

quarter of the unit-cell contents. The structure is packed in (100) layers of $[\text{Ni}(\text{C}_2\text{H}_2\text{ClO}_2)_2(\text{H}_2\text{O})_4]$ groups linked by hydrogen bonds (Table 2). The two non-equivalent water molecules coordinated to the Ni atom act in different ways in the packing of the compound; thus one molecule is linked by hydrogen bonds to two non-coordinated water molecules, whereas the other is linked by a weak hydrogen bond to a non-coordinated water molecule and by strong hydrogen bonds to O atoms of the chloroacetate ion. This could explain the distortion of the octahedral coordination.

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Structure of Bis(2,2'-bipyridine)monobromocopper(II) Bromide

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Abstract. $[\text{CuBr}(\text{C}_{10}\text{H}_8\text{N}_2)_2]\text{Br}$, $M_r = 535.7$, monoclinic, $a = 11.463$ (3), $b = 11.246$ (2), $c = 17.785$ (4) Å, $\beta = 121.50$ (2)°, $V = 1954.9$ (8) Å³, $Z = 4$, $D_c = 1.82$ Mg m⁻³, $F(000) = 1052$; space group $P2_1/c$ from systematic absences ($h0l$ if $l = 2n + 1$, $0k0$ if $k = 2n + 1$); Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å, $\mu = 5.51$ mm⁻¹. Final $R = 0.022$ for 1567 reflections with $I > 3\sigma(I)$. The structure of the $[\text{CuBr}(\text{C}_{10}\text{H}_8\text{N}_2)_2]^+$ ion is similar to that in $[\text{CuBr}(\text{C}_{10}\text{H}_8\text{N}_2)_2]\text{BF}_4$, except for significant differences between the bond distances and angles in the CuN_2Br plane, presumably caused by lattice interactions.

Introduction. The electrochemical oxidation of metals in non-aqueous media provides a convenient route to many inorganic and organometallic complexes (Tuck, 1979). When copper is oxidized in this way into acetonitrile solutions containing phenyl bromide and 2,2'-bipyridine (bpy), the products include $\text{CuBr}\cdot\text{bpy}$ and $\text{CuBr}_2\cdot 2\text{bpy}$ (Said & Tuck, 1980). The present paper reports an X-ray analysis of the latter substance which is shown to be one of a series of compounds containing a $[\text{Cu}(\text{bpy})_2X]^+$ cation. While the present work was in progress, the structure of $[\text{Cu}(\text{bpy})_2\text{Br}]\text{BF}_4$ was reported by Hathaway & Murphy (1980). There are significant differences between the structures

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of the cations in these two systems, and possible reasons for this are outlined.

The preparation and isolation of $\text{CuBr}_2\cdot 2\text{bpy}$ have been described (Said & Tuck, 1980).

A crystal $0.03 \times 0.02 \times 0.02$ mm was mounted on a Syntex $P2_1$ diffractometer equipped with a Mo X-ray tube and a highly oriented graphite monochromator. The data were collected and processed by the methods described by Khan, Steevensz, Tuck, Noltes & Corfield (1980). 3862 reflections ($2\theta_{\text{max}} = 50^\circ$, $hkl/hk\bar{l}$) were measured and reduced to 1567 [$I > 3\sigma(I)$] unique reflections. The data were corrected for absorption, Lorentz and polarization effects, the minimum and maximum absorption corrections being 2.02 and 2.76.

The positions of the Cu and Br atoms were obtained from a sharpened Patterson synthesis, and the subsequent difference map revealed the positions of all other non-hydrogen atoms. The structure was refined anisotropically by full-matrix least-squares methods to $R = 0.031$, $R_w = 0.036$. A difference map at this stage showed the peaks for all the H atoms, which were included in the subsequent refinement. The four H atoms attached to C(1), C(10), C(11), and C(20) were refined isotropically; all others were included in ideal positions ($\text{C}-\text{H} = 0.95$ Å, $\text{CCH} = 120.0^\circ$) and in these cases only the temperature factors were refined.

