Crystal and Molecular Structure of Bis[(acetato)aquo(pyridine)]nickel(II)

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Crystals of the title compound are orthorhombic, space group *Pbca*, $Z = 4$, $a = 8{\cdot}938(3)$, $b = 14{\cdot}983(6)$, $c = 12{\cdot}599(5)$ Å. The molecular structure was solved from diffractometer data by Fourier techniques, and refined by least-squares methods to R 0·08 for 865 independent reflections. It consists of a centrosymmetric monomer with the nickel(II) ion octahedrally co-ordinated by the pyridine and water ligands and by two unidentate acetate groups. Hydrogen bonds link the unco-ordinated oxygen atoms of the acetate ions to water molecules in the same and neighbouring molecules. Ni–N is 2·100, Ni–O(water) 2·102, Ni–O(AcO) 2·050 Å. The angles around the nickel atom are all *ca.* 90°. The nickel–ligand bond lengths are compared to those in related six-co-ordinate nickel(II) complexes.

As part of a study of tetragonally distorted octahedral complexes of first-row transition elements with carboxylate groups and other ligands we have repeated Davis and Logan's preparation [1] of the complex $Ni(py)_2(H_2O)_2(AcO)_2$ (py = pyridine). We now describe the results of an X-ray diffraction analysis of the crystal and molecular structure of this compound. Studies [2] of the spectroscopic and magnetic properties of this and related compounds will be reported later.

EXPERIMENTAL

The compound was prepared as described previously [1] and recrystallised from chloroform as diamond-shaped plates, bounded by {111} and {010}.

Crystal Data.—$C_{14}H_{20}N_2NiO_6$, $M = 370{\cdot}87$, Orthorhombic, $a = 8{\cdot}938(3)$, $b = 14{\cdot}983(6)$, $c = 12{\cdot}599(5)$ Å, $U = 1687$ Å^3, $D_m = 1{\cdot}38$, $Z = 4$, $D_c = 1{\cdot}387$, $F(000) = 766$. Space group *Pbca* from systematic absences. Cu-K_α radiation, $\lambda = 1{\cdot}5418$ Å; $\mu(\text{Cu-}K_\alpha) = 17{\cdot}84$ cm^{-1}. Cell dimensions were calculated from 2θ measurements for axial reflections.

Intensity data were recorded for a crystal of dimensions *ca.* 0·4 × 0·6 (diamond diagonals) × 0·15 mm, mounted about the a axis, by use of a General Electric XRD 6 diffractometer equipped with manual goniometer, pulse-height analyser, and scintillation counter. The stationary-crystal–stationary-counter technique was used, with a counting time of 10 s. Backgrounds were taken from a

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[1] T. L. Davis and A. V. Logan, *J. Amer. Chem. Soc.*, 1940, **62**, 1276.

[2] J. Drew and P. Thornton, unpublished results.

graph prepared by measuring individual backgrounds for some 200 reflections over the range of 2θ used. Two standard reflections were checked regularly during data collection and these showed a small drop in intensities which was allowed for during data processing. A total of 1250 reflections with $2\theta \leqslant 120°$ were measured of which 865 were considered observed having $I_{\text{net}} > 3\sigma$ where $\sigma = [I_{\text{net}} + 2\ \text{Background} + (0{\cdot}03\ I_{\text{net}})^2]^{\frac{1}{2}}$. Although the absorption coefficient for the compound was small, a fairly large crystal was used, and so absorption corrections were applied.

Structure Analysis.—The requirement that the nickel atom is sited at a centre of symmetry precluded the need for a Patterson synthesis. The structure was solved from two electron-density syntheses, computed with signs determined (*a*) by the nickel atom only and (*b*) with the addition of the three light atoms assumed to form the asymmetric portion of the octahedral co-ordination. Refinement by full-matrix least-squares was quite straightforward, terminating at *R* 0·10 with isotropic temperature factors and *R* 0·08 when anisotropic factors were used for the Ni, N, C, and O atoms. Hydrogen atoms of the pyridine molecule were included in the structure-factor calculations (assuming B_{iso} 5·0 Å^2) but were not refined. During the last cycles of refinement a weighting scheme of the type $\sqrt{\omega} = 1$ for $F_o < F^*$ and $\sqrt{\omega} = F^*/F_o$ for $F_o > F^*$ was used, with F^* set at 30·0. At the end of refinement, all parameter shifts were $< 0{\cdot}2\sigma$. The final list of positional and thermal parameters are given in Tables 1 and 2. Final values of observed and calculated structure factors are listed in Supplementary Publication No SUP 20418 (5 pp., 1 microfiche *).

