Crystal and Molecular Structures of Bisbenzoatobis(2-methylpyridine)-nickel(II) and Bisbenzoatobis(quinoline)nickel(II)

By **Michael B. Hursthouse,*** Department of Chemistry, Queen Mary College, Mile End Road, London E1 4NS
Douglas B. New, Department of Science and Humanities, Braintree College of Further Education, Church Lane, Braintree CM7 5SN

The crystal and molecular structures of the title compounds have been determined from single-crystal *X*-ray data measured on a manual diffractometer. The 2-methylpyridine complex (I) is monoclinic, space group $P2_1/a$, with a = 16.70(3), b = 14.42(2), c = 11.39(2) Å, β = 120.36(2)°, and Z = 4; the quinoline complex (II) is also monoclinic, space group $P2_1/a$ with a = 14.06(2), b = 9.75(2), c = 10.36(2) Å, β = 113.3(2)°, and Z = 2. Structures were solved by the heavy-atom method and least-squares refinement has reached R 0.057 for (I) (1 558 significant reflections) and 0.047 for (II) (1 210 reflections). Both complexes are monomeric with distorted octahedral co-ordination geometries but compound (I) has a *cis*-configuration whilst (II) has a centrosymmetric *trans*-configuration. The Ni–O and Ni–N distances in the two complexes fall in the narrow ranges 2.083—2.127 and 2.072—2.087 Å. The adoption of the two different structures is suggested to be due to solid-state packing effects.

CATTERICK and Thornton have recently described the synthesis, magnetic properties, and electronic spectra of a series of complexes of nickel(II) carboxylates of general formula $[Ni(O_2CR)_2L_2]$ (L = pyridine and related ligands).[1] The experimental data indicated the adoption by most of the complexes of a monomeric structure with a *trans*-configuration, except in the case of $[Ni(O_2CPh)_2(2\text{-Mepy})_2]$ which seemed to have a *cis*-configuration. In order to confirm these assignments, and to explore the possible reasons for the adoption of the *cis*-structure in the one instance, we have determined the structure of the 2-methylpyridine complex and also of the complex $[Ni(O_2CPh)_2(quin)_2]$, for which a *trans* configuration was indicated.

EXPERIMENTAL

Crystal Data.—(I), $C_{26}H_{24}O_4N_2Ni$, M = 487.2, Monoclinic, a = 16.70(3), b = 14.42(2), c = 11.39(2), β = 120.36(2)°, U = 2 366(5) Å^3, D_m = 1.40 (by flotation), Z = 4, D_c = 1.37, F(000) = 1 016. Space group $P2_1/a$ Cu-K_α radiation, λ = 1.5418 Å, μ(Cu-K_α) = 14.2 cm^{-1}.

(II) $C_{32}H_{24}O_4N_2Ni$, M = 559.3, Monoclinic, a = 14.06(2), b = 9.75(2), c = 10.36(2), β = 113.32(2)°, U = 1 303(4) Å^3, D_m = 1.6, Z = 2, D_c = 1.42, F(000) = 580. Space group $P2_1/a$, Cu-K_α radiation, μ(Cu-K_α) = 14.5 cm^{-1}.

For both analyses the crystals were set with b axes parallel to the ϕ axis of a General Electric manual diffractometer. Cell dimensions were determined by careful measurement of axial 2θ values and the ϕ angle interval between a^* and c^*. Intensity data were collected by the stationary-crystal–stationary-counter technique, a counting time of 10 s, and Cu-K_α radiation in a manner described previously.[2] For compound (I) 2 029 independent reflections ($\theta \leqslant 45°$) were measured, of which 1 558 were considered significant having $I > 2.58\ \sigma(I)$. For compound (II) 1 754 independent reflections ($\theta \leqslant 55°$) were measured of which 1 210 were considered significant.