Full-matrix least-squares refinement yielded a final $R = 0.022$, $R_w = 0.027$. In the last cycle the maximum shift/error ratio was 0.01 and the final difference map was devoid of significant features.

Scattering factors for all atoms, including the anomalous-dispersion correction for Cu and Br, were obtained from Ibers & Hamilton (1974). All calculations were carried out on an IBM 3031 computer with *SHELX* (Sheldrick, 1977) (Fourier and least-squares calculation), *XANADU* (Roberts & Sheldrick, 1975) (mean plane), and *ORTEP* (Johnson, 1965) (thermal-ellipsoid diagram).

Table 1. Final fractional coordinates and isotropic thermal parameters for $[\text{CuBr}(\text{C}_{10}\text{H}_8\text{N}_2)]\text{Br}$, with standard deviations in parentheses

	x	y	z	U_{eq}/U ($\text{\AA}^2 \times 10^3$)†
Cu	0.12536 (7)	0.04954 (6)	0.37987 (4)	37.1 (4)
Br(1)	0.12853 (7)	-0.16645 (6)	0.38256 (4)	57.2 (4)
Br(2)	0.36898 (6)	0.38714 (6)	0.61949 (3)	49.1 (4)
N(1)	0.2844 (4)	0.0569 (4)	0.5020 (3)	40 (3)
N(2)	0.2562 (4)	0.1554 (4)	0.3600 (3)	36 (3)
N(3)	-0.0379 (5)	0.0478 (4)	0.2593 (3)	42 (3)
N(4)	0.0002 (4)	0.1644 (4)	0.3978 (3)	39 (3)
C(1)	0.2885 (7)	-0.0001 (6)	0.5695 (4)	49 (4)
C(2)	0.4083 (6)	-0.0070 (6)	0.6510 (4)	53 (4)
C(3)	0.5216 (7)	0.0428 (6)	0.6617 (4)	51 (4)
C(4)	0.5202 (5)	0.1055 (5)	0.5934 (3)	44 (3)
C(5)	0.3961 (5)	0.1105 (5)	0.5129 (3)	35 (3)
C(6)	0.3787 (5)	0.1727 (5)	0.4347 (3)	33 (3)
C(7)	0.4772 (6)	0.2454 (6)	0.4357 (4)	50 (4)
C(8)	0.4488 (7)	0.3002 (6)	0.3584 (5)	57 (5)
C(9)	0.3259 (7)	0.2811 (6)	0.2829 (4)	58 (5)
C(10)	0.2316 (7)	0.2086 (6)	0.2855 (4)	50 (4)
C(11)	-0.0478 (7)	-0.0139 (6)	0.1915 (4)	55 (4)
C(12)	-0.1709 (8)	-0.0237 (7)	0.1117 (4)	65 (5)
C(13)	-0.2831 (7)	0.0270 (6)	0.1024 (4)	64 (4)
C(14)	-0.2758 (6)	0.0888 (5)	0.1712 (4)	50 (4)
C(15)	-0.1498 (6)	0.1012 (5)	0.2490 (3)	41 (3)
C(16)	-0.1278 (6)	0.1743 (5)	0.3239 (4)	41 (3)
C(17)	-0.2224 (7)	0.2521 (6)	0.3208 (5)	56 (4)
C(18)	-0.1843 (9)	0.3256 (7)	0.3927 (5)	73 (6)
C(19)	-0.0551 (8)	0.3153 (6)	0.4663 (5)	66 (5)
C(20)	0.0336 (7)	0.2344 (6)	0.4665 (4)	50 (4)
H(1)	0.195 (6)	-0.048 (5)	0.554 (4)	70 (20)
H(10)	0.140 (5)	0.194 (4)	0.237 (3)	50 (20)
H(11)	0.034 (6)	-0.058 (5)	0.207 (3)	50 (20)
H(20)	0.127 (6)	0.219 (6)	0.506 (4)	90 (20)
H(2)	0.410	-0.047	0.699	70 (20)
H(3)	0.605	0.036	0.717	60 (20)
H(4)	0.600	0.143	0.601	60 (20)
H(7)	0.563	0.257	0.489	30 (10)
H(8)	0.515	0.351	0.358	130 (30)
H(9)	0.306	0.317	0.229	50 (20)
H(12)	-0.175	-0.066	0.064	80 (20)
H(13)	-0.368	0.020	0.048	40 (20)
H(14)	-0.356	0.123	0.166	30 (10)
H(17)	-0.312	0.256	0.270	90 (30)
H(18)	-0.247	0.382	0.391	90 (30)
H(19)	-0.028	0.364	0.516	60 (20)

