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

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The crystal structure of 2,2′-bipyridinium tetrabromocobaltate(II) has been established by successive Fourier analyses. The atomic parameters were refined by least-squares techniques, using the three-dimensional X-ray data, to an *R* factor of 0.127 for 1461 non-zero reflections. The complex crystallizes in the space group $P2_1/c$ with four formula units in the unit cell with dimensions of $a=8.42$, $b=14.00$, $c=12.88$ Å, and $\beta=98.7°$. The crystal consists of slightly distorted tetrahedral $[CoBr_4]^{2-}$ anions and 2,2′-bipyridinium cations, in which two pyridinium ring planes are inclined toward one another at an angle of 39°. The two N^+–H groups in the cation participate in N^+–H···Br$^-$ type hydrogen bonds (N···Br=3.23 Å and 3.31 Å). The mean value of the four Co–Br bond lengths is 2.42 Å.

In the course of the preparation of the bromo-analogue of *trans*-$[CoCl_2(bipy)_2]Cl$,[1,2] (bipy=2,2′-bipyridine), we isolated green crystals whose color is quite similar to that of the *trans*-$[CoBr_2en_2]Br\cdot HBr\cdot 2H_2O$.[3] However, the absorption spectra and elemental analyses of the compound suggested that this salt does not contain a complex cation of *trans*-$[CoBr_2(bipy)_2]^+$, but is a novel compound with the chemical formula of $[bipyH_2]\cdot[CoBr_4]$. Subsequently, this salt could be prepared by the direct reaction of 2,2′-bipyridine with $CoBr_2\cdot 6H_2O$ in concentrated hydrobromic acid. The chloro-analogue of this compound, $[bipyH_2][CoCl_4]$, can also be obtained by a similar method. Instead of characterizing the compound by means of the usual methods, such as a study of the IR or electronic spectra, we have undertaken an X-ray crystal analysis of $[bipyH_2][CoBr_4]$. We have already presented preliminary accounts of our work;[4] here the crystal structure of this compound will be given in detail.

Experimental

1) Preparation of Complexes. a) [bipyH$_2$][CoX$_4$] (X=Cl, Br): Both compounds were prepared by mixing equivalent amounts of the appropriate metal halide and bipyridine in conc. hydrohalogenic acid. The products were then recrystallized from the hot conc. HX solution. They are moderately hygroscopic.

2,2′-Bipyridinium Tetrabromocobaltate(II),

Yellowish-green crystals were obtained from the deep blue solution as needles.

Found: C, 22.35; H, 1.98; N, 5.16%. Calcd for $C_{10}H_{10}N_2Br_4Co=[bipyH_2][CoBr_4]$: C, 22.35; H, 1.87; N, 5.21%.

2,2′-Bipyridinium Tetrachlorocobaltate(II),

Large blue crystals were obtained from a deep blue solution in the form of plates.

Found: C, 33.61; H, 2.93; N, 7.99%. Calcd for $C_{10}H_{10}N_2Cl_4Co=[bipyH_2][CoCl_4]$: C, 33.45; H, 2.79; N, 7.80%.

b) Pyridinium Tetrabromocobaltate(II), [pyH]$_2$[CoBr$_4$] (py=pyridine): This compound was prepared following the method of Percival and Wardlaw.[5]

Found: C, 23.67; H, 2.67; N, 5.65%. Calcd for $C_{10}H_{12}N_2Br_4Co=[pyH]_2[CoBr_4]$: C, 22.29; H, 2.25; N, 5.20%.

