Crystal and Molecular Structure of 2-Acetylpyridine[9-(2-pyridyl)-4,8-diazadec-8-en-1-amine]nickel(II) Diperchlorate

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Crystals of the title compound (I) are monoclinic, space group $P2_1/c$, a = 16·591(10), b = 10·203(20), c = 16·164(10) Å, β = 102·65(3)°, Z = 4. The structure was refined by full-matrix least-squares to R 0·076 for 2343 unique reflexions measured by diffractometer. In the cation there is distorted octahedral co-ordination of nickel by the quadridentate ligand and a 2-acetylpyridine molecule in the keto-form. There is evidence for disorder of the perchlorate anions. Ni–N Distances are 2·07—2·09 Å for the quadridentate ligand; for the acetylpyridine, Ni–N 2·138(11), Ni–O 2·124(11), and C=O 1·236 (13) Å.

As part of a study of transition-metal complexes of Schiff-base ligands derived from acetylpyridines and triamines,[1,2] we have determined the structure of the title compound by single-crystal X-ray diffraction. Very few ligands have been synthesised wherein Schiff-base formation has occurred at only one end of a polyamine.[3] The title compound (I) is formed in excellent yield by an *in situ* synthesis,[2] and not by metal-catalysed partial hydrolysis of a preformed ligand;[3-5] probable reasons for this have been discussed.[2,6]

EXPERIMENTAL

The complex (I) was prepared by the method of ref. 2 in a yield of 85%. Crystals obtained by recrystallisation from water were triclinic. The monoclinic crystals used for the structure determination were grown by slow evaporation of the reaction mixture after removal of ethanol. Intensities were determined on a Stoe Stadi-2 two-circle diffractometer (layers $h0$—$11l$ and $hk0$—10) with Mo-K_α radiation and a graphite-crystal monochromator from two crystals (dimensions *ca.* 0·14 × 0·19 × 0·28 and 0·14 × 0·24 × 0·32 mm) mounted on fibres. Data were collected in an approximately 'constant-count' mode; where a prescan indicated that the count could not be achieved within a specified time, the reflexion was ignored. A stationary-background–ω scan–stationary-background technique was employed, with variable reflexion width, and with the background measurement time proportional to the step measurement time. Of a total of 7786 reflexions measured, 187 having $I < 3\sigma(I)$ were rejected. Data from different layers were placed on a common scale by linear least-squares, and equivalent reflexions averaged to give 2343 unique observed reflexions. Lorentz, polarisation, and absorption corrections were applied. Unit-cell dimensions were obtained from a least-squares fit to diffractometer zero-layer angle measurements for the two crystals.

RESULTS

Crystal Data.—$C_{20}H_{29}Cl_2N_5NiO_9$, M = 613·1, Monoclinic, a = 16·591(10), b = 10·203(20), c = 16·164(10) Å, β = 102·65(3)°, U = 2670 Å^3, D_o = 1·50, Z = 4, D_c = 1·52, $F(000)$ = 1252. Mo-K_α radiation, λ = 0·71069 Å, μ(Mo-K_α) = 9·82 cm^{-1}. Space group $P2_1/c$ from systematic absences: $h0l$ with l odd, $0k0$ with k odd.

