

The Crystal Structure and Absolute Configuration of (+)₅₈₉-Tris(2,2'-bipyridyl)nickel(II) Chloride (+)₅₈₉-Tartrate Hydrate, [Ni(C₁₀H₈N₂)₃]₂Cl₂·C₄H₄O₆·nH₂O

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(Received 30 January 1976; accepted 28 May 1976)

The crystal form of the title compound is monoclinic, *C*2, with *a* = 23·600 (1), *b* = 13·199 (1), *c* = 23·099 (1) Å, β = 103·68 (2)° and *Z* = 4. The final refinement was performed by the diagonal least-squares method to an *R* value of 0·096 for 4531 data measured on a Hilger & Watts four-circle diffractometer. The absolute configuration of the complex was assigned as *A* for the (+)₅₈₉-isomer based on the (+)₅₈₉-tartrate ion as an internal reference. This result gives an additional case of the absolute configuration agreeing with that determined by circular dichroism analysis. Each complex ion exhibits approximate *D*₃ symmetry with the threefold axis almost perpendicular to (100). Water molecules form a two-dimensional network, but some water molecules and one Cl⁻ ion are in disorder.

Introduction

The absolute configurations of tris(1,10-phenanthrolyl) and tris(2,2'-bipyridyl) complexes were investigated by Hanazaki & Nagakura (1969), McCaffery, Mason & Norman (1969), and Mason & Norman (1969) by the method of circular dichroism, and their results are in agreement with the X-ray determinations of (-)₅₈₉-[Fe(phen)₃]²⁺ (phen = 1,10-phenanthrolyl) by Templeton, Zalkin & Ueki (1971) and of (+)₅₈₉-[Ni(phen)₃]²⁺ by Butler & Snow (1966). Ferguson, Hawkins, Kane-Maguire & Lip (1969) discussed the spectra of the complex and the reliability of the circular dichroism method. Thus it is desirable that the spectral assignment and the absolute configuration should be confirmed.

Previously, we have determined the crystal structure of the racemic [Ni(bipy)₃]SO₄ (bipy = 2,2'-bipyridyl) complex (Wada, Sakabe & Tanaka, 1976) in order to confirm the spectral assignment of the exciton splitting band. In the present study the crystal structure of (+)₅₈₉-[Ni(bipy)₃]₂Cl₂ (+)₅₈₉-tartrate·nH₂O was investigated.

Experimental

Optically active [Ni(bipy)₃]²⁺ was prepared according to the method described by Morgan & Burstall (1931) with a small modification. Purified [Ni(bipy)₃]Cl₂ (2·5g) was dissolved in water (55ml), a large amount of (+)₅₈₉-ammonium tartrate (30g) was added to it, and the mixture was kept at 0°C. After a few days, [Ni(bipy)₃]₂Cl₂·C₄H₄O₆·nH₂O was separated as red crystals of prismatic shape. The specific gravity was measured by the flotation method and it suggested that 12 water molecules were contained in an asymmetric unit.

Cl content calculated for [Ni(C₃₀H₂₄N₆)₂Cl₂·C₄H₄O₆·12H₂O is 4·3%; found

by analysis: 4·8%. The specific rotation of this compound was obtained as +831° from measurement with a Jasco automatic polarimeter DIP-SL using the Na *D* line.

Preliminary rotation and Weissenberg photographs showed that the crystal belongs to the monoclinic system, and systematic absences were recognized for general reflexions *hkl*: *h* + *k* = 2*n* + 1. This indicates that the space group is *C*2, *C*2/*m*, or *C**m*; however, it was uniquely determined to be *C*2 since the crystal contains one of the enantiomers. The crystal data are listed in Table 1.

Table 1. Crystal data

[Ni(C ₁₀ H ₈ N ₂) ₃] ₂ Cl ₂ ·C ₄ H ₄ O ₆ ·nH ₂ O	
F.W. 1489·5*	<i>D</i> _m = 1·419 g cm ⁻³
<i>a</i> = 23·600 ± 0·001 Å	<i>D</i> _x = 1·415*
<i>b</i> = 13·199 ± 0·001	<i>Z</i> = 4
<i>c</i> = 23·099 ± 0·001	Monoclinic <i>C</i> 2
β = 103·68 ± 0·02°	<i>F</i> (000) = 3112*
<i>V</i> = 6991·2 Å ³	μ(Cu Kα) = 22·0 cm ⁻¹ *

* Value calculated with *n* assumed to be 12.

Intensity data were collected with a Hilger & Watts four-circle diffractometer with Ni-filtered Cu Kα radiation and the ω-2θ step scan technique. Intensities of 4990 reflexions were obtained within θ = 72° and were converted into structure amplitudes in the usual way.

