

## Reactions of Copper(II) and Nickel(II) Compounds of 6-Methyl-2-picolyamine with Acetone, Including an X-ray Structural Analysis of $[\text{Ni}(\text{C}_{20}\text{H}_{28}\text{N}_4)(\text{NO}_3)]\text{NO}_3$

DONALD F. COOK and E. DONALD MCKENZIE\*

Chemistry Department, The University, Sheffield S3 7HF, U.K.

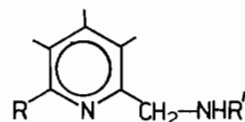
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### Abstract

The reaction with acetone of nickel(II) and copper(II) bis-chelated compounds of 6-methyl-2-pyridylmethylamine gives compounds of the quadridentate  $[\text{N}_4]$  ligand 2,6-diaza-1,7-bis-(6'-methyl-2'-pyridyl)-3,5,5-trimethyl-hept-2-ene(Q). In the nickel series also, a bis-chelated perchlorate of the terdentate ligand 2-aza-1-(6'-methyl-2'-pyridyl)-3-methyl-hex-2-ene-5-one was obtained. In the copper series, five-coordinate species  $[\text{Cu}(Q)\text{X}]\text{X}$  ( $\text{X} = \text{Br}, \text{I}, \text{NCS}$ ) and  $[\text{Cu}(Q)\text{X}]\text{ClO}_4$  ( $\text{X} = \text{Cl}$ ) were isolated. If left in acetone, these undergo further reaction, with increasing ease in the order  $\text{Cl} < \text{Br} < \text{I}$ . An intermediate formation of a transient brown colour suggests the possible involvement of a copper(I) intermediate. The nature of the products was established by an X-ray analysis of the structure of  $[\text{Ni}(Q)\text{NO}_3]\text{NO}_3$ . Crystals are orthorhombic,  $a = 20.36(2)$ ,  $b = 13.38(1)$ ,  $c = 8.226(5)$  Å, space group  $Pna2_1$ . Using two-circle diffractometer data (1598 reflections), the structure was solved by Patterson and Fourier methods, and refined by block diagonal least-squares methods to a final  $R$  of 0.030. The expected quadridentate ligand was found in the *cis-β* configuration about the metal, with coordination sphere completed by a bidentate nitrate. Bond-lengths and angles within the molecular cation were unexceptionable considering the small 'bite' of the chelated nitrate group of only  $59^\circ$ .

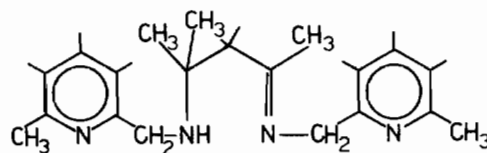
### Introduction

During an extended study [1] of the metal(II) compounds of the picolyamines I, with special reference to steric effects, we found that several 6-methyl-2-picolyamine (I)



I (= L for  $\text{R} = \text{Me}$ ,  $\text{R}' = \text{H}$ )

(for  $\text{R} = \text{Me}$ ,  $\text{R}' = \text{H}$ , labelled L) compounds of copper(II) reacted with acetone, apparently forming compounds of the quadridentate ligand II (labelled Q), in a reaction of the type described by Curtis and



II (= Q)

co-workers in a series of papers [2, 3].

To characterise the reaction in this case, the observations were extended to a range of copper(II) and nickel(II) compounds of 6-methyl-2-picolyamine, and the nature of the main reaction product has been confirmed by an X-ray analysis of one of the nickel compounds.

### Experimental

#### Preparation of Compounds

##### $[\text{CuQCl}]\text{ClO}_4$

The compound [1, 4]  $[\text{CuL}_2\text{Cl}]\text{ClO}_4$  (1 g) was suspended in acetone (100 ml) and the mixture heated to reflux (3 h). The green solution, so formed, did not deposit crystals on cooling. After several days, diethyl ether was used to precipitate the green product.

##### Reaction of $[\text{CuL}_2\text{Br}]\text{ClO}_4$

After 2 months at ambient temperature in contact with acetone, very little of this blue compound

\*Author to whom correspondence should be addressed. Present address: Chemistry Department, University of Queensland, St Lucia, Queensland, 4067, Australia.

[1, 4] had reacted. The filtrate was green, but contained insufficient material for recovery to be attempted.

#### [CuQCl]Cl

This compound was not fully characterised, being very soluble in acetone and not precipitated with diethyl ether. The reactant [1, 4]  $\text{CuL}_2\text{Cl}_2$  dissolved readily in acetone, giving a green solution. Evaporation of the solvents after 24 h gave a green powder which we assume to be an impure sample of the product.

#### [CuQBr]Br

When the blue compound [1, 4]  $\text{CuL}_2\text{Br}_2$  (1 g) was suspended in acetone (100 ml), a green solution formed quickly from the dissolution of part only of the solid. This solution within 10 min turned brown, but reverted to a green after several hours. The cycle (slowly  $\rightarrow$  brown, and then more slowly  $\rightarrow$  green) could be repeated by the addition of fresh samples of reagent acetone.

After several days, small green crystals of the product were noticed, but complete dissolution of the blue reactant and replacement by the green product took 2 months at  $\sim 20^\circ\text{C}$ .

