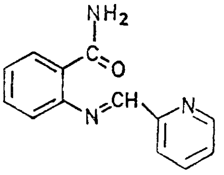
Crystal Structure and Physicochemical properties of a Mixed-chelated Nickel Complex: Aquo-{*o*-[(2-pyridylmethylene)amino]benzamide}-[2-(2-pyridyl)-1,2,3,4-tetrahydroquinazolin-4-one]nickel(II) Dinitrate Tetrahydrate

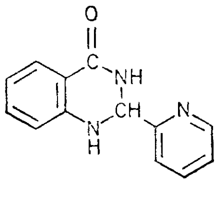
By **Anna Bonamartini Corradi, Clotilde Grasselli Palmieri, Mario Nardelli,*** and **Corrado Pelizzi**, Istituto di Chimica Generale ed Inorganica, Centro di Studio per la Strutturistica Diffrattometrica del C.N.R., Parma, Italy

The title compound has been prepared and its spectroscopic and magnetic properties and *X*-ray structure have been studied. The structure was solved from diffractometer data by Patterson and Fourier methods and refined by least-squares techniques to R 6·3% for 6530 independent reflexions. Crystals are triclinic, space group $P\bar{1}$, with unit-cell dimensions: a = 15·49(1), b = 13·00(1), c = 8·99(1) Å, α = 95·3(1), β = 105·3(1), γ = 110·8(1)°, Z = 2. Co-ordination around Ni is octahedral and involves two different organic ligands and a water molecule. The *o*-aminobenzamide ligand is terdentate [Ni–O(1) 2·028, Ni–N 2·082, 2·067 Å] and the quinazolinone ligand is bidentate (Ni–N 2·164, 2·068 Å). Packing is determined by a hydrogen bond system and by van der Waals contacts.

THE terdentate ligand *o*-[(2-pyridylmethylene)amino]-benzamide (I) has been prepared by condensing *o*-aminobenzamide with pyridine-2-carbaldehyde. When this compound is dissolved in methanol solution in presence of nickel(II) nitrate, it partly undergoes a cyclisation reaction to give (II). A metal complex (III) containing the two different organic ligands, the Schiff's base (I) and the cyclic derivative (II), is formed, as deduced from an *X*-ray structural analysis which we now report.



(I)



(II)

EXPERIMENTAL

Preparation of (I).—Equimolar quantities of *o*-aminobenzamide and pyridine-2-carbaldehyde, in benzene were heated under reflux for 2 h. The crude product, obtained by evaporating the solution almost to dryness, was recrystallized from hot acetone, m.p. 155 °C (Found: C, 69·35; H, 5·1; N, 18·9. Calc. for $C_{13}H_{11}N_3O$: C, 69·3; H, 5·35; N, 18·65%).

Preparation of Ni^{II} *Complex*.—(I) dissolved in methanol, was slowly added to nickel nitrate hexahydrate (molar ratio 2 : 1) in methanol. The solution was heated under reflux for 30 min, allowed to evaporate at room temperature, for 2 days, when brown prismatic crystals had been deposited. [Found: C, 43·2; H, 4·45; N, 15·35; Ni, 8·1. $Ni(C_{26}H_{22}N_6O_2)(NO_3)_2(H_2O)_5$ requires C, 43·2; H, 4·45; N, 15·5; Ni, 7·75]. The room-temperature magnetic susceptibility was measured on a Gouy balance. Diamagnetic corrections were calculated from Pascal's constants.[1]

I.r. and electronic spectra were recorded on Perkin-Elmer 457 and 402 spectrophotometers respectively. *X*-Ray intensity data were collected on a Siemens AED single-crystal computer-controlled diffractometer.

Crystal Properties.—The compound gives brown triclinic flattened prisms showing pleochroic effects: when examined with plane-polarized light, looking down [010], the colour changes from brown to pale yellow when the electric vector vibrates perpendicular or parallel to the elongation, [001], respectively. Cell dimensions were determined from rotation and Weissenberg photographs, and refined from diffractometer measurements.

Crystal Data.—$C_{26}H_{23}N_8NiO_{13}$, M = 723, a = 15·49(1), b = 13·00(1), c = 8·99(1) Å, α = 95·3(1), β = 105·3(1), γ = 110·8(1)°, U = 1607 Å^3, D_m = 1·52, Z = 2, D_c = 1·49, $F(000)$ = 712. Space group $P\bar{1}$. Cu-K_α radiation, λ = 1·5418 Å; μ(Cu-K_α) = 15·2 cm^{-1}.