Determination of the structure and refinement

The positions of the two Ni atoms were located from a Patterson map. 12 N atoms were found in the following Fourier map, calculated by Sim's (1959) method. It was found that the arrangement of the Ni and N atoms is similar to that in the crystal of racemic [Ni(bipy)₃]SO₄·7·5H₂O (Wada *et al.*, 1976). Therefore, the positions of the other ligand atoms were estimated from the structure of the sulphate complex. The atoms

in the tartrate ion were easily located on the successive Fourier map. However, there were no peaks large enough to be assigned to the Cl⁻ ions except for two at (0.50, 0.70, 0.50) and (0.05, 0.70, 0.02); the former on the twofold axis, the latter near the other twofold axis with a peak height of about half the expected value for Cl(2). Therefore, Cl(2) was assumed to be in disorder between two sites related by the twofold axis. The remaining 16 peaks were refined on the assumption that they were water molecules, but four of them turned out to have occupancies of 0.5, as is stated below. These peaks were then allotted to 14 water molecules, but only 12 were found by the specific gravity measurement. Two of them might be missing Cl⁻ ions, since the weights of Cl(1) and Cl(2) were each 0.5. It was difficult to distinguish between the molecules and the disordered Cl⁻ ions.

Since the asymmetric unit contains so many atoms, the refinement was started by applying a constrained least-squares method (Scheringer, 1963). The *R* index converged to 0.20 after 15 cycles by using 464 data with

Table 2. Fractional coordinates ($\times 10^4$) and isotropic thermal parameters (\AA^2)

Estimated standard deviations are given in parentheses. The occupancies are assumed to be 0.5 for the atoms marked with an asterisk.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
Complex 1				
Ni(1)	299 (1)	2081 (2)	1759 (1)	4.80 (4)
N(A1)	-256 (5)	1561 (10)	2288 (5)	3.6 (2)
C(A2)	-791 (7)	1093 (15)	2089 (8)	5.0 (4)
C(A3)	-1141 (8)	811 (15)	2488 (8)	5.0 (4)
C(A4)	-936 (8)	1040 (15)	3089 (8)	5.0 (4)
C(A5)	-394 (7)	1492 (14)	3294 (7)	4.6 (4)
C(A6)	-67 (6)	1778 (12)	2887 (6)	3.8 (3)
C(A7)	493 (6)	2303 (11)	3057 (6)	3.5 (3)
C(A8)	776 (7)	2545 (14)	3646 (7)	4.7 (4)
C(A9)	1315 (8)	3001 (15)	3785 (8)	5.2 (4)
C(A10)	1582 (7)	3264 (15)	3320 (8)	5.0 (4)
C(A11)	1277 (7)	3023 (14)	2727 (7)	4.6 (3)
N(A12)	760 (5)	2567 (10)	2609 (5)	3.7 (3)
N(B1)	-155 (5)	3431 (10)	1517 (5)	3.5 (2)
C(B2)	-664 (7)	3738 (12)	1641 (7)	3.9 (3)
C(B3)	-984 (7)	4561 (13)	1382 (7)	4.4 (3)
C(B4)	-766 (7)	5137 (14)	977 (7)	4.5 (4)
C(B5)	-213 (6)	4860 (12)	864 (7)	3.9 (3)
C(B6)	69 (6)	4018 (11)	1131 (6)	3.1 (3)
C(B7)	628 (6)	3679 (11)	1019 (6)	3.0 (3)
C(B8)	926 (7)	4219 (13)	682 (7)	4.3 (3)
C(B9)	1444 (7)	3841 (14)	577 (7)	4.7 (4)
C(B10)	1646 (7)	2951 (14)	826 (7)	4.4 (3)
C(B11)	1335 (7)	2402 (12)	1189 (7)	4.0 (3)
N(B12)	833 (5)	2794 (9)	1269 (5)	3.5 (2)
N(C1)	-187 (5)	1297 (10)	1002 (5)	3.6 (2)
C(C2)	-690 (7)	1631 (13)	647 (7)	4.5 (3)
C(C3)	-1040 (7)	1012 (14)	213 (7)	4.4 (3)
C(C4)	-857 (7)	46 (14)	175 (7)	4.7 (4)
C(C5)	-337 (7)	-298 (13)	536 (7)	4.4 (3)
C(C6)	-6 (6)	323 (12)	970 (6)	3.4 (3)
C(C7)	529 (6)	22 (12)	1383 (6)	3.6 (3)
C(C8)	819 (7)	-886 (14)	1344 (7)	4.6 (4)
C(C9)	1317 (8)	-1160 (14)	1736 (8)	4.9 (4)
C(C10)	1552 (8)	-443 (15)	2218 (8)	5.2 (4)
C(C11)	1256 (7)	490 (14)	2237 (7)	4.7 (4)
N(C12)	757 (5)	672 (10)	1830 (5)	3.8 (3)