Structure Solution and Refinement.—Interpretation of an E map obtained by multisolution Σ2 refinement gave co-ordinates for the nickel and chlorine atoms which were consistent with the Patterson function; the carbon, nitrogen, and oxygen atoms, and 19 of the 29 hydrogen atoms in the molecule, were located from successive difference electron-density syntheses. Anisotropic temperature factors for the nickel, chlorine, perchlorate oxygen, and methyl carbon atoms produced a significant decrease in the R index, but the use of an Ni^{2+} scattering factor caused no change in R, so complex neutral-atom scattering factors[7] were employed for all atoms to preserve the correct electron count. Methyl-group hydrogen atoms were omitted; the remaining hydrogens were inserted in geometrically calculated positions (assuming C–H 1·08, and N–H 0·99 Å) and the structure refined, using an overall hydrogen atom temperature factor, so that the C–H (or N–H) bonds remained constant in magnitude and direction but not necessarily location in the unit cell. The structure was refined by full-matrix least-squares with the weighting scheme $w = \Sigma[\sigma^2(N) + 0{\cdot}001N^2]^{-1}/[7{\cdot}91 + |F_o| + 0{\cdot}00718\,F_o{}^2]$, where N is the net peak count, and the summation is over equivalent reflexions. The refinement converged to $R' = \Sigma w^{\frac{1}{2}}|F_o - F_c|/\Sigma w^{\frac{1}{2}}F_o = 0{\cdot}081$, with a corresponding unweighted index R 0·076, for 216 independent parameters. The final difference electron-density synthesis did reveal several peaks close to the perchlorate oxygen and chlorine atoms, indicating perchlorate-group disorder; this is not unusual for perchlorates of large cations,[8] and may account for the high final R index. On the basis of the consistency of the data from the two crystals and our experience of other structures determined by the same techniques we would have expected a final R index in the range 0·04—0·05. Final parameters are given in Tables 1 and 2, bond lengths and angles are presented in Tables 3 and 4. Estimated standard deviations are random-error estimates calculated using the full covariance matrix, and include contributions from the errors in the unit-cell dimensions. Shortest non-bonded distances and final observed and calculated structure factors are listed in Supplementary Publication No. SUP 21236 (15 pp., 1 microfiche).‡

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

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TABLE 1

Fractional atomic co-ordinates (× 10^4), and isotropic temperature factors ($Å^2 \times 10^3$)

	x/a	y/b	z/c	U
Ni	2373(1)	9160(1)	3607(1)	
Cl(1)	4685(2)	3065(3)	1536(2)	
Cl(2)	856(2)	3691(3)	2877(2)	
O(1)	4977(5)	3920(10)	986(6)	
O(2)	5293(9)	2730(17)	2183(8)	
O(3)	4417(8)	1915(11)	1085(9)	
O(4)	3912(8)	3411(19)	1632(10)	
O(5)	1451(6)	2987(10)	2577(7)	
O(6)	503(10)	4526(18)	2262(10)	
O(7)	1146(12)	4078(15)	3692(10)	
O(8)	217(10)	2947(21)	2947(12)	
O(9)	2439(4)	7361(7)	2964(4)	70(2)
N(1)	1505(4)	8523(8)	4260(5)	62(2)
C(2)	1073(6)	7344(12)	4136(7)	79(3)
H(2)	1145	6703	3626	77(8)
C(3)	548(7)	6985(13)	4666(8)	94(4)
H(3)	207	6076	4572	77(8)
C(4)	476(7)	7811(13)	5285(8)	96(4)
H(4)	87	7521	5708	77(8)
C(5)	870(7)	8998(13)	5417(9)	95(4)
H(5)	789	9645	5922	77(8)
C(6)	1391(5)	9335(9)	4865(6)	60(3)
C(7)	1873(6)	10569(9)	4935(6)	63(3)
C(8)	1769(8)	11566(14)	5574(8)	
N(9)	2367(4)	10693(7)	4442(5)	55(2)
C(10)	2862(6)	11874(11)	4467(7)	71(3)
H(10)	3070	12180	5118	77(8)
H(10′)	2486	12637	4113	77(8)
C(11)	3630(7)	11644(12)	4086(7)	85(3)
H(11)	3972	10828	4415	77(8)
H(11′)	4008	12516	4193	77(8)
C(12)	3447(7)	11339(12)	3160(7)	82(3)
H(12)	2926	11920	2842	77(8)
H(12′)	3982	11583	2912	77(8)
N(13)	3247(4)	9933(8)	2985(5)	61(2)
H(13)	3730	9394	3256	77(8)
C(14)	3112(6)	9703(13)	2071(7)	84(3)
H(14)	3115	8658	1965	77(8)
H(14′)	3607	10151	1835	77(8)
C(15)	2324(8)	10237(15)	1590(9)	109(4)
H(15)	2307	10126	922	77(8)
H(15′)	2315	11266	1743	77(8)
C(16)	1541(7)	9614(13)	1766(8)	92(4)
H(16)	1017	10004	1317	77(8)
H(16′)	1569	8566	1686	77(8)
N(17)	1438(4)	9910(8)	2652(5)	63(2)
H(17)	1419	10873	2721	77(8)
H(17′)	908	9522	2716	77(8)
N(18)	3267(4)	8041(7)	4478(5)	55(2)
C(19)	3658(6)	8407(11)	5242(7)	67(3)
H(19)	3594	9407	5436	77(8)
C(20)	4168(6)	7521(13)	5828(7)	81(3)
H(20)	4474	7814	6461	77(8)
C(21)	4238(7)	6350(12)	5548(8)	81(3)
H(21)	4612	5653	5969	77(8)
C(22)	3867(6)	5943(11)	4763(7)	78(3)
H(22)	3954	4954	4561	77(8)
C(23)	3375(5)	6821(10)	4225(6)	60(3)
C(24)	2946(6)	6563(10)	3350(6)	65(3)
C(25)	3113(9)	5314(13)	2897(10)	

