Crystal and Molecular Structure of Bis(8-amino-2-methylquinoline)-nitratonickel(II) Nitrate

By **Leslie F. Power,*** and **A. Martin Tait,** Chemistry Department, James Cook University of North Queensland, Townsville, Queensland 4811, Australia
James Pletcher and **Martin Sax,** Biocrystallography Laboratory, Veterans Administration Hospital, Pittsburgh, Pennsylvania 15240, U.S.A.

An *X*-ray diffraction study of the title compound has been carried out and the structure solved by direct methods. Crystals are monoclinic, space group $P2_1/c$, $Z = 4$, $a = 15.905(3)$, $b = 8.040(5)$, $c = 10.736(3)$ Å, $\beta = 117.78(4)°$. The structure was refined by block-diagonal least-squares to *R* and *R′* both 4.2%. The nitrato-group in the cation acts as a bidentate ligand. The presence of the methyl group on the organic ligand produces various distortions of bond lengths and angles, and in the geometrical arrangement about the metal.

COMPLEXES of some transition metals with the ligand 8-amino-2-methylquinoline (amq) have been described previously.[1-6] In the first of this series [1] it was pointed out that molecular models of bis-chelated octahedral complexes of the ligand indicated that the presence of the methyl group in the 2-position would sterically hinder any configuration in which the aromatic nitrogens are mutually *cis*. Of the two possible geometric configurations in which the aromatic nitrogen atoms are mutually *trans*, it was concluded that a *cis*-octahedral disposition of the two ligand molecules would be favoured because no methyl–amine interactions are thereby generated, and although the methyl groups shield the remaining *cis*-octahedral co-ordinating positions to some degree, effective co-ordination to these positions would be determined by the relative sizes of the atoms to be co-ordinated.

The magnetic moment, diffuse reflectance spectrum, and absorption spectrum of the complex $[Ni(amq)_2(NO_3)_2]$ supported an octahedral configuration.[1] From the i.r. spectrum it was concluded that one nitrate group was ionic and the other was bidentate and hence that the complex could be formulated as $[Ni(amq)_2NO_3]NO_3$.

As an *X*-ray analysis of the compound $[Pd(dmp)(NO_2)_2]$ (dmp = 2,9-dimethyl-1,10-phenanthroline) [7] had shown that steric strain could be accommodated by various small extensions in bond lengths and angles and by a slight buckling of the aromatic molecule, it was decided to investigate by *X*-ray diffraction the compound $[Ni(amq)_2(NO_3)_2]$ to verify the suggested formulation and configuration, and to identify any changes which may accommodate the possible steric strain. A preliminary description of the structure of the compound has been reported.[8]

EXPERIMENTAL

Crystal Data.—$NiC_{20}H_{20}N_6O_6$, $M = 499.14$, Monoclinic, $a = 15.905(3)$, $b = 8.040(5)$, $c = 10.736(3)$ Å, $\beta = 117.78(4)°$, $U = 2\,105$ Å^3, $D_m = 1.57$ (by flotation), $Z = 4$, $D_c = 1.57$. Cu-K_α radiation, $\lambda = 1.5418$ Å; $\mu(\text{Cu-}K_\alpha) = 18.5\ \text{cm}^{-1}$. Space group, $P2_1/c$ from systematic absences.

The compound was prepared as described previously.[1] Six small blue-green crystals of the compound were grown from a methanol solution, in a conical flask capped with a

---

[1] M. Litzow, L. Power, and A. Tait, *J. Chem. Soc.* (*A*), 1970, 275.

[2] M. Litzow, L. Power, and A. Tait, *Austral. J. Chem.*, 1970, **23**, 1375.

[3] M. Litzow, L. Power, and A. Tait, *Austral. J. Chem.*, 1970, **23**, 1383.

[4] M. Litzow, L. Power, and A. Tait, *J. Chem. Soc.* (*A*), 1970, 2907.

[5] M. Litzow, L. Power, and A. Tait, *J. Chem. Soc.* (*A*), 1970, 3226.

[6] J. King and L. Power, *Austral. J. Chem.*, 1972, **25**, 1863.

[7] J. Fridrichsons, A. McL. Mathieson, and L. Power, *J. Cryst. Mol. Struct.*, 1971, **1**, 333.

[8] L. F. Power and A. M. Tait, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 337.

polythene film, kept refrigerated for *ca.* 3 months. Three of these crystals were monoclinic and three triclinic, with axial dimensions almost identical with those of the monoclinic form. The triclinic crystals appeared to possess a little more blue colour than the monoclinic crystals. This structural analysis has been carried out on the monoclinic form. The space group and initial unit-cell dimensions were determined from Weissenberg photographs.