Attempts to speed the preparation by heating were not successful. Powdered  $\text{CuL}_2\text{Br}_2$  in refluxing acetone gave the colour changes green  $\rightarrow$  brown  $\rightarrow$  green as above and green crystals began to separate after 1 h. However, before all of the blue reactant had dissolved at this temperature, the colour of the solution had changed to an olive-green, and the green product crystals also had redissolved. No crystals separated from the cooled solution and the material that precipitated when diethyl ether was added was a greenish-brown amorphous material with very broad IR bands. *Anal.* Found: C, 37.0; H, 4.0; N, 9.0; Br, 26.2%.

#### [CuQI]I

When the dark-brown  $\alpha$ -form [1] of  $[\text{CuL}_2]\text{I}$  was covered with acetone, a dark-brown solution formed immediately and an olive-green material began to separate. However, when the mixture was set aside overnight, further reaction occurred: all of the green material redissolved, the solution was dark-brown, and only a small quantity of light brown solid remained. *Anal.* Found: C, 28.4; H, 2.6; N, 7.5; I, 26.9%. The X-ray powder diffraction from that [1] of  $[\text{CuL}_2]\text{I}$ . Calcd: C, 38.7; H, 4.6; N, 12.9; I, 29.2%.

The olive-green quadridentate species noted above, was isolated using large crystals [1] of  $[\text{CuL}_2(\text{H}_2\text{O})]\text{I}_2$ . When these were suspended in acetone, the olive-green product soon formed as a finely-divided material, the suspension of which in acetone was readily separated from the large

crystals of the reactant. The product was filtered off immediately and washed with acetone.

All products were characterised by X-ray powder photography. The analytical data on three independent samples suggested approximately 25% contamination with a  $\text{Cu}(\text{I})$  species.

When the filtrate from the final separation of this olive-green material was set aside (1 week), the dark-brown solution contained a lacrymatory material, and a small amount of amorphous brown solid had separated. *Anal.* Found: C, 40.6; H, 3.3; N, 8.1; halide, negligible.

When brown [1]  $[\text{CuL}_2]\text{I}$  was suspended in acetone and  $\text{I}_2$  added, a deep-brown solution formed. However, this did not give the expected acetone reaction product: dark-brown crystals of  $\alpha$ - $[\text{CuL}_2]\text{I}$  were formed instead.

#### [CuQ(NCS)]SCN

The green compounds [1]  $[\text{CuL}_2(\text{NCS})_2]$  dissolved readily in acetone. An initial green solution turned brown  $\sim 15$  min after mixing, but within 30 min had reverted to a clear grass-green. After 24 h the product was precipitated with diethyl ether, giving a finely-divided yellow-green product. Some larger crystals were obtained when the mother liquors were set aside overnight.

#### Reaction of $\text{CuL}_2(\text{ClO}_4)_2$

When a suspension (1 g) in acetone (100 ml) was heated under reflux (24 h), much of the solid remained unreacted. A green solution did form in acetone (no brown intermediate was observed), but when this solution was evaporated, blue crystals of the starting material only were obtained.

In a second reaction, acetonitrile (30 ml) was added to the mixture. A deep blue solution formed readily, and this turned green when set aside overnight. On the addition of diethyl ether, a green gum formed. With repeated trituration, this eventually solidified, and the product (although green from some contamination) proved to be (IR spectra, X-ray diffraction, and analyses) the starting material  $\text{CuL}_2(\text{ClO}_4)_2$ .

#### [NiQ(NCS)<sub>2</sub>] and [NiQ(NO<sub>3</sub>)]NO<sub>3</sub>

Both products were prepared by heating the parent compounds [1, 5]  $\text{NiL}_2\text{X}_2$  (1 g) in acetone (100 ml) under reflux. Reaction was slow and both products crystallised from the hot solutions during the reaction. They were isolated after 4 days of refluxing.

#### [NiQL](ClO<sub>4</sub>)<sub>2</sub>

The tris-chelated [1, 5] perchlorate (1 g) dissolved readily in acetone (25 ml) at  $\sim 20^\circ\text{C}$ . Purple crystals of a compound, which appears to be  $[\text{NiQL}](\text{ClO}_4)_2$ , soon crystallised out. These were filtered off after  $1\frac{1}{2}$  h.

$$[\text{Ni}(\text{Q}(\text{py})_2)(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}]$$

The previous compound was dissolved in methanol, pyridine was added, and the new compound was precipitated with diethyl ether.

$$[\text{NiT}_2](\text{ClO}_4)_2$$

The bis-chelated perchlorate [1, 5]  $\text{NiL}_2(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ , slowly dissolved in acetone over a 5-day period. The originally blue solution turned brown after  $\sim 3$  days. The product was isolated by the addition of diethyl ether, and was recrystallised from methanol. X-ray powder photography was used to prove that the recrystallised and crude materials were of the same species.

### Physical Measurements

Details of the instruments used are in ref. [6].

### The X-ray Structure Analysis

Crystals of lilac  $[\text{Ni}(\text{Q})\text{NO}_3]\text{NO}_3$  were obtained directly from the acetone reaction mixture. Sampling relied on microscopic examination of what appeared to be a homogeneous product. The data crystal was mounted along the *c* axis, and had dimensions  $0.14 \times 0.15 \times 0.37$  mm.

