As expected, the molecule has a symmetrical *cis* coordination analogous to that of Ni(debd)$(N_3)_2$ (Paap *et al.*, 1985). The Cd—Cl and the Cd—N bonds are comparable with literature values (Cannas, Marongiu & Saba, 1980; Kleywegt, Wiesmeijer, Van Driel, Driessen, Reedijk & Noordik, 1985). The pyrazole rings are planar to within 0·02 Å. Comparison of the ligand geometry of the title compound with that of Ni(debd)$(N_3)_2$ shows no significant differences between the two. However, the metal coordination spheres differ significantly. The Cd octahedron is more distorted than the Ni octahedron. This can be seen from comparison of the N(12)—*M*—N(12′) angle, which is 151° in the Cd compound and 171° in the Ni compound. The steric constraints of the ligand obviously make it more suitable to accommodate the smaller Ni^{2+} ion (coordination distances ~2·15 Å) than the larger Cd^{2+} ion (coordination distances ~2·50 Å). On the other hand, the more distorted octahedron is able to accommodate the larger Cl^- anions, which do not bind to the smaller ion in combination with the debd ligand.

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Structure of Tris-μ-[bis(8-quinolinolato)hydrogen(I)-*N*,*O*]-dinickel(II) Thiocyanate Monohydrate

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Abstract. $[Ni_2\{H(C_9H_6NO)_2\}_3](SCN).H_2O$, $M_r = 1061{\cdot}4$, monoclinic, $C2/c$, $a = 21{\cdot}269\,(3)$, $b = 15{\cdot}004\,(1)$, $c = 15{\cdot}481\,(2)$ Å, $\beta = 101{\cdot}732\,(9)°$, $V = 4837{\cdot}2\,(9)$ Å^3, $Z = 4$, $D_m = 1{\cdot}47\,(1)$, $D_x = 1{\cdot}46$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 0{\cdot}88$ mm^{-1}, $F(000) = 2192$, $T = 298$ K, $R = 0{\cdot}045$ for 4747 unique observed reflections. The crystal contains dinuclear cations made up of two Ni complexes joined face to face by three strong O—H···O hydrogen bonds of distances 2·402 (2) and 2·448 (2) Å. The counter SCN^- is orientationally disordered, its N atom lying on a twofold (2) axis and the remaining C and S atoms each being located on the two sites related by 2 symmetry. A water molecule is hydrogen-bonded to an SCN^- ion to form an O(*W*)···N—C—S linear array. These dinuclear cations and the disordered, hydrated thiocyanate anions are arranged in the NaCl-type structure.

Introduction. In previous papers the crystal structures of the novel dimeric nickel 8-quinolinol complexes with triiodide and perchlorate anions were reported (Kiriyama, Fukuda, Yamagata & Sekido, 1985; Kiriyama, Yamagata, Yonetani & Sekido, 1986). Both structures contain the unique dinuclear cation in which two nickel complexes with three bidentate 8-quinolinol ligands in facial conformation are joined face to face by three very strong O—H···O hydrogen bonds. These facts suggest that the hydrogen-bonded dinuclear cations are essential for the nickel 8-quinolinol complexes in the presence of anions and excess 8-quinolinol in organic solvents. The present structural study was extended to the corresponding thiocyanate complex. Better crystals were obtained and a more accurate structure determination could be carried out.

Experimental. Yellow nickel(II) chloride (10 mmol in 30 ml of ethanol) and 8-quinolinol (60 mmol in 30 ml of ethanol) were added to a sodium thiocyanate solution (20 mmol in 200 ml ethanol) dropwise with stirring.