The crystal used measured *ca.* 0.52 × 0.20 × 0.09 mm. It was mounted with the *b* axis approximately coincident with the ψ axis of a Picker four-angle diffractometer system equipped with a scintillation counter, by use of Cu-K_α radiation. Accurate unit-cell parameters were obtained from a least-squares fit to the angular settings for 20 centred reflections. Intensities were corrected for Lorentz and polarization effects. Of 3 813 reflections recorded, 2 871 were considered observed having $I \geqslant 3\sigma(I)$ where $\sigma(I) = [S + 4(B_1 + B_2)]^{\frac{1}{2}}$, S is the total number of counts accumulated during a 2θ scan over a 3° scan at 2° min^{-1}, B_1 is the total number of counts in 22.5 s at the initial setting, and B_2 is the total number of counts in 22.5 s at the terminal setting. The intensity I is given by $I = [S - 2(B_1 + B_2)]$. No absorption correction was applied.

Structure Solution and Refinement.—A Wilson plot was calculated to place the structure factors on an absolute scale and to determine the overall temperature factor. Signs for 387 generated E values > 1.5 were determined manually using symbolic addition and these signs were all subsequently shown to agree with the observed signs. An E map allowed the location of all non-hydrogen atoms and a structure factor calculation based on these positions yielded R 32%. Seven successive block-diagonal least-squares cycles reduced the R to 10.7% at which stage the introduction of anisotropic temperature factor refinement reduced R to 6.4%. A final Fourier map allowed the location of all hydrogen atoms and three cycles of block-diagonal least-squares reduced R and R' to 4.2%. All refinements were based on F_o^2 and the weighting scheme used minimised $\Sigma\omega(F_o^2 - F_c^2)^2$ where $\omega = F_o^{-2}$.

Scattering factors for non-hydrogen atoms were taken from ref. 9, and for hydrogen from ref. 10. Allowance was made for the anomalous dispersion correction of nickel using the real part only. Final positional and thermal parameters

TABLE 1

Atomic co-ordinates (× 10⁴) and thermal * parameters

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni	2 637(1)	2 509(1)	228(1)	33(1)	123(1)	21(1)	−3(1)	22(4)	−5(1)
C(1)	1 316(2)	836(5)	−1 204(2)	29(2)	129(6)	26(1)	1(5)	22(2)	−3(5)
C(2)	876(3)	−477(5)	−1 715(2)	39(2)	139(7)	34(2)	−29(6)	28(3)	−17(5)
C(3)	650(3)	−390(5)	−2 540(2)	48(2)	179(8)	33(2)	−41(7)	32(3)	−56(6)
C(4)	828(3)	999(6)	−2 854(2)	43(2)	232(9)	24(1)	−9(7)	30(3)	−26(6)
C(5)	1 295(2)	2 392(5)	−2 345(2)	34(2)	165(6)	24(1)	10(7)	26(2)	4(5)
C(6)	1 494(3)	3 895(6)	−2 616(2)	48(2)	214(9)	32(4)	28(7)	40(3)	42(6)
C(7)	1 932(3)	5 131(5)	−2 084(2)	52(2)	164(8)	32(4)	−4(7)	44(3)	36(6)
C(8)	2 228(3)	4 904(5)	−1 243(2)	40(2)	139(7)	32(4)	5(6)	36(3)	16(5)
C(9)	2 752(3)	6 266(5)	−655(3)	66(3)	128(7)	45(6)	−38(8)	49(4)	0(6)
C(10)	1 563(2)	2 263(5)	−1 507(2)	39(2)	127(6)	28(4)	9(5)	24(2)	−2(5)
N(1)	1 523(2)	892(4)	−368(2)	35(2)	137(5)	20(3)	−18(5)	28(2)	2(4)
N(2)	2 052(2)	3 510(4)	−963(2)	35(2)	119(5)	25(1)	−4(4)	27(2)	1(4)
C(21)	2 662(2)	4 180(5)	1 587(2)	35(2)	153(7)	23(1)	5(6)	31(2)	−4(5)
C(22)	2 726(3)	5 517(5)	2 066(2)	49(2)	164(7)	36(2)	6(7)	42(3)	−17(6)
C(23)	3 339(3)	5 457(6)	2 910(2)	62(3)	212(9)	33(2)	−16(8)	45(3)	−59(6)
C(24)	3 835(3)	4 057(6)	3 264(2)	50(2)	265(9)	24(1)	−14(8)	30(3)	−23(6)
C(25)	3 790(2)	2 647(5)	2 786(2)	41(2)	180(7)	24(1)	−1(7)	29(3)	14(6)
C(26)	4 272(3)	1 146(6)	3 096(2)	49(2)	200(8)	26(1)	0(7)	17(3)	37(6)
C(27)	4 197(3)	−97(6)	2 586(2)	47(2)	164(8)	38(2)	19(7)	18(3)	56(6)
C(28)	3 646(2)	100(5)	1 727(2)	35(2)	132(7)	37(2)	1(6)	28(3)	8(5)
C(29)	3 575(3)	−1 279(5)	1 165(3)	52(3)	134(7)	46(2)	31(7)	35(4)	0(6)
C(210)	3 215(2)	2 750(5)	1 931(2)	34(2)	134(6)	25(1)	−14(6)	27(2)	1(5)
N(21)	2 033(2)	4 106(4)	722(2)	40(2)	131(5)	25(1)	24(5)	24(2)	16(4)
N(22)	3 184(2)	1 500(4)	1 418(2)	34(1)	120(5)	23(1)	6(4)	20(2)	11(4)
O(21)	3 689(2)	1 370(4)	−14(2)	47(1)	184(5)	33(1)	14(5)	36(2)	−14(4)
O(22)	3 974(2)	3 681(4)	639(2)	42(1)	191(5)	32(1)	−38(5)	28(2)	−15(5)
O(23)	5 044(2)	2 632(6)	363(2)	42(2)	422(10)	64(2)	−17(7)	63(3)	21(7)
N(23)	4 270(2)	2 577(5)	338(2)	39(2)	232(7)	30(1)	12(6)	31(2)	34(5)
O(1)	250(2)	1 902(5)	379(2)	65(2)	358(10)	56(2)	61(8)	32(3)	−9(7)
O(2)	−359(4)	2 956(9)	−717(3)	165(5)	915(27)	135(4)	372(19)	220(8)	491(17)
O(3)	−1 215(2)	2 506(5)	−146(2)	56(2)	210(6)	95(2)	57(6)	99(3)	85(6)
N(3)	−473(2)	2 442(5)	−193(2)	63(2)	184(6)	43(1)	63(7)	63(3)	120(7)