Table 2 (cont.)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
Complex 2				
Ni(2)	17 (1)	6932 (2)	3362 (1)	4.58 (4)
N(D1)	548 (5)	6364 (10)	2822 (5)	3.8 (3)
C(D2)	1052 (7)	5838 (14)	3003 (7)	4.8 (4)
C(D3)	1412 (8)	5577 (15)	2618 (8)	5.5 (4)
C(D4)	1228 (8)	5888 (15)	2028 (8)	5.0 (4)
C(D5)	708 (7)	6395 (14)	1832 (7)	4.6 (4)
C(D6)	378 (6)	6654 (12)	2247 (7)	3.9 (3)
C(D7)	-161 (6)	7262 (11)	2084 (6)	3.2 (3)
C(D8)	-409 (7)	7569 (13)	1507 (7)	4.4 (3)
C(D9)	-933 (7)	8113 (15)	1380 (8)	5.0 (4)
C(D10)	-1173 (7)	8396 (13)	1858 (7)	4.2 (3)
C(D11)	-915 (6)	8079 (13)	2408 (6)	3.8 (3)
N(D12)	-413 (5)	7533 (9)	2536 (5)	3.2 (2)
N(E1)	512 (5)	8238 (10)	3608 (5)	3.5 (2)
C(E2)	1029 (7)	8432 (13)	3479 (7)	4.3 (3)
C(E3)	1349 (8)	9329 (16)	3674 (8)	5.5 (4)
C(E4)	1118 (8)	10011 (15)	4028 (8)	5.3 (4)
C(E5)	565 (7)	9804 (14)	4134 (7)	4.6 (4)
C(E6)	282 (6)	8903 (12)	3937 (6)	3.6 (3)
C(E7)	-291 (6)	8624 (12)	4023 (6)	3.3 (3)
C(E8)	-613 (7)	9249 (13)	4312 (7)	4.4 (3)
C(E9)	-1167 (7)	8973 (14)	4389 (8)	4.8 (4)
C(E10)	-1361 (7)	8014 (14)	4188 (7)	4.4 (3)
C(E11)	-1032 (6)	7425 (12)	3906 (7)	3.8 (3)
N(E12)	-511 (5)	7728 (9)	3829 (5)	3.4 (2)
N(F1)	448 (5)	6087 (10)	4118 (5)	3.9 (3)
C(F2)	942 (7)	6394 (13)	4520 (7)	4.5 (4)
C(F3)	1228 (7)	5729 (13)	4980 (7)	4.5 (3)
C(F4)	1018 (7)	4771 (13)	5017 (7)	4.5 (3)
C(F5)	499 (7)	4479 (13)	4593 (7)	4.3 (3)
C(F6)	221 (6)	5151 (12)	4144 (6)	3.5 (3)
C(F7)	-303 (6)	4890 (12)	3693 (6)	3.3 (3)
C(F8)	-603 (7)	3989 (14)	3694 (7)	4.7 (4)
C(F9)	-1106 (7)	3810 (14)	3268 (7)	4.8 (4)
C(F10)	-1291 (7)	4552 (13)	2818 (7)	4.5 (4)
C(F11)	-971 (6)	5430 (12)	2831 (6)	3.5 (3)
N(F12)	-488 (5)	5593 (9)	3267 (5)	3.0 (2)
Tartrate ion				
O(T1)	2394 (6)	5755 (11)	-144 (6)	6.3 (3)
O(T2)	2014 (5)	7145 (10)	-576 (5)	5.0 (2)
C(T3)	2181 (6)	6603 (12)	-140 (6)	3.6 (3)
C(T4)	2126 (6)	6958 (14)	483 (6)	4.0 (3)
O(T5)	1753 (5)	7834 (9)	421 (5)	4.5 (2)
C(T6)	2734 (6)	7198 (13)	852 (7)	4.2 (3)
O(T7)	3009 (5)	7955 (10)	579 (5)	5.8 (3)
C(T8)	2686 (7)	7632 (13)	1483 (7)	4.3 (3)
O(T9)	2800 (5)	8552 (10)	1591 (5)	5.8 (3)
O(T10)	2483 (5)	7024 (11)	1793 (5)	5.8 (3)
Chloride ions and water molecules				
Cl(1)	5000	6922 (6)	5000	5.5 (1)
Cl(2)*	487 (3)	7145 (7)	213 (3)	4.3 (2)
O(W1)	2050 (6)	136 (12)	976 (6)	7.2 (4)
O(W2)	2977 (6)	1264 (11)	1679 (6)	6.9 (3)
O(W3)	2893 (5)	4326 (10)	705 (5)	5.2 (3)
O(W4)	2470 (5)	4966 (10)	1692 (6)	5.8 (3)
O(W5)	2610 (7)	873 (13)	3637 (7)	8.1 (4)
O(W6)	2680 (7)	2083 (17)	2661 (7)	9.6 (4)
O(W7)	2341 (8)	1644 (15)	4697 (8)	9.8 (5)
O(W8)	2816 (6)	4114 (12)	2796 (7)	7.6 (4)
O(W9)	2804 (7)	8824 (14)	3885 (7)	8.8 (4)
O(W10)	2463 (8)	7518 (14)	2955 (8)	9.7 (5)
O(W11)	2796 (9)	5620 (17)	3628 (9)	11.2 (6)
O(W12)	2410 (9)	8568 (17)	4966 (10)	12.3 (5)
O(W13)*	785 (13)	6689 (26)	472 (14)	8.4 (8)
O(W14)*	3639 (15)	6878 (34)	4512 (15)	10.4 (10)
O(W15)*	2306 (14)	4953 (28)	4436 (15)	8.8 (8)
O(W16)*	2525 (14)	5497 (26)	3988 (14)	8.3 (8)