Data Collection.—Intensity data were collected by the θ—2θ scan technique by use of Cu-K_α radiation. The sample was aligned with its [001] axis along the ϕ axis of the diffractometer and all reflexions with $2\theta \leqslant 140°$ were collected. In this way 6530 reflexions were measured, of which only 5650, having $I > 2\sigma(I)$, were used in the analysis. No absorption correction was used, the cross-section of the crystal being 0·12 × 0·07 mm². After the usual data reduction, intensities were put on an absolute scale, first by Wilson's method, then by comparison with the calculated values.

Structure Analysis.—The structure was solved by the heavy-atom technique, starting from the nickel co-ordinates obtained from a three-dimensional Patterson calculation. A three-dimensional Fourier synthesis then gave the co-ordinates of all other non-hydrogen atoms. Least-squares refinement was then commenced, the function minimized being $\Sigma w|\Delta F|^2$. In this way R improved to 8·3%, when a difference-Fourier calculation enabled resolution of all hydrogen-atom positions. Further refinement reduced R to the final value of 6·3%. Final atomic co-ordinates and thermal parameters are given in Tables 1 and 2. Observed and calculated structure factors, are listed in Supplementary Publication No. SUP 20793 (28 pp., 1 microfiche).

---

* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue.

[1] J. Lewis and R. G. Wilkins, ' Modern Co-ordination Chemistry,' Interscience, New York, 1964, p. 403.

TABLE 1

Fractional atomic co-ordinates ($\times 10^4$) and thermal parameters * ($\times 10$ Å^2) for non-hydrogen atoms, with estimated standard deviations in parentheses

	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ni	2048(1)	3232(1)	1801(1)	35(1)	38(1)	29(1)	15(1)	12(1)	7(1)
O(1)	3491(2)	3872(2)	3030(3)	22(1)	40(1)	17(1)	14(1)	8(1)	5(1)
O(2)	5127(2)	6167(2)	1382(3)	22(1)	33(1)	22(1)	9(1)	6(1)	−1(1)
O(3)	640(2)	3348(3)	7176(4)	41(1)	50(2)	51(2)	26(1)	−2(1)	0(1)
O(4)	401(3)	4648(3)	8405(5)	63(2)	74(2)	55(2)	38(2)	2(2)	−14(2)
O(5)	−429(3)	3887(4)	6014(4)	59(2)	108(3)	44(2)	57(2)	0(1)	12(2)
O(6)	4046(4)	10012(4)	6422(7)	94(3)	20(3)	132(4)	7(2)	61(3)	2(3)
O(7)	3207(5)	9142(5)	7746(8)	225(6)	92(3)	105(5)	97(4)	131(5)	62(3)
O(8)	2630(3)	9345(4)	5358(7)	85(3)	91(3)	116(4)	44(2)	20(3)	−40(3)
O(9)	1993(2)	1926(2)	3012(3)	35(1)	35(1)	35(1)	16(1)	17(1)	18(1)
O(10)	570(3)	8711(3)	4817(4)	65(2)	45(2)	57(2)	23(1)	17(2)	3(1)
O(11)	368(2)	417(3)	3267(4)	43(1)	54(2)	55(2)	10(1)	21(1)	16(1)
O(12)	3454(3)	1106(4)	3441(5)	88(3)	84(2)	71(2)	60(2)	27(2)	16(2)
O(13)	4295(4)	481(5)	1260(7)	116(4)	107(4)	117(1)	58(3)	50(3)	22(3)
N(1)	4218(2)	3551(3)	5302(3)	29(1)	40(1)	20(1)	19(1)	7(1)	5(1)
N(2)	1813(2)	4098(2)	3618(3)	26(1)	29(1)	19(1)	15(1)	10(1)	6(1)
N(3)	543(2)	2612(2)	1057(3)	24(1)	30(1)	25(1)	10(1)	8(1)	8(1)
N(4)	2213(2)	4511(2)	396(3)	20(1)	23(1)	19(1)	10(1)	8(1)	3(1)
N(5)	3738(2)	4749(2)	−32(3)	19(1)	24(1)	19(1)	8(1)	8(1)	1(1)
N(6)	2190(2)	2408(2)	−143(3)	26(1)	22(1)	20(1)	11(1)	10(1)	3(1)
N(7)	200(2)	3971(3)	7201(4)	28(1)	43(2)	31(1)	18(1)	6(1)	4(1)
N(8)	3275(4)	9473(4)	6536(7)	94(3)	58(2)	89(3)	44(2)	49(3)	10(2)
C(1)	3720(2)	4062(3)	4494(4)	20(1)	33(2)	21(1)	10(1)	9(1)	7(1)
C(2)	3463(2)	4885(3)	5375(4)	28(1)	28(2)	19(1)	11(1)	10(1)	6(1)
C(3)	4176(3)	5674(3)	6669(4)	29(1)	33(2)	20(1)	8(1)	8(1)	7(1)
C(4)	3992(3)	6515(3)	7432(4)	42(2)	29(2)	24(2)	8(1)	9(1)	3(1)
C(5)	3087(3)	6555(3)	6936(5)	52(2)	33(2)	28(2)	21(2)	13(2)	3(1)
C(6)	2361(3)	5764(3)	5698(4)	39(2)	36(2)	25(2)	21(1)	10(1)	4(1)
C(7)	2541(2)	4916(3)	4909(4)	28(1)	28(1)	17(1)	13(1)	9(1)	5(1)
C(8)	916(2)	3816(3)	3505(4)	26(1)	34(2)	26(1)	15(1)	11(1)	8(1)
C(9)	194(2)	3011(3)	2118(4)	24(1)	33(2)	29(2)	12(1)	12(1)	11(1)
C(10)	−797(3)	2680(4)	1903(5)	25(2)	46(2)	43(2)	14(1)	12(1)	13(2)
C(11)	−1438(3)	1925(4)	550(6)	27(2)	46(2)	50(2)	11(1)	7(2)	18(2)
C(12)	−1079(3)	1527(4)	−526(5)	31(2)	37(2)	40(2)	7(1)	2(1)	10(2)
C(13)	−80(3)	1888(3)	−229(5)	28(2)	32(2)	31(2)	5(1)	5(1)	5(1)
C(14)	2644(2)	5653(3)	1219(4)	28(1)	24(1)	18(1)	13(1)	9(1)	7(1)
C(15)	2036(3)	6134(3)	1793(4)	36(2)	30(2)	29(2)	21(1)	14(1)	9(1)
C(16)	2541(3)	7212(3)	2697(5)	47(2)	34(2)	34(2)	25(2)	16(2)	7(1)
C(17)	3524(3)	7819(3)	3016(5)	50(2)	27(2)	38(2)	18(2)	13(2)	0(1)
C(18)	4079(3)	7352(3)	2415(5)	38(2)	26(1)	32(2)	12(1)	9(1)	2(1)
C(19)	3644(2)	6271(3)	1534(4)	27(1)	25(1)	20(1)	12(1)	8(1)	4(1)
C(20)	4224(2)	5735(3)	948(4)	24(1)	27(1)	17(1)	9(1)	8(1)	6(1)
C(21)	2684(1)	4270(3)	−755(4)	21(1)	24(1)	17(1)	8(1)	8(1)	3(1)
C(22)	2395(2)	3013(3)	−1218(4)	18(1)	26(1)	18(1)	10(1)	6(1)	2(1)
C(23)	2402(3)	2544(3)	−2663(4)	34(2)	32(2)	24(1)	12(1)	13(1)	1(1)
C(24)	2236(3)	1423(3)	−2974(5)	41(2)	32(2)	29(2)	14(1)	15(1)	1(1)
C(25)	2050(3)	807(3)	−1857(6)	46(2)	26(2)	46(2)	16(1)	14(2)	−1(1)
C(26)	2017(3)	1321(3)	−454(5)	43(2)	25(1)	28(2)	14(1)	14(1)	5(1)