Both structures were solved by the application of the standard heavy-atom method and refined by full-matrix least-squares. Methyl hydrogen positions in compound (I) were determined from a difference-Fourier map. All other hydrogen atoms were included at calculated positions assuming C–H 1.08 Å and an isotropic temperature factor of 1.2 times the average value of the U_{ii} terms for the carbon atoms to which they were attached. With all non-hydrogen atoms assigned anisotropic temperature factors compound (I) gave a final stationary R value of 0.057, and compound (II) 0.045. During the latter stages of refinement, a Hughes type weighting scheme[3] was used with a value for F^* of 30 (on an absolute scale) for compound (I), and 50 for compound (II) giving the best agreement analysis.

TABLE 1

Final atomic parameters (× 10^4) for (I), with estimated standard deviations in parentheses here and throughout this paper

Atom	x/a	y/b	z/c
Ni	5 938(9)	18 790(10)	−9 351(13)
O(1)	548(4)	1 357(4)	754(6)
O(2)	1 720(4)	2 197(4)	1 026(5)
C(11)	1 327(7)	1 744(7)	1 536(10)
C(12)	1 789(6)	1 640(6)	3 027(9)
C(13)	1 293(6)	1 419(7)	3 657(10)
C(14)	1 756(8)	1 352(8)	5 082(12)
C(15)	2 695(9)	1 483(8)	5 835(10)
C(16)	3 187(7)	1 686(7)	5 202(11)
C(17)	2 745(6)	1 796(7)	3 805(10)
O(3)	741(4)	2 933(4)	−2 079(6)
O(4)	5(4)	3 197(4)	−988(6)
C(21)	322(6)	3 474(7)	−1 721(10)
C(22)	203(6)	4 467(6)	−2 166(9)
C(23)	532(7)	4 771(9)	−3 010(12)
C(24)	402(9)	5 710(11)	−3 400(14)
C(25)	20(10)	6 310(9)	−2 939(15)
C(26)	−318(9)	6 009(10)	−2 124(13)
C(27)	−227(7)	5 076(9)	−1 734(10)
N(1)	−710(5)	1 403(5)	−2 426(8)
C(1)	−1 336(7)	1 373(7)	−1 981(10)
C(2)	−2 216(8)	1 126(9)	−2 709(14)
C(3)	−2 547(8)	909(9)	−4 074(17)
C(4)	−1 958(9)	931(8)	−4 592(11)
C(5)	−1 019(8)	1 195(7)	−3 705(13)
C(6)	−339(7)	1 231(8)	−4 243(10)
N(2)	1 328(4)	747(5)	−1 018(6)
C(10)	954(6)	−88(6)	−1 116(9)
C(20)	1 350(7)	−903(7)	−1 156(10)
C(30)	2 203(7)	−864(8)	−1 130(11)
C(40)	2 591(7)	−13(9)	−1 038(10)
C(50)	2 184(6)	787(7)	−0 965(9)
C(60)	2 592(6)	1 737(7)	−0 828(10)

Tables 1 and 2 list fractional co-ordinates for compounds (I) and (II). Computations were performed on the Univers-

---

[1] J. Catterick and P. Thornton, *J.C.S. Dalton*, 1976, 233.

[2] J. Drew, M. B. Hursthouse, and P. Thornton, *J.C.S. Dalton*, 1972, 1658.

[3] E. W. Hughes, *J. Amer. Chem. Soc.*, 1941, **63**, 1737.

ity of London CDC 7600 computer by use of the ' X-Ray '72 ' package.[4] Neutral atom scattering factors were taken from ref. 5. Temperature factor coefficients, hydrogen atom co-ordinates, bond lengths and angles in the ligands, and observed and calculated structure factors are listed in Supplementary Publication No. SUP 21958 (19 pp., 1 microfiche).*

TABLE 2

Final atomic parameters ($\times 10^4$) for (II)