### Crystal Data

$\text{C}_{20}\text{H}_{28}\text{N}_6\text{NiO}_6$ ,  $M = 507.2$ , orthorhombic,  $a = 20.36(2)$ ,  $b = 13.38(1)$ ,  $c = 8.226(5)$  Å,  $U = 2241(4)$  Å<sup>3</sup>,  $D_m = 1.50$  g cm<sup>-3</sup> (floatation),  $Z = 4$ ,  $D_c = 1.50$  g cm<sup>-3</sup>,  $F(000) = 1064$ . Space group  $Pna2_1$  ( $C_{2v}^9$ , No. 33) from systematic absences (photography). MoK $\alpha$  radiation,  $\lambda = 0.71069$  Å,  $\mu(\text{MoK}\alpha) = 9.15$  cm<sup>-1</sup>.

Cell dimensions were from a least squares analysis of the  $\omega$  positions of 60 general order reflections.

X-ray data with  $6.5 < 2\theta < 50^\circ$  were collected from a crystal mounted along the *c* axis on a Stöe Stadi-2 automatic diffractometer in the stationary-counter-moving-crystal mode, using graphite-monochromated MoK $\alpha$  radiation.

Angular step-scan ranges for the reflections were systematically varied to allow for variations in peak-width. A counting time of 1.0 s was used, generally for each  $0.01^\circ$  increment of scan. However, for scan ranges  $\geq 2.0^\circ$ , variable increments of scan were set so that the total number of equal steps for each scan did not exceed 200. Background counts were accumulated for 30 s at each extremity of the scan.

Reflections with intensity  $I < 3\sigma(I)$  were ignored, as were those with background differences  $\Delta > 3\sigma_B$ . Lorentz and polarisation corrections were applied, but no allowance was made for absorption or extinction. The complete set comprised 1598 reflections.

The structure was solved by conventional Patterson and Fourier techniques, and refinement, using

block-diagonal least-squares methods, proceeded smoothly to a final  $R$  of 0.030. Anisotropic thermal parameters were used for all non-hydrogen atoms; unit weights were used throughout; anomalous dispersion corrections [7] (both  $\Delta f'$  and  $\Delta f''$ ) were applied to all atomic scattering factors.

Hydrogen atoms, being observed in a difference Fourier at  $\sim 0.3$  eÅ<sup>-3</sup> were included (at 0.98 Å from C or N), but not varied, in the final refinement. The hydrogens for the various methyls were located by calculating the electron-density at regularly spaced points ( $10^\circ$  intervals) on the circle defined by the tetrahedral angle to the C–C vector and a distance 0.98 Å from the carbon. In all cases, these suggested localisation (restricted rotation) of the methyls. Accordingly, calculated positions were chosen for hydrogens on the best fit to the observed electron densities of sets of 3 hydrogens  $120^\circ$  apart. Fixed B's of 6.0 were used.

The final difference Fourier had a highest peak of 0.1 eÅ<sup>-3</sup> near the Ni atom.

Atomic scattering factors were taken from Vol. IV of International Tables [8]. Programmes used are part of the Sheffield X-ray system. The final structural parameters with estimated standard deviations, are listed in Table I. Structure factors are listed in a Table available from the Editor.

## Results and Discussion

A range of different anions was studied, since these can lead, through different reactivities and solubilities, to different reaction products. The various reactions attempted and the results are summarised in Table II. All solids were characterised by elemental analyses (C, H, N and halide or sulphur), IR spectra and X-ray powder photography. Listings of the analyses, and some IR and electronic spectral data are in Table IIa, available from the Editor.

Many of the reactants gave the metal(II) compounds of the *quadridentate ligand II*. Such products were readily characterised by the IR spectra: a sharp band appearing at  $\sim 1660$  cm<sup>-1</sup> characterising the azomethine group; and, in the NH region, the more complex spectra of the  $\text{-NH}_2$  species were replaced generally by a single sharp band in the region 3100–3300 cm<sup>-1</sup>, characterising the quadridentate with its single secondary amine. This 'band' was a doublet for  $[\text{Cu}(\text{Q})(\text{NCS})]\text{SCN}$ .

The electronic spectra (diffuse reflectance on the solids) characterise the nickel(II) species as octahedral. That of the nitrate, with its lack of splitting of the low energy bands, was consistent with the observed *cis*  $[\text{NiN}_4\text{O}_2]$  structure, although the first band was of much lower intensity than the second (ratio  $\sim 1:3$ ). The thiocyanate has a typical  $[\text{NiN}_6]$  spectrum. The copper(II) species

TABLE I. Final Atomic Parameters (fractional coordinates  $\times 10^4$ ) with e.s.d.s. in parentheses. The Anisotropic Thermal Parameters ( $\times 10^5$ ) are in the Form  $\exp[-h^2b_{11} + k^2b_{22} + l^2b_{33} + klb_{23} + hlb_{13} + hkb_{12}]$ . Hydrogen Positions ( $\times 10^3$ ) were Calculated at C-H and N-H = 0.98 Å.