	x	y	z	B/Å²		x	y	z	B/Å²
H(2)	711(25)	−1 345(48)	−1 514(20)	3.6(8)	H(22)	2 343(25)	6 543(47)	1 804(20)	4.0(8)
H(3)	372(25)	−1 428(47)	−2 894(20)	3.3(8)	H(23)	3 331(26)	6 423(49)	3 246(21)	3.7(8)
H(4)	708(26)	998(52)	−3 354(22)	4.3(9)	H(24)	4 190(30)	3 882(58)	3 850(25)	6.1(11)
H(6)	1 317(24)	4 082(45)	−3 151(20)	2.9(8)	H(26)	4 618(31)	1 005(60)	3 696(25)	6.3(11)
H(7)	2 077(27)	6 255(52)	−2 277(22)	4.9(10)	H(27)	4 491(31)	−1 104(59)	2 769(25)	5.8(11)
H[N(11)]	1 567(28)	−237(54)	−127(23)	4.5(10)	H[N(211)]	1 899(23)	4 975(45)	479(19)	3.1(8)
H[N(12)]	1 040(25)	1 391(49)	−291(21)	3.4(9)	H[N(212)]	1 458(28)	3 666(53)	607(23)	4.0(10)
H(91)	2 667(39)	7 212(83)	−819(32)	7.6(17)	H(291)	3 800(31)	−2 154(67)	1 352(26)	6.3(12)
H(92)	2 802(25)	6 168(49)	−140(21)	5.2(8)	H(292)	3 866(26)	−1 112(51)	860(22)	5.2(9)
H(93)	3 445(44)	6 118(83)	−561(36)	11.4(19)	H(293)	2 954(45)	−1 504(85)	9 838(36)	12.3(20)

* The temperature factor is of the form $\exp[-10^{-4}(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

---

[9] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

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

are given in Table 1. Measured and calculated structure factors are listed in Supplementary Publication No. SUP 21486 (21 pp., 1 microfiche).*