† U_{eq} for the nonhydrogen atoms is calculated from the refined anisotropic thermal parameters (deposited) ($U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} \times a_i^* a_j^* a_i \cdot a_j$).

Table 2. Bond distances (\AA) and angles ($^\circ$)

Cu—Br(1)	2.429 (2)	Cu—N(3)	1.977 (6)
Cu—N(1)	1.978 (6)	Cu—N(4)	2.075 (8)
Cu—N(2)	2.085 (7)	N(3)—C(11)	1.34 (1)
N(1)—C(1)	1.34 (1)	N(3)—C(15)	1.34 (1)
N(1)—C(5)	1.34 (1)	C(11)—C(12)	1.39 (1)
C(1)—C(2)	1.38 (1)	C(12)—C(13)	1.34 (2)
C(2)—C(3)	1.33 (1)	C(13)—C(14)	1.37 (1)
C(3)—C(4)	1.40 (1)	C(14)—C(15)	1.39 (1)
C(4)—C(5)	1.40 (1)	C(15)—C(16)	1.47 (1)
C(5)—C(6)	1.47 (1)	C(16)—C(17)	1.37 (1)
C(6)—C(7)	1.39 (1)	C(17)—C(18)	1.39 (2)
C(7)—C(8)	1.38 (1)	C(18)—C(19)	1.38 (2)
C(8)—C(9)	1.36 (1)	C(19)—C(20)	1.36 (1)
C(9)—C(10)	1.37 (1)	N(4)—C(20)	1.33 (1)
N(2)—C(10)	1.34 (1)	N(4)—C(16)	1.37 (1)
N(2)—C(6)	1.35 (1)	C(11)—H(11)	0.97 (9)
C(1)—H(1)	1.10 (9)	C(20)—H(20)	0.94 (9)
C(10)—H(10)	0.97 (7)		
Br(1)—Cu—N(1)	91.4 (2)	Br(1)—Cu—N(3)	90.4 (2)
Br(1)—Cu—N(2)	124.7 (2)	Br(1)—Cu—N(4)	128.6 (2)
N(1)—Cu—N(2)	80.3 (3)	N(3)—Cu—N(4)	80.4 (3)
N(1)—Cu—N(3)	177.3 (3)		
N(1)—Cu—N(4)	96.9 (3)		
N(2)—Cu—N(3)	100.3 (3)		
N(2)—Cu—N(4)	106.7 (3)		
Cu—N(1)—C(1)	123.0 (6)	Cu—N(3)—C(11)	124.5 (7)
Cu—N(1)—C(5)	116.2 (6)	Cu—N(3)—C(15)	116.1 (6)
C(1)—N(1)—C(5)	120 (1)	C(11)—N(3)—C(15)	119 (1)
Cu—N(2)—C(6)	112.6 (6)	Cu—N(4)—C(16)	112.5 (6)
Cu—N(2)—C(10)	128.6 (6)	Cu—N(4)—C(20)	128.2 (7)
C(6)—N(2)—C(10)	119 (1)	C(16)—N(4)—C(20)	119 (1)
N(1)—C(1)—C(2)	121 (1)	N(3)—C(11)—C(12)	122 (1)
C(1)—C(2)—C(3)	119 (1)	C(11)—C(12)—C(13)	119 (1)
C(2)—C(3)—C(4)	121 (1)	C(12)—C(13)—C(14)	120 (1)
C(3)—C(4)—C(5)	117 (1)	C(13)—C(14)—C(15)	119 (1)
C(4)—C(5)—N(1)	121 (1)	C(14)—C(15)—N(3)	121 (1)
C(4)—C(5)—C(6)	123 (1)	C(14)—C(15)—C(16)	124 (1)
C(6)—C(5)—N(1)	116 (1)	C(16)—C(15)—N(3)	115 (1)
C(5)—C(6)—N(2)	115 (1)	C(15)—C(16)—N(4)	115 (1)
C(5)—C(6)—C(7)	124 (1)	C(15)—C(16)—C(17)	124 (1)
C(7)—C(6)—N(2)	121 (1)	C(17)—C(16)—N(4)	121 (1)
C(6)—C(7)—C(8)	119 (1)	C(16)—C(17)—C(18)	119 (1)
C(7)—C(8)—C(9)	120 (1)	C(17)—C(18)—C(19)	119 (1)
C(8)—C(9)—C(10)	119 (1)	C(18)—C(19)—C(20)	119 (1)
C(9)—C(10)—N(2)	122 (1)	C(19)—C(20)—N(4)	122 (1)
N(1)—C(1)—H(1)	116 (6)	N(3)—C(11)—H(11)	113 (5)
C(2)—C(1)—H(1)	123 (5)	C(12)—C(11)—H(11)	125 (5)
N(2)—C(10)—H(10)	112 (5)	N(4)—C(20)—H(20)	104 (6)
C(9)—C(10)—H(10)	126 (5)	C(19)—C(20)—H(20)	133 (6)