Atom	$x/a$	$y/b$	$z/c$
Ni	1336.6(3)	2111.6(4)	2482.4(16)
O(1)	1495(2)	2598(3)	-42(5)
O(2)	980(2)	1216(3)	446(5)
O(3)	1176(2)	1672(4)	-2049(5)
O(4)	4576(3)	1349(5)	-710(10)
O(5)	4551(3)	2852(4)	-11(8)
O(6)	4050(2)	2395(5)	-2143(6)
N(1)	2110(2)	1094(3)	2594(7)
N(2)	931(2)	1200(3)	4112(5)
N(3)	574(2)	3125(3)	2495(8)
N(4)	1834(2)	3365(3)	3423(6)
N(5)	1213(2)	1822(3)	-590(6)
N(6)	4394(2)	2210(4)	-977(6)
C(1)	2885(3)	2013(5)	875(9)
C(2)	2703(3)	1112(4)	1838(8)
C(3)	3136(3)	318(5)	1926(8)
C(4)	2974(3)	-499(5)	2862(8)
C(5)	2384(3)	-518(4)	3654(8)
C(6)	1960(3)	291(4)	3528(7)
C(7)	1332(3)	304(4)	4450(8)
C(8)	66(4)	461(5)	5818(10)
C(9)	352(3)	1242(4)	4692(7)
C(10)	-112(3)	2070(5)	4250(8)
C(11)	152(3)	3147(4)	3996(7)
C(12)	-448(3)	3812(5)	3708(9)
C(13)	529(3)	3504(5)	5481(7)
C(14)	876(3)	4090(4)	2065(7)
C(15)	1570(2)	4176(3)	2715(7)
C(16)	1907(3)	5064(4)	2562(11)
C(17)	2541(3)	5103(5)	3139(9)
C(18)	2801(3)	4317(5)	3975(9)
C(19)	2427(3)	3443(5)	4138(8)
C(20)	2662(3)	2590(5)	5179(10)
H(1a)	254	252	99
H(1b)	330	228	127
H(1c)	293	183	-27
H(3)	356	33	135
H(4)	328	-106	296
H(5)	227	-111	431
H(7a)	108	-29	415
H(7b)	143	29	561
H(8a)	14	66	695
H(8b)	-41	40	561
H(8c)	28	-18	561
H(10a)	-33	187	323
H(10b)	-44	211	512
H(12a)	-72	382	469
H(12b)	-30	449	345
H(12c)	-70	355	280
H(13a)	24	351	643
H(13b)	90	305	568
H(13c)	69	418	529
H(14a)	89	415	88
H(14b)	61	463	253
H(16)	172	564	200
H(17)	279	572	304

(continued on facing page)

TABLE I (continued)

Atom	$x/a$		$y/b$		$z/c$	
H(18)	324		437		443	
H(20a)	276		284		627	
H(20b)	232		208		524	
H(20c)	306		230		470	
H(N3)	24		292		170	

	$b_{11}$	$b_{22}$	$b_{33}$	$b_{23}$	$b_{13}$	$b_{12}$
Ni	151(0)	306(0)	863(1)	89(2)	-9(2)	-13(1)
O(1)	295(2)	476(4)	1290(11)	205(11)	90(8)	-69(4)
O(2)	248(2)	476(4)	1611(12)	31(12)	-140(8)	-123(4)
O(3)	454(3)	1228(7)	1068(14)	-498(14)	-315(9)	514(7)
O(4)	756(4)	1115(8)	2877(22)	39(24)	422(18)	379(10)
O(5)	690(4)	846(6)	2929(22)	-101(22)	-771(16)	-495(8)
O(6)	339(2)	2225(11)	1644(19)	1374(23)	-251(10)	-151(9)
N(1)	179(2)	331(3)	1063(10)	-46(18)	-94(11)	24(4)
N(2)	230(2)	442(4)	767(11)	204(11)	-12(8)	-101(5)
N(3)	172(1)	396(4)	1033(9)	61(19)	-210(12)	55(4)
N(4)	152(2)	444(4)	1122(12)	-302(12)	45(8)	-25(5)
N(5)	264(2)	568(5)	890(11)	30(13)	-192(8)	200(5)
N(6)	259(2)	877(7)	1237(14)	255(17)	113(10)	-177(7)
C(1)	212(2)	511(6)	2064(20)	-169(20)	326(12)	34(7)
C(2)	178(2)	493(6)	1469(16)	-397(16)	-249(10)	87(6)
C(3)	225(3)	595(6)	1653(19)	-494(17)	-409(11)	261(7)
C(4)	408(3)	664(6)	1186(21)	-254(18)	-473(12)	445(8)
C(5)	442(4)	368(5)	1216(17)	221(17)	-246(14)	340(7)
C(6)	270(3)	345(5)	1053(14)	-107(15)	-189(11)	-21(6)
C(7)	347(3)	441(5)	1282(16)	512(16)	-10(13)	-14(7)
C(8)	375(4)	843(9)	2043(24)	626(25)	403(16)	-464(10)
C(9)	246(2)	522(6)	823(13)	-68(15)	34(10)	-272(6)
C(10)	208(2)	800(7)	1373(17)	-441(21)	210(11)	-80(8)
C(11)	173(2)	461(5)	1172(16)	-336(15)	42(9)	53(6)
C(12)	183(2)	869(8)	2055(22)	-581(24)	-42(13)	237(7)
C(13)	238(3)	634(7)	1086(16)	-379(17)	59(11)	-40(7)
C(14)	259(2)	314(5)	1640(21)	260(15)	-19(10)	111(6)
C(15)	244(2)	387(4)	881(14)	-110(15)	236(11)	7(5)
C(16)	356(3)	484(5)	1386(15)	-332(26)	263(19)	-258(6)
C(17)	384(3)	660(7)	1916(21)	-567(19)	791(14)	-488(8)
C(18)	203(3)	887(8)	2002(23)	-1356(24)	273(13)	-248(8)
C(19)	190(2)	690(7)	1279(16)	-835(18)	-127(10)	53(7)
C(20)	304(3)	667(7)	2223(22)	-639(23)	-698(15)	271(8)

are assigned five-co-ordinate structures on the basis of stoichiometry, electronic spectra, and parallels with a wide range of related compounds [9].