TABLE 2

Bond lengths (Å), with estimated standard deviations in parentheses

Bond	(I)	Bond	(I)	(II)	(III)
C(1)–C(2)	1.375(5)	C(21)–C(22)	1.373(6)	1.371(5)	1.362(5)
C(1)–C(10)	1.413(5)	C(21)–C(210)	1.408(5)	1.416(4)	1.411(4)
C(2)–C(3)	1.406(5)	C(22)–C(23)	1.412(6)	1.410(4)	1.408(8)
C(3)–C(4)	1.354(6)	C(23)–C(24)	1.359(7)	1.379(4)	1.348(8)
C(4)–C(5)	1.427(6)	C(24)–C(25)	1.422(6)	1.422(5)	1.414(6)
C(5)–C(6)	1.401(6)	C(25)–C(26)	1.399(6)	1.416(4)	1.414(6)
C(5)–C(10)	1.415(4)	C(25)–C(210)	1.424(5)	1.423(4)	1.411(5)
C(6)–C(7)	1.349(6)	C(26)–C(27)	1.348(6)	1.365(6)	1.346(6)
C(7)–C(8)	1.419(5)	C(27)–C(28)	1.427(6)	1.408(5)	1.399(5)
C(8)–C(9)	1.489(6)	C(28)–C(29)	1.492(6)		
C(8)–N(2)	1.321(5)	C(28)–N(22)	1.320(5)	1.314(5)	1.345(5)
N(2)–C(10)	1.383(4)	N(22)–C(210)	1.372(5)	1.370(4)	1.374(4)
N(1)–C(1)	1.431(4)	N(21)–C(21)	1.443(4)		
Ni–N(1)	2.056(3)	Ni–N(21)	2.061(3)		
Ni–N(2)	2.124(3)	Ni–N(22)	2.131(3)		

(I) This work, (II) 5-acetoxy-6-methoxy-8-nitroquinoline (ref. 12), (III) tetra-n-butylammonium tribromo(quinoline)-nickelate(II) (ref. 11).

DISCUSSION

Bond lengths and angles together with their estimated standard deviations are listed in Tables 2—4. Figure 1 shows a drawing of the complex and the labelling of the atoms. The packing within the unit cell is shown as a projection on the *bc* plane in Figure 2. Equations for the least-squares planes through various portions of the molecule are shown in Table 5 together with deviations of relevant atoms from them.

TABLE 3

Bond angles (°), with estimated standard deviations in parentheses

Angle	(I)	Angle	(I)	(II)	(III)
C(10)–C(1)–C(2)	119.3(3)	C(210)–C(21)–C(22)	120.0(4)	123.9(3)	119.3(4)
C(1)–C(2)–C(3)	120.6(4)	C(21)–C(22)–C(23)	120.2(4)	119.1(3)	121.3(4)
C(2)–C(3)–C(4)	120.9(4)	C(22)–C(23)–C(24)	120.8(4)	119.3(3)	120.4(4)
C(3)–C(4)–C(5)	120.5(4)	C(23)–C(24)–C(25)	120.5(4)	121.9(3)	120.3(5)
C(4)–C(5)–C(6)	124.6(4)	C(24)–C(25)–C(26)	124.6(4)	123.3(3)	122.0(4)
C(4)–C(5)–C(10)	118.2(4)	C(24)–C(25)–C(210)	118.3(4)	119.2(3)	119.2(4)
C(5)–C(10)–C(1)	120.0(3)	C(25)–C(210)–C(21)	119.9(3)	116.5(3)	119.5(3)
C(5)–C(10)–N(2)	122.4(3)	C(25)–C(210)–N(22)	122.2(3)	123.4(3)	121.0(3)
C(10)–C(5)–C(6)	117.2(4)	C(210)–C(25)–C(26)	117.1(4)	117.4(4)	118.8(3)
C(5)–C(6)–C(7)	119.8(4)	C(25)–C(26)–C(27)	119.7(4)	118.5(4)	119.1(4)
C(6)–C(7)–C(8)	120.5(4)	C(26)–C(27)–C(28)	121.1(4)	119.7(4)	120.0(4)
C(7)–C(8)–C(9)	120.0(4)	C(27)–C(28)–C(29)	120.7(4)		
C(7)–C(8)–N(2)	121.6(4)	C(27)–C(28)–N(22)	120.6(4)	124.6(4)	123.0(3)
C(9)–C(8)–N(2)	118.4(4)	C(29)–C(28)–N(22)	116.7(4)		
C(8)–N(2)–C(10)	118.3(3)	C(28)–N(22)–C(210)	119.2(3)	116.2(3)	118.2(3)
N(2)–C(10)–C(1)	117.4(3)	N(22)–C(210)–C(21)	117.9(3)	119.9(3)	119.5(3)

Despite the fact that quinoline is a ligand which participates in a wide variety of transition-metal complexes, there have been only three accurate crystal-structure analyses of co-ordination compounds containing quinoline derivatives.[11-13] A preliminary account has also been published of the crystal structure of bis(2-methyl-8-quinolinato)aluminium(III).[14]

The structure determination of the present complex has shown that the crystal consists of a lattice of discrete octahedral bis(8-amino-2-methylquinoline)nitratonickel(II) cations and nitrate anions. The molecule provides an example of how strain due to steric interactions may be accommodated by several small changes in bond lengths and bond angles, instead of by considerable distortion in one part of the molecule. Leybold models have shown that least steric interaction between the two quinoline ring systems occurs for bis-chelated molecules when the two organic ligands are disposed in a *cis*-octahedral arrangement, with the aromatic nitrogen atoms disposed mutually *trans*. Such an arrangement, however, would lead to shielding of the remaining *cis*-co-ordinating positions in an octahedral complex by the methyl groups, so that for effective co-ordination to occur at these sites, distortion must occur to remove the shielding methyl groups. The structure determination of this compound has revealed that the steric shielding is relieved by a combination of: (i) a slight buckling and twisting within both quinoline ring systems, (ii) a displacement of the quinoline ring systems from a regular *cis*-octahedral arrangement, (iii) an increase in length of the Ni–N(2) and Ni–N(22) bonds, and (iv) the deviation from planarity of the nickel atom and atoms (N1), N(2), O(22), and N(22).