Interatomic distances $< 3.0 \text{ \AA}$

Br(2)···H(2)(1 - x, 0.5 + y, 1.5 - z)	2.98
Br(2)···H(12)(-x, 0.5 + y, 0.5 - z)	2.88
Br(2)···H(18)(-x, 1 - y, 1 - z)	2.91

The final atomic coordinates* are given in Table 1, bond lengths and angles in Table 2, and selected mean planes in Table 3. Fig. 1 illustrates the structure of the

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35801 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Equations of the planes of best fit given in the form $lX + mY + nZ = p$ with reference to the cell axes; p and deviations of the atoms are given in Å

E.s.d.'s for all distances are 0.001 Å.

Plane (1): N(1), C(1)–C(5)

$$-0.2422X + 0.8226Y + 0.5144Z = 3.618$$

r.m.s.d. = 0.039; N(1) –0.049; C(1) 0.019; C(2) 0.0493; C(3) –0.011; C(4) –0.047; C(5) 0.037

Plane (2): N(2), C(6)–C(10)

$$-0.3791X + 0.7886Y + 0.4842Z = 2.780$$

r.m.s.d. = 0.004; N(2) 0.0049; C(6) –0.006; C(7) 0.001; C(8) 0.004; C(9) –0.004; C(10) –0.001

Plane (3): N(3), C(11)–C(15)

$$0.2007X + 0.8313Y - 0.5184Z = -2.128$$

r.m.s.d. = 0.013; N(3) –0.007; C(11) –0.017; C(12) 0.002; C(13) 0.011; C(14) –0.008; C(15) 0.020

Plane (4): N(4), C(16)–C(20)

$$0.3301X + 0.6931Y - 0.6408Z = -3.247$$

r.m.s.d. = 0.009; N(4) –0.003; C(16) 0.013; C(17) –0.015; C(18) 0.007; C(19) 0.003; C(20) –0.005