The quadridentate ligand in such compounds has been proven by an X-ray structural analysis of  $[\text{NiQ}(\text{NO}_3)]\text{NO}_3$ . The molecular geometry of the cation is shown, together with the atom labelling scheme, in Fig. 1. (Hydrogens attached to carbon are given the number of that atom).

The analysis showed the expected quadridentate  $[\text{N}_4]$  ligand, and in the *cis- $\beta$*  configuration. The octahedron of the high-spin  $[\text{NiN}_4\text{O}_2]$  species is completed by the oxygens of a bidentate nitrate.

The *cis- $\beta$*  configuration of the amine ligand is an obvious result of steric effects: the methyls of the

terminal pyridyls effectively prevent planar coordination, and the 'bend' occurs at the tetrahedral secondary nitrogen  $[\text{N}(3)]$ . The conformation of the six-membered mono-ene chelate ring is defined by the deviations of the atoms from the  $[\text{Ni}, \text{N}(2), \text{N}(3)]$  plane (Table IV).

Observed nickel-nitrogen bond lengths (Table III) are in the usual range for high-spin nickel(II), with no apparent lengthening of the Ni-N (pyridyl) bonds resulting from the bulkiness of the 6-Me groups. The nickel is not coplanar with the pyridyl groups: it is 0.18 Å out of the plane of the pyridyl of N(1) and 0.87 Å out of the plane of the pyridyl of N(4). The pyridyl of N(4) is much more significantly distorted than that of N(1) (Table V), a

TABLE II. The Reaction Products.<sup>a</sup>

Reactant	X	Conditions <sup>b</sup>	Acetone addition products
[CuL <sub>2</sub> X]ClO <sub>4</sub>	Cl	reflux (3 h)	Green [CuQL]ClO <sub>4</sub>
	Br	R.T. (3 mth)	—
CuL <sub>2</sub> X <sub>2</sub>	Cl	R.T. (24 h)	Green [CuQL]Cl
	Br	R.T. (2 mth) <sup>c</sup>	Green [CuQBr]Br
	I	R.T. (min)	Olive-green [CuQI]I
	NCS	R.T. (2 h)	Yellow-green [CuQ(NCS)]SCN
	ClO <sub>4</sub>	R.T. (2 mth) reflux	—
NiL <sub>2</sub> X <sub>2</sub> ·nH <sub>2</sub> O	NCS	reflux (4 day)	Lilac <i>cis</i> -[NiQ(NCS) <sub>2</sub> ]
	NO <sub>3</sub>	reflux (4 day)	Lilac [NiQ(NO <sub>3</sub> )]NO <sub>3</sub>
	ClO <sub>4</sub>	R.T. (5 day)	Lilac [NiT <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>
[NiL <sub>3</sub> ](ClO <sub>4</sub> ) <sub>2</sub>		R.T. (2 h)	Purple [NiQL](ClO <sub>4</sub> ) <sub>2</sub>

<sup>a</sup>L, Q and T are the ligands of the diagrams I, II and III. <sup>b</sup>Usually the solid reactant (1 g) was added to 100 ml acetone. R.T. = room temperature (15 → 20 °C). Further details for each are in the Experimental section. <sup>c</sup>The slowness of this reaction seems to be associated with the low solubility of the reactant. Some product was observed within 2 days.

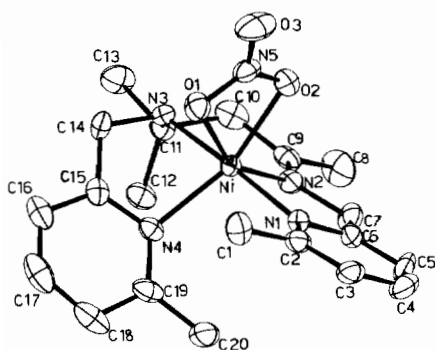


Fig. 1. The molecular cation and the atom-labelling scheme.

result of the configuration adopted. However, all such distortions are relatively small: the more rigid ligand framework seems to preclude the sorts of distortion found by Power *et al.* [10] in a closely related molecular species [Ni(2-methyl-8-aminoquinoline)<sub>2</sub>NO<sub>3</sub>]NO<sub>3</sub>.

In the present structure, however, the bulkiness (B-strain [11]) of the attached methyls may be responsible for the rather long Ni—O distances (for the chelating nitrate): at 2.201(4) and 2.185(4) Å, they are at the longer extremity of observed Ni—O (nitrate) distances (seven previous bidentate examples [10, 12]; sixteen independent distances;

TABLE III. Interatomic Distances (Å) and Angles (°) with e.s.d.s in Parentheses.