TABLE 4

Bond lengths and angles for nitrate groups, with estimated standard deviations in parentheses, for (I)

Distance		Angle	
N(23)–O(21)	1.289(5)	O(21)–N(23)–O(23)	121.5(4)
N(23)–O(22)	1.259(5)	O(22)–N(23)–O(23)	123.0(4)
N(23)–O(23)	1.211(8)	O(22)–N(23)–O(21)	115.5(3)
Ni–O(21)	2.133(3)	Ni–O(21)–N(23)	91.0(2)
Ni–O(22)	2.116(3)	Ni–O(22)–N(23)	92.6(2)
N(3)–O(1)	1.231(5)	O(1)–N(3)–O(3)	119.9(5)
N(3)–O(2)	1.154(7)	O(2)–N(3)–O(3)	126.0(5)
N(3)–O(3)	1.222(5)	O(2)–N(3)–O(1)	113.9(4)

(i) Deformation amongst resonating systems appears to be characteristic of overcrowded aromatic and heterocyclic molecules. Thus, folding of a system of three

---

* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1974, Index issue.

[11] W. DeW. Horrocks, jun., D. H. Templeton, and A. Zalkin, *Inorg. Chem.*, 1968, **7**, 2203.

[12] M. Sax and R. Desiderato, *Acta Cryst.*, 1967, **23**, 319.

[13] P. Jose, S. Ooi, and Q. Fernando, *J. Inorg. Nuclear Chem.*, 1969, **31**, 1971.

[14] Y. Kushi and Q. Fernando, *Chem. Comm.*, 1969, 555.

TABLE 5

Equations of least-squares best planes in the form $AX = BY + CZ = D$, where X, Y, and Z are orthogonal (Å) co-ordinates and $X = ax$, $Y = by$, and $Z = cz$. Deviations (Å) of atoms from the planes are given in square brackets

		A	B	C	D
Plane (1):	C(5)—(10), N(2)	0.9165	−0.3756	−0.3054	2.4771
	[C(5) 0.020, C(6) 0.008, C(7) −0.022, C(8) −0.003, C(9) 0.010, C(10) −0.024, N(2) 0.011]				
Plane (2):	C(25)—(29), C(210), N(22)	0.9279	0.3684	−0.4833	3.8537
	[C(25) 0.022, C(26) 0.011, C(27) −0.025, C(28) −0, C(29) 0.007, C(210) −0.034, N(22) 0.019]				
Plane (3):	C(1)—(5), C(10)	0.9004	−0.3895	−0.2483	2.2016
	[C(1) −0.014, C(2) −0.010, C(3) 0.022, C(4) −0.010, C(5) −0.013, C(10) 0.025, N(1) −0.131]				
Plane (4):	C(21)—(25), C(210)	0.9195	0.3730	−0.5386	3.5627
	[C(21) 0.018, C(22) 0.006, C(23) 0.014, C(24) −0.024, C(25) −0.021, C(210) 0.043, N(21) −0.035]				
Plane (5):	C(1)—(10), N(2)	0.9020	−0.3979	−0.2526	2.1948
	[C(1) −0.058, C(2) −0.033, C(3) 0.045, C(4) 0.036, C(5) 0.011, C(6) −0.031, C(7) −0.053, C(8) 0.008, C(9) 0.027, C(10) 0.005, N(2) 0.048, N(1) −0.223, Ni 0.576]				
Plane (6):	C(21)—(29), C(210), N(22)	0.9142	0.3840	−0.5236	3.6240
	[C(21) −0.066, C(22) −0.032, C(23) 0.053, C(24) 0.046, C(25) 0.003, C(26) −0.036, C(27) −0.056, C(28) 0.010, C(29) 0.033, C(210) −0.010, N(22) 0.057, N(21) −0.198, Ni 0.672]				
Plane (7):	N(3), O(1)—(3)	0.0316	0.9076	0.3557	1.6556
	[N(3) −0.020, O(1) 0.006, O(2) 0.007, O(3) 0.007, Ni 0.458]				
Plane (8):	N(23), O(21)—(23)	0.0222	0.5060	−0.7732	0.7080
	[N(23) −0.004, O(21) 0.001, O(22) 0.001, O(23) 0.001, Ni 0.075]				
Plane (9):	Ni, N(2), O(21), N(22), N(21)	0.6052	0.7236	0.0115	4.1869
	[Ni −0.135, N(2) −0.141, O(21) 0.214, N(22) −0.164, N(21) 0.226]				
Plane (10):	Ni, O(22), N(2), N(1), N(22)	−0.6588	0.7123	0.5212	1.2333
	[Ni 0.129, O(22) −0.199, N(2) 0.149, N(1) −0.210, N(22) 0.132]				