TABLE 1

Fractional atomic co-ordinates *

	x	*y*	*z*
Ni	0·0000	0·0000	0·0000
O(1)	0·2465(6)	−0·0274(4)	0·2034(4)
O(2)	0·2210(6)	0·0199(4)	0·0361(4)
O(3)	−0·0382(6)	−0·0682(4)	0·1436(4)
N	0·0491(7)	−0·1244(4)	−0·0676(5)
C(1)	0·1842(10)	−0·1409(6)	−0·1107(7)
C(2)	0·2227(12)	−0·2228(7)	−0·1532(9)
C(3)	0·1172(14)	−0·2910(7)	−0·1506(9)
C(4)	−0·0198(12)	−0·2762(6)	−0·1068(10)
C(5)	−0·0487(10)	−0·1922(6)	−0·0657(8)
C(6)	0·2911(8)	0·0122(5)	0·1224(7)
C(7)	0·4416(10)	0·0615(7)	0·1270(8)
H(1)	0·2614	−0·0927	−0·1134
H(2)	0·3397	−0·2380	−0·1539
H(3)	0·1464	−0·3564	−0·1531
H(4)	−0·0715	−0·3300	−0·1040
H(5)	−0·1821	−0·1746	−0·0624

* Estimated standard deviations are given in parentheses throughout this paper.

All calculations were performed on the University of London CDC 6600 computer using the '*X*-Ray '67 ' system,[3] except the absorption corrections. These were computed using the program ' ICABS ', a local version prepared by Dr. P. G. H. Troughton of Imperial College of the original program of Coppens *et al.*[4] Scattering factors for neutral atoms were taken from ref. 5.

TABLE 2

Anisotropic thermal parameters (× 10^4) *

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Ni	76(2)	43(1)	53(1)	0	0	−1
O(1)	55(7)	56(4)	42(4)	−17(4)	−6(5)	14(3)
O(2)	46(6)	43(3)	34(3)	1(4)	−3(4)	−2(2)
O(3)	66(7)	34(3)	37(3)	−6(4)	0	5(3)
N	65(9)	27(3)	41(5)	2(4)	3(5)	−5(3)
C(1)	98(13)	45(5)	54(7)	14(7)	8(8)	−10(5)
C(2)	138(17)	56(6)	83(8)	37(9)	−4(9)	−20(6)
C(3)	207(22)	39(5)	89(10)	32(9)	−41(11)	−32(6)
C(4)	136(16)	32(5)	98(9)	9(7)	−27(10)	−16(5)
C(5)	91(12)	32(4)	70(7)	3(6)	−17(8)	6(5)
C(6)	42(10)	29(4)	60(7)	−1(5)	4(6)	−8(4)
C(7)	65(11)	71(7)	60(7)	−35(7)	−13(7)	6(6)

For all hydrogen atoms isotropic thermal parameter, *B* 5·0 Å^2.

* Values in the temperature factor expression: $\exp -(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + 2b_{12}hk + 2b_{13}hl + 2b_{23}kl)$.

DISCUSSION

The bond lengths and angles together with standard deviations in the molecule are shown in Table 3, and the atom labelling in the Figure. The compound is monomeric, with the nickel atom at a centre of symmetry, co-ordinated by both pyridine and both water molecules and by the two acetate ions, which are unidentate.

TABLE 3

Bond lengths and angles

(*a*) Bond lengths (Å)

Ni–N	2·100(6)	C(4)–C(5)	1·382(12)
Ni–O(2)	2·050(5)	C(5)–N	1·339(10)
Ni–O(3)	2·102(5)	C(1)–N	1·344(10)
O(2)–C(6)	1·260(9)	C(1)–H(1)	1·000(9)
O(1)–C(6)	1·247(10)	C(2)–H(2)	1·069(10)
C(6)–C(7)	1·534(11)	C(3)–H(3)	1·019(10)
C(1)–C(2)	1·382(14)	C(4)–H(4)	0·932(9)
C(2)–C(3)	1·389(15)	C(5)–H(5)	1·187(8)
C(3)–C(4)	1·352(15)		

(*b*) Contact distances (Å) *

O(3) · · · O(1)	2·723(7)	O(3′) · · · O(1)	2·791(7)

(*c*) Bond angles (°)

O(2)–Ni–O(3)	92·0(2)	C(1)–N–C(5)	117·1(7)
N–Ni–O(2)	90·9(2)	N–C(1)–C(2)	122·8(8)
N–Ni–O(3)	87·3(2)	C(1)–C(2)–C(3)	117·8(9)
Ni–O(2)–C(6)	131·0(5)	C(2)–C(3)–C(4)	120·2(9)
O(2)–C(6)–O(1)	126·4(6)	C(3)–C(4)–C(5)	117·9(7)
O(2)–C(6)–C(7)	115·1(7)	C(4)–C(5)–N	124·0(8)
O(1)–C(6)–C(7)	118·5(7)		

* Primed atoms are related to unprimed atoms whose coordinates are listed in Table 1 by the symmetry operation $\frac{1}{2} + x, y, \frac{1}{2} - z$

Comparison with other tetragonally distorted six-coordinate nickel(II)–pyridine complexes shows that the Ni–N bond length [2·100(6) Å] is possibly significantly shorter than that [2·112(5) Å] found[6] in $\text{Ni(py)}_2\text{(acac)}_2$

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* See Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. are supplied as full size copies).