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Greenish light-blue crystals were obtained from the filtrate. Density measured by flotation (kerosine–methyl iodide–ethyl iodide mixture); crystal $0{\cdot}3 \times 0{\cdot}3 \times 0{\cdot}3$ mm; Rigaku AFC-5 diffractometer, graphite-monochromated Mo $K\alpha$ radiation, 50 kV–150mA; unit-cell parameters determined from least squares of setting angles of 50 reflections in 2θ range 20–30°; systematic absences: hkl for $h + k$ odd, $h0l$ for l odd, space group $C2/c$ or Cc. Three kinds of reflection pairs within $2\theta_{\max} = 40°$ measured, agreement factors between $|F(\pm hkl)|$ and $|F(\pm h{-}kl)|$, $|F(\pm hkl)|$ and $|F(\mp hk{-}l)|$, and $|F(\pm h{-}kl)|$ and $|F(\mp hk{-}l)|$ 0·016, 0·013 and 0·013, respectively, leading to $C2/c$. Additional reflections (h $-27{\rightarrow}27$, k $0{\rightarrow}19$, l $-20{\rightarrow}20$) within $2\theta_{\max} = 55°$ measured, 13 354 total reflections, 5560 unique reflections for $C2/c$, $R_{\rm int} = 0{\cdot}024$, 4757 with $|F_o| > 3\sigma(F_o)$; standard reflections 280, 002 and 600, intensity variation <2·8%; corrections for Lorentz–polarization and absorption (North, Phillips & Mathews, 1968), absorption correction factors on F: 1·001–1·081. Structure solved by direct methods (*MULTAN*78, Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) and refined by full-matrix least squares on F with anisotropic thermal parameters for non-H atoms; O atom of water, O(*W*), and all H atoms except for H atoms of water found in difference Fourier maps, H atoms of 8-quinolinol included as fixed contributions ($B_{\rm iso} = 5{\cdot}0$ Å^2), H(*A*) and H(*B*) of hydroxy groups and O(*W*) atom refined isotropically; $\sum w(|F_o| - |F_c|)^2$ minimized for 341 parameters. Final $R = 0{\cdot}045$, $wR = 0{\cdot}036$, $S = 2{\cdot}04$, $w = 1/\sigma^2(F_o)$; $(\Delta/\sigma)_{\max} = 0{\cdot}06$; ten reflections with low angles and high intensities removed in final refinement because of possible extinction effects. Highest residual in final difference Fourier synthesis 0·78 e Å^{-3}. The presence of water molecules of crystallization was judged not only by the X-ray method but also by chemical, thermal and spectroscopic analyses, as described later. Complex neutral scattering factors and anomalous-dispersion terms from *International Tables for X-ray Crystallography* (1974); computations using 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.

Discussion. Final positional and isotropic thermal parameters are listed in Table 1* and selected interatomic distances and angles in Table 2.

Table 1. *Final atomic coordinates and isotropic thermal parameters* (Å^2)