Plane (5): Cu, Br(1), N(2), N(4)

$$0.6613X + 0.0134Y + 0.7500Z = 5.329$$

r.m.s.d. = 0.004; Cu –0.007; Br(1) 0.0024; N(2) 0.0023; N(4) 0.0024

Plane (6): Cu, Br(1), N(1), N(3)

$$-0.6034X - 0.0074Y + 0.7974Z = 4.067$$

r.m.s.d. = 0.013; Cu –0.022; Br(1) 0.001; N(1) 0.011; N(3) 0.011

Angles between planes (1) and (2) = 8.3°; (3) and (4) = 12.9°; Cu, N(1), N(2) and Cu, N(3), N(4) = 74.2°; (5) and (6) = 78.5° (e.s.d.'s are ~1.5°).

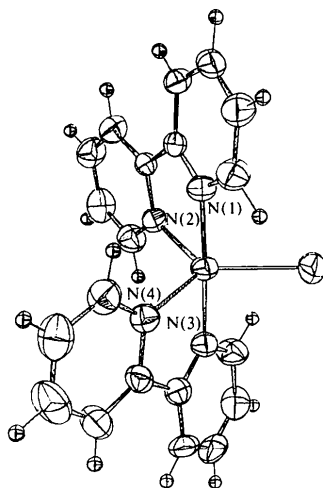


Fig. 1. The structure of the $[\text{Cu}(\text{bpy})_2\text{Br}]^+$ cation. The atoms are drawn as 50% probability ellipsoids with the numbering system of Hathaway & Murphy (1980).

$[\text{CuBr}(\text{C}_{10}\text{H}_8\text{N}_2)_2]^+$ ion; the atom numbering is the same as that used by Hathaway & Murphy (1980).

Discussion. The present structure is one of a relatively large group of $[\text{Cu}(\text{bpy})_2X]$ complexes whose

molecular structures have been reported. The results for $X = \text{Cl}, \text{Br}$ or I have been reviewed by Hathaway & Murphy (1980), and we return to these compounds below, but the following structures have also been determined: $X = \text{NO}_2$ (Proctor & Stephens, 1969), NH_3 (Stephens, 1972), thiourea (Ferrari, Corradi, Fava, Palmieri, Nardelli & Pelizzi, 1973), H_2O (Harrison, Hathaway & Kennedy, 1979), NO_3 (Nakai, 1980) and acetate (Hathaway, Ray, Kennedy, O'Brien & Murphy, 1980). While significant differences occur in these structures in terms of the $\text{N}(2)\text{—Cu—N}(4)$ and related angles and distances, there are, equally, certain consistencies; specifically, the bite of the 2,2'-bipyridine ligand at Cu is $80 \pm 1^\circ$, and the $\text{N}(1)\text{—Cu—N}(3)$ angles are $177 \pm 2.5^\circ$.

The thrust of the discussion of the results has frequently been the stereochemistry of the CuN_4X coordination kernel, and in particular whether this is best described as a distortion from trigonal-bipyramidal or square-pyramidal symmetry. One might have hoped that an examination of such a series of related complexes would have cast light on the effect of differing ligands. In practice, the present results, and those for other cations in which halide ligands are bonded to the $\text{Cu}(\text{bpy})_2$ moiety, show that there are remarkable and non-systematic changes in the stereochemistry around the Cu atom, and that the reason for these changes is not at all obvious.

Structural studies for $[\text{Cu}(\text{bpy})_2X]^+$ ($X = \text{Cl}, \text{Br}, \text{I}$) have been published; in each case the cation is balanced by a different anion, and in some cases the presence or absence of water in the structure may be significant. The main differences between individual $[\text{Cu}(\text{bpy})_2X]^+$ species apparently reside in the N_2CuX plane, since the comparisons made by Hathaway & Murphy (1980) show that $\text{Cu—N}(\text{apical})$ distances are both equal and constant between the different cations (unweighted mean 1.989 ± 0.008 Å), and that the $\text{N}(1)\text{—Cu—N}(3)$ angles are also sensibly constant. The remaining results for the equatorial plane are shown in Table 4.