linear fused rings due to hydrogen–hydrogen repulsions is known for the compounds 9,9′-bifluorenylidene [15] and β-9,9′-bixanthenylidene.[16] Folding of the molecule 2,9-dimethyl-1,10-phenanthroline occurs in the planar complex [Pd(dmp)$(NO_2)_2$] [7] and Freeman and Snow [17] have noted a similar effect in the bis(2,2′-bipyridyliminato)-palladium(II) complex. In the complex, tetra-n-butylammonium tribromo(quinoline)nickelate(II),[11] the co-ordinated quinoline is accurately planar, presumably reflecting the absence of any steric interactions in the tetrahedral complex. On the other hand, Sax and Desiderato [12] have reported that the quinoline ring system in the compound 5-acetoxy-6-methoxy-8-nitroquinoline is decidedly non-planar and suggest that the lack of planarity arises from steric interactions of the substituents.

Calculation of the least-squares planes shows that pyridine ring (1) lies at 3.5° to benzene ring (1) whereas pyridine ring (2) lies at 3.9° to benzene ring (2).

(ii) For a regular octahedral complex involving a *cis*-octahedral arrangement of two bidentate ligands, the dihedral angle between the least-squares planes through the two bidentate ligand systems is theoretically 90°. In this compound the angle between the two quinoline ring systems is 49.4°, representing a marked degree of distortion, the effect of which is to move the two methyl groups away from each other and from the remaining *cis*-octahedral co-ordinating positions.

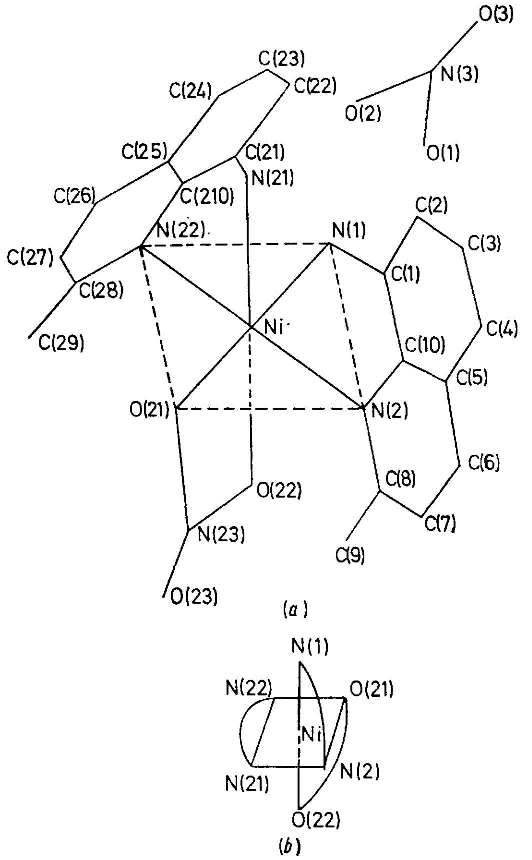

FIGURE 1 (a) The molecule $[Ni(amq)_2(NO_3)]NO_3$ viewed down the *a* axis showing the labelling of the atoms, and (b) the idealised octahedron about nickel

(iii) This distortion is also reflected in the different Ni–N bond lengths. The Ni–N(2) and Ni–N(22) distances are 2.124 and 2.061 Å respectively. The single-bond radii for nickel(II) and nitrogen are 1.39 and 0.70 Å.[18] The observed Ni–N bond distance is 2.029(3) Å in tetra-n-butylammonium tribromo(quinoline)nickelate(II) [11] and Horrocks *et al.* suggest that the distance is consistent with a definite shortening of bond lengths in tetrahedral complexes as compared to their octahedral counterparts.

(iv) The least-squares planes, about the nickel, reflect the highly-distorted six-co-ordinate structure. Table 5 lists the deviations of the co-ordinating atoms from the respective least-squares planes.

---

[15] S. C. Nyburg, *Acta Cryst.*, 1954, **7**, 719.

[16] J. F. D. Mills and S. C. Nyburg, *J. Chem. Soc.*, 1963, 308.

[17] H. C. Freeman and N. R. Snow, *Acta Cryst.*, 1965, **18**, 845.