2) Electronic Spectra of Solids. Specimens of $[bipyH_2][CoBr_4]$ and $[pyH]_2[CoBr_4]$ were ground with nujol and placed between two plates of opal glass, and their transmission spectra were measured with a Hitachi EPU-2A photoelectric spectrophotometer.[6]

3) X-Ray Data Measurement. The specimens used in the present investigation were coated with vaseline in order to prevent decomposition caused by atmospheric moisture. Oscillation and Weissenberg photographs taken with Ni$K\alpha$ radiation exhibited a monoclinic symmetry with space group $P2_1/c$. The lattice parameters were obtained from (*hk*0) and (*h*0*l*) Weissenberg photographs on which Al wire patterns had been superimposed; then they were refined by a least-squares method. In order to collect the three-dimensional intensity data, equi-inclination Weissenberg photographs were taken with Co-filtered Ni$K\alpha$ radiation from 0*kl* to 5*kl* and from *hk*0 to *hk*6, using a multiple-film technique. The intensities were visually estimated by the use of a standard scale. Thus, 1461 independent non-zero reflections were observed. These relative intensities were corrected for Lorentz and polarization factors, a spot-shape correction being made for upper layers. An absorption correction was applied to the data around the *c* axis, using a cylindrical approximation, since μR is equal to about 3.5. All the intensities were then placed on a common scale by a least-squares method. The crystal data are summarized in Table 1.

TABLE 1. CRYSTAL DATA

Formula	$C_{10}H_{10}N_2CoBr_4$
monoclinic	$a=8.42\pm0.01$ Å
	$b=14.00\pm0.02$
	$c=12.88\pm0.01$
	$\beta=98.7\pm0.2°$
Space Group	$P2_1/c$
Z	4
Dx	2.38 g/cm^3
μ	190 cm^{-1} (for Ni$K\alpha$)

1) F. M. Jaeger and J. A. van Dijk, *Z. Anorg Allg. Chem.*, **227**, 273 (1936).

2) Recently it was elucidated that the Jaeger's *trans*-$[CoCl_2\cdot bipy_2]Cl$ should be formulated as *cis*-$[CoCl_2bipy_2]_2\cdot[CoCl_4]$ (J.G. Gibson, R. Laird, and E. D. McKenzie, *J. Chem. Soc., A*, **1969**, 2089).

3) S. Ooi, Y. Komiyama, Y. Saito, and H. Kuroya, This Bulletin, **32**, 263 (1959).

4) S. Koda, S. Ooi, and H. Kuroya, *ibid.*, **43**, 971 (1970).

5) E. G. V. Percival and W. Wardlaw, *J. Chem. Soc.*, **1929**, 1505.

6) K. Shibata, "Methods of Biochemical Analysis," Vol. VII, Interscience Publishers, New York, N. Y. (1959), p. 77.

Structure Determination

The coordinates of the three bromine atoms were determined by an elaborate examination of the twenty largest peaks in the three-dimensional Patterson function. The positions of all the remaining atoms (except hydrogen) were found by successive three-dimensional Fourier analyses,[7] all the atoms of the pyridine rings being assumed provisionally to be carbon atoms at this stage. The refinement of the crystal structure was carried out by a block-diagonal-matrix, least-squares method.[8] Three cycles of refinement using isotropic temperature factors for all the atoms reduced the conventional R factor to 0.16.

The atoms in the close vicinity of each bromine atom were thoroughly examined in order to pick out the nitrogen atoms among the pyridine ring atoms, for it is quite reasonable to suppose that there must be N^+–H···Br^--type hydrogen bonds in the crystal. We found two ring atoms which are in close contact, 3.23 Å and 3.31 Å, with Br(1) and Br(4) respectively. They were identified as the nitrogen atoms on the basis of close contacts as well as the favorable directions of the hydrogen atoms.

In the further refinement, the anisotropic thermal parameters were applied to the heavy atoms. Four cycles of the least-squares calculation resulted in a convergence, with R=0.127, for all the 1461 non-zero reflections.