There are clearly significant differences between replicate sets of results for any given cation, notably in the Cu—Cl distance and $\text{N}(2)\text{—Cu—N}(4)$ angle in $[\text{Cu}(\text{bpy})_2\text{Cl}]^+$, the $\text{Cu—N}(2,4)$ distances and $\text{N}(2)\text{—Cu—N}(4)$ angle in $[\text{Cu}(\text{bpy})_2\text{Br}]^+$, and in each pair of comparable results for the iodo complex. In addition, $[\text{Cu}(\text{bpy})_2\text{Br}]\text{BF}_4$ is the only structure in which the $\text{Cu—N}(2)$ and $\text{Cu—N}(4)$ distances differ by more than the sum of the experimental errors, leaving aside the older determination on $[\text{Cu}(\text{bpy})_2\text{I}]\text{I}$. Although there is no evidence in any system of an interaction between cation and anion of the type referred to as semi-coordination (Tomlinson, Hathaway, Billing & Nichols, 1969), it is difficult to see what factor other than anion–cation interaction can be responsible for the significant differences identified in Table 4. Hathaway *et al.* (1980) revealed that the detailed structure of

Table 4. *Structural results for the CuN₂X plane in [Cu(bpy)₂X]⁺ cations (X = Cl, Br, I)*

X	Balancing anion, etc.	Cu-X bond length (Å)	Cu-N(2); N(4) bond lengths (Å)	N(2)-Cu-N(4) angle (°)	Reference
Cl	S ₂ O ₆ ²⁻ ; 6H ₂ O	2.292 (4)	2.092 (6); 2.106 (5)	107.3 (2)	(a)
Cl	Cl ⁻ ; 6H ₂ O	2.361 (4)	2.077 (10); 2.087 (11)	122.8 (4)	(b)
Br	BF ₄ ⁻	2.419 (3)	2.068 (8); 2.114 (9)	99.4 (3)	(c)
Br	Br ⁻	2.429 (2)	2.085 (7); 2.075 (8)	106.7 (3)	(d)
I	ClO ₄ ⁻	2.675 (4)	2.090 (8); 2.100 (7)	114.3 (3)	(c)
I	I ⁻	2.697	1.961; 2.106	113.8	(e)

References: (a) Harrison, Hathaway & Kennedy (1979); (b) Stephens & Tucker (1973); (c) Hathaway & Murphy (1980); (d) present work; (e) Barclay, Hoskins & Kennard (1963).

[Cu(bpy)₂OAc]⁺ is significantly dependent upon the nature of the anion (BF₄⁻ or ClO₄⁻·H₂O). Until the differences between (say) [Cu(bpy)₂Br]Br and [Cu(bpy)₂Br]BF₄ can be rationalized, there seems little point in trying to discuss different [Cu(bpy)₂L]^{+,2+} structures in any systematic manner.

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Structure of (1R,2R,4S,7S,8R,9R,11S,14S)-1,2,4,7,8,9,11,14-Octamethyl-1,4,8,11-tetraazacyclotetradecanenickel(II) Perchlorate

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Abstract. [Ni(C₁₈H₄₀N₄)(ClO₄)₂], tetragonal, *P*4₃2₁2, *a* = 8.872 (1), *c* = 33.368 (2) Å, *U* = 2626.5 (2) Å³, *Z* = 4, *D_m* = 1.44, *D_x* = 1.44 Mg m⁻³, μ(Cu Kα) =

3.30 mm⁻¹, *R* = 0.034 and *R_w* = 0.044 for 2343 independent reflexions. The Ni^{II} ion is surrounded by a square-planar array of N atoms. The 14-membered ring takes a basket configuration with all four NH groups on the same side of the coordination plane. The absolute configurations of the eight chiral centers have been determined.

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