Atom	*x/a*	*y/b*	*z/c*
Ni	0	0	0
O(1)	1 541(3)	659(4)	872(4)
O(2)	0 548(2)	887(4)	2 047(3)
C(1)	1 395(4)	1 118(5)	1 936(5)
C(2)	2 209(4)	1 986(5)	2 981(5)
C(3)	2 101(4)	2 404(6)	4 201(5)
C(4)	2 836(5)	3 303(7)	5 108(6)
C(5)	3 653(4)	3 771(7)	4 816(6)
C(6)	3 765(4)	3 317(7)	3 610(7)
C(7)	3 048(4)	2 417(6)	2 709(6)
N(1)	−0 476(3)	1 955(4)	−819(4)
C(10)	−1 184(4)	2 535(6)	−459(6)
C(11)	−1 546(5)	3 874(7)	−807(7)
C(12)	−1 161(5)	4 629(6)	−1 611(7)
C(13)	−0 414(4)	4 047(6)	−2 032(6)
C(14)	−0 083(4)	2 698(6)	−1 624(5)
C(15)	0 671(4)	2 092(6)	−2 023(6)
C(16)	1 062(5)	2 830(7)	−2 814(6)
C(17)	0 741(5)	4 179(8)	−3 236(7)
C(18)	0 021(5)	4 776(7)	−2 841(7)

RESULTS AND DISCUSSION

Figure 1 illustrates the molecular structure of compound (I) together with the atom labelling scheme used.[6]

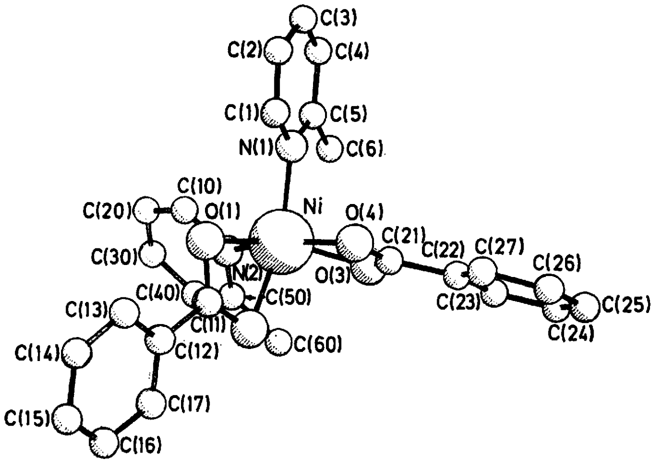

FIGURE 1 The molecular structure of (I)

Table 3 gives bond lengths and angles in the co-ordination sphere computed from the data of Table 1.

The co-ordination around the nickel atom is distorted octahedral, with two chelating benzoate groups and two 2-methylpyridine molecules arranged in a *cis*-configuration as previously suggested.[1] The main distortion is due to the restricted ' bite ' of the chelating ligand with angles at the metal of 62.4 and 62.1°. These values and the mean Ni–O bond lengths (2.115 Å) are very similar to those found for the only other nickel complex containing a chelating carboxylate group.[7] The values indicate fairly close approach of the ligands in these complexes compared with those involving other metals.[8] This may be due, in part, to the absence of any hydrogen-bonding which has been suggested to be a constraining factor on the ability of a carboxylate group to approach a metal atom.[9] Although all Ni–O bond distances are essentially equivalent, the two independent benzoate ligands show small but significant differences in chelation geometry and conformation. Ligand (1) [containing O(1) and O(2)] shows an accurately planar Ni,O_2,C ring, but a dihedral angle of 21.6° between this plane and that of the phenyl ring. Ligand (2) [containing O(3) and O(4)] shows a small fold of 2.9° about the O · · · O line, and a dihedral angle of 2.9° between the O_2,C plane and that of the phenyl ring.

