

Fig. 1. PLUTO drawings of the two complexes and numbering schemes.

the atom at the apex of the pyramid [Br(1)] to positions such that the angles they make with the Cu and the bromine atom are about 120°. In this complex N(2)—Cu—Br(1) = 139.5 (3) and N(4)—Cu—Br(1) = 106.9 (3)°.

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Structure of a Hydrogen-Bonded Dinuclear Nickel 8-Quinolinol Complex

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Abstract. 8-Hydroxyquinolinium bis{[tris- μ -[bis(8-quinolinolato)hydrogen(1)-*N,O*]-dinickel(II)} triperchlorate, [C₉H₈NO][Ni₂{H(C₉H₆NO)₂]₃]₂(ClO₄)₃, *M_r* = 2415.2, monoclinic, *Cc*, *a* = 45.313 (3), *b* = 13.143 (1), *c* = 18.675 (1) Å, β = 98.87 (1)°, *V* = 10989 (1) Å³, *Z* = 4, *D_m* = 1.48 (1), *D_x* = 1.46 Mg m⁻³, λ (Cu *K*α) = 1.5418 Å, μ = 2.102 mm⁻¹, *F*(000) = 4968, *T* = 295 K, *R* = 0.0837 for 4668 observed reflections. Each Ni^{II} atom is octahedrally coordinated by three bidentate 8-quinolinol ligands in the facial conformation and two such complexes form a dinuclear cation through three strong O...H...O hydrogen bonds with distances ranging from 2.35 (2) to 2.55 (2) Å, as found in the triiodide analogue. The uncoordinated 8-quinolinol is linked by hydrogen bonds to two perchlorate ions, while the remaining perchlorate ion is disordered over two positions with nearly equal occupancies. Thus, the two anionic species, [(C₉H₈NO)(ClO₄)₂]⁻ and ClO₄⁻ are

held alternately between layers consisting of only cationic complexes [Ni₂{H(C₉H₆NO)₂]₃⁺ parallel to (100).

Introduction. The previous X-ray study on the nickel 8-quinolinol complex with the triiodide anion (Kiriya, Fukuda, Yamagata & Sekido, 1985) revealed that the complex cations of nickel with three bidentate 8-quinolinol ligands in facial conformation form a dinuclear cation of [Ni₂{H(C₉H₆NO)₂]₃⁺ joined face to face by three strong O...H...O hydrogen bonds. Such unique dimer formation was noted as the first example for metal 8-quinolinol complexes. We prepared successively nickel 8-quinolinol complexes with perchlorate anions in order to ascertain whether or not such a dinuclear cation would be formed in the presence of another anion such as perchlorate. Its chemical composition was too complex to be confirmed

by chemical and spectroscopic analyses. Therefore the stoichiometry and stereochemistry of this compound were determined by X-ray diffraction.

Experimental. Nickel(II) perchlorate hexahydrate (10 mmol in 20 ml of ethanol) was mixed with 8-quinolinol (80 mmol in 100 ml of ethanol) by dropwise addition. The mixture was stirred and filtered. The light-green filtrate was concentrated and set aside to crystallize. After several days, a light-green precipitate was deposited. It was attempted to recrystallize the precipitate from ethanol, but this process resulted in an unexpected reaction producing an unknown blue-green precipitate. No solvent other than ethanol could be used for crystal growth because of the compound's poor solubility. So we picked single crystals from the precipitate, that is clusters of fine crystals, and obtained only one suitable crystal, but of small size ($0.1 \times 0.13 \times 0.12$ mm), for X-ray use. Density by flotation (*m*-xylene–1,2-dibromoethylene mixture); Rigaku AFC-5 diffractometer, Ni-filtered $\text{Cu K}\alpha$ radiation, 40 kV–200 mA; unit-cell parameters determined from least squares of setting angles of 44 reflections in 2θ range $35\text{--}55^\circ$; 8149 unique reflections, $\omega\text{--}2\theta$ scan technique, ω -scan width $(1.2 + 0.15 \tan \theta)^\circ$, $2\theta_{\text{max}} = 120^\circ$ (h 0→50, k 0→14, l –20→20), relatively weak intensities observed: 4668 (57%) with $|F_o| \geq 3\sigma(F_o)$, of 2508 in range $100 \leq 2\theta \leq 120^\circ$ only 957 (38.2%) had $|F_o| \geq 3\sigma(F_o)$; peak widths at half-height less than 0.17° , no peak splitting; standard reflections 22,0,0, 574, and 020, scale factors for intensity variation ranged from 0.984 to 1.007; Lorentz–polarization and empirical absorption corrections, correction factors on F : 1.008–1.043 (North, Phillips & Mathews, 1968). Structure solved by heavy-atom method and refined by block-diagonal least squares on F with anisotropic temperature factors for all non-H atoms except for O atoms of perchlorates and C atoms of uncoordinated 8-quinolinol; population of disordered perchlorate anions estimated from peak heights of Cl atoms in Fourier map, O(44) fixed at position derived from Fourier synthesis with $B_{\text{iso}} = 10.0 \text{ \AA}^2$; H-atom coordinates calculated on basis of $X\text{--}H = 1.0 \text{ \AA}$, $X = \text{C}$ and N with sp^2 hybridization, $\text{O--H} = 1.0 \text{ \AA}$ on $\text{O}\cdots\text{O}$ line and included as fixed atoms with $B_{\text{iso}} = 5.0 \text{ \AA}^2$ in final cycles of refinement; $\sum w(|F_o| - |F_c|)^2$ minimized for 1376 parameters, $R = 0.0837$, $wR = 0.0833$, $w = [\sigma^2(F_o) + 0.051|F_o|]^{-1}$, $S = 1.93$, data/parameter = 3.39, $(\Delta/\sigma)_{\text{max}} = 0.6$ except for perchlorate anions where $(\Delta/\sigma)_{\text{max}} = 2.0$. Residual electron density in difference Fourier map -0.41 to 0.83 e \AA^{-3} ; the two largest peaks were in the vicinity of the two disordered perchlorate anions, but no other convincing disorder model could be assigned. Equivalent refinement of the enantiomeric model converged with $R = 0.0841$, no significant change in the overall geometry. The relatively high R value resulted from a large number of