TABLE 2

Anisotropic temperature factors ($Å^2 \times 10^3$) *

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ni	46(1)	42(1)	48(1)	−2(1)	13(1)	2(1)
Cl(1)	62(2)	86(2)	78(2)	17(2)	16(2)	−10(1)
Cl(2)	70(2)	70(2)	100(3)	8(2)	30(2)	10(1)
O(1)	106(6)	141(8)	101(7)	42(6)	25(5)	−45(5)
O(2)	208(12)	288(18)	147(10)	129(12)	−75(10)	−71(13)
O(3)	212(12)	90(8)	191(12)	−6(8)	39(10)	−32(8)
O(4)	163(11)	303(19)	251(16)	1(15)	151(12)	23(11)
O(5)	127(7)	139(9)	162(9)	12(7)	69(7)	40(6)
O(6)	255(15)	315(21)	221(15)	163(15)	130(13)	201(16)
O(7)	319(20)	171(13)	159(12)	−64(11)	6(13)	76(12)
O(8)	239(15)	296(24)	287(21)	−11(17)	158(16)	−98(16)
C(8)	121(10)	108(10)	95(10)	−51(8)	20(8)	24(8)
C(25)	144(11)	69(8)	146(13)	−45(9)	68(10)	5(8)

* In the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{13}hla^*c^* + 2U_{12}hka^*b^*)]$.