$\sin \theta/\lambda < 0.25$. Refinement was continued by a diagonal least-squares method, and Fourier and difference-Fourier syntheses were carried out. No large peaks could be found on the difference-Fourier map, but the Fourier map suggested that the occupancies of the four water molecules: O(W13), O(W14), O(W15), and O(W16), were less than 1.0, so they were assigned an occupancy of 0.5. Final refinement was performed with 4531 unweighted data with $|F_o| > 3\sigma(|F_o|)$ by the diagonal least-squares method and the R index converged to 0.096.

Final atomic parameters are listed in Table 2 with their estimated standard deviations.* The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1968).

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31936 (25 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. *Bijvoet inequalities*

h	k	l	$ F(hkl) ^2$	$I_o(hkl)$
			$ F(h\bar{k}l) ^2$	$I_o(h\bar{k}l)$
5	7	2	1.101	> 1
5	3	9	1.129	> 1
1	3	9	1.210	> 1
8	4	1	0.902	< 1
10	2	1	0.905	< 1
7	1	3	0.814	< 1
7	7	4	0.897	< 1
9	1	4	1.207	> 1
6	6	8	1.463	> 1

Determination of the absolute configuration

The absolute structure of the crystal was determined based on the tartrate ion as an internal reference. The coordinate system was chosen so that the (+)₅₈₉-tartrate ion has the configuration (2*R*, 3*R*) in the crystal. It was definitely concluded that the configuration *A* should be assigned to the (+)₅₈₉-[Ni(bipy)₃]²⁺ complex isomer. Fig. 1 shows the framework of the complex, taking the absolute configuration into consideration.

The absolute configuration was checked further by application of the Bijvoet method. The intensity ratios for nine Bijvoet pairs were calculated by including the imaginary part of the anomalous dispersion terms of Ni and Cl, and were compared with those observed (Table 3). This shows that the Bijvoet method gives a correct result under the limited conditions which include the disorder of water molecules and Cl⁻ ions, and the isotropic approximation in the refinement. This result is in agreement with earlier results on the absolute configuration of bipyridyl and phenanthrolyl complexes determined by Hanazaki & Nagakura (1969) by circular dichroism analysis, and by Templeton, Zalkin & Ueki (1966) and Butler & Snow (1971) by the X-ray method.

Discussion of the structure

Bond lengths and angles are given in Table 4 with their estimated standard deviations. In the complex ions the average values of the bond lengths Ni-N, N-C, C-C and C-C' (connecting two pyridine rings) and the bond angle N-Ni-N are: 2.11, 1.36, 1.40

Table 4. *Bond lengths (Å) and bond angles (°)*

Estimated standard deviations are given in parentheses.