TABLE 3

Bond lengths and angles in the co-ordination sphere (I)

(*a*) Bond lengths (Å)

Ni–O(1)	2.103(8)	Ni–O(2)	2.119(5)
Ni–O(3)	2.096(7)	Ni–O(4)	2.127(7)
Ni–N(1)	2.087(6)	Ni–N(2)	2.072(8)

(*b*) Bond angles (°)

O(1)–Ni–O(2)	62.4(2)	O(3)–Ni–O(4)	62.1(3)
O(1)–Ni–O(4)	96.6(3)	O(2)–Ni–O(3)	100.2(2)
O(2)–Ni–O(4)	89.3(2)	N(1)–Ni–N(2)	95.8(3)
O(1)–Ni–N(1)	97.0(3)	O(1)–Ni–N(2)	93.2(3)
O(2)–Ni–N(2)	89.3(2)	O(3)–Ni–N(1)	97.7(3)
O(3)–Ni–N(2)	106.6(3)	O(4)–Ni–N(1)	89.6(3)

The Ni–N bond lengths are just a little shorter than those found for [Ni(py)$_2$(acac)$_2$][2.112(5) Å] [9] and [Ni(py)$_2$(H$_2$O)$_2$(O)$_2$][2.100(6) Å] [2] (py = pyridine, acac = acetylacetonate). The configurations adopted by the 2-methylpyridine ligands are strongly affected by intra- and inter-molecular non-bonded contacts so that the Ni–N–C bond-angles are not equal. Figure 2(a) illustrates relevant angles and interatomic contacts involving the methyl group on the 2-methylpyridine ligand containing N(2), and Figure 1(b) the same for the ligand containing N(1).

The tilt about N(2) is 4.2° so that C(50) and C(60) are pushed away from the Ni,O(2),O(3) plane and C(10) is

---

* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1976, Index issue.

[4] ' X-Ray ' System, Version of June 1972, Technical Report TR 192, Computer Science Center, University of Maryland, June 1972.

[5] ' International Tables for X-Ray Crystallography,' vol. 3, Kynoch Press, Birmingham, 1962.

[6] W. D. S. Motherwell, Program PLUTO, University of Cambridge.

[7] P. O. Whimp, M. F. Bailey, and N. F. Curtis, *J. Chem. Soc.* (*A*), 1970, 1956.

[8] W. H. Zachariasen and H. A. Plettinger, *Acta Cryst.*, 1959, **12**, 525; L. A. Aslanov, I. K. Abdul'minve, and M. A. Porai-Koshits, *Russ. J. Phys. Chem.*, 1973, **47**, 601; J. N. van Niekerk, F. R. L. Schoening, and J. H. Talbot, *Acta Cryst.*, 1953, **6**, 720; A. C. Skapski and F. A. Stephens, *J.C.S. Dalton*, 1974, 390; L. S. Kolomnikov, A. I. Gusev, G. G. Aleksandrov, T. S. Lobeeva, Yu. T. Struchkov, and M. W. Vol'pin, *J. Organometallic Chem.*, 1973, **59**, 349; W. K. Dean, G. L. Simon, P. M. Treichel, and L. F. Dahl, *ibid.*, **50**, p. 193; D. F. Christian, G. R. Clark, W. R. Roper, J. M. Waters, and K. R. Whittle, *J.C.S. Chem. Comm.*, 1972, 458; P. O. Whimp, M. F. Bailey, and N. F. Curtis, *J. Chem. Soc.* (*A*), 1970, 1956.

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

closer to the nickel atom. In the case of N(1) the tilt is 8.6° so that the distances of C(5) and C(6) from the Ni,N(2),O(3) plane are significantly greater than in the corresponding case for N(2). The difference might be accounted for by the different orientations of the two methyl groups but could also be affected by the intermolecular contacts between C(4),C(5) and C(14),C(16) which are directed in such a way as to enhance the tilt for 2-methylpyridine ligand (1), whereas those between C(10), C(20), and C(1) act in the opposite sense and thus tend to reduce the tilt of ligand (2).