The atomic scattering factors used were taken from the International Tables for X-ray Crystallography. The final atomic coordinates and thermal parameters are given in Tables 2(a) and (b). All the numerical calculations were carried out on a FACOM 270-30 computer of our university. Tables of the observed and calculated structure factors are preserved by the Chemical Society of Japan.[9]

Results and Discussion

The crystal consists of 2,2′-bipyridinium cations and tetrahedral $[CoBr_4]^{2-}$anions. Figures 1 and 2 show the crystal structure viewed along the a and c axes respectively. As is shown in the figures, the structure is composed of regions of anions and cations, both elongated along the c axis. The arrangement of these ions

Table 2(a). The final atomic parameters (e.s.d's in parentheses)

Atom	x/a	y/b	z/c	B(Å^2)
Br(1)	0.2365(5)	0.2281(3)	0.0051(3)	*
Br(2)	−0.0068(5)	0.3132(3)	0.2204(3)	*
Br(3)	0.2540(6)	0.0714(3)	0.2582(4)	*
Br(4)	0.4813(5)	0.3224(3)	0.2528(3)	*
Co	0.2356(8)	0.2312(5)	0.1941(5)	*
N(1)	0.1128(34)	0.6758(20)	0.0615(23)	0.9(5)
N(2)	0.3491(34)	0.8129(20)	−0.0890(23)	0.8(5)
C(1)	0.2531(41)	0.6996(24)	0.0338(28)	0.8(6)
C(2)	0.3805(47)	0.6363(28)	0.0449(32)	1.6(7)
C(3)	0.3572(51)	0.5440(30)	0.0823(35)	2.0(8)
C(4)	0.2169(49)	0.5252(28)	0.1117(34)	1.8(7)
C(5)	0.0870(51)	0.5833(30)	0.0977(34)	2.1(8)
C(6)	0.2633(42)	0.8055(24)	−0.0087(29)	0.9(6)
C(7)	0.1928(42)	0.8790(25)	0.0364(29)	0.9(6)
C(8)	0.2154(51)	0.9709(30)	−0.0079(35)	2.1(8)
C(9)	0.2977(47)	0.9769(27)	−0.0920(33)	1.6(7)
C(10)	0.3694(52)	0.9017(31)	−0.1249(36)	2.3(8)

* Anisotropic temperature factors are listed in Table 2(b).

Table 2(b). The anisotropic temperature factors in the form of $\exp(-B_{11}h^2-B_{22}k^2-B_{33}l^2-B_{12}hk-B_{13}hl-B_{23}kl)$ (e.s.d's. in parentheses)

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Br(1)	0.0050(5)	0.0014(2)	0.0021(3)	0.0011(6)	0.0006(7)	0.0004(4)
Br(2)	0.0053(6)	0.0030(2)	0.0016(3)	0.0026(6)	0.0001(8)	−0.0010(4)
Br(3)	0.0106(7)	0.0007(2)	0.0038(3)	0.0007(6)	0.0035(9)	0.0016(4)
Br(4)	0.0051(6)	0.0017(2)	0.0024(3)	−0.0008(5)	−0.0008(8)	−0.0019(4)
Co	0.0097(9)	0.0020(3)	0.0045(5)	0.0004(9)	0.0018(13)	−0.0003(6)

7) The computer program used was kindly offered by Mr. Makoto Fukuyo of Osaka City University.

8) The computer program used was a modified version of HBLS-IV which was adapted for use with a FACOM 270-30 computer by Mr. Ken Hirotsu of Osaka City University.

9) The complete data of the F_o–F_c table are kept as Document No. 7107 at the office of the Chemical Society of Japan. A copy may be secured by citing the document number and by remitting, in advance, ¥150 for photoprints. Pay by check or money order payable to: The Chemical Society of Japan.