* Anisotropic thermal parameters are in the form: $\exp[-0{\cdot}25(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^*\cos\gamma^* + 2B_{13}hla^*c^*\cos\beta^* + 2B_{23}klb^*c^*\cos\alpha^*)]$

Atomic scattering factors were taken from ref. 2 for non-hydrogen atoms and from ref. 3 for hydrogen atoms. All calculations were performed on a CDC 6600 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale (Bologna) using programs written by Immirzi.[4]

RESULTS AND DISCUSSION

I.R. Spectrum.—Table 3 lists the main i.r. absorption bands (4000—250 cm^{-1}) and their relative assignments for (I) and for the Ni^{II} complex (III). The ligand spectrum displays characteristic bands which may be assigned to ν(NH), ν(C⋮C), and ν(C⋮N).

The spectrum of the nickel complex differs from that of the ligand in several features. In the 3000 cm^{-1} region a broad intense and multiple band is present which can be assigned to ν(OH) and ν(NH). The frequencies of the four bands due to pyridine are increased significantly from the values for the free ligand as a consequence of Ni–N co-ordination. The shifts of two amide bands (at 1655 and 1560 cm^{-1}) to lower frequences indicate metal co-ordination through the amide-oxygen atom. The two bands at 1380s and 823m cm^{-1} can be attributed to ν(N–O) and δ(NO$_3$) respectively indicating ionic nitrate groups.

Electronic Spectrum.—In the visible region only two bands (430 and 890 nm) are observed, which can be attributed to $^3T_{1g}(P) \leftarrow {}^3A_{2g}(\nu_3)$ and $^3T_{1g} \leftarrow {}^3A_{2g}(\nu_2)$ transitions, for Ni^{2+} in an octahedral field. The u.v. region shows a band at 230—240 nm attributable to a π–π*

---

[2] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[3] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[4] A. Immirzi, *Ricerca sci.*, 1967, **37**, 743.

transition and an intense band at 330—340 nm which is probably due primarily to an M→L charge transfer and also to an *n*-π* transition.