weak reflections with large errors due to the small size of the crystal and also to the disorder. Scattering factors and anomalous-dispersion terms from *International Tables for X-ray Crystallography* (1974); computations using the programs of *The Universal Crystallographic Computing System–Osaka* (1979) and their modifications on an ACOS 1000 computer at the Information Processing Center of Kobe University and an ACOS 850 computer at the Crystallographic Research Center, Institute for Protein Research, Osaka University.

Discussion. Final positional and thermal parameters are given in Table 1* and selected interatomic distances and angles in Table 2. The complex cation with the atom-numbering scheme, hydrogen-bonded 8-quinolinol with two perchlorates and the crystal structure viewed along the b axis are shown in Figs. 1(a), 1(b) and 2, respectively.

The asymmetric unit consists of four Ni atoms, twelve bidentate 8-quinolinol ligands, one uncoordinated 8-quinolinol and three perchlorate ions. It was confirmed that the perchlorate complex possesses the same hydrogen-bonded dinuclear cation, $[\text{Ni}_2\{\text{H}(\text{C}_9\text{H}_6\text{NO})_2\}_3]^+$, as that found in the triiodide complex (Kiriyaama, Fukuda, Yamagata & Sekido, 1985). Thus, in the dimeric unit, octahedral tris chelates in a mutually *cis* configuration are joined face to face through their oxygen faces by hydrogen bonds. The details of the dimensions in the two crystallographically independent dinuclear cations agree well with those found in the triiodide complex. The average values of Ni–N and Ni–O bond distances and N–Ni–O intraligand angles are 2.06 (6) and 2.07 (4) Å and 79.5 (13°), respectively. The C, N and O atoms in each 8-quinolinol ligand lie close to a plane with the largest deviation being 0.21 (2) Å. The dihedral angles between tris chelate planes are in the range 69.3 (4)– 88.8 (5°). The average $\text{O}\cdots\text{H}\cdots\text{O}$ distance is 2.44 (7) Å which corresponds to the low end of the range reported in the literature. Although the bridging H atoms were not located in the difference Fourier map, these hydrogen bonds may be symmetrical, judging from the very short $\text{O}\cdots\text{O}$ distances and also from the fact that no significant differences in corresponding Ni–O and C–O distances were disclosed for each pair of hydrogen-bonded 8-quinolinol ligands, *A–D*, *B–E*, *C–F*, *G–J*, *H–K*, and *I–L*, within the experimental errors.

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, intramolecular bond distances and angles, and least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42489 (37 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Final atomic coordinates and equivalent isotropic thermal parameters (\AA^2) for non-H atoms
$$B_{eq} = \frac{4}{3} \sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