Ni(1)—N(A1)	2.107 (13)	C(B6)—C(B7)	1.47 (2)	Ni(2)—N(F12)	2.113 (12)	C(E10)—C(E11)	1.37 (2)
—N(A12)	2.108 (11)	C(B7)—C(B8)	1.37 (2)	N(D1)—C(D2)	1.36 (2)	C(E11)—N(E12)	1.34 (2)
—N(B1)	2.087 (13)	—N(B12)	1.34 (2)	—C(D6)	1.35 (2)	N(F1)—C(F2)	1.37 (2)
—N(B12)	2.104 (13)	C(B8)—C(B9)	1.39 (3)	C(D2)—C(D3)	1.41 (3)	—C(F6)	1.35 (2)
—N(C1)	2.119 (11)	C(B9)—C(B10)	1.34 (2)	C(D3)—C(D4)	1.39 (2)	C(F2)—C(F3)	1.42 (2)
—N(C12)	2.137 (13)	C(B10)—C(B11)	1.43 (2)	C(D4)—C(D5)	1.38 (2)	C(F3)—C(F4)	1.37 (2)
N(A1)—C(A2)	1.38 (2)	C(B11)—N(B12)	1.35 (2)	C(D5)—C(D6)	1.41 (3)	C(F4)—C(F5)	1.43 (2)
—C(A6)	1.38 (2)	N(C1)—C(C2)	1.35 (2)	C(D6)—C(D7)	1.48 (2)	C(F5)—C(F6)	1.40 (2)
C(A2)—C(A3)	1.43 (3)	—C(C6)	1.36 (2)	C(D7)—C(D8)	1.38 (2)	C(F6)—C(F7)	1.46 (2)
C(A3)—C(A4)	1.39 (2)	C(C2)—C(C3)	1.40 (2)	—N(D12)	1.37 (2)	C(F7)—C(F8)	1.38 (2)
C(A4)—C(A5)	1.39 (2)	C(C3)—C(C4)	1.36 (3)	C(D8)—C(D9)	1.40 (2)	—N(F12)	1.35 (2)
C(A5)—C(A6)	1.40 (2)	C(C4)—C(C5)	1.39 (2)	C(D9)—C(D10)	1.40 (3)	C(F8)—C(F9)	1.37 (2)
C(A6)—C(A7)	1.46 (2)	C(C5)—C(C6)	1.38 (2)	C(D10)—C(D11)	1.34 (2)	C(F9)—C(F10)	1.42 (2)
C(A7)—C(A8)	1.40 (2)	C(C6)—C(C7)	1.45 (2)	C(D11)—N(D12)	1.36 (2)	C(F10)—C(F11)	1.38 (2)
—N(A12)	1.38 (2)	C(C7)—C(C8)	1.39 (2)	N(E1)—C(E2)	1.35 (2)	C(F11)—N(F12)	1.35 (2)
C(A8)—C(A9)	1.37 (2)	—N(C12)	1.35 (2)	—C(E6)	1.35 (2)	O(T1)—C(T3)	1.23 (2)
C(A9)—C(A10)	1.41 (3)	C(C8)—C(C9)	1.35 (2)	C(E2)—C(E3)	1.42 (3)	O(T2)—C(T3)	1.22 (2)
C(A10)—C(A11)	1.42 (2)	C(C9)—C(C10)	1.47 (3)	C(E3)—C(E4)	1.41 (3)	C(T3)—C(T4)	1.55 (2)
C(A11)—N(A12)	1.33 (2)	C(C10)—C(C11)	1.42 (3)	C(E4)—C(E5)	1.41 (3)	C(T4)—O(T5)	1.44 (2)
N(B1)—C(B2)	1.35 (2)	C(C11)—N(C12)	1.34 (2)	C(E5)—C(E6)	1.39 (2)	—C(T6)	1.52 (2)
—C(B6)	1.38 (2)	Ni(2)—N(D1)	2.104 (14)	C(E6)—C(E7)	1.46 (2)	C(T6)—O(T7)	1.42 (2)
C(B2)—C(B3)	1.40 (2)	—N(D12)	2.093 (11)	C(E7)—C(E8)	1.39 (2)	—C(T8)	1.59 (2)
C(B3)—C(B4)	1.39 (3)	—N(E1)	2.084 (12)	—N(E12)	1.33 (2)	C(T8)—O(T9)	1.26 (2)
C(B4)—C(B5)	1.44 (2)	—N(E12)	2.111 (13)	C(E8)—C(E9)	1.41 (3)	—O(T10)	1.24 (2)
C(B5)—C(B6)	1.37 (2)	—N(F1)	2.120 (12)	C(E9)—C(E10)	1.39 (3)		

Table 4 (cont.)