TABLE 2

Final atomic fractional co-ordinates ($\times 10^3$) and isotropic thermal parameters ($\times 10$ Å^2) for hydrogen atoms, with estimated standard deviations in parentheses

	x/*a*	*y*/*b*	*z*/*c*	*B*
H(1)	244(3)	176(3)	318(5)	49(10)
H(2)	153(3)	148(3)	295(5)	38(9)
H(3)	122(4)	883(4)	506(6)	73(14)
H(4)	23(4)	810(4)	433(6)	77(14)
H(5)	24(4)	76(5)	368(7)	82(16)
H(6)	41(5)	−25(5)	372(8)	108(20)
H(7)	387(4)	105(4)	265(6)	69(14)
H(8)	293(4)	46(5)	329(7)	80(16)
H(9)	477(4)	74(4)	253(6)	69(14)
H(10)	435(3)	98(4)	42(6)	69(13)
H(11)	429(3)	301(3)	484(5)	38(9)
H(12)	439(3)	364(3)	618(5)	40(9)
H(13)	478(3)	562(3)	703(5)	35(9)
H(14)	448(3)	710(3)	822(5)	46(10)
H(15)	301(3)	723(4)	733(5)	49(11)
H(16)	171(3)	581(3)	524(5)	38(9)
H(17)	68(3)	412(3)	403(5)	35(9)
H(18)	−99(3)	296(3)	267(5)	47(10)
H(19)	−215(3)	164(4)	28(6)	56(12)
H(20)	−145(3)	104(4)	−146(6)	57(12)
H(21)	20(3)	156(3)	−91(5)	44(10)
H(22)	139(3)	564(3)	150(5)	33(9)
H(23)	217(3)	756(3)	308(5)	40(10)
H(24)	389(3)	864(3)	362(5)	40(10)
H(25)	474(3)	775(3)	248(5)	40(8)
H(26)	402(3)	450(3)	−26(5)	36(9)
H(27)	261(3)	461(3)	−161(5)	39(9)
H(28)	166(3)	437(3)	−8(5)	32(9)
H(29)	259(3)	296(3)	−332(5)	35(9)
H(30)	234(4)	105(4)	−398(6)	68(14)
H(31)	192(3)	9(3)	−196(5)	46(10)
H(32)	189(3)	87(3)	34(4)	32(9)

H(1) and (2) are on O(9), H(3) and (4) on O(10), H(5) and (6) on O(11), H(7) and (8) on O(12), and H(9) and (10) on O(13).

TABLE 3

Selected i.r. bands with tentative assignments for (I) and for the nickel complex (III)

(I)	(III)	Assignment
	3390br, s	ν(OH)
3340m		ν(NH)
3180m	3180br, s	
1670s	1655vs	Amide (I)
1650s		
1625s	1560m	Amide (II)
1590m	1608m	py (I)
1573m	1580m	py (II)
1500s	1500m	ν(C=N)
1478m	1475m	py (III)
1450m	1445m	py (IV)
	1380vs	ν(NO)
1292m		Amide (III)
	823w	δ(NO_3)

br = Broad, m = medium, sh = shoulder, s = strong, vs = very strong.

Magnetic Data.—The observed magnetic moment (3·08 B.M.) is in agreement with the values generally found for octahedral Ni^{II} complexes.

X-*Ray Structure.*—Co-ordination around nickel is octahedral and involves two different organic ligands and a water molecule (Figure 1). The ligand (I) is terdentate through the pyridine nitrogen, the azomethine nitrogen, and the amide oxygen, to form five- and six-membered chelate rings. The five-membered ring, [Ni, N(2), C(8), C(9), N(3)] is planar and lies almost in the same plane of the pyridine ring [N(3), C(9)—(13)] the dihedral angle they form being 2·4°. In the six-membered ring [Ni, O(1), C(1), C(2), C(7), N(2)] the atoms C(1), C(7), and O(1) are out of the mean plane by —0·36, 0·21, 0·19 Å. Ligand (II) is bidentate and co-ordinates through the pyridine and quinazoline nitrogen atoms forming a five-membered chelate ring [Ni, N(4), C(21), C(22), N(6)] which is nearly planar [displacements from the mean plane: Ni —0·01, N(4) 0·17, N(6) 0·63, C(21) —0·27, C(22) 0·05 Å].