	x	y	z	B_{eq} or B
Ni(1)	0.00034	0.22343 (28)	0.99977	4.28 (11)
Ni(2)	0.05714 (7)	0.27593 (27)	0.81215 (17)	3.76 (10)
Ni(3)	0.79104 (7)	0.22161 (26)	0.73432 (16)	3.24 (9)
Ni(4)	0.73256 (7)	0.27790 (27)	0.91951 (16)	3.41 (9)
Cl(1)	0.9199 (2)	-0.2130 (7)	0.6878 (3)	9.1 (3)
Cl(2)	0.3734 (2)	0.2481 (9)	0.0400 (4)	13.2 (5)
O(8A)	-0.0130 (3)	0.3032 (11)	0.9080 (7)	4.5 (5)
O(8B)	0.0423 (3)	0.2847 (10)	1.0191 (7)	3.4 (4)
O(8C)	0.0175 (3)	0.1094 (10)	0.9390 (7)	4.1 (5)
O(8D)	0.0114 (3)	0.2778 (11)	0.8015 (6)	4.0 (4)
O(8E)	0.0601 (3)	0.3575 (10)	0.9090 (7)	4.3 (5)
O(8F)	0.0561 (3)	0.1363 (9)	0.8705 (6)	2.6 (4)
O(8G)	0.7474 (3)	0.2772 (10)	0.7194 (6)	4.0 (4)
O(8H)	0.8031 (3)	0.3061 (9)	0.8321 (6)	3.1 (4)
O(8I)	0.7754 (3)	0.1088 (10)	0.7940 (7)	3.3 (4)
O(8J)	0.7304 (3)	0.3523 (9)	0.8227 (6)	2.8 (4)
O(8K)	0.7776 (3)	0.2748 (10)	0.9348 (6)	3.5 (4)
O(8L)	0.7337 (3)	0.1436 (11)	0.8678 (7)	4.2 (4)
O(8M)	0.3954 (5)	0.1669 (14)	-0.1669 (10)	3.6 (6)
N(1A)	-0.0195 (3)	0.3511 (13)	1.0365 (8)	3.5 (5)
N(1B)	0.0160 (3)	0.1543 (13)	1.0958 (8)	3.2 (5)
N(1C)	-0.0395 (3)	0.1271 (13)	0.9766 (8)	3.5 (5)
N(1D)	0.0465 (3)	0.2113 (11)	0.7103 (7)	2.8 (5)
N(1E)	0.0580 (4)	0.4222 (15)	0.7768 (10)	5.4 (7)
N(1F)	0.1027 (4)	0.2483 (13)	0.8374 (9)	4.6 (6)
N(1G)	0.7725 (4)	0.1558 (11)	0.6342 (7)	4.0 (6)
N(1H)	0.8056 (4)	0.3525 (12)	0.6909 (8)	3.4 (5)
N(1I)	0.8255 (4)	0.1354 (12)	0.7508 (9)	3.7 (5)
N(1J)	0.7321 (3)	0.4269 (11)	0.9553 (7)	2.6 (5)
N(1K)	0.7411 (3)	0.2226 (14)	1.0221 (8)	4.2 (5)
N(1L)	0.6883 (3)	0.2437 (12)	0.8988 (7)	3.4 (5)
N(1M)	0.3915 (4)	0.0560 (28)	-0.0695 (11)	13.0 (14)
Cl(3) ^a	0.6290 (3)	0.1676 (10)	0.0913 (8)	7.1 (5)
Cl(4) ^a	0.6638 (4)	0.3634 (14)	0.1469 (8)	9.6 (6)
C(2A)	-0.0208 (5)	0.3763 (16)	1.1066 (11)	4.5 (7)
C(3A)	-0.0317 (4)	0.4663 (16)	1.1261 (12)	4.1 (7)
C(4A)	-0.0340 (5)	0.5504 (16)	1.0710 (12)	4.3 (7)
C(5A)	-0.0342 (6)	0.6033 (17)	0.9558 (14)	6.0 (9)
C(6A)	-0.0331 (5)	0.5765 (17)	0.8784 (11)	4.8 (8)
C(7A)	-0.0261 (5)	0.4788 (18)	0.8619 (12)	5.2 (8)
C(8A)	-0.0208 (4)	0.4076 (15)	0.9225 (11)	3.4 (6)
C(9A)	-0.0240 (4)	0.4331 (17)	0.9907 (11)	3.9 (7)
C(10A)	-0.0303 (5)	0.5311 (16)	1.0042 (11)	3.8 (7)
C(2B)	0.0019 (5)	0.0950 (14)	1.1412 (11)	3.8 (7)
C(3B)	0.0156 (5)	0.0506 (17)	1.1991 (10)	4.0 (7)
C(4B)	0.0468 (5)	0.0635 (17)	1.2170 (11)	4.7 (8)
C(5B)	0.0942 (6)	0.1399 (19)	1.1923 (13)	5.7 (9)
C(6B)	0.1073 (5)	0.1968 (24)	1.1484 (13)	7.7 (11)
C(7B)	0.0906 (5)	0.2422 (18)	1.0877 (11)	4.7 (8)
C(8B)	0.0597 (4)	0.2331 (15)	1.0691 (10)	2.8 (6)
C(9B)	0.0459 (4)	0.1641 (15)	1.1136 (10)	3.1 (6)
C(10B)	0.0674 (5)	0.1105 (15)	1.1731 (10)	4.0 (7)
C(2C)	-0.0630 (5)	0.1399 (19)	1.0034 (13)	5.1 (8)
C(3C)	-0.0871 (5)	0.0755 (17)	0.9919 (14)	5.4 (8)
C(4C)	-0.0825 (5)	-0.0011 (18)	0.9605 (11)	4.4 (7)
C(5C)	-0.0510 (6)	-0.1048 (18)	0.8855 (13)	5.7 (9)
C(6C)	-0.0247 (5)	-0.1168 (16)	0.8594 (13)	5.0 (8)
C(7C)	0.0006 (5)	-0.0380 (16)	0.8787 (12)	4.8 (8)
C(8C)	-0.0047 (4)	0.0434 (16)	0.9238 (11)	3.7 (7)
C(9C)	-0.0342 (4)	0.0417 (14)	0.9378 (9)	2.9 (6)
C(10C)	-0.0578 (5)	-0.0263 (15)	0.9269 (11)	4.2 (7)
C(2D)	0.0632 (5)	0.1890 (18)	0.6612 (11)	5.0 (8)
C(3D)	0.0585 (5)	0.1529 (19)	0.5970 (12)	5.3 (8)
C(4D)	0.0296 (6)	0.1500 (17)	0.5742 (12)	5.4 (8)
C(5D)	-0.0248 (6)	0.1617 (21)	0.5978 (13)	6.5 (9)
C(6D)	-0.0401 (4)	0.1749 (18)	0.6425 (12)	4.6 (7)
C(7D)	-0.0339 (4)	0.2221 (17)	0.7195 (12)	4.7 (7)
C(8D)	-0.0020 (5)	0.2354 (16)	0.7381 (11)	4.2 (7)
C(9D)	0.0170 (4)	0.2052 (12)	0.6857 (9)	2.4 (5)
C(10D)	0.0095 (5)	0.1703 (16)	0.6196 (10)	3.9 (7)
C(2E)	0.0572 (7)	0.4545 (19)	0.7062 (12)	6.9 (10)
C(3E)	0.0521 (6)	0.5535 (20)	0.6878 (12)	6.0 (9)
C(4E)	0.0494 (5)	0.6254 (15)	0.7410 (12)	4.7 (7)
C(5E)	0.0459 (5)	0.6616 (15)	0.8858 (11)	3.7 (7)
C(6E)	0.0456 (6)	0.6283 (16)	0.9480 (12)	5.2 (8)
C(7E)	0.0512 (5)	0.5306 (15)	0.9606 (11)	4.4 (7)
C(8E)	0.0579 (5)	0.4586 (19)	0.9011 (14)	6.1 (9)
C(9E)	0.0559 (4)	0.4962 (15)	0.8245 (10)	3.1 (6)
C(10E)	0.0492 (5)	0.6041 (16)	0.8167 (14)	4.9 (8)
C(2F)	0.1256 (5)	0.2964 (16)	0.8247 (12)	4.4 (7)
C(3F)	0.1545 (5)	0.2634 (20)	0.8452 (14)	6.2 (9)
C(4F)	0.1597 (5)	0.1978 (19)	0.8910 (13)	5.7 (9)
C(5F)	0.1420 (5)	0.0653 (18)	0.9622 (13)	5.5 (8)