$$B_{\rm eq} = \tfrac{4}{3}\textstyle\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$
Ni	0·46180 (1)	0·23875 (2)	0·09648 (2)	2·59 (1)
O(8*A*)	0·46022 (6)	0·13479 (9)	0·18271 (9)	3·03 (2)
O(8*B*)	0·42017 (7)	0·31835 (9)	0·17712 (9)	2·94 (2)
O(8*C*)	0·55342 (6)	0·28061 (9)	0·16582 (8)	2·90 (2)
N(1*A*)	0·37432 (8)	0·17923 (11)	0·04230 (11)	3·16 (3)
C(2*A*)	0·3346 (1)	0·1952 (2)	−0·0332 (2)	4·27 (4)
C(3*A*)	0·2725 (1)	0·1577 (2)	−0·0541 (2)	5·66 (5)
C(4*A*)	0·2514 (1)	0·1077 (2)	0·0062 (2)	5·67 (6)
C(5*A*)	0·2745 (1)	0·0390 (2)	0·1570 (2)	5·60 (7)
C(6*A*)	0·3185 (1)	0·0223 (2)	0·2329 (2)	5·21 (5)
C(7*A*)	0·3821 (1)	0·0540 (2)	0·2446 (2)	3·99 (4)
C(8*A*)	0·4003 (1)	0·1045 (1)	0·1803 (1)	3·03 (3)
C(9*A*)	0·3544 (1)	0·1256 (1)	0·1025 (1)	3·14 (4)
C(10*A*)	0·2915 (1)	0·0899 (2)	0·0889 (2)	4·33 (5)
N(1*B*)	0·44733 (7)	0·35082 (11)	0·01984 (11)	2·70 (2)
C(2*B*)	0·4603 (1)	0·3638 (1)	−0·0592 (1)	3·40 (3)
C(3*B*)	0·4461 (1)	0·4451 (2)	−0·1052 (2)	4·07 (4)
C(4*B*)	0·4191 (1)	0·5123 (2)	−0·0671 (2)	3·89 (4)
C(5*B*)	0·3766 (1)	0·5675 (1)	0·0624 (2)	4·30 (5)
C(6*B*)	0·3640 (1)	0·5498 (2)	0·1434 (2)	4·61 (5)
C(7*B*)	0·3779 (1)	0·4658 (2)	0·1844 (1)	3·74 (4)
C(8*B*)	0·4059 (1)	0·3998 (1)	0·1438 (1)	2·79 (3)
C(9*B*)	0·4195 (1)	0·4179 (1)	0·0585 (1)	2·67 (3)
C(10*B*)	0·4046 (1)	0·5015 (1)	0·0173 (2)	3·34 (4)
N(1*C*)	0·51993 (8)	0·17429 (11)	0·02669 (11)	3·02 (3)
C(2*C*)	0·5019 (1)	0·1226 (2)	−0·0431 (2)	4·00 (4)
C(3*C*)	0·5461 (1)	0·0845 (2)	−0·0882 (2)	5·01 (4)
C(4*C*)	0·6099 (1)	0·0995 (2)	−0·0595 (2)	4·77 (5)
C(5*C*)	0·6962 (1)	0·1715 (2)	0·0512 (2)	5·34 (6)
C(6*C*)	0·7127 (1)	0·2238 (2)	0·1233 (2)	5·41 (6)
C(7*C*)	0·6656 (1)	0·2624 (2)	0·1648 (2)	3·98 (4)
C(8*C*)	0·6018 (1)	0·2461 (1)	0·1316 (1)	2·84 (3)
C(9*C*)	0·5839 (1)	0·1907 (1)	0·0565 (1)	2·88 (3)
C(10*C*)	0·6314 (1)	0·1533 (2)	0·0154 (2)	3·80 (4)
S*	0·3793 (2)	0·2171 (3)	0·7596 (2)	6·77 (3)
N(11)	0·5000	0·2696 (4)	0·7500	9·11 (9)
C(22)*	0·4503 (3)	0·2460 (4)	0·7492 (4)	5·76 (8)
O(*W*)*	0·3736 (7)	0·2157 (11)	0·7579 (9)	12·5 (4)†
H(*A*)	0·500	0·132 (2)	0·250	7·0 (10)†
H(*B*)	0·433 (1)	0·299 (2)	0·264 (2)	7·0 (7)†

* Occupancy factors are 0·5.
† Isotropic temperature factor.

The structure analysis showed the stoichiometry of this complex to be $[Ni_2\{H(C_9H_6NO)_2\}_3](SCN).H_2O$, the asymmetric unit being one half of it. The complex cation is shown in Fig. 1(*a*) together with the atom-numbering scheme. The coordination of each Ni^{II} atom is a distorted octahedron, where three O atoms and three N atoms of three bidentate 8-quinolinol ligands occupy the six coordination sites in the facial conformation. Two such facial isomers related by the crystallographic twofold axis form a dinuclear cation joined face to face by three strong O—H···O hydrogen bonds. Similar dinuclear cations have already been found in the triiodide and perchlorate analogues, in both of which the cations have no crystallographic symmetry. All of these, however, have pseudo 32 symmetry, and no distinct structure differences are found among them. The rotation angles of the two oxygen faces around the pseudo threefold axis are *ca* 25° for the thiocyanate and triiodide complexes and 30° for the perchlorate complex. One of the two independent bridging H atoms, H(*A*), appears to sit on the twofold axis to form a symmetric hydrogen bond, whereas H(*B*) is close to O(8*C*) rather than O(8*B*$^{\rm i}$), forming an asymmetric hydrogen bond.

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and calculations of least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42770 (36 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