The co-ordination octahedron is not perfectly regular, as indicated by the bond angles at nickel which are in the range 79·2—97·2°. The Ni–O distances are in agreement with those usually found in other Ni-complexes; nevertheless the distance involving the oxygen of the co-ordinated water is slightly longer than the one involving that of the carbonyl. Ni–N Distances involving trigonal nitrogen atoms are practically equal and sensibly shorter than Ni–N(4) which involves the tetrahedral quinazoline nitrogen.

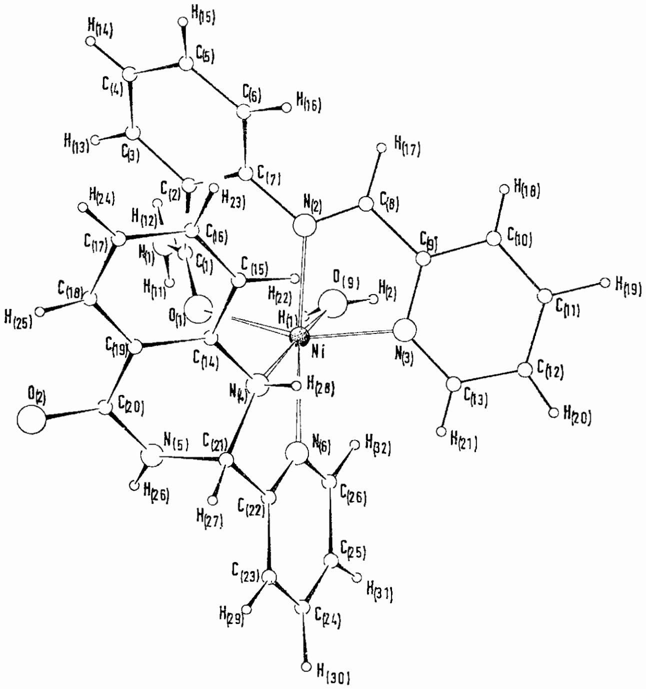


FIGURE 1 Clinographic projection of the cation

The aromatic rings are all planar and bond distances in them are generally in good agreement with those usually found in aromatic systems. In the N(2), C(7)—(9) bridging group, the double bond is localized mainly between N(2)–C(8), even if some conjugation is spread through the C(7)–N(2) and C(8)–C(9) bonds which are slightly shorter than the single bonds [theoretical values: $\sigma(\mathrm{C}sp^2\text{–}\mathrm{N}sp^2)$ 1·44, $\sigma(\mathrm{C}sp^2\text{–}\mathrm{C}sp^2)$ 1·48 Å].