Table 1 (cont.)

	x	y	z	B_{eq} or B
C(6F)	0.1176 (5)	0.0199 (16)	0.9900 (12)	4.6 (8)
C(7F)	0.0874 (6)	0.0335 (16)	0.9547 (12)	5.2 (8)
C(8F)	0.0846 (5)	0.1100 (15)	0.9037 (10)	3.5 (6)
C(9F)	0.1059 (5)	0.1736 (17)	0.8845 (10)	4.2 (7)
C(10F)	0.1399 (6)	0.1520 (17)	0.9127 (13)	5.4 (8)
C(2G)	0.7861 (6)	0.1033 (17)	0.5952 (11)	5.1 (8)
C(3G)	0.7690 (6)	0.0492 (16)	0.5303 (12)	5.5 (9)
C(4G)	0.7416 (6)	0.0525 (16)	0.5149 (12)	5.6 (9)
C(5G)	0.6949 (6)	0.1246 (20)	0.5545 (11)	6.0 (9)
C(6G)	0.6820 (6)	0.1949 (20)	0.5997 (14)	6.9 (10)
C(7G)	0.6988 (5)	0.2569 (19)	0.6570 (11)	5.6 (8)
C(8G)	0.7286 (5)	0.2341 (15)	0.6649 (10)	3.7 (6)
C(9G)	0.7416 (5)	0.1709 (15)	0.6200 (10)	3.3 (6)
C(10G)	0.7294 (5)	0.1244 (16)	0.5617 (11)	4.1 (7)
C(2H)	0.8110 (5)	0.3684 (19)	0.6243 (11)	4.9 (8)
C(3H)	0.8139 (5)	0.4788 (17)	0.6024 (11)	4.5 (7)
C(4H)	0.8208 (6)	0.5478 (19)	0.6447 (12)	5.9 (9)
C(5H)	0.8235 (7)	0.6042 (18)	0.7838 (13)	6.9 (10)
C(6H)	0.8174 (5)	0.5793 (16)	0.8429 (12)	4.9 (8)
C(7H)	0.8118 (4)	0.4759 (15)	0.8675 (10)	3.2 (6)
C(8H)	0.8089 (4)	0.4007 (15)	0.8204 (10)	3.1 (6)
C(9H)	0.8125 (4)	0.4254 (13)	0.7461 (11)	2.9 (6)
C(10H)	0.8188 (5)	0.5297 (18)	0.7249 (12)	5.4 (8)
C(2I)	0.8530 (6)	0.1439 (18)	0.7267 (14)	6.1 (9)
C(3I)	0.8744 (5)	0.0587 (25)	0.7419 (15)	8.1 (11)
C(4I)	0.8705 (5)	-0.0255 (15)	0.7923 (11)	4.4 (7)
C(5I)	0.8365 (5)	-0.1219 (19)	0.8538 (13)	5.5 (8)
C(6I)	0.8075 (5)	-0.1271 (16)	0.8684 (11)	4.5 (7)
C(7I)	0.7872 (5)	-0.0532 (15)	0.8554 (10)	3.9 (7)
C(8I)	0.7935 (4)	0.0352 (13)	0.8167 (9)	2.7 (6)
C(9I)	0.8208 (5)	0.0499 (14)	0.7885 (10)	3.4 (6)
C(10I)	0.8413 (4)	-0.0336 (18)	0.8126 (11)	4.1 (7)
C(2J)	0.7327 (4)	0.4653 (15)	1.0215 (10)	3.1 (6)
C(3J)	0.7363 (5)	0.5710 (16)	1.0369 (11)	4.5 (7)
C(4J)	0.7395 (6)	0.6355 (19)	0.9865 (13)	6.2 (9)
C(5J)	0.7423 (5)	0.6695 (18)	0.8710 (12)	5.3 (8)
C(6J)	0.7395 (7)	0.6283 (21)	0.7986 (14)	7.3 (10)
C(7J)	0.7368 (6)	0.5137 (19)	0.7814 (12)	5.6 (9)
C(8J)	0.7359 (4)	0.4535 (13)	0.8321 (8)	1.8 (5)
C(9J)	0.7367 (4)	0.4931 (14)	0.8992 (10)	2.8 (6)
C(10J)	0.7383 (5)	0.5938 (16)	0.9184 (11)	3.6 (7)
C(2K)	0.7218 (5)	0.1876 (17)	1.0650 (10)	4.4 (7)
C(3K)	0.7372 (6)	0.1515 (18)	1.1437 (12)	5.3 (8)
