

Fig. 2. A projection of the crystal structure along *b*.

The crystal structure can be described in terms of successive layers of anions and cations parallel to (001) as shown in Fig. 2. There is no close contact less than 2.9 Å. The perchlorate thermal parameters are extraordinarily large. The thermal ellipsoids do not represent the electron density of the perchlorate O atoms properly. In fact, in the final difference synthesis, diffuse residual electron densities are found around the Cl atoms, suggesting some other possible locations of the O atoms. The perchlorate ions exhibit orientational disorder as often found in the X-ray crystal structures of the perchlorate salts (e.g. Bang, 1977).

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Tetraaquabis(monochloroacetato)nickel(II) Dihydrate

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Abstract. [Ni(C₂H₂ClO₂)₂(H₂O)₄].2H₂O, *M_r* = 353.78, orthorhombic, *Fddd*, *a* = 26.009 (2), *b* = 16.396 (2), *c* = 12.080 (2) Å, *Z* = 16, *D_o* = 1.82, *D_c* = 1.82 Mg m⁻³. The structure has been solved by direct methods, and refined by block-diagonal least squares to an *R* value of 0.048 for 825 independent reflections. The Ni atom displays an octahedral coordination and the structure is packed in layers with the hydrate water molecules acting as bridges between different layers.

Introduction. It was suspected that the structure of the title compound was similar to that obtained by van Niekerk & Schoening (1953) for nickel(II) acetate tetrahydrate but the study of the IR and UV spectra was inconclusive. For this reason it was decided to determine its crystal structure by X-ray diffraction.

Blue crystals suitable for X-ray studies were obtained by recrystallization from an aqueous solution. The dimensions of the crystal selected were 0.2 × 0.2 × 0.2

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mm. Lattice parameters were determined by least-squares refinement of the θ values for 25 reflections measured with a Philips PW 1100 four-circle diffractometer on which all further experimental work was carried out. Monochromated Mo *K* α radiation, pulse-height discrimination and the ω -scan mode [scan width = 1.3°(θ), scan speed = 0.05°(θ) s⁻¹] were used. 838 independent reflections were collected in the range 2 ≤ θ ≤ 24°, of which 825 were considered as observed according to the criterion $I \geq 2\sigma(I)$. Only Lorentz-polarization corrections were made.

The structure was solved by direct methods with the *MULTAN* 77 system of computer programs (Main, Woolfson, Lessinger, Germain & Declercq, 1977). 120 reflections were used in the phase-determining procedure. An *E* map calculated with the set of signs with the highest combined figure of merit revealed peaks for all non-hydrogen atoms. Refinement was carried out by means of the program *SSFLS* (Solans & Miravittles,

Table 1. Positional parameters ($\times 10^5$; for H $\times 10^3$) and isotropic thermal parameters

	x	y	z	U_{eq}/U (\AA^2)*
Ni	0	0	0	0.009 (1)
Cl(1)	7116 (6)	28969 (9)	23288 (13)	0.046 (2)
C(2)	4226 (24)	24586 (34)	11419 (54)	0.04 (1)
C(3)	3861 (18)	15401 (32)	11725 (47)	0.03 (1)
O(4)	1390 (13)	-12364 (23)	3593 (29)	0.03 (1)
O(5)	5835 (18)	-11449 (25)	19320 (37)	0.08 (1)
O(6)	6400 (15)	323 (24)	-9537 (31)	0.03 (1)
O(7)	4149 (13)	3769 (20)	14059 (29)	0.03 (1)
O(8)	12500	12500	26114 (47)	0.04 (1)
O(9)	37755 (21)	12500	12500	0.03 (1)
H(C21)	61 (3)	-271 (4)	44 (6)	0.01 (2)
H(C22)	7 (2)	277 (4)	105 (5)	0.01 (2)
H(O61)	90 (2)	-49 (3)	-95 (5)	0.01 (2)
H(O62)	82 (3)	42 (5)	-63 (7)	0.08 (2)
H(O71)	91 (3)	53 (5)	86 (6)	0.04 (2)
H(O72)	45 (4)	-18 (7)	184 (8)	0.04 (2)
H(O8)	106 (2)	104 (4)	227 (5)	0.04 (2)
H(O9)	394 (2)	127 (5)	174 (5)	0.01 (2)

* For the non-hydrogen atoms $U_{eq} = 1/(6\pi^2) \sum_i \sum_j \beta_{ij} a_i \cdot a_j$.