There are significant differences in the Ni—N and Ni—O distances among the three 8-quinolinol ligands. The Ni—O(8*C*) distance is longer by about 0·06 Å than the other Ni—O distances, while the Ni—N(1*A*) distance is longer by about 0·04 Å than the others. The Ni—O distances are relatively longer than the Ni—N distances. In order to look more closely at the coordination geometry, the Ni^{II}—N(or O) distances in complexes with octahedral coordination of three N and three O atoms were taken from the files of the Cambridge Crystallographic Data Centre (Allen, Bellard, Brice, Cartwright, Doubleday, Higgs, Hummelink, Hummelink-Peters, Kennard, Motherwell, Rodgers & Watson, 1979). The Ni—N and Ni—O distances averaged for 18 independent octahedra are 2·09 (4) and 2·09 (4) Å, respectively. Slight, but significant deviations are found between Ni—N [$-NH_2$, 2·10 (2) Å] and Ni—N [$\gtrdot$N, 2·07 (6) Å] and between Ni—O [$-O^-$, 2·06 (3) Å] and Ni—O [O(water), 2·10 (6), =O, 2·09 (2) Å] distances. These observations seem to be consistent with the present results, *i.e.* the Ni—O(8*C*) distance may reflect the close approach of the H(*B*) atom to O(8*C*), and the shortening of the Ni—N bonds relative to the Ni—O bonds may be associated with the electron-rich N atoms in the aromatic ring.

The C and N atoms in each 8-quinolinol ligand lie close to a plane with the maximum deviation

Table 2. *Interatomic distances* (Å) *and angles* (°)

(1) Metal coordinations

Ni—N(1*A*)	2·080 (2)	Ni—O(8*A*)	2·058 (1)
Ni—N(1*B*)	2·045 (2)	Ni—O(8*B*)	2·054 (1)
Ni—N(1*C*)	2·043 (2)	Ni—O(8*C*)	2·120 (1)
N(1*A*)—Ni—O(8*A*)	78·75 (6)	N(1*A*)—Ni—N(1*B*)	95·87 (7)
N(1*A*)—Ni—O(8*B*)	91·94 (6)	N(1*A*)—Ni—N(1*C*)	99·87 (7)
N(1*A*)—Ni—O(8*C*)	170·42 (6)	O(8*A*)—Ni—N(1*B*)	168·33 (6)
O(8*A*)—Ni—O(8*B*)	88·89 (5)	O(8*A*)—Ni—N(1*C*)	94·34 (6)
O(8*A*)—Ni—O(8*C*)	91·76 (5)	N(1*B*)—Ni—O(8*B*)	80·90 (6)
N(1*B*)—Ni—N(1*C*)	96·79 (7)	N(1*B*)—Ni—O(8*C*)	93·70 (6)
O(8*B*)—Ni—N(1*C*)	168·15 (6)	O(8*B*)—Ni—O(8*C*)	89·17 (5)
N(1*C*)—Ni—O(8*C*)	79·35 (6)		

(2) 8-Quinolinol ligands

	A	*B*	*C*
N(1)—C(2)	1·317 (3)	1·323 (3)	1·322 (3)
C(2)—C(3)	1·413 (4)	1·412 (3)	1·402 (4)
C(3)—C(4)	1·342 (4)	1·353 (3)	1·357 (4)
C(4)—C(10)	1·413 (4)	1·411 (3)	1·410 (4)
C(5)—C(10)	1·408 (4)	1·413 (3)	1·405 (4)
C(5)—C(6)	1·369 (4)	1·360 (4)	1·351 (4)
C(6)—C(7)	1·410 (4)	1·416 (4)	1·418 (4)
C(7)—C(8)	1·370 (3)	1·373 (3)	1·373 (3)
C(8)—C(9)	1·423 (3)	1·434 (3)	1·418 (3)
C(9)—C(10)	1·416 (3)	1·414 (3)	1·414 (3)
C(9)—N(1)	1·363 (3)	1·365 (3)	1·367 (3)
C(8)—O(8)	1·346 (3)	1·338 (2)	1·352 (2)
C(2)—N(1)—C(9)	118·9 (2)	119·2 (2)	119·0 (2)
N(1)—C(2)—C(3)	122·1 (2)	122·0 (2)	122·3 (2)
C(2)—C(3)—C(4)	119·5 (3)	119·3 (2)	119·7 (3)
C(3)—C(4)—C(10)	120·6 (3)	120·7 (2)	120·0 (3)
C(6)—C(5)—C(10)	120·4 (3)	120·1 (2)	120·6 (3)
C(5)—C(6)—C(7)	121·3 (3)	121·7 (2)	121·5 (3)
C(6)—C(7)—C(8)	120·0 (2)	120·5 (2)	119·6 (2)
C(7)—C(8)—C(9)	119·4 (2)	118·3 (2)	119·4 (2)
C(8)—C(9)—C(10)	120·5 (2)	121·0 (2)	120·4 (2)
C(10)—C(9)—N(1)	122·5 (2)	122·2 (2)	122·0 (2)
C(9)—C(10)—C(4)	116·2 (2)	116·6 (2)	117·1 (2)
C(9)—C(10)—C(5)	118·3 (2)	118·5 (2)	118·5 (2)
C(4)—C(10)—C(5)	125·5 (3)	124·9 (2)	124·4 (2)
C(8)—C(9)—N(1)	117·0 (2)	116·8 (2)	117·7 (2)
C(7)—C(8)—O(8)	125·0 (2)	124·6 (2)	124·0 (2)
C(9)—C(8)—O(8)	115·6 (2)	117·1 (2)	116·6 (2)