C(4K)	0.7665 (6)	0.1397 (18)	1.1630 (11)	5.4 (8)
C(5K)	0.8143 (5)	0.1573 (18)	1.1327 (11)	5.1 (8)
C(6K)	0.8362 (5)	0.1906 (19)	1.0810 (12)	5.6 (8)
C(7K)	0.8189 (5)	0.2286 (19)	1.0137 (11)	5.0 (7)
C(8K)	0.7903 (4)	0.2396 (15)	0.9959 (10)	3.0 (6)
C(9K)	0.7706 (5)	0.2112 (16)	1.0446 (10)	4.3 (7)
C(10K)	0.7866 (5)	0.1692 (16)	1.1176 (11)	3.8 (6)
C(2L)	0.6660 (5)	0.3021 (21)	0.9208 (11)	5.8 (9)
C(3L)	0.6352 (5)	0.2929 (19)	0.8836 (13)	5.5 (8)
C(4L)	0.6289 (6)	0.2103 (23)	0.8304 (15)	7.8 (11)
C(5L)	0.6502 (5)	0.0645 (22)	0.7586 (12)	6.9 (10)
C(6L)	0.6714 (6)	0.0018 (20)	0.7511 (14)	6.6 (10)
C(7L)	0.7001 (5)	0.0389 (19)	0.7839 (13)	5.7 (9)
C(8L)	0.7071 (5)	0.1169 (16)	0.8305 (11)	4.2 (7)
C(9L)	0.6792 (4)	0.1664 (15)	0.8494 (10)	3.2 (6)
C(10L)	0.6533 (4)	0.1370 (19)	0.8139 (11)	4.6 (8)
C(2M)	0.3898 (6)	0.0311 (20)	-0.0122 (13)	6.1 (6)*
C(3M)	0.3869 (7)	-0.0756 (23)	0.0003 (16)	8.2 (8)*
C(4M)	0.3897 (6)	-0.1509 (20)	-0.0445 (13)	6.0 (6)*
C(5M)	0.3961 (6)	-0.1721 (20)	-0.1739 (13)	6.6 (7)*
C(6M)	0.3980 (6)	-0.1228 (21)	-0.2365 (14)	6.8 (7)*
C(7M)	0.4012 (7)	-0.0282 (26)	-0.2583 (17)	9.7 (9)*
C(8M)	0.3979 (6)	0.0481 (20)	-0.1917 (14)	6.5 (7)*
C(9M)	0.3950 (6)	-0.0013 (13)	-0.1186 (12)	3.6 (5)*
C(10M)	0.3934 (7)	-0.1070 (17)	-0.1141 (13)	5.9 (7)*
O(11)	0.9453 (4)	-0.2626 (16)	0.7253 (10)	9.1 (6)*
O(12)	0.8960 (4)	-0.2022 (15)	0.7296 (10)	8.4 (5)*
O(13)	0.9113 (4)	-0.2552 (14)	0.6224 (9)	7.0 (5)*
O(14)	0.9280 (5)	-0.0953 (17)	0.6755 (12)	10.6 (6)*
O(21)	0.3932 (4)	0.2348 (16)	-0.0148 (11)	9.6 (6)*
O(22)	0.3452 (5)	0.2175 (18)	0.0092 (12)	11.2 (7)*
O(23)	0.3753 (5)	0.3337 (17)	0.0667 (11)	10.3 (6)*
O(24)	0.3840 (5)	0.1784 (19)	0.1006 (13)	12.4 (7)*
O(31) ^a	0.6132 (5)	0.1159 (18)	0.1333 (12)	2.5 (5)*
O(32) ^a	0.645 (1)	0.105 (3)	0.054 (2)	10.4 (13)*
O(33) ^a	0.648 (2)	0.226 (5)	0.139 (3)	16.4 (19)*
O(34) ^a	0.615 (1)	0.219 (4)	0.049 (3)	12.8 (14)*
O(41) ^a	0.6811 (7)	0.4200 (23)	0.1368 (15)	5.0 (7)*
O(42) ^a	0.6707 (9)	0.2387 (32)	0.1705 (22)	9.7 (12)*
O(43) ^a	0.639 (1)	0.330 (4)	0.102 (3)	13.3 (16)*
O(44) ^{a,b}	0.656	0.419	0.205	10.0*

(a) Occupancy factors were set at 0.5. (b) Atom was not refined.

* Isotropic temperature factor.