[18] L. Pauling, ' The Nature of the Chemical Bond,' 3rd edn., Cornell University Press, Ithaca, New York, 1960, ch. 7—9.

The distortion is also evident in the angles about the nickel atom. For instance N(21)–Ni–N(22) and O(22)–Ni–O(21) are 80.0 and 60.8°, whilst N(21)–Ni–O(21) is only 159.6(2)°. The presence of the bidentate nitrato-group is primarily responsible for the two last-mentioned angles.

For a theoretical O(22)–Ni–O(21) angle of 90°, the O(21)–O(22) distance would have to be 2.975 Å and O(21)–N(23)–O(22) would necessarily be >120°. Instead this distance is only 2.154(6) Å and, as mentioned later, the angle is only 115.5°. The twisting of the two organic ligand molecules relative to each other is reflected in the large deviation of the Ni atom from the least-squares planes of the quinoline ring systems (0.576 and 0.672 Å).

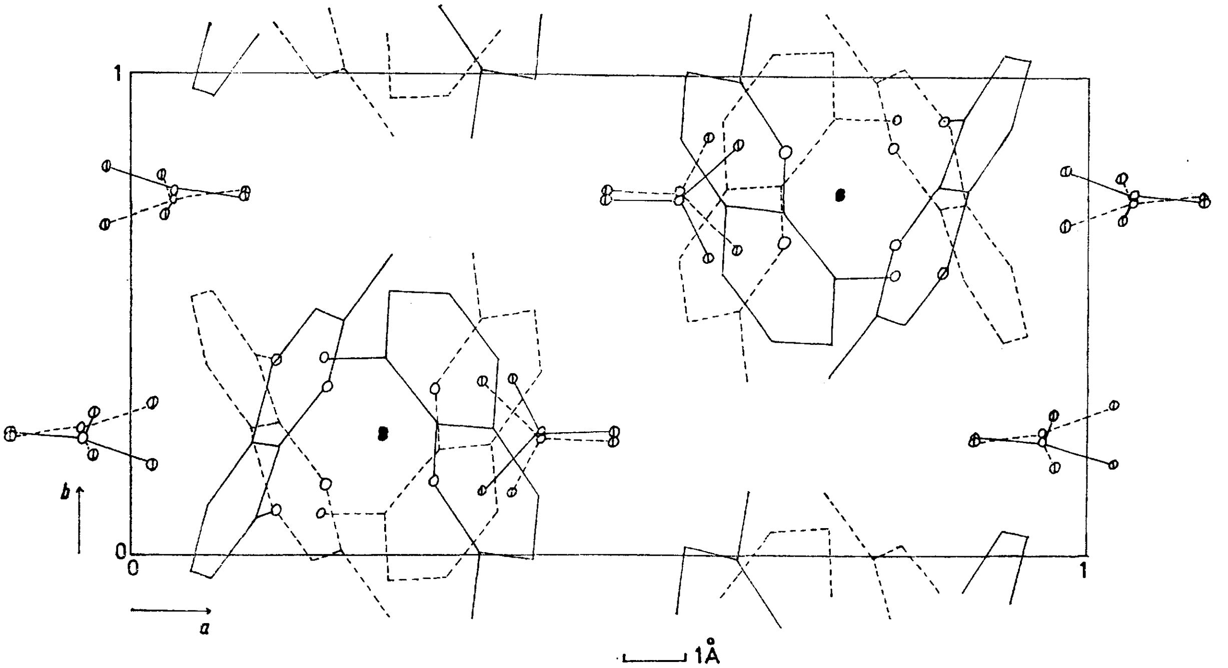

FIGURE 2 The projection of the unit cell on the *bc* plane

The 8-Amino-2-methylquinoline Moieties.—The crystal structures of 5-acetoxy-6-methoxy-8-nitroquinoline[12] and tetra-n-butylammonium tribromo(quinoline)nickelate(II)[11] have been examined; the bond lengths in the quinoline ring systems of these two compounds [referred to as (II) and (III)] and those in the present compound (I) are compared in Table 2.

There are significant variations in the C–C and C–N bond lengths in the quinoline ring systems of compound (I) which are analogous to those found in naphthalene.[19] Agreement of the bond lengths for the two quinoline ring systems of compound (I) is within experimental error and compares favourably with the bond distances of compounds (II) and (III). The bond-length variations correlate well with those predicted[20] by the SCF MO theory. As predicted by the theory, the introduction of a heteroatom does not introduce any marked changes in the C–C bond length pattern from those observed for naphthalene.[19] Agreement is satisfactory, both for the present results and for those of compounds (II) and (III), particularly with respect to trends. Co-ordination to the nickel atom appears to have little effect on the bond lengths in the quinoline structures. The internal bond angles (Table 3) of the quinoline systems agree. Table 3 also compares angles for compounds (II) and (III).