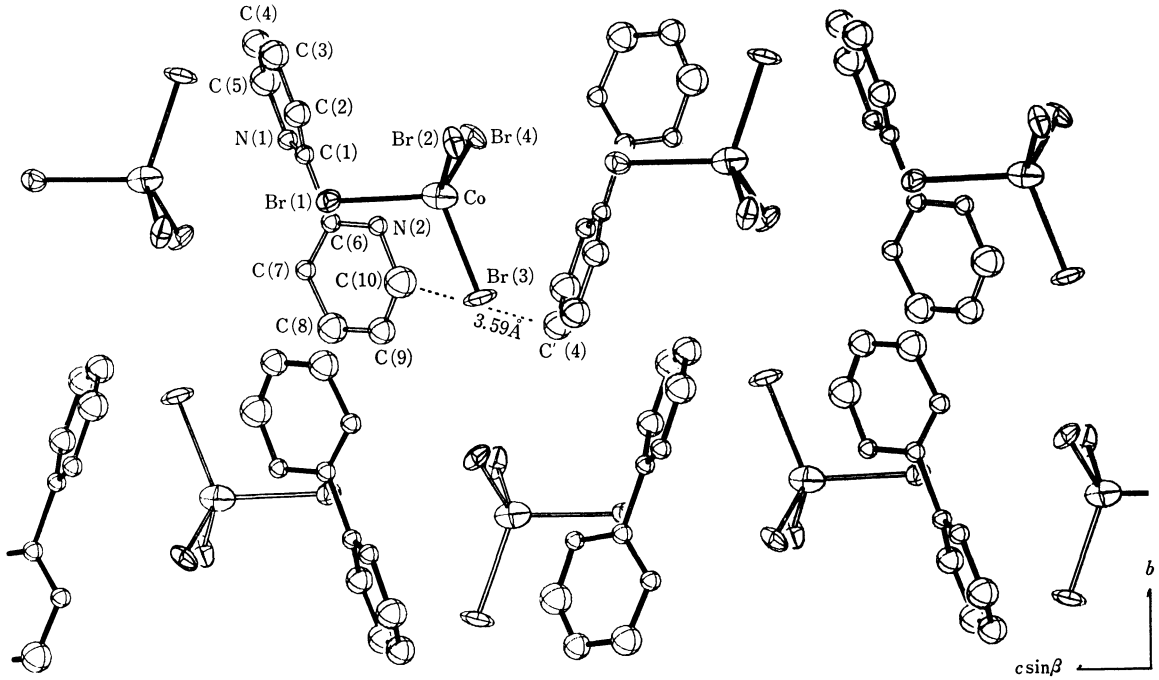

Fig. 1. The crystal structure viewed along the *a* axis.