Similar dinuclear cations with hydrogen-bonding bridges were found in the crystals of $[\text{Co}_2(\text{eta})_3(\text{etaH})_3](\text{ClO}_4)_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ and $[\text{Ni}_2(\text{eta})_2(\text{etaH})_4](\text{ClO}_4)_2$ (where etaH represents 2-aminoethanol and eta the anion formed by removing the proton from 2-aminoethanol) (Bertrand, Eller, Fujita, Lively & Van Derveer,

1979). However, there are distinct differences in the geometry of these dinuclear cations. The cations in $[\text{Co}_2(\text{eta})_3(\text{etaH})_3](\text{ClO}_4)_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ occupy the sites of twofold symmetry, and the two tris chelates are oriented so that their oxygen faces form a trigonal prism with three $\text{O}\cdots\text{O}$ distances of 2.38 (1) Å once and 2.445 (7) Å twice. In $[\text{Ni}_2(\text{eta})_2(\text{etaH})_4](\text{ClO}_4)_2$, because of $\bar{3}$ symmetry of the cation, the two tris chelates are oriented such that their oxygen faces form an octahedron with six equivalent $\text{O}\cdots\text{O}$ distances of 2.73 (2) Å for one set of ligands and 2.68 (5) Å for the other disordered set. On the other hand, in the present complex the overall conformational geometry can be approximated to 32 symmetry. And two oxygen faces are rotated with respect to each other around the pseudo threefold axis by *ca* 30° from the positions of a trigonal prism. Such a situation was encountered in the triiodide analogue where the rotation angle (ϕ) was found to be *ca* 25°. These oxygen arrangements are just intermediate between trigonal prismatic ($\phi = 0^\circ$) and octahedral ($\phi = 60^\circ$) ones owing to mainly steric interactions between large, planar 8-quinolinyl ligands.

Table 2. Selected interatomic distances (Å) and angles (°)