(3) Hydrogen bonds

O(8*A*)—O(8A^{i})	2·402 (2)	O(8*C*)—O(8B^{i})	2·448 (2)
O(8*A*)—H(*A*)	1·20 (1)	O(8*C*)—H(*B*)	1·10 (3)
O(8B^{i})—H(*B*)	1·35 (3)		
O(8*A*)—H(*A*)—O(8A^{i})	177 (1)	O(8*C*)—H(*B*)—O(8B^{i})	176 (2)
C(8*A*)—O(8*A*)—Ni	112·2 (1)	C(8*A*)—O(8*A*)—O(8A^{i})	121·4 (1)
Ni—O(8*A*)—O(8A^{i})	117·5 (1)	C(8*B*)—O(8*B*)—Ni	112·9 (1)
C(8*B*)—O(8*B*)—O(8C^{i})	125·7 (1)	Ni—O(8*B*)—O(8C^{i})	115·4 (1)
C(8*C*)—O(8*C*)—Ni	112·5 (1)	C(8*C*)—O(8*C*)—O(8B^{i})	116·0 (1)
Ni—O(8*C*)—O(8B^{i})	125·0 (1)		

(4) SCN^- ions

S—C	1·610 (8)	C—N	1·112 (7)
N—O(*W*)	2·83 (2)		
S—C—N	173·1 (6)		

Symmetry code: (i) $-x, y, \frac{1}{2}-z$.

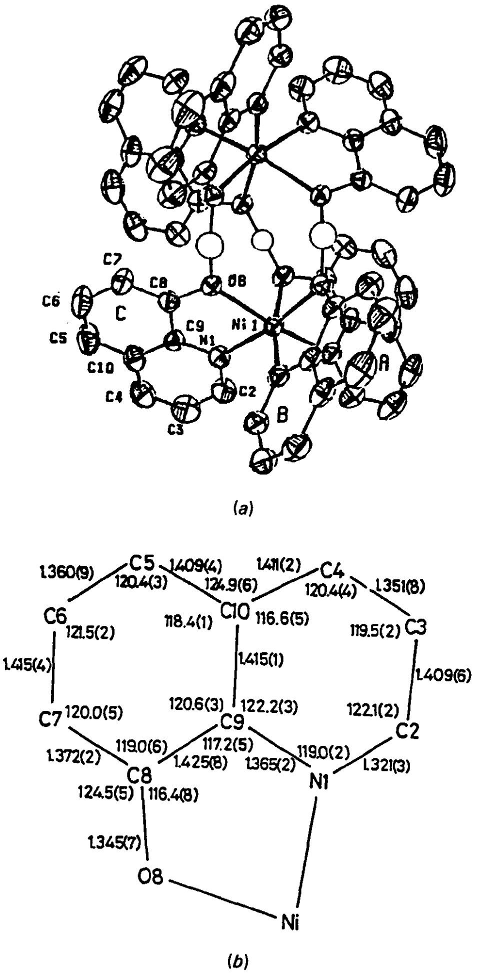

Fig. 1. (*a*) *ORTEP* drawing (Johnson, 1976) of the $[Ni_2\{H(C_9H_6NO)_2\}_3]^+$ cation with atom-numbering scheme. Thermal ellipsoids are shown at the 50% probability level; (*b*) mean interatomic distances (Å) and angles (°) for the 8-quinolinol ligands.