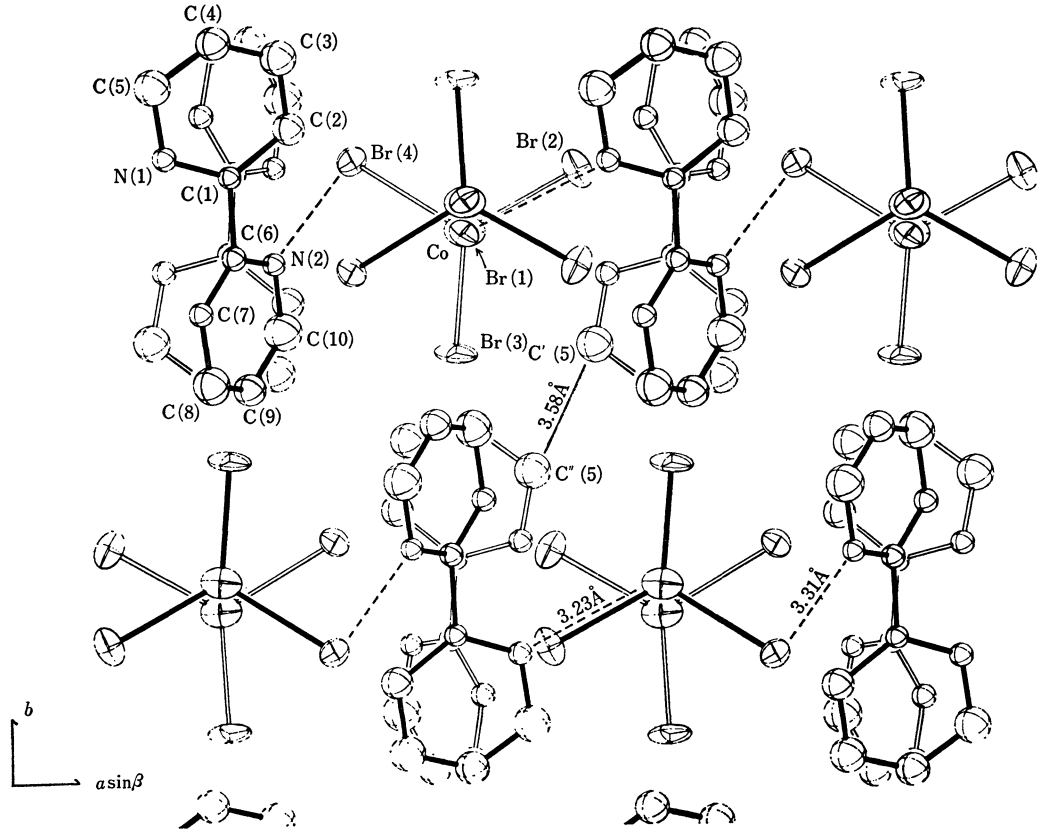

Fig. 2. The crystal structure viewed along the *c* axis.

in a checkered pattern is clearly illustrated in Fig. 2. Two-dimensional linkages are also formed by a N^+—H··· Br^--type hydrogen bonding extended along the *a* axis. These linkages are indicated by dashed lines in Fig. 2. The distances of the hydrogen bonds, 3.23 Å and 3.31Å, are in the range expected for this type. Apart from these, the closest intermolecular contacts are C′(5)··· C″(5) (=3.58 Å) and C′(4)···C(10) (=3.59 Å) (see Figs. 1 and 2). The interatomic distances and angles are listed in Tables 3(a) and (b).

It is known that the conformation of the 2,2′-bipyridine molecule is coplanar in the crystalline state, the

Table 3(a). Bond lengths (Å) and their standard deviations

Co-Br(1)=2.436(8)	Co-Br(2)=2.409(8)
Co-Br(4)=2.452(9)	Co-Br(3)=2.382(8)
C(1)-C(2)=1.38(5)	C(6)-C(7)=1.36(5)
C(2)-C(3)=1.40(6)	C(7)-C(8)=1.43(6)
C(3)-C(4)=1.32(6)	C(8)-C(9)=1.37(6)
C(4)-C(5)=1.35(6)	C(9)-C(10)=1.32(6)
C(5)-N(1)=1.41(5)	C(10)-N(2)=1.35(5)
C(1)-N(1)=1.33(5)	C(6)-N(2)=1.35(5)
C(1)-C(6)=1.59(5)	

Table 3(b). Bond angles (°) and their standard deviations

Br(1)-Co-Br(2)=106.1(5)	
Br(1)-Co-Br(3)=108.7(3)	
Br(1)-Co-Br(4)=100.9(5)	
Br(2)-Co-Br(3)=114.3(4)	
Br(2)-Co-Br(4)=113.7(3)	
Br(3)-Co-Br(4)=112.0(3)	
C(1)-N(1)-C(5)=121(3)	C(6)-N(2)-C(10)=116(3)
C(2)-C(1)-N(1)=121(3)	C(7)-C(6)-N(2)=126(3)
C(1)-C(2)-C(3)=119(4)	C(6)-C(7)-C(8)=115(4)
C(2)-C(3)-C(4)=117(4)	C(7)-C(8)-C(9)=119(4)
C(3)-C(4)-C(5)=126(4)	C(8)-C(9)-C(10)=121(4)
C(4)-C(5)-N(1)=116(4)	C(9)-C(10)-N(2)=123(4)
C(2)-C(1)-C(6)=124(3)	C(1)-C(6)-C(7)=121(3)
C(6)-C(1)-N(1)=115(3)	C(1)-C(6)-N(2)=113(3)