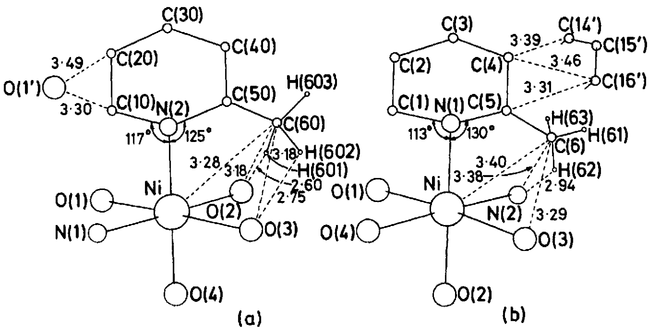

FIGURE 2 (a and b) Schematic representation of the intramolecular non-bonded contacts involving the two 2-methylpyridine ligands in (I)

The molecular packing is depicted in Figure 3. There are only six intermolecular contacts <3.5 Å; five of these have already been discussed, the sixth is C(30) · · · O(2) 3.294(14) Å.

In molecules of compound (II) the central nickel atom has distorted octahedral co-ordination from two symmetrically chelating benzoate groups and two quinoline donor ligands in a *trans*-configuration. Table 4 lists bond-lengths and angles computed from the data of Table 2. These relate to Figure 4,[10] which shows the atom labelling scheme.

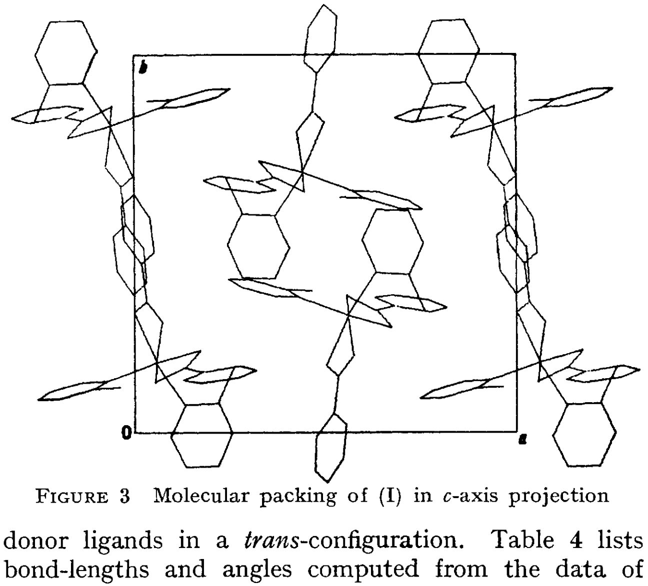

FIGURE 3 Molecular packing of (I) in *c*-axis projection

Chelation is nearly symmetrical with the Ni–O bond-lengths slightly shorter than for the 2-methylpyridine analogue (I), but the angles subtended at the metal (62.4°) and the oxygen atoms (88.7 and 89.0°) are in close agreement. The fold about the O · · · O line (7.2°) is significantly greater than that found for either benzoate ligand in the 2-methylpyridine complex, whilst the dihedral angle between the O_2C plane and the phenyl ring (11.0°) is of intermediate value.

TABLE 4

Bond lengths and angles in the co-ordination sphere for (II)

(*a*) Bond lengths (Å)			
Ni–O(1)	2.096(3)	Ni–O(2)	2.083(3)
Ni–N(1)	2.080(4)		
(*b*) Bond angles (°)			
O(1)–Ni–O(2)	62.4(1)	O(1)–Ni–N(1)	90.3(1)
O(2)–Ni–N(1)	87.0(1)		