0·056 (3) Å while the O atoms deviate slightly from these planes [0·179 (3) Å for O(8*A*), 0·036 (2) Å for O(8*B*) and 0·046 (2) Å for O(8*C*)]. The corresponding bond lengths and angles in the three ligands are in close agreement with each other (Table 2). The mean distances and angles are illustrated in Fig. 1(*b*). These values, except for those for C—O, are consistent with those averaged for five 8-quinolinolato ligands found in the literature whose structures have been determined with high precision (Scheidt, 1973; Hanson & Hughes, 1981; Giacomelli, Floriani, Duarte, Chiesi-Villa & Guastini, 1982). The C—O distances [1·338 (2)–1·352 (2) Å] are somewhat longer than the mean values of 1·331 (6) Å in the 8-quinolinolate ions, possibly owing to the formation of very short O—H···O hydrogen bonds. These results suggest that the exocyclic C—O bonds have little effect on quinoline-ring bonds, therefore the observed distances may be typical for the quinoline ring system of 8-quinolinol.

The overall crystal structure is quite similar to that of the triiodide complex in that the dinuclear cations and $\mathrm{SCN^-}$ anions (instead of $\mathrm{I_3^-}$ ions) are in the alternate arrangement analogous to the NaCl structure, as shown in Fig. 2 (Kiriyama *et al.*, 1985). In this crystal, however, the nearly linear $\mathrm{SCN^-}$ counteranion is disordered, possibly owing to its shorter length 2·72 Å compared with the I(1)—I(2)—I(3) distance 5·82 Å. The C and S atoms each lie on two sites related by the twofold axis with equal population, centered at the N atom lying on this symmetry axis. The water molecule is hydrogen-bonded to an adjacent $\mathrm{SCN^-}$ ion and consequently the linear O(*W*)···$\mathrm{NCS^-}$ group is also orientationally disordered. The O(*W*)···S distance 5·32 Å is comparable to the I(1)···I(3) distance in the triiodide analogue. The structure is mainly achieved by electrostatic and van der Waals interactions. The two kinds of intermolecular S···H distance [S···H(C2*A*), 2·66 Å and S···H(C6*C*), 2·77 Å] are considerably shorter than the sum of the van der Waals radii 3·0 Å (Bondi, 1964), suggesting weak C—H···S hydrogen bonds. Such intermolecular C—H···S interactions are rarely observed in crystals (Taylor & Kennard, 1982).

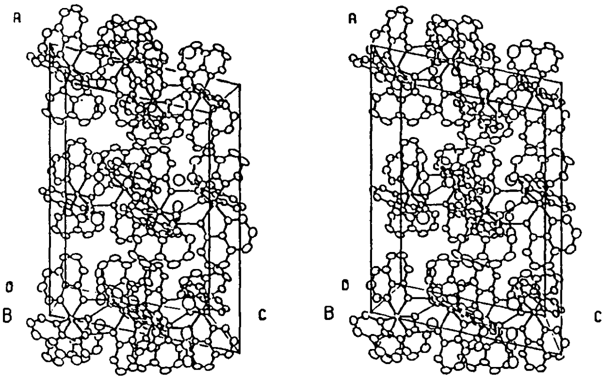

Fig. 2. Stereodrawing of the crystal structure viewed along the *b* axis. Only one orientation of the disordered, hydrated $\mathrm{SCN^-}$···O(*W*) ion is shown for simplicity.

The present X-ray analysis showed that the crystal is a monohydrate. Other evidence is as follows: (1) The measured density agrees well with that calculated for a monohydrate rather than that for an anhydrate. (2) Chemical analyses: found: C 62·21, H 3·99, N 9·25%; calc. for the anhydrate: C 63·31, H 3·77, N 9·40%; calc. for the monohydrate: C 62·24, H 3·89, N 9·24%. (3) IR spectra: antisymmetric stretching band 3650 and 3300 cm^{-1}, the former assignable to free O—H groups and the latter to hydrogen-bonded O—H groups of water molecules; the broad band at 1620 cm^{-1} accompanied by a quite broad shoulder centering at about 1680 cm^{-1}; the absorption at 1620 cm^{-1} assigned to the stretching mode of the very strong O—H···O hydrogen bonds, because it commonly occurs in all the three complexes concerned; the broad shoulder superimposed near 1680 cm^{-1} attributable to the bending mode of water molecules. (4) Thermal analyses: TG and DTA, an endothermic anomaly is observed between 308 and 428 K, the attendant weight loss corresponds to the gradual liberation of one water molecule per chemical formula.

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