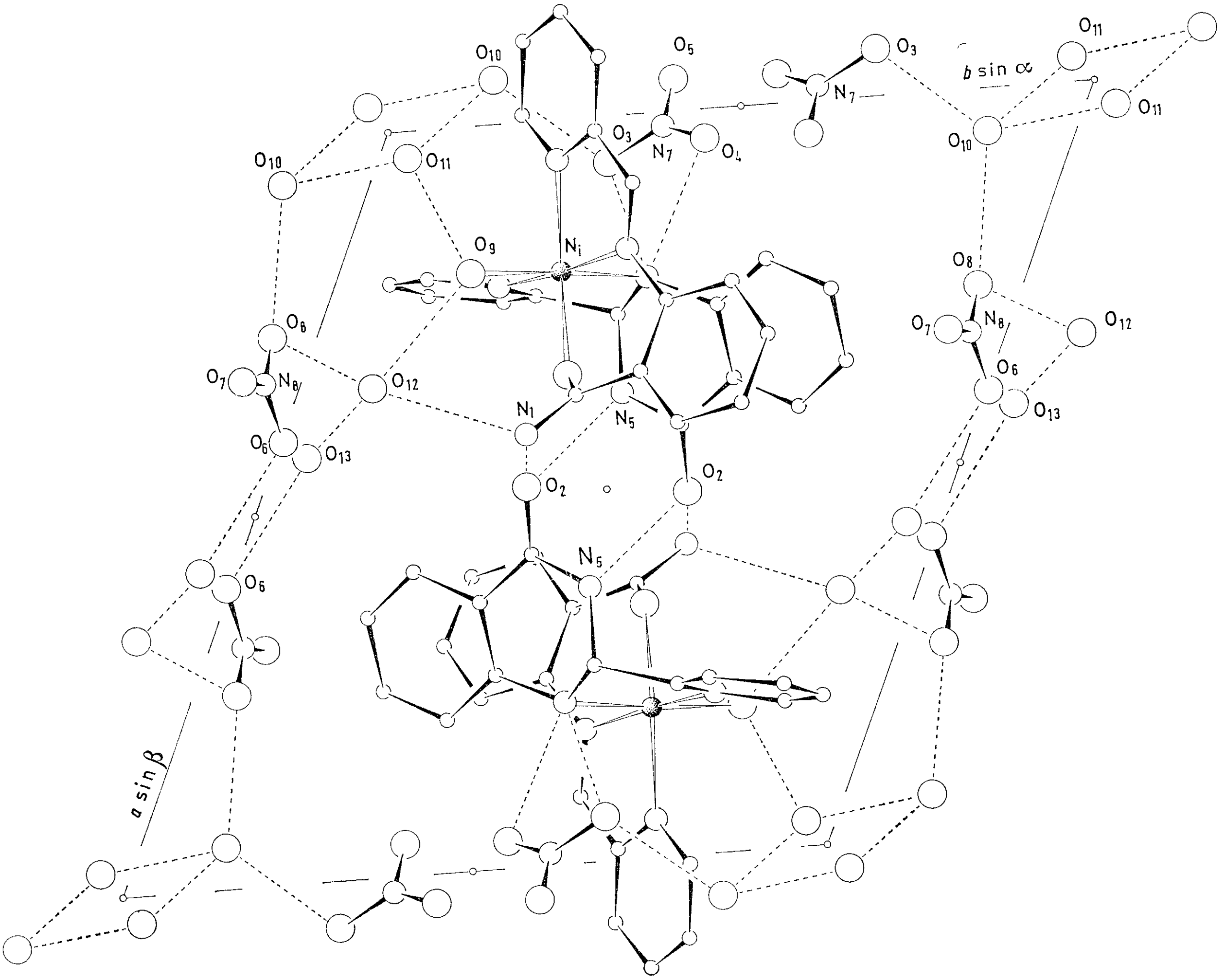


FIGURE 2 Projection of the structure along [001]

The amide group is planar and rotated by 46° with respect to the benzene ring to which it is attached. In the quinazoline ligand, the pyridine ring is rotated by 67·4° with respect to the benzene plane of the quinazoline moiety. There is some π-delocalization along O(2), C(20), N(5). The N(4) atom assumes a tetrahedral configuration as a consequence of co-ordination, the angles around it (including those involving hydrogen) being in the range 101—117°. Bond angles around the oxygen atom of the co-ordinated water molecule [Ni–O(9)–H(1) 116·7, Ni–O(9)–H(2) 127·5, H(1)–O(9)–H(2) 115·3°] indicate some trigonal instead of tetrahedral character, and this is possibly due to some π character in the Ni–O(9) bond. This water molecule forms two hydrogen bonds with the O(11) and O(12) water molecules. These molecules and that corresponding to O(10) and O(13), form the hydrogen bond system shown in Figures 2 and 3. This system also involves the oxygen atoms of the nitrate ions, as well as those of the water molecules. Contacts involving hydrogen are given in Table 4. The two NO_3^- groups are not equivalent, one [N(8), O(6)—(8)] showing some disorder, as indicated by the exceptionally high thermal parameters. Packing is due to hydrogen bonds and to normal van der Waals contacts, the most significant of which are quoted in Table 5.

TABLE 4

Bond distances (Å) and angles (°), with standard deviations in parentheses

(*a*) In the co-ordination polyhedron			
(i) Distances			
Ni–O(1)	2·028(3)	Ni–N(3)	2·067(4)
Ni–O(9)	2·089(4)	Ni–N(4)	2·164(4)
Ni–N(2)	2·082(4)	Ni–N(6)	2·068(4)
(ii) Angles			
O(1)–Ni–O(9)	84·0(8)	O(9)–Ni–N(6)	93·6(3)
O(1)–Ni–N(2)	89·4(2)	N(2)–Ni–N(3)	79·2(3)
O(1)–Ni–N(4)	93·1(3)	N(2)–Ni–N(4)	96·7(3)
O(1)–Ni–N(6)	94·6(3)	N(3)–Ni–N(4)	94·7(3)
O(9)–Ni–N(2)	90·0(3)	N(3)–Ni–N(6)	97·2(3)
O(9)–Ni–N(3)	89·5(3)	N(4)–Ni–N(6)	79·9(2)
(*b*) In the ligand (I)			
(i) Distances			
O(1)–C(1)	1·246(4)	C(7)–N(2)	1·407(4)
N(1)–C(1)	1·312(6)	N(2)–C(8)	1·277(5)
C(1)–C(2)	1·498(6)	C(8)–C(9)	1·447(5)
C(2)–C(3)	1·387(5)	C(9)–C(10)	1·392(6)
C(3)–C(4)	1·390(7)	C(10)–C(11)	1·371(6)
C(4)–C(5)	1·376(7)	C(11)–C(12)	1·382(8)
C(5)–C(6)	1·367(5)	C(12)–C(13)	1·389(6)
C(6)–C(7)	1·405(7)	C(13)–N(3)	1·311(5)
C(7)–C(2)	1·394(6)	N(3)–C(9)	1·361(5)

TABLE 4 (*Continued*)