[3] ' *X*-Ray '67 ' System of Crystallographic Programs, eds. J. M. Stewart, F. A. Kundell, and J. C. Baldwin, University of Maryland Technical Report 67—58, 1967; revised July 1970.

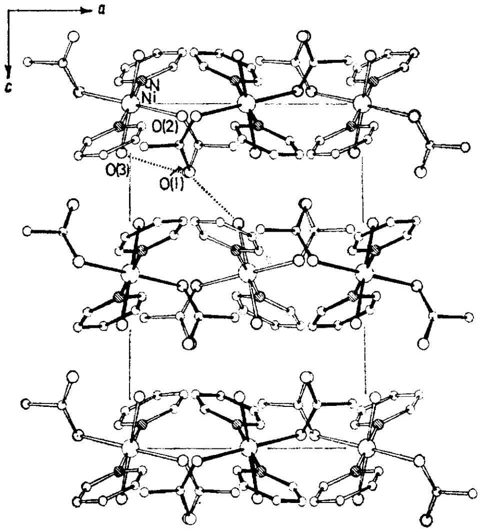
[4] P. Coppens, L. Leiservwitz, and D. Rabinowich, *Acta Cryst.*, 1965, **18**, 1035.

[5] ' International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

[6] R. C. Elder, *Inorg. Chem.*, 1968, **7**, 2316.

(acac = acetylacetonate). If this difference is meaningful it could be rationalised by considering that the acetylacetonate ion in the latter complex interacts more strongly with the Ni^{2+} ion than do acetate and water. There would then be a smaller residual positive charge remaining on the metal for attracting the pyridine ligands, which would therefore not be held so closely to the nickel as in the aquoacetate.

It is less easy to make a similar comparison with the Ni–N distance [7] of 2·11 Å in $Ni(py)_2[(EtO)_2PS_2]_2$, but the bidentate anion may well exert a greater interaction with the metal ion than do acetate and water. Spectroscopic confirmation of this is complicated by the nephelauxetic effect of the sulphur atoms and the distortion of the NiN_2S_4 chromophore from D_{4h} to D_{2h} symmetry by the small S–Ni–S angle of 81°.



Crystal structure of $Ni(py)_2(H_2O)_2(AcO)_2$ projected along the *b* axis. Hydrogen bonding is indicated by dotted lines

Ni–N Bond lengths of 2·00 and 2·03 Å have been reported [8,9] for $Ni(py)_4Cl_2$ and $Ni(py)_4(NCS)_2$ respectively, although one would expect, on a similar argument to that used in the above comparison with $Ni(py)_2(acac)_2$, that the Ni–N distance would be longer for these compounds than for $Ni(py)_2(H_2O)_2(AcO)_2$. The structures for the tetrakispyridine complexes were obtained by two-dimensional methods and may well need revision.

Ni–O distances in carboxylate complexes vary greatly, from 1·98 Å in a five-co-ordinate complex [10] to 2·18 Å in the bis(glycylglycinato)nickel(II) anion,[11] but no consistent trend can be seen. The chief complicating factors are that most of the complexes are of amino-acids or other ligands possessing another co-ordinating group in addition to carboxylate, and that hydrogen bonding occurs in the majority of the compounds and possibly affects the bond lengths. The only nickel(II) carboxylate complex containing unidentate non-bridging carboxylate ligands for which a crystal structure has been reported is $Ni(H_2O)_4(AcO)_2$, in which the Ni–O(acetate) bond length was found [12] to be 2·067(3) Å. The difference between this value and ours [2·050(5) Å] is, again, possibly significant. In the tetrahydrate both carboxylate oxygens are hydrogen bonded, but in $Ni(py)_2(H_2O)_2(AcO)_2$ only the nonco-ordinated oxygen is hydrogen bonded, and the co-ordinated oxygen is freer to approach the nickel atom more closely.

Hydrogen bonding may also be invoked to account for the scatter of reported nickel–water bond lengths from 1·991 in $[Ni(H_2O)_2\{[CH_2]_4(NNO_2)_2\}]$ [13] to 2·167 Å in $[Ni(H_2O)_2(NH_2\{CH_2\}_2CO_2)_2]$.[14] Our distance (2·102 Å) is rather longer than the reported [15] mean (2·08 Å). Each water molecule is involved in two hydrogen bonds, one (2·723 Å) to an unco-ordinated acetate oxygen in the same molecule, and one (2·791 Å) to a similar oxygen in a neighbouring molecule (Figure). Thus both lone pairs on the unco-ordinated oxygen are used in hydrogen bonds, one intra- the other inter-molecular, and each molecule is joined to two neighbours through hydrogen bonds.

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