N(A1)—Ni(1)—N(A12)	79.2 (5)	C(B7)—N(B12)—C(B11)	121 (1)	Ni(2)—N(D12)—C(D11)	128 (1)
—N(B1)	94.7 (5)	Ni(1)—N(C1)—C(C2)	125 (1)	C(D7)—N(D12)—C(D11)	119 (1)
—N(B12)	172.4 (5)	—C(C6)	113 (1)	Ni(2)—N(E1)—C(E2)	125 (1)
—N(C1)	91.7 (5)	C(C2)—N(C1)—C(C6)	121 (1)	—C(E6)	115 (1)
—N(C12)	92.6 (5)	N(C1)—C(C2)—C(C3)	122 (2)	C(E2)—N(E1)—C(E6)	120 (1)
N(A12)—Ni(1)—N(B1)	96.3 (5)	C(C2)—C(C3)—C(C4)	117 (1)	N(E1)—C(E2)—C(E3)	122 (2)
—N(B12)	97.0 (5)	C(C3)—C(C4)—C(C5)	121 (2)	C(E2)—C(E3)—C(E4)	118 (2)
—N(C1)	167.5 (5)	C(C4)—C(C5)—C(C6)	121 (2)	C(E3)—C(E4)—C(E5)	119 (2)
—N(C12)	93.0 (5)	N(C1)—C(C6)—C(C5)	118 (1)	C(E4)—C(E5)—C(E6)	120 (2)
N(B1)—Ni(1)—N(B12)	79.0 (5)	—C(C7)	117 (1)	N(E1)—C(E6)—C(E5)	121 (2)
—N(C1)	93.0 (4)	C(C5)—C(C6)—C(C7)	125 (1)	—C(E7)	115 (1)
—N(C12)	169.1 (5)	C(C6)—C(C7)—C(C8)	124 (1)	C(E5)—C(E6)—C(E7)	124 (2)
N(B12)—Ni(1)—N(C1)	92.9 (5)	—N(C12)	117 (1)	C(E6)—C(E7)—C(E8)	123 (1)
—N(C12)	94.3 (5)	C(C8)—C(C7)—N(C12)	119 (1)	—N(E12)	119 (1)
N(C1)—Ni(1)—N(C12)	78.7 (5)	C(C7)—C(C8)—C(C9)	123 (2)	C(E8)—C(E7)—N(E12)	118 (1)
Ni(1)—N(A1)—C(A2)	127 (1)	C(C8)—C(C9)—C(C10)	117 (2)	C(E7)—C(E8)—C(E9)	122 (2)
—C(A6)	115 (1)	C(C9)—C(C10)—C(C11)	119 (1)	C(E8)—C(E9)—C(E10)	116 (2)
C(A2)—N(A1)—C(A6)	119 (1)	C(C10)—C(C11)—N(C12)	119 (2)	C(E9)—C(E10)—C(E11)	120 (2)
N(A1)—C(A2)—C(A3)	122 (1)	Ni(1)—N(C12)—C(C7)	113 (1)	C(E10)—C(E11)—N(E12)	122 (1)
C(A2)—C(A3)—C(A4)	118 (2)	—C(C11)	124 (1)	Ni(2)—N(E12)—C(E7)	113 (1)
C(A3)—C(A4)—C(A5)	121 (2)	C(C7)—N(C12)—C(C11)	123 (1)	—C(E11)	126 (1)
C(A4)—C(A5)—C(A6)	120 (2)	N(D1)—Ni(2)—N(D12)	79.8 (5)	C(E7)—N(E12)—C(E11)	121 (1)
N(A1)—C(A6)—C(A5)	121 (1)	—N(E1)	94.7 (5)	Ni(2)—N(F1)—C(F2)	125 (1)
—C(A7)	115 (1)	—N(E12)	170.6 (5)	—C(F6)	114 (1)
C(A5)—C(A6)—C(A7)	124 (1)	—N(F1)	93.7 (5)	C(F2)—N(F1)—C(F6)	122 (1)
C(A6)—C(A7)—C(A8)	124 (2)	—N(F12)	92.4 (5)	N(F1)—C(F2)—C(F3)	120 (2)
—N(A12)	118 (1)	N(D12)—Ni(2)—N(E1)	93.1 (4)	C(F2)—C(F3)—C(F4)	120 (1)