The Nitrato- and Nitrate Groups.—The structural determination has shown that the complex contains a co-ordinated bidentate nitrato-group (Figure 1). So far as is known the results presented here constitute the first *X*-ray analysis of a metal complex containing both an ionic nitrate and a bidentate nitrato-group. Only one other co-ordination complex involving an organic ligand, $[Co(Me_3PO)_2(NO_3)_2]$, has been shown by *X*-ray structural determinations to contain bidentate nitrato-groups,[21] although there have been a few crystal structures of simple salts containing bidentate nitrato-groups.[22] Bond lengths and angles for both NO_3 groups are shown in Table 4.

(a) *Nitrato-group*. The nitrato-group is planar, the sum of the O–N–O angles being 360°, and all atoms showing only minor deviations from the least-square plane. The nickel atom lies 0.075 Å out of the plane. The O–N–O angles are distorted so that the O(21)–N(23)–O(22) angle decreases to 115.5° while the external angles

---

[19] D. W. J. Cruickshank and R. A. Sparks, *Proc. Roy. Soc.*, 1960, **A258**, 270.

[20] K. Nishimoto and L. S. Foster, *Theor. Chim. Acta*, 1966, **4**, 155.

[21] F. A. Cotton and R. H. Soderberg, *J. Amer. Chem. Soc.*, 1963, **85**, 2402.

[22] J. E. Fleming and H. Lynton, *Chem. and Ind.*, 1960, 1415; S. C. Wallwork, *Proc. Chem. Soc.*, 1959, 311; F. S. Mathews and W. N. Lipscomb, *J. Amer. Chem. Soc.*, 1958, **80**, 4745.

increase to 122 ± 1°. The angles agree well with those found in the complex [Co(Me$_3$PO)$_2$(NO$_3$)$_2$] [21] and presumably result from the effect of co-ordination. The effect of co-ordination also significantly lengthens the O(21)–N(23) and O(22)–N(23) bond lengths [1.289(5) and 1.259(5) Å] relative to O(23)–N(23) [1.211(5) Å]. A similar lengthening of the N–O (co-ordinated *vs.* unidentate) bonds in the complexes [Ni(tri)(H$_2$O)$_2$NO$_3$]NO$_3$ (ref. 23) (tri = tribenzo[*b,f,j*][1.5.9]triazacyclododecine) and [{Cu-(C$_5$H$_5$NO)$_2$(NO$_3$)$_2$}$_2$] (ref. 24) has been found. Cotton and Soderberg,[21] however, have shown that the N–O bond lengths of the bidentate nitrato-groups in [Co-(Me$_3$PO)$_2$(NO$_3$)$_2$] remain equal at 1.22(3) Å, a value equal to the most probable value for the N–O bond lengths for unco-ordinated nitrate ions.[25] The Ni–O(21) and Ni–O(22) bond distances support the bidentate co-ordination of the nitrate group and compare favourably with analogous Co–O distances.[21]

(*b*) *Nitrate group*. As shown in Table 4, two of the N–O bonds in the ionic nitrate group are as expected, whilst N(3)–O(2) (1.154 Å) is inordinately short. The complex [Ni(tri)(H$_2$O)$_2$NO$_2$]NO$_3$ (ref. 23) also possesses one very short N–O (ionic) bond length of 1.15 Å, whilst the remaining N–O (ionic) bond lengths are 1.21 and 1.26 Å. The authors made no comment on this disparity. In the present structure, however, the thermal parameters of O(2) are much larger than those of any of the other atoms. We have considered that there may have been a NO$_3^-$/NO$_2^-$ equilibrium in the crystal and have allowed the occupancy factor of O(2) to vary in the least-squares refinement, but this has done little to improve the bond length or to reduce the thermal parameters. We can but attribute these disparities to some errors in the reflection data.

An analysis of intramolecular distances reveals no close contacts which could account for the observed distortions in the molecule, or for the possible disorder of the oxygen atom in the ionic nitrate group. There is no evidence for hydrogen bonding of the ionic nitrate group oxygen atoms to the hydrogen atoms of the amine groups.

We thank the U.S. Public Health Service, National Institutes of Health, and the Australian Research Grants Committee for financial support of this work.

[4/2352 *Received*, 11*th November*, 1974]

---

[23] E. B. Fleischer and E. Klem, *Inorg. Chem.*, 1965, **4**, 637.

[24] S. Scavincar and B. Matkovic, *Acta Cryst.*, 1969, **B25**, 2047.

[25] A. F. Wells, ' Structural Inorganic Chemistry,' 3rd edn., Oxford University Press, London, 1962, p. 627.