The Crystal and Molecular Structure of 2,2′-Bipyridinium Tetrabromocobaltate(II)

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2,2′-Bipyridine (=bip) reacts with $CoBr_2$ in a HBr solution to yield a moderately stable crystalline compound. Elemental analysis indicates the composition $[bipH_2][CoBr_4]$; this formula was confirmed by the X-ray analysis. We wish here to report the structural features of the $[CoBr_4]^{2-}$ ion and the conformation of the bipyridinium ion in the crystal.

Crystal data: monoclinic, space group $P2_1/c$: $a=8.420\pm0.005$, $b=14.00\pm0.01$, $c=12.878\pm0.006$ Å, $\beta=98.6\pm0.1°$; $Z=4$, $Dc=2.34$ g·cm^{-3}, $\mu=187.0$ cm^{-1} (for Ni$K\alpha$). Multiple-film equi-inclination Weissenberg photographs were taken with Ni$K\alpha$ radiation about the a and c axes, while the intensities of 1551 independent reflections were obtained by visual estimation.

The structure was solved by Patterson and Fourier methods, and the positional and isotropic thermal parameters were refined by the least-squares procedure. The conventional R-factor is 15.7% at this stage; further refinements are now in progress.

The crystal consists of bipyridinium cations and $[CoBr_4]^{2-}$ anions. In the anions, each cobalt atom is surrounded tetrahedrally by four bromine atoms. The mean value of the four Co–Br bond distances is 2.42 Å; this is presumably the first example found for the Co(II)–Br length. It is known that the configuration of the 2,2′-bipyridine molecule in the crystalline state is planar, the two nitrogen atoms being in the *trans* positions with respect to the C–C bond connecting the two pyridine rings.[1] However, this is not the case for our bipyridinium ion. As is shown in the figure, the pyridine rings are inclined toward one another, thus departing from the *trans*-coplanar configuration; the dihedral angle between the ring planes is 37.4°. The bipyridinium cation is isoelectronic with biphenyl, in which the angle of twisting is 45°.[2] The small discrepancy in those values may be attributable to the formation of rather strong hydrogen bonds between the two N^+–H groups in the cation and bromine atoms (N^+–H···Br^-=3.24 and 3.32 Å respectively). The bond distances and angles in the rings are normal within the range of standard deviation (~0.06 Å).

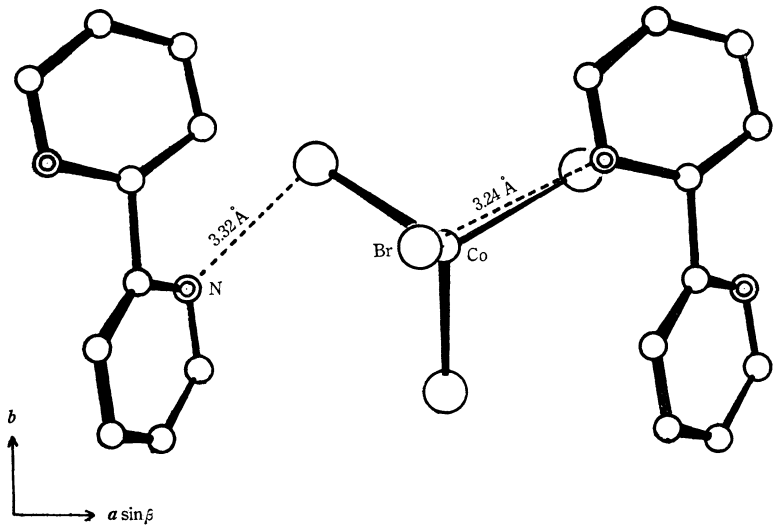

Fig. 1. The crystal structure viewed along the c axis.

1) L. L. Merritt, Jr., and E. D. Schroeder, *Acta Crystallogr.*, **9**, 801 (1956).

2) P. W. Allen and L. E. Sutton, *ibid.*, **3**, 46 (1950).