C(A8)—C(A7)—N(A12)	118 (1)	N(D12)—Ni(2)—N(E12)	93.5 (5)	C(F3)—C(F4)—C(F5)	118 (2)
C(A7)—C(A8)—C(A9)	122 (2)	—N(F1)	170.2 (5)	C(F4)—C(F5)—C(F6)	121 (2)
C(A8)—C(A9)—C(A10)	119 (2)	—N(F12)	94.8 (4)	N(F1)—C(F6)—C(F5)	119 (1)
C(A9)—C(A10)—C(A11)	118 (2)	N(E1)—Ni(2)—N(E12)	79.0 (5)	—C(F7)	118 (1)
C(A10)—C(A11)—N(A12)	122 (2)	—N(F1)	94.7 (5)	C(F5)—C(F6)—C(F7)	123 (1)
Ni(1)—N(A12)—C(A7)	113 (1)	—N(F12)	170.2 (5)	C(F6)—C(F7)—C(F8)	123 (1)
—C(A11)	125 (1)	N(E12)—Ni(2)—N(F1)	93.8 (5)	—N(F12)	116 (1)
C(A7)—N(A12)—C(A11)	122 (1)	—N(F12)	94.7 (5)	C(F8)—C(F7)—N(F12)	121 (1)
Ni(1)—N(B1)—C(B2)	127 (1)	N(F1)—Ni(2)—N(F12)	78.1 (4)	C(F7)—C(F8)—C(F9)	120 (2)
—C(B6)	114 (1)	Ni(2)—N(D1)—C(D2)	127 (1)	C(F8)—C(F9)—C(F10)	118 (2)
C(B2)—N(B1)—C(B6)	118 (1)	—C(D6)	114 (1)	C(F9)—C(F10)—C(F11)	119 (1)
N(B1)—C(B2)—C(B3)	123 (2)	C(D2)—N(D1)—C(D6)	119 (1)	C(F10)—C(F11)—N(F12)	121 (1)
C(B2)—C(B3)—C(B4)	118 (2)	N(D1)—C(D2)—C(D3)	123 (2)	Ni(2)—N(F12)—C(F7)	115 (1)
C(B3)—C(B4)—C(B5)	119 (2)	C(D2)—C(D3)—C(D4)	117 (2)	—C(F11)	125 (1)
C(B4)—C(B5)—C(B6)	119 (2)	C(D3)—C(D4)—C(D5)	121 (2)	C(F7)—N(F12)—C(F11)	120 (1)
N(B1)—C(B6)—C(B5)	122 (1)	C(D4)—C(D5)—C(D6)	119 (2)	O(T1)—C(T3)—O(T2)	126 (2)
—C(B7)	116 (1)	N(D1)—C(D6)—C(D5)	121 (1)	—C(T4)	114 (1)
C(B5)—C(B6)—C(B7)	122 (1)	—C(D7)	116 (1)	O(T2)—C(T3)—C(T4)	121 (1)
C(B6)—C(B7)—C(B8)	123 (1)	C(D5)—C(D6)—C(D7)	123 (1)	C(T3)—C(T4)—O(T5)	110 (1)
—N(B12)	116 (1)	C(D6)—C(D7)—C(D8)	123 (1)	—C(T6)	108 (1)
C(B8)—C(B7)—N(B12)	121 (1)	—N(D12)	117 (1)	O(T5)—C(T4)—C(T6)	111 (1)
C(B7)—C(B8)—C(B9)	120 (2)	C(D8)—C(D7)—N(D12)	120 (1)	C(T4)—C(T6)—O(T7)	112 (1)
C(B8)—C(B9)—C(B10)	118 (2)	C(D7)—C(D8)—C(D9)	120 (2)	—C(T8)	109 (1)
C(B9)—C(B10)—C(B11)	121 (2)	C(D8)—C(D9)—C(D10)	118 (2)	O(T7)—C(T6)—C(T8)	107 (1)
C(B10)—C(B11)—N(B12)	118 (1)	C(D9)—C(D10)—C(D11)	119 (2)	C(T6)—C(T8)—O(T9)	118 (2)
Ni(1)—N(B12)—C(B7)	115 (1)	C(D10)—C(D11)—N(D12)	123 (2)	—O(T10)	115 (2)
—C(B11)	124 (1)	Ni(2)—N(D12)—C(D7)	113 (1)	O(T9)—C(T8)—O(T10)	127 (2)