two nitrogen atoms being in the *trans* positions with respect to the C–C bond connecting the two pyridine rings.[10] However, this is not the case with our bipyridinium cation. As may be seen in Figs. 1 and 2, the bipyridinium cation lacks planarity. The individual pyridinium moiety is planar; the equation of the best plane through the six atoms N(1), C(1), C(2), C(3), C(4), and C(5), is:

$$0.162X + 0.332\,Y + 0.929\,Z = 3.99,$$

and that of the plane of the six atoms N(2), C(6), C(7), C(8), C(9), and C(10) is:

$$0.742\,X + 0.140\,Y + 0.655\,Z = 3.17,$$

where X, Y, and Z are the rectangular coordinates in Å units, X standing for $x+z\cos\beta$; Y, for y, and Z, for $z\sin\beta$. C(1) shows the maximum deviation of 0.04 Å from the former plane, and both C(9) and C(10) are in the maximum deviation from the latter plane by 0.04 Å. These two ring planes are inclined at an angle of 39° to each other. This dihedral angle is comparable with those found in (bipyH$_2$)SeOCl$_4$,[11] within the accuracy of the standard deviations.

The coordination around the cobalt atom is almost a regular tetrahedron. However, in the four Co–Br bonds, two of them (Co–Br(1)=2.436 Å and Co–Br(4) =2.452 Å) are longer than the other two (Co–Br(2)= 2.409 Å and Co–Br(3)=2.382 Å). The differences in the bond lengths between these two groups are possibly significant in view of the e.s.d.'s. The elongation in the former group must result from the hydrogen bonding in which the corresponding bromine atoms participate.

In the solid state, the color of [bipyH$_2$][CoBr$_4$] is green, while that of the analogous complex, [pyH]$_2$·[CoBr$_4$], is blue. As can be seen from Fig. 3, in which their transmission spectra are shown, the remarkable color difference between them is attributable to the absorption bands in the higher frequency region; a detailed discussion will be given in subsequent papers.

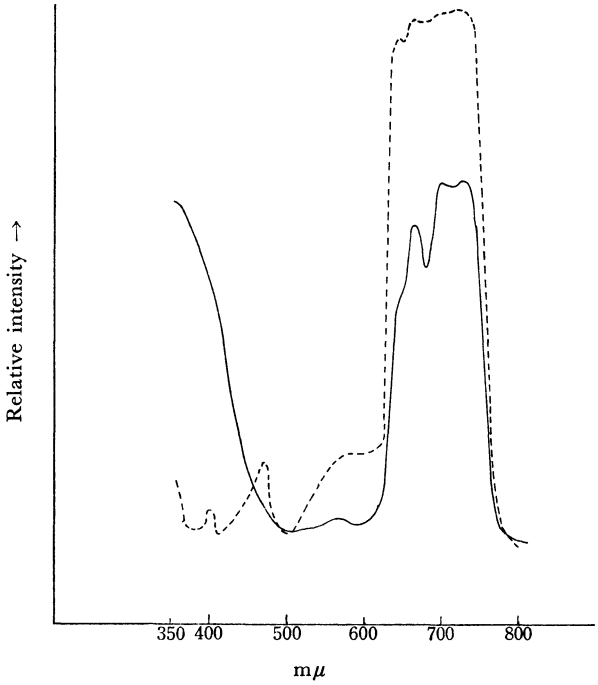

Fig. 3. Transmission spectra of [bipyH$_2$][CoBr$_4$]: —— and [pyH]$_2$[CoBr$_4$]: ----.

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

11) Bi-Cheng Wang and A. W. Cordes, *Inorg. Chem.*, **9**, 1643 (1970).