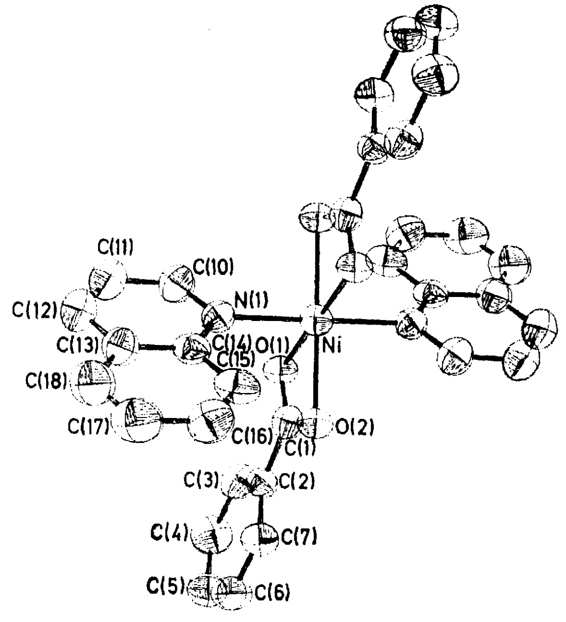

FIGURE 4 The molecular structure of (II); thermal ellipsoids scaled to enclose 50% probabilities

The Ni–N bond length is identical to the mean value found for compound (I). The quinoline molecule is displaced from a symmetrical orientation about the nitrogen atom by 4.5°, in the same way as in (I). This is illustrated in Figure 5, which shows the close non-bond-

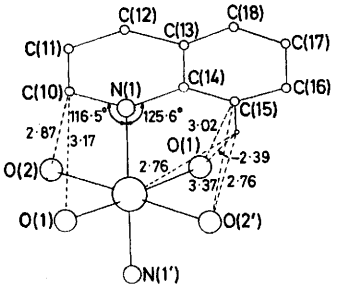

FIGURE 5 Schematic representation of the intramolecular non-bonded contacts involving the quinoline ligand in (II)

---

[10] C. K. Johnson, ORTEP, Oak Ridge National Laboratory, Report ORNL 3794, Oak Ridge, Tennessee.

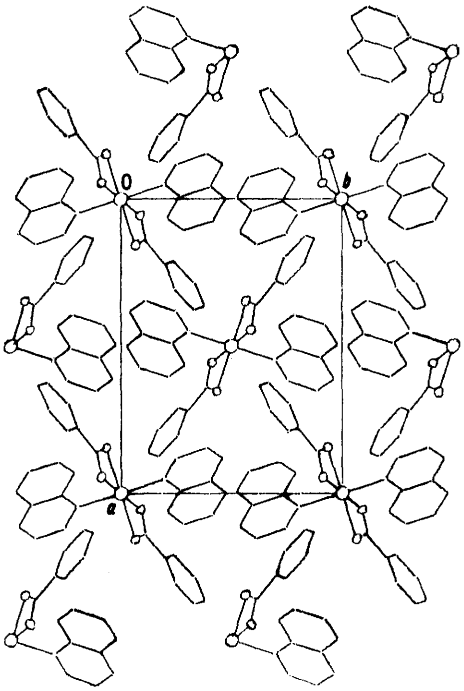

FIGURE 6 Molecular packing of (II) in *c*-axis projection

ing contacts. There is only one intermolecular C $\cdots$ C contact <3.5 Å (3.44 Å) involving C(5) and C(15) in molecules related by the glide plane, but this does not seem to have any significant effect on the molecular conformation. The molecular packing is illustrated in Figure 6.

Detailed examination of the interligand non-bonded interactions was made in order to see if the different molecular structures adopted by the two complexes could be attributed to these effects. Our feelings are that this is probably not so and that one must seek alternative explanations. In view of the similarities in Ni–O and Ni–N bond lengths in the two species, it is very unlikely that any electronic factors are involved. It only remains, therefore, to suggest that the differences might arise purely from packing considerations. This is a strong possibility here since both molecules contain a number of aromatic rings whose packing requirements will dominate in the choice of crystal structure. Furthermore, the complexes dissociate in solution, and can only be considered to exist in the solid state.

We thank Dr. P. Thornton for helpful discussions and Dr. J. Catterick for providing crystals of (I) and (II).

[6/1510 *Received, 4th August,* 1976]