(ii) Angles

C(1)–O(1)–Ni	116·9(5)	C(8)–N(2)–Ni	114·2(5)
O(1)–C(1)–N(1)	119·7(7)	C(7)–N(2)–C(8)	120·0(7)
O(1)–C(1)–C(2)	121·8(7)	N(2)–C(8)–C(9)	117·8(7)
N(1)–C(1)–C(2)	118·5(8)	C(8)–C(9)–C(10)	121·0(7)
C(7)–C(2)–C(3)	118·5(7)	C(8)–C(9)–N(3)	116·2(7)
C(2)–C(3)–C(4)	120·7(8)	N(3)–C(9)–C(10)	122·9(9)
C(3)–C(4)–C(5)	120·2(9)	C(9)–N(3)–Ni	112·4(5)
C(4)–C(5)–C(6)	120·2(8)	Ni–N(3)–C(13)	128·9(7)
C(5)–C(6)–C(7)	120·1(8)	C(9)–C(10)–C(11)	117·3(6)
C(6)–C(7)–C(2)	120·1(9)	C(10)–C(11)–C(12)	119·2(9)
C(6)–C(7)–N(2)	121·5(8)	C(11)–C(12)–C(13)	120·1(9)
C(2)–C(7)–N(2)	118·4(7)	C(12)–C(13)–N(3)	121·5(8)
C(7)–N(2)–Ni	125·8(6)	C(13)–N(3)–C(9)	118·7(8)

(*c*) In the ligand (II)

(i) Distances

C(14)–C(15)	1·401(7)	N(5)–C(21)	1·454(4)
C(15)–C(16)	1·381(6)	C(21)–N(4)	1·485(5)
C(16)–C(17)	1·377(6)	N(4)–C(14)	1·425(5)
C(17)–C(18)	1·398(8)	C(21)–C(22)	1·517(5)
C(18)–C(19)	1·377(5)	C(22)–C(23)	1·388(6)
C(19)–C(14)	1·402(5)	C(23)–C(24)	1·374(6)
C(19)–C(20)	1·482(7)	C(24)–C(25)	1·368(7)
C(20)–O(2)	1·240(5)	C(25)–C(26)	1·394(7)
C(20)–N(5)	1·320(5)	C(26)–N(6)	1·329(5)
		N(6)–C(22)	1·334(5)

(ii) Angles

C(19)–C(14)–C(15)	120·2(8)	C(21)–N(4)–C(14)	113·7(6)
C(19)–C(14)–N(4)	119·5(6)	Ni–N(4)–C(14)	117·2(4)
N(4)–C(14)–C(15)	120·2(7)	Ni–N(4)–C(21)	108·3(4)
C(14)–C(15)–C(16)	118·9(8)	N(4)–C(21)–C(22)	110·2(5)
C(14)–C(16)–C(17)	121·0(8)	N(6)–C(22)–C(23)	122·6(8)
C(16)–C(17)–C(18)	120·2(9)	C(23)–C(22)–C(21)	120·5(7)
C(17)–C(18)–C(19)	119·7(9)	N(6)–C(22)–C(21)	116·8(6)
C(18)–C(19)–C(14)	119·9(7)	C(22)–C(23)–C(24)	118·9(8)
C(20)–C(19)–C(14)	119·2(7)	C(23)–C(24)–C(25)	118·6(9)
C(20)–C(19)–C(18)	120·9(8)	C(24)–C(25)–C(26)	119·6(9)
O(2)–C(20)–C(19)	122·2(8)	C(25)–C(26)–N(6)	121·9(9)
O(2)–C(20)–N(5)	120·7(7)	C(22)–N(6)–C(26)	118·4(7)
C(20)–N(5)–C(21)	123·3(7)	C(26)–N(6)–Ni	125·3(6)
N(5)–C(21)–N(4)	110·1(5)	Ni–N(6)–C(22)	116·0(5)

(*d*) In the nitrate groups

(i) Distances

N(7)–O(3)	1·232(6)	N(8)–O(6)	1·188(8)
N(7)–O(4)	1·223(6)	N(8)–O(7)	1·223(10)
N(7)–O(5)	1·206(5)	N(8)–O(8)	1·200(8)

(ii) Angles

O(3)–N(7)–O(4)	120·2(9)	O(6)–N(8)–O(7)	121·1(1·5)
O(4)–N(7)–O(5)	121·7(9)	O(7)–N(8)–O(8)	128·0(1·6)
O(3)–N(7)–O(5)	118·1(9)	O(6)–N(8)–O(8)	110·9(1·0)