1.46 Å and 79.0° for complex 1, and 2.10, 1.35, 1.40, 1.47 Å and 79.0° for complex 2. These values are in good agreement with the corresponding values found in the same complex in the sulphate compound (Wada *et al.*, 1976).

The two crystallographically independent complex ions are approximately related to each other by a non-crystallographic twofold screw axis at $x=0.0158$, $z=0.2561$ and parallel to the b axis. Both complex ions exhibit an approximate D_3 symmetry with their threefold axes almost perpendicular to (100).

The complex ions are arranged in layers parallel to

(100) as shown in Fig. 2. The tartrate ions and the water molecules are located between these layers, and compose a two-dimensional network of hydrogen bonds as shown in Figs. 3 and 4. This net is linked to the next by two chains of hydrogen bonds through Cl^- ions. This layered structure resembles that found in racemic $[\text{Ni}(\text{bipy})_3]\text{SO}_4 \cdot 7.5\text{H}_2\text{O}$ (Wada *et al.*, 1976).

The computer programs used in this study were devised in our laboratory by C. Katayama and A. Wada. *RSDA-4* of a local version of *UNICS* (Sakurai,

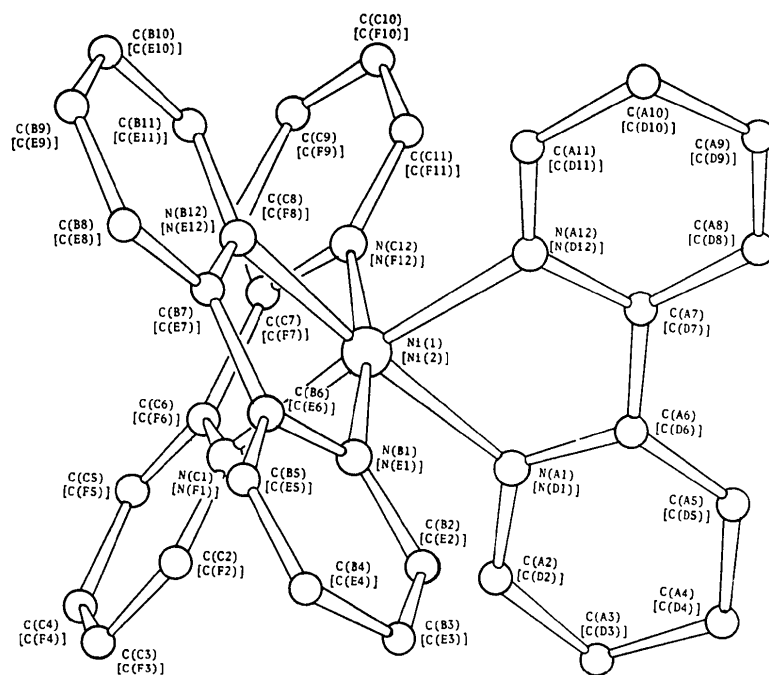


Fig. 1. Framework of the complex ion, taking the absolute configuration *A* into consideration.

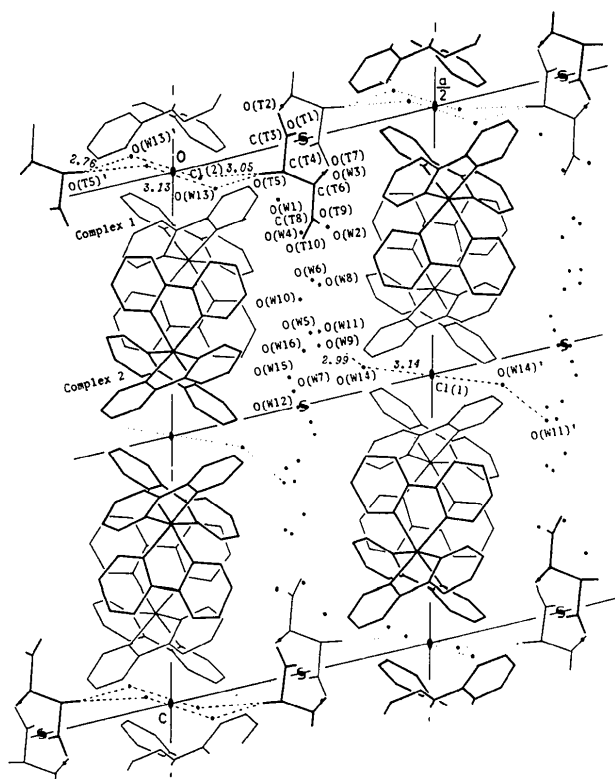


Fig. 2. Crystal structure projected along *b*. Water molecules are drawn with dots. Broken lines show the hydrogen-bonded chains linking the hydrogen-bonded nets parallel to (100).

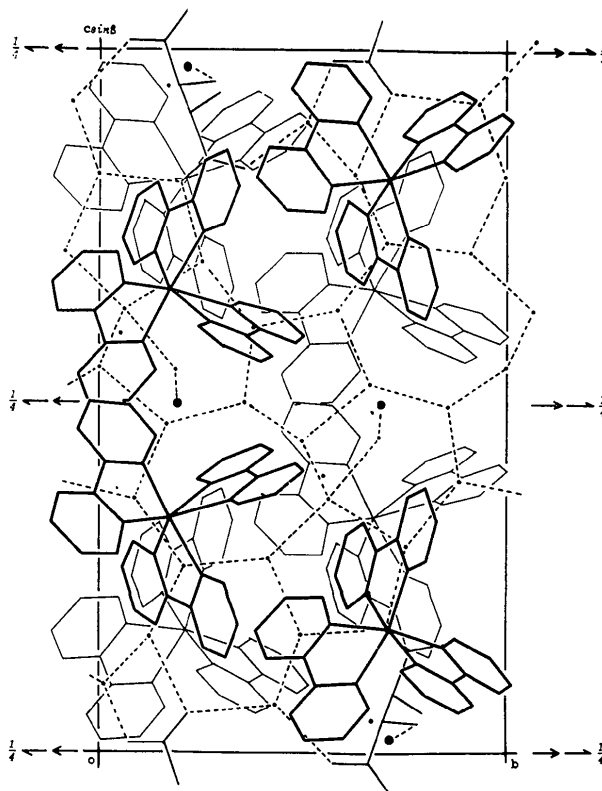


Fig. 3. Crystal structure projected along *a*. Hydrogen bonds are drawn with broken lines and chloride ions are drawn with shaded circles. Tartrate ions and water molecules lying in $x \approx 0.75$ are omitted.