Ni—N(1)	2.084(5)	N(1)—Ni—N(2)	83.3(2)	N(2)—Ni—N(3)	95.0(2)
Ni—N(2)	1.991(5)	N(1)—Ni—N(3)	177.2(2)	N(2)—Ni—N(4)	116.1(2)
Ni—N(3)	2.062(5)	N(1)—Ni—N(4)	98.2(2)	N(2)—Ni—O(1)	151.3(2)
Ni—N(4)	2.105(4)	N(1)—Ni—O(1)	97.1(2)	N(2)—Ni—O(2)	92.5(2)
Ni—O(1)	2.201(4)	N(1)—Ni—O(2)	85.7(2)	N(3)—Ni—N(4)	80.6(2)
Ni—O(2)	2.185(4)	N(4)—Ni—O(1)	92.3(2)	N(3)—Ni—O(1)	85.5(2)
		N(4)—Ni—O(2)	151.4(2)	N(3)—Ni—O(2)	96.6(2)
		O(1)—Ni—O(2)	59.1(1)		
N(1)—C(2)	1.359(7)	Ni—N(1)—C(2)	129.9(4)	C(2)—N(1)—C(6)	118.3(5)
N(1)—C(6)	1.356(7)	Ni—N(1)—C(6)	111.8(4)		
C(2)—C(1)	1.489(9)	N(1)—C(2)—C(1)	118.5(5)	C(1)—C(2)—C(3)	119.5(5)
C(2)—C(3)	1.381(8)	N(1)—C(2)—C(3)	122.0(5)		
C(3)—C(4)	1.378(9)	C(2)—C(3)—C(4)	119.0(6)		
C(4)—C(5)	1.367(9)	C(3)—C(4)—C(5)	119.6(6)		
C(5)—C(6)	1.389(8)	C(4)—C(5)—C(6)	119.6(6)	N(1)—C(6)—C(5)	121.4(5)
C(6)—C(7)	1.486(8)	C(5)—C(6)—C(7)	120.3(5)	N(1)—C(6)—C(7)	118.4(5)
C(7)—N(2)	1.477(8)	C(6)—C(7)—N(2)	112.8(5)	C(7)—N(2)—Ni	113.3(4)
N(2)—C(9)	1.275(7)	C(7)—N(2)—C(9)	118.4(5)	Ni—N(2)—C(9)	127.6(4)
C(8)—C(9)	1.509(9)	N(2)—C(9)—C(8)	123.8(5)	C(8)—C(9)—C(10)	114.7(5)
C(9)—C(10)	1.501(8)	N(2)—C(9)—C(10)	121.5(5)		
C(10)—C(11)	1.552(8)	C(9)—C(10)—C(11)	120.2(5)	C(10)—C(11)—C(12)	106.6(5)

(continued on facing page)

TABLE III (continued)

C(11)–C(12)	1.528(9)	C(10)–C(11)–C(13)	111.0(5)	C(12)–C(11)–C(13)	110.2(5)
C(11)–C(13)	1.520(8)	C(10)–C(11)–N(3)	106.8(4)	C(12)–C(11)–N(3)	109.9(5)
N(3)–C(11)	1.504(7)	C(13)–C(11)–N(3)	112.2(4)	Ni–N(3)–C(11)	116.6(3)
N(3)–C(14)	1.475(7)	C(11)–N(3)–C(14)	114.7(4)	Ni–N(3)–C(14)	105.1(3)
C(14)–C(15)	1.514(8)	N(3)–C(14)–C(15)	111.8(4)		
C(15)–C(16)	1.377(8)	C(14)–C(15)–C(16)	119.9(5)	N(4)–C(15)–C(14)	117.6(4)
C(16)–C(17)	1.375(10)	C(15)–C(16)–C(17)	118.0(6)	N(4)–C(15)–C(16)	122.5(5)
C(17)–C(18)	1.361(10)	C(16)–C(17)–C(18)	120.6(7)		
C(18)–C(19)	1.405(9)	C(17)–C(18)–C(19)	118.9(6)		
C(19)–C(20)	1.503(9)	C(18)–C(19)–C(20)	121.2(6)	C(18)–C(19)–N(4)	120.4(6)
C(19)–N(4)	1.349(7)	C(20)–C(19)–N(4)	118.4(5)	C(19)–N(4)–C(15)	119.0(5)
N(4)–C(15)	1.344(7)	C(19)–N(4)–Ni	130.7(4)	C(15)–N(4)–Ni	107.0(3)
O(1)–N(5)	1.268(6)	O(1)–N(5)–O(2)	117.1(4)	Ni–O(1)–N(5)	91.5(3)
O(2)–N(5)	1.267(6)	O(2)–N(5)–O(3)	122.2(5)	Ni–O(2)–N(5)	92.2(3)
O(3)–N(5)	1.220(7)	O(1)–N(5)–O(3)	120.6(5)		
O(4)–N(6)	1.228(9)	O(4)–N(6)–O(5)	118.0(6)		
O(5)–N(6)	1.216(8)	O(5)–N(6)–O(6)	121.5(6)		
O(6)–N(6)	1.214(8)	O(4)–N(6)–O(6)	120.5(6)		