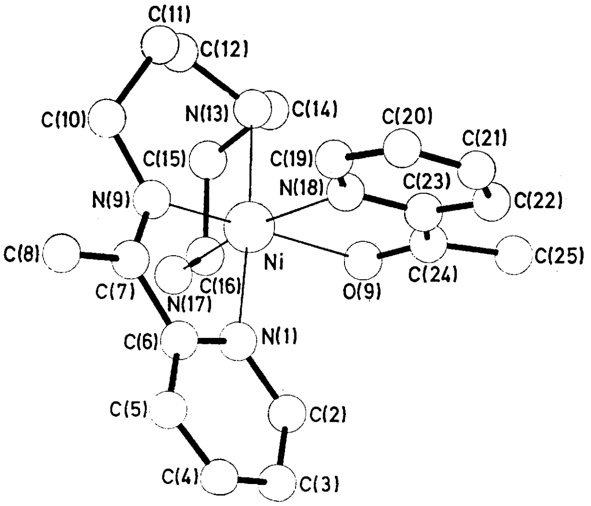

FIGURE 1 The cation, showing the atom numbering system used in the analysis

DISCUSSION

The nickel ion displays a somewhat distorted octahedral co-ordination. The C(24)–C(25) [1·52(2) Å] and C(24)–O(9) [1·24(1) Å] bond lengths confirm that the 2-acetylpyridine is co-ordinated in the keto-form. In 2-acetylpyridine hydrochloride the corresponding bond lengths are 1·49(4) and 1·25(3) Å respectively;[9] metal complexes of both the keto and enol forms of this ligand have been described,[10] but no crystal structures have been reported. In bis(pyridine-2-carboxamido)-nickel(II) [C=O 1·32(2), Ni–N 1·92(1), Ni–O 1·87(1) Å][11]

TABLE 3

Bond lengths (Å)

Ni–O(9)	2·124(11)	C(6)–C(7)	1·483(16)
Ni–N(1)	2·068(12)	C(7)–C(8)	1·487(18)
Ni–N(9)	2·068(11)	C(7)–N(9)	1·267(14)
Ni–N(13)	2·091(11)	N(9)–C(10)	1·454(15)
Ni–N(17)	2·080(11)	C(10)–C(11)	1·550(17)
Ni–N(18)	2·138(11)	C(11)–C(12)	1·494(18)
Cl(1)–O(1)	1·406(11)	C(12)–N(13)	1·486(17)
Cl(1)–O(2)	1·329(14)	N(13)–C(14)	1·465(16)
Cl(1)–O(3)	1·402(14)	C(14)–C(15)	1·471(18)
Cl(1)–O(4)	1·372(14)	C(15)–C(16)	1·529(20)
Cl(2)–O(5)	1·391(12)	C(16)–N(17)	1·509(16)
Cl(2)–O(6)	1·342(15)	N(18)–C(19)	1·317(14)
Cl(2)–O(7)	1·359(17)	N(18)–C(23)	1·334(14)
Cl(2)–O(8)	1·330(17)	C(19)–C(20)	1·442(17)
N(1)–C(2)	1·392(16)	C(20)–C(21)	1·292(19)
N(1)–C(6)	1·326(14)	C(21)–C(22)	1·349(17)
C(2)–C(3)	1·398(18)	C(22)–C(23)	1·383(16)
C(3)–C(4)	1·333(18)	C(23)–C(24)	1·462(16)
C(4)–C(5)	1·370(19)	C(24)–C(25)	1·524(18)
C(5)–C(6)	1·415(18)	C(24)–O(9)	1·236(13)

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the anionic ligand is more tightly bound than the neutral acetylpyridine ligand in (I) [Ni–N(18) 2·14(1), Ni–O(9) 2·12(1) Å] and the co-ordinated carbonyl group has correspondingly more single-bond character. Intermediate values [C=O 1·27(1), Ni–N 2·07(1), Ni–O 2·05(1) Å] are found[12] in bisaquabis(pyridine-2-carboxylato)nickel(II).

TABLE 4

Bond angles (°)