Ni(1)—O(8A)	2.02 (1)	Ni(1)—O(8B)	2.05 (1)
Ni(1)—O(8C)	2.10 (1)	Ni(1)—N(1A)	2.07 (2)
Ni(1)—N(1B)	2.04 (2)	Ni(1)—N(1C)	2.19 (2)
Ni(2)—O(8D)	2.05 (1)	Ni(2)—O(8E)	2.09 (1)
Ni(2)—O(8F)	2.14 (1)	Ni(2)—N(1D)	2.07 (2)
Ni(2)—N(1E)	2.04 (2)	Ni(2)—N(1F)	2.08 (2)
Ni(3)—O(8G)	2.09 (1)	Ni(3)—O(8H)	2.14 (1)
Ni(3)—O(8I)	2.05 (1)	Ni(3)—N(1G)	2.11 (2)
Ni(3)—N(1H)	2.05 (2)	Ni(3)—N(1I)	1.91 (2)
Ni(4)—O(8J)	2.04 (1)	Ni(4)—O(8K)	2.02 (1)
Ni(4)—O(8L)	2.02 (1)	Ni(4)—N(1J)	2.07 (2)
Ni(4)—N(1K)	2.03 (2)	Ni(4)—N(1L)	2.03 (2)
O(8A)—C(8A)	1.45 (2)	O(8B)—C(8B)	1.31 (2)
O(8C)—C(8C)	1.32 (2)	O(8D)—C(8D)	1.36 (3)
O(8E)—C(8E)	1.34 (3)	O(8F)—C(8F)	1.39 (2)
O(8G)—C(8G)	1.35 (2)	O(8H)—C(8H)	1.30 (2)
O(8I)—C(8I)	1.29 (2)	O(8J)—C(8J)	1.36 (2)
O(8K)—C(8K)	1.28 (2)	O(8L)—C(8L)	1.34 (3)
O(8A)—O(8D)	2.44 (2)	O(8B)—O(8E)	2.51 (2)
O(8C)—O(8F)	2.35 (2)	O(8G)—O(8I)	2.40 (2)
O(8H)—O(8K)	2.42 (2)	O(8J)—O(8L)	2.55 (2)
O(8M)—O(12)	2.59 (3)	N(1M)—O(21)	2.56 (3)
O(8M)—N(1M)	2.36 (3)		
O(8A)—Ni(1)—O(8B)	95.4 (5)	O(8A)—Ni(1)—O(8C)	89.9 (6)
O(8A)—Ni(1)—N(1A)	76.8 (6)	O(8A)—Ni(1)—N(1B)	174.8 (6)
O(8A)—Ni(1)—N(1C)	90.2 (6)	O(8B)—Ni(1)—O(8C)	88.1 (5)
O(8B)—Ni(1)—N(1A)	93.5 (6)	O(8B)—Ni(1)—N(1B)	80.4 (6)
O(8B)—Ni(1)—N(1C)	167.7 (6)	O(8C)—Ni(1)—N(1A)	166.7 (6)
O(8C)—Ni(1)—N(1B)	92.9 (6)	O(8C)—Ni(1)—N(1C)	80.9 (6)
N(1A)—Ni(1)—N(1B)	100.3 (6)	N(1A)—Ni(1)—N(1C)	98.5 (6)
N(1B)—Ni(1)—N(1C)	94.6 (6)	O(8D)—Ni(2)—O(8E)	90.3 (5)
O(8D)—Ni(2)—O(8F)	87.6 (5)	O(8D)—Ni(2)—N(1D)	80.0 (6)
O(8D)—Ni(2)—N(1E)	91.6 (7)	O(8E)—Ni(2)—N(1F)	167.9 (6)
O(8E)—Ni(2)—O(8F)	90.1 (5)	O(8E)—Ni(2)—N(1D)	168.6 (6)
O(8E)—Ni(2)—N(1E)	78.1 (7)	O(8F)—Ni(2)—N(1F)	88.0 (6)
O(8F)—Ni(2)—N(1D)	95.5 (5)	O(8F)—Ni(2)—N(1E)	168.2 (6)
O(8F)—Ni(2)—N(1F)	80.4 (6)	N(1D)—Ni(2)—N(1E)	95.9 (7)
N(1D)—Ni(2)—N(1F)	102.7 (6)	N(1E)—Ni(2)—N(1F)	99.8 (7)
O(8G)—Ni(3)—O(8H)	92.5 (5)	O(8G)—Ni(3)—O(8I)	85.8 (5)
O(8G)—Ni(3)—N(1G)	77.7 (6)	O(8G)—Ni(3)—N(1H)	90.6 (6)
O(8G)—Ni(3)—N(1I)	164.0 (6)	O(8H)—Ni(3)—O(8I)	88.6 (5)
O(8H)—Ni(3)—N(1G)	169.8 (6)	O(8H)—Ni(3)—N(1H)	81.2 (6)
O(8H)—Ni(3)—N(1I)	94.3 (6)	O(8I)—Ni(3)—N(1G)	93.6 (6)
O(8I)—Ni(3)—N(1H)	169.0 (6)	O(8I)—Ni(3)—N(1I)	79.9 (6)
N(1G)—Ni(3)—N(1H)	95.8 (6)	N(1G)—Ni(3)—N(1I)	95.9 (7)
N(1H)—Ni(3)—N(1I)	104.8 (7)	O(8J)—Ni(4)—O(8K)	92.6 (5)
O(8J)—Ni(4)—O(8L)	89.8 (5)	O(8J)—Ni(4)—N(1J)	80.3 (5)
O(8J)—Ni(4)—N(1K)	169.1 (6)	O(8J)—Ni(4)—N(1L)	91.5 (6)
O(8K)—Ni(4)—O(8L)	87.1 (5)	O(8K)—Ni(4)—N(1J)	91.9 (6)
O(8K)—Ni(4)—N(1K)	79.4 (6)	O(8K)—Ni(4)—N(1L)	165.7 (6)
O(8L)—Ni(4)—N(1J)	170.0 (6)	O(8L)—Ni(4)—N(1K)	97.1 (6)
O(8L)—Ni(4)—N(1L)	79.2 (6)	N(1J)—Ni(4)—N(1K)	92.5 (6)
N(1J)—Ni(4)—N(1L)	102.2 (6)	N(1K)—Ni(4)—N(1L)	98.0 (7)
Ni(1)—O(8A)—O(8D)	120.4 (7)	Ni(1)—O(8A)—C(8A)	112.4 (11)
O(8D)—O(8A)—C(8A)	115.8 (11)	Ni(1)—O(8B)—O(8E)	114.3 (6)
Ni(1)—O(8B)—C(8B)	111.2 (11)	O(8E)—O(8B)—C(8B)	123.1 (11)
Ni(1)—O(8C)—O(8F)	123.7 (7)	Ni(1)—O(8C)—C(8C)	104.7 (12)
O(8F)—O(8C)—C(8C)	125.9 (12)	Ni(2)—O(8D)—O(8A)	120.0 (7)
Ni(2)—O(8D)—C(8D)	112.8 (12)	O(8A)—O(8D)—C(8D)	124.5 (12)
Ni(2)—O(8E)—O(8B)	121.9 (7)	Ni(2)—O(8E)—C(8E)	114.8 (14)
O(8B)—O(8E)—C(8E)	116.3 (14)	Ni(2)—O(8F)—O(8C)	119.0 (6)
Ni(2)—O(8F)—C(8F)	110.5 (11)	O(8C)—O(8F)—C(8F)	116.1 (11)
Ni(3)—O(8G)—O(8I)	116.9 (7)	Ni(3)—O(8G)—C(8G)	115.4 (12)
O(8I)—O(8G)—C(8G)	122.4 (12)	Ni(3)—O(8H)—O(8K)	119.9 (6)
Ni(3)—O(8H)—C(8H)	112.8 (11)	O(8K)—O(8H)—C(8H)	115.5 (11)
Ni(3)—O(8I)—O(8L)	120.8 (6)	Ni(3)—O(8I)—C(8I)	117.8 (11)
O(8L)—O(8I)—C(8I)	116.2 (11)	Ni(4)—O(8J)—O(8K)	122.5 (6)
Ni(4)—O(8J)—C(8J)	111.8 (10)	O(8K)—O(8J)—C(8J)	115.5 (10)
Ni(4)—O(8K)—O(8H)	118.7 (6)	Ni(4)—O(8K)—C(8K)	116.0 (11)
O(8H)—O(8K)—C(8K)	124.2 (12)	Ni(4)—O(8L)—O(8J)	119.5 (7)
Ni(4)—O(8L)—C(8L)	112.9 (12)	O(8J)—O(8L)—C(8L)	110.8 (12)