TABLE IV. Least-Squares Planes.<sup>a</sup>

	<i>l</i>	<i>m</i>	<i>n</i>	<i>d</i>	
Plane (1): N(1), C(2)–(6) [N(1) 0.016, C(2) –0.013, C(3) 0.005, C(4) 0.000, C(5) 0.003, C(6) –0.011, N(2) –0.019, C(1) –0.050, C(7) –0.077, Ni 0.179]	–0.4263	–0.4261	–0.7980	–4.1728	
Plane (2): N(4), C(15)–(19) [N(4) 0.044, C(15) –0.013, C(16) –0.029, C(17) 0.039, C(18) –0.008, C(19) –0.034, N(3) –0.178, C(20) –0.217, C(14) –0.058, Ni 0.871]	0.3843	–0.3271	–0.8634	–2.5133	
Plane (3): N(5), O(1)–(3) [N(5) 0.003, O(1) –0.001, O(2) –0.001, O(3) –0.001, Ni –0.086]	–0.8716	0.4896	–0.0234	–0.9500	
Plane (4): N(6), O(4)–(6) [N(6) –0.013, O(4) 0.004, O(5) 0.004, O(6) 0.005]	–0.8237	–0.1743	0.5395	–8.3061	
Plane (5): Ni, N(1), N(2) [C(6) –0.128, C(7) –0.092, C(9) –0.110]	0.4161	0.5303	0.7387	4.1395	
Plane (6): Ni, N(2), N(3) [C(7) –0.039, C(8) –0.258, C(9) –0.150, C(10) –0.277, C(11) 0.540, C(12) 0.269, C(13) 2.025, C(14) 0.670]	0.4475	0.5069	0.7368	4.1549	
Plane (7): Ni, N(3), N(4) [C(14) –0.843, C(15) –0.720, C(11) 1.343]	–0.2404	–0.2827	0.9286	0.4439	
Angles between planes (°)					
1–2	48.4	3–4	51.7	4–1	90.3
1–5	173.1	3–5	96.9	4–2	136.5
2–7	143.3	3–6	99.2		
5–6	2.2	3–7	87.2	4–5	92.1
5–7	64.1	3–1	79.5	4–6	93.4
6–7	64.3	3–2	118.3	4–7	41.6

<sup>a</sup>The equations are in the form  $lX + mY + nZ = d$  (where  $X$ ,  $Y$ , and  $Z$  are coordinates in Å referred to the axes  $a$ ,  $b$  and  $c$ ). Deviations (Å) of various atoms from these planes are listed in parentheses.

average Ni–O = 2.13 Å). In conformity, the O(1)–Ni–O(2) angles of 59.1(1)° is a little smaller than usual, although the O(1)–N(5)–O(2) angle, at 117.1(4)°, agrees well with the other structural

determinations. Another indication of steric effects in the bonding of this symmetrically bidentate nitrate group is a 'twist' of ~10° from the expected position in the octahedron: the 'twist' is shown,

TABLE V. Inter- and Intramolecular Close Contacts (Å).<sup>a</sup>

(a) The H-bond			
N(3)–O(5)	I <sup>b</sup>		3.209(8)
H(N3)–O(5)	II		2.24
N(3)–H(N3)···O(5)		168.5°	
(b) Others associated with H-bond			
N(3)–O(4)	I		3.403(9)
H(N3)–O(4)	II		2.59
N(3)–H(N3)···O(4)		140.1°	
N(5)–O(5)	I		3.444(8)
O(2)–O(5)	I		3.187(7)
O(6)–C(10)	III		3.497(9)
(c) Other intermolecular contacts			
O(1)–C(4)	IV		3.261(8)
O(2)–C(8)	V		3.109(9)
O(3)–C(7)	VI		3.429(8)
O(3)–C(8)	VI		3.291(9)
O(3)–C(9)	VI		3.216(7)
O(3)–C(13)	VI		3.446(8)
O(3)–C(17)	VII		3.356(9)
C(2)–C(17)	VII		3.366(9)
C(3)–C(12)	II		3.436(9)
C(3)–C(17)	VII		3.421(9)
C(3)–C(18)	VII		3.366(9)
C(4)–C(19)	VII		3.470(9)
(d) Intramolecular contacts			
O(1)–C(1)	3.029(8)	N(4)–C(11)	3.468(7)
O(1)–C(14)	2.931(7)	N(4)–C(13)	3.156(7)
O(1)–C(15)	3.102(6)	N(6)–C(1)	3.442(8)
O(2)–C(6)	3.456(7)	C(1)–C(19)	3.428(9)
O(6)–C(1)	3.472(9)	C(2)–C(20)	3.398(9)
N(1)–C(19)	3.451(8)	C(9)–C(13)	3.118(8)
N(1)–C(20)	3.130(9)	C(13)–C(14)	3.002(8)
N(2)–C(13)	3.383(7)	C(13)–C(15)	3.239(8)

<sup>a</sup>These refer to contacts, not specifically defined by the molecular framework, that is, those which might affect configuration and fine details of geometry. Only those referring to O, N, and C at distances <3.5 Å are listed. Except for the H-bond, hydrogen atom contacts are not included. <sup>b</sup>The second atom in each case is at a position defined by: I:  $x - 1/2, 1/2 - y, z$ ; II:  $1/2 + x, 1/2 - y, z$ ; III:  $1/2 + x, 1/2 - y, z - 1$ ; IV:  $1/2 - x, 1/2 + y, z - 1/2$ ; V:  $-x, -y, z - 1/2$ ; VI:  $x, y, z - 1$ ; VII:  $1/2 - x, y - 1/2, z - 1/2$ .

for example, in the angles at Ni which O(1) and O(2) make with N(1) and N(3) (Table III). It is a result of the close intermolecular contacts of O(1) with C(1), C(14), and C(15) (Table V).

Despite the preference of nickel(II) for the octahedral six-coordinate geometry over a five-coordinate one in the high-spin configuration, it seems perfectly happy to accept such strained four-membered chelate rings. Bidentate nitrates [13], nitrites [14] and carboxylates [15] seem to be a not uncommon feature of nickel stereochemistry.

There is a weak H-bond in the crystalline solid (Table V and Fig. 2): the secondary nitrogen N(3) is H-bonded to O(5) of the ionic nitrate [N(3)–O(5) = 3.209(8) Å]. Such bonding is reflected in the IR spectra: whereas [NiQ(NCS)<sub>2</sub>] has  $\nu_{\text{NH}}$  at 3306  $\text{cm}^{-1}$ , this nitrate has  $\nu_{\text{NH}}$  at 3180  $\text{cm}^{-1}$ .