N(1)–Ni–O(9)	95·4(5)	H(11′)–C(11)–C(10)	108·1
N(9)–Ni–O(9)	168·9(3)	C(12)–N(13)–Ni	115·0(7)
N(9)–Ni–N(1)	78·5(5)	C(12)–C(11)–C(10)	115·1(10)
N(13)–Ni–O(9)	88·6(5)	C(12)–C(11)–H(11)	107·6
N(13)–Ni–N(1)	176·0(3)	C(12)–C(11)–H(11′)	108·4
N(13)–Ni–N(9)	97·6(5)	H(12)–C(12)–C(11)	109·2
N(17)–Ni–O(9)	93·7(5)	H(12′)–C(12)–C(11)	108·7
N(17)–Ni–N(1)	90·3(5)	N(13)–C(12)–C(11)	112·3(11)
N(17)–Ni–N(9)	95·6(5)	N(13)–C(12)–H(12)	108·5
N(17)–Ni–N(13)	89·3(5)	N(13)–C(12)–H(12′)	108·6
N(18)–Ni–O(9)	76·0(5)	H(13)–N(13)–Ni	99·0
N(18)–Ni–N(1)	87·5(5)	H(13)–N(13)–C(12)	109·1
N(18)–Ni–N(9)	94·4(5)	C(14)–N(13)–Ni	117·1(7)
N(18)–Ni–N(13)	93·6(5)	C(14)–N(13)–C(12)	108·9(9)
N(18)–Ni–N(17)	169·2(3)	C(14)–N(13)–H(13)	106·7
O(2)–Cl(1)–O(1)	110·5(8)	H(14)–C(14)–N(13)	108·2
O(3)–Cl(1)–O(1)	107·7(8)	H(14′)–C(14)–N(13)	109·2
O(3)–Cl(1)–O(2)	107·1(11)	C(15)–C(14)–N(13)	113·3(11)
O(4)–Cl(1)–O(1)	111·9(10)	C(15)–C(14)–H(14)	108·4
O(4)–Cl(1)–O(2)	123·0(11)	C(15)–C(14)–H(14′)	108·2
O(4)–Cl(1)–O(3)	94·4(11)	H(15)–C(15)–C(14)	108·4
O(6)–Cl(2)–O(5)	107·3(8)	H(15′)–C(15)–C(14)	107·1
O(7)–Cl(2)–O(5)	111·1(10)	C(16)–N(17)–Ni	114·2(7)
O(7)–Cl(2)–O(6)	122·5(12)	C(16)–C(15)–C(14)	116·2(13)
O(8)–Cl(2)–O(5)	112·1(12)	C(16)–C(15)–H(15)	107·8
O(8)–Cl(2)–O(6)	101·5(15)	C(16)–C(15)–H(15′)	107·8
O(8)–Cl(2)–O(7)	101·7(14)	H(16)–C(16)–C(15)	108·3
C(2)–N(1)–Ni	126·3(8)	H(16′)–C(16)–C(15)	109·2
H(2)–C(2)–N(1)	119·6	N(17)–C(16)–C(15)	111·8(11)
C(3)–C(2)–N(1)	120·5(12)	N(17)–C(16)–H(16)	108·8
C(3)–C(2)–H(2)	119·8	N(17)–C(16)–H(16′)	109·2
H(3)–C(3)–C(2)	121·1	H(17)–N(17)–Ni	108·6
C(4)–C(3)–C(2)	117·7(14)	H(17)–N(17)–C(16)	108·6
C(4)–C(3)–H(3)	121·2	H(17′)–N(17)–Ni	108·1
H(4)–C(4)–C(3)	117·8	H(17′)–N(17)–C(16)	107·9
C(5)–C(4)–C(3)	123·9(14)	C(19)–N(18)–Ni	126·5(8)
C(5)–C(4)–H(4)	118·3	H(19)–C(19)–N(18)	118·8
C(5)–C(6)–N(1)	121·2(11)	C(20)–C(19)–N(18)	122·5(11)
H(5)–C(5)–C(4)	121·6	C(20)–C(19)–H(19)	118·8
C(6)–N(1)–Ni	114·0(7)	H(20)–C(20)–C(19)	122·4
C(6)–N(1)–C(2)	119·7(10)	C(21)–C(20)–C(19)	115·8(12)
C(6)–C(5)–C(4)	116·9(14)	C(21)–C(20)–H(20)	121·8
C(6)–C(5)–H(5)	121·5	H(21)–C(21)–C(20)	118·1
C(7)–N(9)–Ni	115·5(7)	C(22)–C(21)–C(20)	123·8(13)
C(7)–C(6)–N(1)	115·2(9)	C(22)–C(21)–H(21)	118·1
C(7)–C(6)–C(5)	123·5(11)	C(22)–C(23)–N(18)	120·8(10)
C(8)–C(7)–C(6)	119·4(11)	H(22)–C(22)–C(21)	120·6
N(9)–C(7)–C(6)	116·7(10)	C(23)–N(18)–Ni	114·7(7)
N(9)–C(7)–C(8)	123·9(11)	C(23)–N(18)–C(19)	118·6(9)
C(10)–N(9)–Ni	124·1(7)	C(23)–C(22)–C(21)	118·5(12)
C(10)–N(9)–C(7)	120·3(9)	C(23)–C(22)–H(22)	120·9
H(10)–C(10)–N(9)	108·9	C(23)–C(24)–O(9)	120·2(10)
H(10′)–C(10)–N(9)	109·0	C(24)–C(23)–N(18)	113·2(10)
C(11)–C(10)–N(9)	111·9(10)	C(24)–C(23)–C(22)	126·0(11)
C(11)–C(10)–H(10)	108·4	C(24)–O(9)–Ni	115·1(7)
C(11)–C(10)–H(10′)	109·2	C(25)–C(24)–O(9)	118·9(11)
H(11)–C(11)–C(10)	108·1	C(25)–C(24)–C(23)	120·9(11)