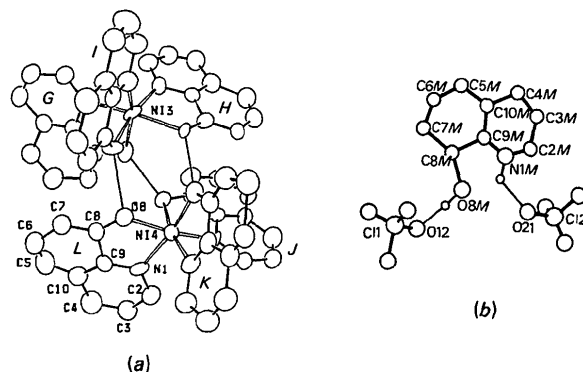


Fig. 1. ORTEP drawings (Johnson, 1976). (a) $[\text{Ni}_2\{\text{H}(\text{C}_9\text{H}_6\text{NO})_2\}_3]^+$ cation containing Ni(3) and Ni(4) atoms; (b) 8-hydroxyquinolinium cation linked to two perchlorate anions by hydrogen bonds.

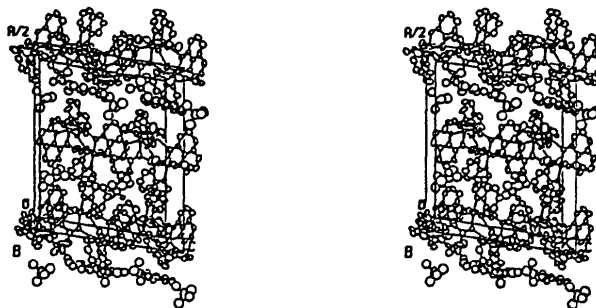


Fig. 2. Stereodrawing of the crystal structure viewed along the *b* axis.

The overall crystal structure can be described in terms of alternating cationic and anionic layers parallel to the (100) plane (Fig. 2). Furthermore, two kinds of dinuclear cationic layers are distinguished, one of which contains atoms Ni(1) and Ni(2) and the other Ni(3) and Ni(4). These are related by a pseudo center of symmetry at (0.145, 0.250, 0.116). Thus the interlayer spaces formed are alternately occupied by two anionic species. In the wide one, an uncoordinated 8-hydroxyquinolinium cation, $[\text{C}_9\text{H}_8\text{NO}]^+$, joins two perchlorate anions through considerably strong hydrogen bonds with distances $\text{N}(1M)-\text{H}\cdots\text{O}(21)$ 2.56 (4) Å and $\text{O}(8M)-\text{H}\cdots\text{O}(12)$ 2.59 (3) Å, as shown in Fig. 1(b). Such a hydrogen-bonding scheme was based on the chemical consideration that perchloric acid is a very strong acid, that is a powerful hydrogen donor. Although the resulting 8-hydroxyquinolinium cations are less common in comparison with neutral and anionic species of 8-quinolinol, their occurrence has been realized in $[\text{C}_9\text{H}_8\text{NO}][\text{Mo}(\text{C}_9\text{H}_6\text{NO})\text{Cl}_3\text{O}]$ (Yamauchi, Huneke & Enemark, 1979) and in $(\text{C}_9\text{H}_8\text{NO})_2[\text{WO}(\text{O})_2\text{F}_4]\cdot 3\text{H}_2\text{O}$ (Ružić-Toroš, Kojić-Prodić, Gabela & Šljukić, 1977). Consequently, the repeat unit contains one 8-hydroxyquinolinium cation and two perchlorate anions and therefore has a net negative charge of one. In the narrow interlayer space, isolated ClO_4^- ions are distributed over two possible sites each with statistically equal population. There are

some close proximities of the perchlorate O atoms to the surrounding 8-quinolinol H atoms, in addition to electrostatic interactions between a cationic layer and its adjacent, anionic layers. For example, estimated distances of $\text{H}(35)\cdots\text{O}(43)$, $\text{H}(83)\cdots\text{O}(42)$ and $\text{H}(25)\cdots\text{O}(31)$ are 2.38, 2.56 and 2.61 Å, respectively.

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Neubestimmung der Struktur von Tribrombis(pyridin-*N*-oxid)thallium(III)

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Abstract. $[\text{TlBr}_3(\text{C}_5\text{H}_5\text{NO})_2]$, $M_r = 634.30$, monoclinic, $C2/c$, $a = 12.998$ (3), $b = 7.105$ (2), $c = 17.036$ (3) Å, $\beta = 103.45$ (3)°, $V = 1530.1$ Å³, $Z = 4$, $D_x = 2.753$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 184.23$ cm⁻¹, $F(000) = 1144$, $T = 213$ K, $R = 0.034$ for 1081 unique observed reflections. The structure consists of neutral monomeric complexes, in which the Tl atom shows a fivefold coordination in the form of a

distorted trigonal bipyramid. The Tl—O distance [2.377 (3) Å] is larger than the sum of the covalent radii (2.21 Å) in accordance with the donor character of the pyridine *N*-oxide ligand.

Einleitung. Wir berichteten kürzlich über die Synthese und Kristallstruktur von $[\text{TlI}_3(3\text{-CH}_3\text{C}_5\text{H}_4\text{NO})_2]$ (Bermejo, Castineiras, Gayoso, Hiller, Englert & Strähle,