1978). The function minimized was $\sum w|F_o| - |F_c|^2$ with Cruickshank's (1965) weights. After several cycles of isotropic and anisotropic refinement to $R = 0.055$, the H atoms were obtained by a difference synthesis. Further refinement cycles gave $R = 0.048$ for 825 reflections ($R = \sum ||F_o| - |F_c|| / \sum |F_o|$).^{*} The final atomic parameters are listed in Table 1.

Discussion. Figs. 1 and 2 show views of the coordination around the Ni^{2+} ion and of the chloroacetate ion, respectively. The Ni^{2+} ion displays the octahedral

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35974 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

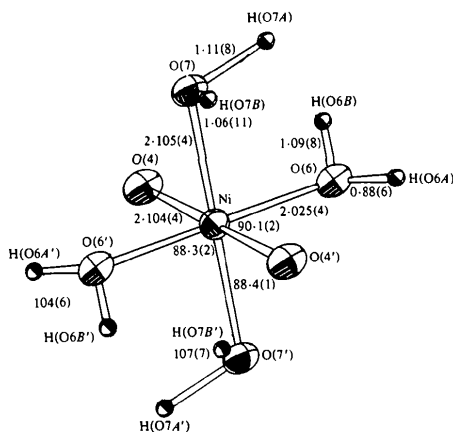


Fig. 1. View of the coordination of the Ni^{2+} ion, with bond distances (\AA) and bond angles ($^\circ$).

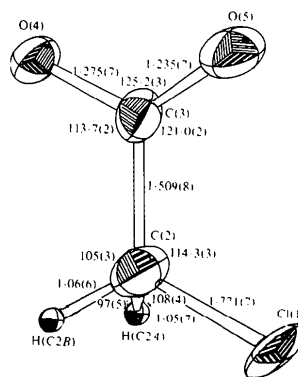


Fig. 2. View of the chloroacetate ion, with bond distances (\AA) and bond angles ($^\circ$).

coordination expected in blue complexes of this ion. The Ni—O distances and O—Ni—O angles are similar to those obtained by van Niekerk & Schoening (1953), Nyburg & Wood (1964) and Lumme & Mutikainen (1980). The short Ni—OH₂ distance [2.025 (4) Å], the H₂O—Ni—OH₂ angle [88.3 (2)°] below 90° and the hydrogen bond between the non-coordinated O atom of the chloroacetate ion with an H₂O linked to a Ni atom (Table 2) have already been observed in nickel(II) acetate tetrahydrate (van Niekerk & Schoening, 1953).

The geometry of the carboxylate group is intermediate between those of the —COO⁻ and —COOH groups (Borthwick, 1980). Fig. 3 shows a projection of a

Table 2. Hydrogen-bond distances (\AA)

O(6) ... O(8) ⁱ	2.746 (5)	O(7) ... O(7) ^v	2.888 (5)
O(6) ... O(9) ⁱⁱ	2.698 (5)	O(8) ... O(7) ^{iv}	2.981 (5)
O(7) ... O(4) ⁱⁱⁱ	2.697 (5)	O(9) ... O(5) ^{vi}	2.763 (6)
O(7) ... O(5) ^v	2.612 (6)		

Symmetry code

- | | | | |
|-------|---------------------------------------|------|---|
| (i) | $x, \frac{1}{4} - y, \frac{1}{4} - z$ | (iv) | x, y, z |
| (ii) | $x - \frac{1}{4}, y, z - \frac{1}{4}$ | (v) | $\frac{1}{2} - x, y, \frac{1}{2} - z$ |
| (iii) | $\bar{x}, \bar{y}, \bar{z}$ | (vi) | $\frac{1}{2} - x, \frac{1}{4} + y, z - \frac{1}{4}$ |

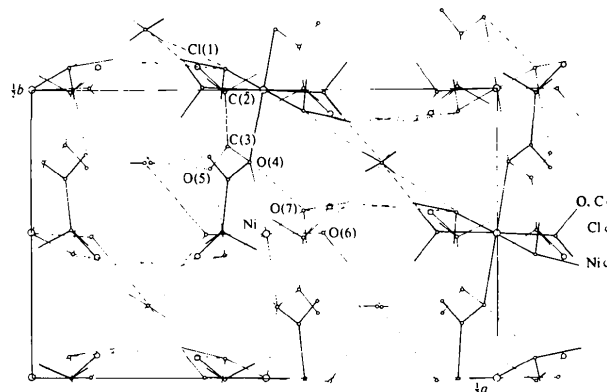


Fig. 3. Projection of a quarter of the unit-cell contents down the c axis.

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.