)	0.0864(18)	0.1695(18)	0.4593(22)
C(5)	0.0537(22)	0.1859(22)	0.6006(38)
C(6)	0.0580(26)	0.1131(31)	0.7126(50)
C(7)	0.1095(26)	0.0339(32)	0.6733(58)
C(8)	0.1479(39)	0.0292(39)	0.5336(55)
C(9)	0.1350(31)	0.0964(28)	0.4311(49)
N(6)	0.3941(18)	0.0933(17)	0.1993(27)
O(1)	0.4484(16)	0.0430(17)	0.1257(29)
O(2)	0.3528(21)	0.0518(22)	0.3008(31)
O(3)	0.3785(21)	0.1659(19)	0.1743(32)
N(7)	0.1975(13)	0.3308(16)	0.8610(18)
O(4)	0.2455(19)	0.3262(20)	0.9767(28)
O(5)	0.2359(24)	0.3119(26)	0.7487(32)
O(6)	0.1116(27)	0.3550(23)	0.8578(28)

Table 2. Bond distances and angles in $[CoBr(en)_2py](NO_3)_2$ (standard deviations in parentheses).

Distance (Å)		Angle (°)	
Co - Br	2.431(8)	Co - N(1) - C(1)	111(2)
Co - N(1)	1.939(27)	N(1) - C(1) - C(2)	110(3)
Co - N(2)	2.004(27)	C(1) - C(2) - N(2)	111(3)
Co - N(3)	1.925(26)	C(2) - N(2) - Co	108(2)
Co - N(4)	1.948(23)	Co - N(3) - C(3)	113(2)
Co - N(5)	2.016(26)	N(3) - C(3) - C(4)	106(3)
N(1) - C(1)	1.48(5)	C(3) - C(4) - N(4)	108(4)
C(1) - C(2)	1.53(7)	C(4) - N(4) - Co	113(2)
C(2) - N(2)	1.52(5)	Co - N(5) - C(5)	114(2)
N(3) - C(3)	1.52(4)	Co - N(5) - C(9)	125(2)
C(3) - C(4)	1.57(6)	N(5) - C(5) - C(6)	120(3)
C(4) - N(4)	1.47(6)	C(5) - C(6) - C(7)	116(4)
N(5) - C(5)	1.40(4)	C(6) - C(7) - C(8)	119(4)
C(5) - C(6)	1.49(6)	C(7) - C(8) - C(9)	123(4)
C(6) - C(7)	1.42(6)	C(8) - C(9) - N(5)	121(4)
C(7) - C(8)	1.40(7)	C(9) - N(5) - C(5)	121(3)
C(8) - C(9)	1.37(7)	O(1) - N(6) - O(2)	113(3)
C(9) - N(5)	1.30(5)	O(1) - N(6) - O(3)	125(3)
N(6) - O(1)	1.26(4)	O(2) - N(6) - O(3)	123(3)
N(6) - O(2)	1.27(4)	O(4) - N(7) - O(5)	120(2)
N(6) - O(3)	1.13(4)	O(4) - N(7) - O(6)	119(2)
N(7) - O(4)	1.19(3)	O(5) - N(7) - O(6)	121(2)
N(7) - O(5)	1.20(4)		
N(7) - O(6)	1.18(4)		

Table 3. Packing distances less than 3.2 Å in $[CoBr(en)_2py](NO_3)_2$.

Distance (Å)	
Br - N(4)	3.11
N(1) - O(1)	3.09
N(1) - O(1)	2.96
N(1) - O(5)	3.03
C(1) - O(5)	3.04
C(2) - O(3)	3.16
N(2) - O(3)	2.79
N(2) - O(4)	2.87
N(3) - O(2)	3.16
N(3) - O(6)	3.07
N(4) - O(3)	3.03
N(4) - O(4)	3.15
N(4) - O(5)	3.00
N(6) - O(6)	3.20

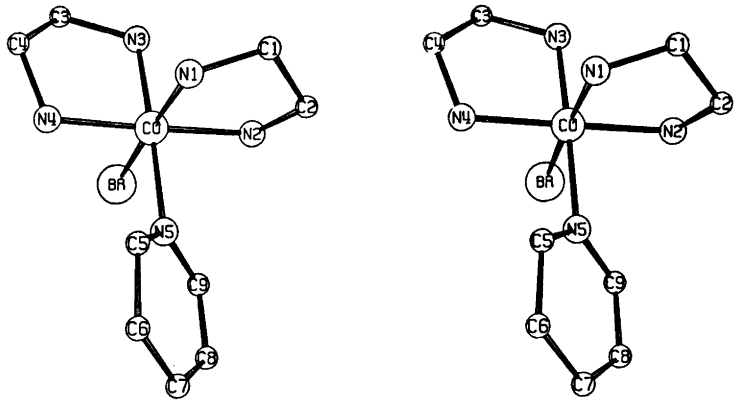

Fig. 1. A stereoscopic view of the ion $[CoBr(en)_2py]^{2+}$.

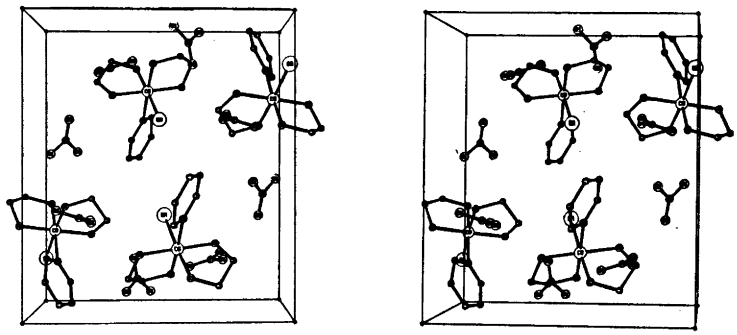

Fig. 2. A stereoscopic view of the structure.

The cobalt atom is octahedrally coordinated by one bromine atom and five nitrogen atoms with the bromine atom and the pyridine group in *cis* position to each other. The Co – Br bond distance is 2.43 Å and the Co – N bond distances are 2.02 Å (to py) and 1.93 – 2.00 Å (to en) with the shorter distances to the nitrogen atoms in *trans* position to the bromido and pyridine groups. The bond angles Co – N5 – C5 of 114° and Co – N5 – C9 of 125° indicate that the pyridine group is repelled by the bromine atom. The distance from Br to C9 is 3.27 Å and the calculated distance from Br to a hydrogen atom bonded to C9 is 2.85 Å.

The large bromidobis(ethylenediamine)pyridinecobalt(III) ions are arranged in a close-packed manner. The nitrate ions occupy holes between the cations. The two different nitrate ions are situated rather close to each other with the shortest distance 3.2 Å between the atoms N6 and O6. Some distances between oxygen atoms of the nitrate ions and nitrogen atoms of the ethylenediamine groups indicate that the structure is held together by hydrogen bonds. The shortest of these distances are 2.8 – 3.0 Å.

The ion $[CoBr(en)_2py]^{2+}$ is shown in Fig. 1 and the unit cell in Fig. 2.

Acknowledgements. This work has been supported by Chalmers University of Technology, which has supplied a grant to cover the costs of the computer work, which was performed at the Göteborg Universities' Computing Centre.

1. *International Tables for X-Ray Crystallography*, 2nd Ed., Kynoch Press, Birmingham 1952, Vol. III.
2. Cromer, D. T. and Waber, J. T. *Acta Crystallogr. 18* (1956) 104.
3. Cruickshank, D. W. J. *The Equation of Structure Refinements*, Glasgow 1964.

Received January 20, 1976.