The N(1),Ni,N(9) five-membered and the N(9),Ni,N(13) six-membered chelate rings can be compared with those in (II) Ni(L)Br_2,H_2O,[13] where the macrocyclic ligand, L, is produced by employing 2,6-diacetylpyridine in the *in situ* preparation.[1,14] In (II) there is approximately square-pyramidal co-ordination of nickel, with shorter Ni–N distances [1·81(1), 1·91(1), and 1·93(2) Å]; most of the strain is born by the five-membered chelate rings, as shown by the bond-angle deviations from those in (I), where the open-chain ligand possesses more degrees of freedom. The six-membered chelate ring in both compounds has the chair conformation, as displayed by the parent triamine in the structure of bis[di(3-aminopropyl)amine]nickel(II) diperchlorate,[15] in which the Ni–N bond lengths corresponding to Ni–N(13) and Ni–N(17) in (I) are 2·23(2) and 2·15(2) Å, indicating that the influence of the other co-ordinating groups is important.

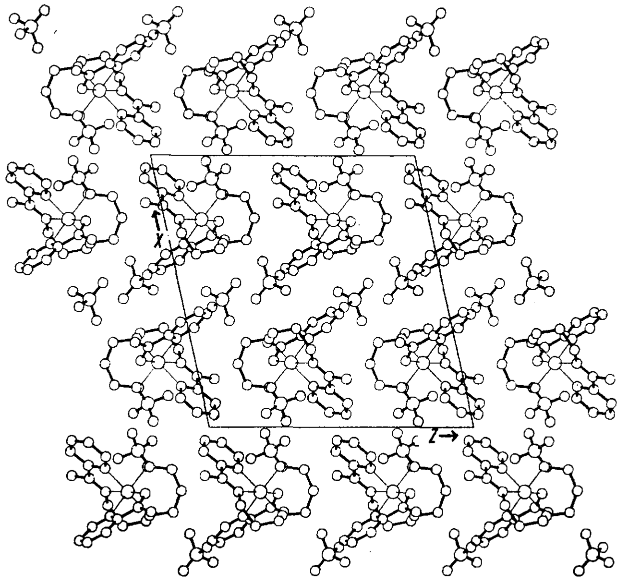

FIGURE 2 Projection of the structure perpendicular to *Y*

Calculations were performed on the Cambridge University IBM 370/165 computer with programs written by G. M. S., and the structural diagrams were drawn by use of the program PLUTO written by Dr. S. Motherwell. We thank the S.R.C. for funds to purchase a diffractometer, and for a maintenance grant (to D. A. S.), and also thank Dr. R. H. Prince for useful discussions.

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