(*e*) Contacts involving hydrogen

(i) Distances

O(9) · · · O(12)	2·78	H(7) · · · O(13)	1·77
H(1) · · · O(12)	2·00	O(13) · · · O(6$^{\mathrm{III}}$)	3·15
O(9) · · · O(11)	2·67	H(9) · · · O(6$^{\mathrm{III}}$)	2·39
H(2) · · · O(11)	1·95	O(13) · · · O(7$^{\mathrm{III}}$)	3·15
O(10) · · · O(8)	2·89	H(10) · · · O(7$^{\mathrm{IV}}$)	2·88
H(3) · · · O(8)	1·98	N(1) · · · O(12)	3·10
O(10) · · · O(3$^{\mathrm{I}}$)	2·77	H(11) · · · O(12)	2·38
H(4) · · · O(3$^{\mathrm{I}}$)	1·99	N(1) · · · O(2$^{\mathrm{III}}$)	2·83
O(11) · · · O(10$^{\mathrm{II}}$)	2·79	H(12) · · · O(2$^{\mathrm{III}}$)	2·08
H(5) · · · O(10$^{\mathrm{II}}$)	2·56	N(5) · · · O(2$^{\mathrm{V}}$)	2·89
O(12) · · · O(13)	2·83	H(26) · · · O(2$^{\mathrm{V}}$)	2·20

TABLE 4 (*Continued*)

(ii) Angles

O(9)–H(1) · · · O(12)	172	O(13)–H(9) · · · O(6$^{\mathrm{III}}$)	123
O(9)–H(2) · · · O(12)	167	O(13)–H(10) · · · O(7$^{\mathrm{IV}}$)	95
O(10)–H(3) · · · O(8)	168	N(1)–H(11) · · · O(12)	144
O(10)–H(4) · · · O(3$^{\mathrm{I}}$)	171	N(1)–H(12) · · · O(2$^{\mathrm{III}}$)	178
O(11)–H(5) · · · O(10$^{\mathrm{II}}$)	120	N(5)–H(26) · · · O(2$^{\mathrm{V}}$)	169
O(12)–H(7) · · · O(13)	161		

Roman numerals as superscripts refer to the following equivalent positions relative to the reference molecule at x, y, z:

I $\bar{x}, 1-y, 1-z$
II $x, y-1, z$
III $1-x, 1-y, 1-z$
IV $x, y-1, z-1$
V $1-x, 1-y, \bar{z}$

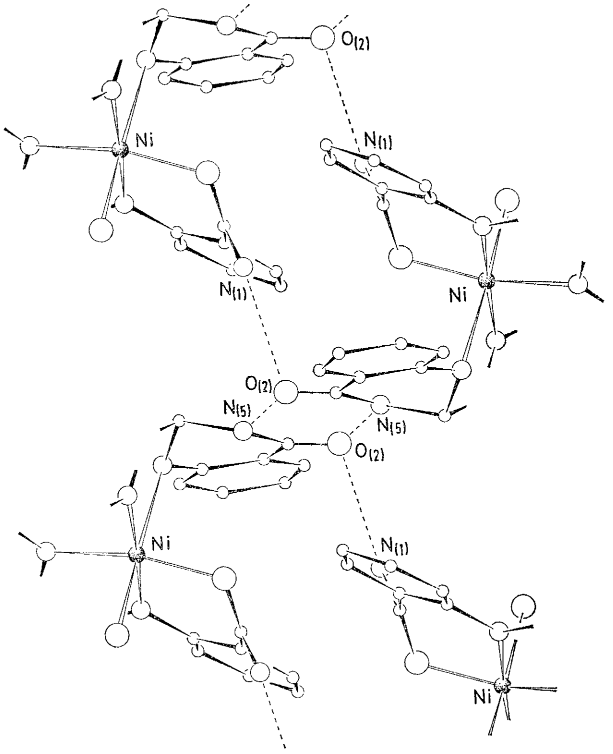


FIGURE 3 Clinographic projection of hydrogen-bonded chains running along [001]

TABLE 5

Significant intermolecular contacts (Å)

O(9) · · · N(1)	3·23	O(11) · · · O(10$^{\mathrm{I}}$)	2·91
O(12) · · · O(9)	3·09	C(21) · · · O(3$^{\mathrm{VI}}$)	2·95
N(4) · · · O(3$^{\mathrm{VI}}$)	3·08	C(22) · · · O(3$^{\mathrm{VI}}$)	2·92
N(4) · · · O(4$^{\mathrm{VI}}$)	2·98	O(12) · · · O(6$^{\mathrm{II}}$)	3·22
O(5) · · · O(10$^{\mathrm{I}}$)	3·31	C(6) · · · O(5$^{\mathrm{I}}$)	3·19
O(8) · · · O(12$^{\mathrm{VII}}$)	3·11		

VI $x, y, z-1$ VII $x, y+1, z$

Bond distances involving hydrogen atoms are in the usual range.

[3/735 *Received, 9th April,* 1973]