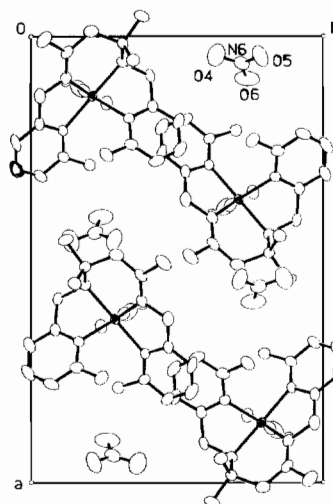
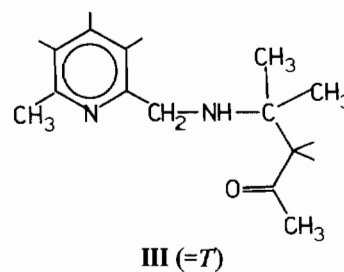


Fig. 2. The packing of the ions in the unit cell, projected down  $c$ .

#### The reactions with Acetone

The reactions of the nickel(II) compounds give the quadridentate ligand for those anions which readily bond covalently to the metal (NCS and  $\text{NO}_3$ ). However, for the perchlorate, with its greater reluctance to covalent bonding, a different species—the bis-terdentate  $[\text{Ni}T_2]^{2+}$  where  $T$  is the ligand **III**—is formed.



There are close parallels with the ethylenediamine and other systems studied by Curtis and co-workers [2, 16–18], allowing for the differences that this ligand ( $L$ ) has only one reactive amine group and the final products cannot be macrocyclic low spin species. The reaction of  $\text{NiL}_2(\text{ClO}_4)_2 \cdot n\text{H}_2\text{O}$  is slow, and  $\text{Ni}(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$  reacts [16] at a similar rate, producing a similar bis-terdentate product.

In another parallel with the ethylenediamine system [2], the tris species here reacts rapidly, but



instead of producing a macrocyclic planar spp., the picolylamine system retains the extra mole of unreacted ligand in an octahedral  $[N_6]$  cation  $[\text{Ni}(Q)(L)]^{2+}$ . Recrystallisation of this from pyridine gives a different product which appears to be  $[\text{Ni}(Q)(\text{py})_2]^{2+}$ .

Whilst the reactions of the nickel compounds were relatively straightforward, those of the copper compounds produced some interesting complications. Where acetone reaction products were obtained, these were always of the quadridentate ligand II; but further reactions were observed which were dependent on anion, and some intermediate colour changes were observed.

Of the reactants tried, only  $[\text{CuL}_2\text{Br}]\text{ClO}_4$  and  $\text{CuL}_2(\text{ClO}_4)_2$  failed to give an isolable acetone reaction product. In both cases, this may be associated with low solubility of the reactants, but we note that, despite its low solubility,  $[\text{CuLBr}]\text{Br}$  did react to give  $[\text{Cu}(Q)\text{Br}]\text{Br}$ . Perhaps this is an indication that a good co-ordinating anion is necessary for the reaction and that the concentration of  $\text{Br}^-$  in the attempted reaction of the bromoperchlorate is insufficient for the catalysis. It is tempting to think of five-co-ordinate  $[\text{CuN}_4\text{X}]^+$  intermediates, but we have [1] good evidence that  $[\text{CuL}_2(\text{NCS})_2]$  is six-co-ordinate in the solid.

When  $\text{CuL}_2(\text{ClO}_4)_2$  was refluxed with acetone, a green solution was obtained. Addition of ether produced a green oil, which took some time of trituration with ether before it solidified. The product was largely unchanged  $\text{CuL}_2(\text{ClO}_4)_2$ , but perhaps  $[\text{CuT}_2](\text{ClO}_4)_2$  was produced in the reaction and that this then was hydrolysed back to the starting material during the attempted isolation.

The various  $[\text{Cu}(Q)\text{X}]^+$  species undergo further reaction to undefined products in increasing order of anion  $\text{Cl} < \text{Br} < \text{I}$ . Such further reaction, for example, prevents the use of elevated temperatures to speed the reaction of  $\text{CuL}_2\text{Br}_2$ . Further details of these reactions are in the Experimental section.

Intermediate colour changes were noted for the reactions of the copper compounds. Generally, the reactants initially gave green solutions, but within 10 min, these turned brown for a time, reverting to a green within several hours. Such reversible colour changes could be reproduced a number of times by adding fresh acetone: the solutions turned brown immediately, then slowly reverted to green.

Whereas the reaction on the addition of fresh acetone to the reactants might signal the presence of some impurity (aldehyde?) in the acetone, this seems a less likely reason for the initial green  $\rightarrow$

brown  $\rightarrow$  green changes. Perhaps these colour changes are signaling a copper(I) intermediate here.

Pertinent to this are some observations with the iodo compounds.  $[\text{CuL}_2\text{I}]\text{I}$  was prepared by treating a suspension of  $[\text{CuL}_2]\text{I}$  in acetone with a slight excess of  $\text{I}_2$  in acetone. There was no sign of acetone reaction occurring in this mixture. Yet when the isolated brown  $[\text{CuL}_2\text{I}]\text{I}$  was suspended again in acetone, the olive-green  $[\text{Cu}(Q)\text{I}]\text{I}$  formed quite readily, and our preparations of the latter always seemed to contain 25% of a copper(I) species.

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