Ammine[1-(2-hydroxyphenyl)-3,5-diphenylformazanato]nickel(II), [Ni(C₁₉H₁₄N₄O)(NH₃)], and [1-(2-hydroxyphenyl)-5-phenyl-3-(p-tolyl)formazanato](pyridine)nickel(II), [Ni(C₅H₅N)(C₂₀H₁₆N₄O)]

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Ammine[1-(2-hydroxyphenyl)-3,5-diphenylformazanato]nickel(II), [Ni(C₁₉H₁₄N₄O)-(NH₃)], and [1-(2-Hydroxyphenyl)-5-phenyl-3-(*p*-tolyl)formazanato](pyridine)nickel(II), [Ni(C₃H₅N)(C₂₀H₁₆N₄O)]

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Abstract. C₁₉H₁₇N₅NiO (NIFORM 2): $M_r = 390.1$, monoclinic, $P2_1/a$, $a = 11.2599(4)$, $b = 13.972(8)$, $c = 11.8702(4)$ Å, $\beta = 109.17(1)^\circ$, $V = 1763.9$ Å³, $Z = 4$, $D_x = 1.47$ g cm⁻³, $\mu(\text{Cu } K\alpha) = 16.99$ cm⁻¹, $\lambda(\text{Cu } K\alpha) = 1.5418$ Å, room temperature, $F(000) = 808$, $R = 0.031$ for 2725 reflexions. C₂₅H₂₁N₅NiO (NIFORM 3): $M_r = 466.2$, monoclinic, $P2_1/c$, $a = 8.411(1)$, $b = 24.938(4)$, $c = 11.235(2)$ Å, $\beta = 111.77(1)^\circ$, $V = 2189.2$ Å³, $Z = 4$, $D_x = 1.41$ g cm⁻³, $\mu(\text{Cu } K\alpha) = 14.62$ cm⁻¹, $\lambda(\text{Cu } K\alpha) = 1.5418$ Å, room temperature, $F(000) = 968$, $R = 0.032$ for 2993 reflexions. Both structures have planar, approximately square coordination of Ni by three N and one O. In NIFORM 2 formazan is coordinated to Ni *via* one terminal and one non-terminal N, giving rise to a five-membered Ni-formazan ring. In NIFORM 3 formazan is coordinated to Ni *via* both terminal N atoms resulting in a six-membered Ni-formazan ring.

Introduction. Formazans are well known for their flexible coordination behaviour (Renkema, 1975; Balt, Renkema, van Capelleveen & Stam, 1976). This is manifest in the formation of intermediates in reactions of Cu^{II} and Ni^{II} with 1-(2-hydroxyphenyl)-3,5-diphenylformazan in ammoniacal environment (Balt, Meuldijk & Renkema, 1980; Meuldijk, 1979). The final products of these reactions have been isolated and their crystal structures (CUFORM and NIFORM 1) have been elucidated (Renkema, Lute & Stam, 1979). In these compounds the doubly negative formazan ion is bonded to the metal ion *via* the two terminal N atoms and the O of the hydroxyphenyl group.

One of the structure determinations described in this paper concerns an intermediate in the reaction leading to NIFORM 1. This intermediate (NIFORM 2) has the same composition as NIFORM 1. The other structure determination reported here is that of NIFORM 3,

which was undertaken in order to investigate the effect on the geometry of the complex of substituting NH₃ by other monodentate ligands.

Experimental. The preparation of the complexes has been described elsewhere (Meuldijk, 1979; Balt *et al.*, 1980). Suitable crystals of both complexes were obtained by evaporation of solutions in a mixture of five parts dichloromethane and one part ethanol. D_m was not measured. NIFORM 2: 15 reflexions (2θ 70–76°) used to measure lattice parameters; $2\theta_{\text{max}} = 130^\circ$, h 0 to 13, k 0 to 16, l -13 to 13; two standard reflexions, no systematic variation; 3135 unique reflexions, 2725 with $I > 2.5\sigma(I)$; Nonius CAD-4 diffractometer with graphite-monochromatized Cu $K\alpha$ radiation; no absorption correction (crystal dimensions $0.8 \times 0.45 \times 0.15$ mm). NIFORM 3: 12 reflexions (2θ 80–85°) used to measure lattice parameters; $2\theta_{\text{max}} = 130^\circ$, h 0 to 9, k 0 to 29, l -13 to 13; two standard reflexions, no systematic variation; 3812 unique reflexions (measured as for NIFORM 2), 2993 with $I > 2.5\sigma(I)$; no absorption correction (crystal dimensions $0.45 \times 0.15 \times 0.08$ mm). Both crystal structures were solved by first locating the Ni atom by means of E^2-1 Patterson syntheses and subsequently calculating four-fold Patterson minimum functions based on the positions of the four Ni atoms in the unit cell, which enabled the remaining non-hydrogen atoms to be found. Refinement (on F) proceeded by block-diagonal least-squares calculations, anisotropic for the Ni, C, N and O atoms and isotropic for the H atoms which had been found from a ΔF synthesis. The final R factors were 0.031 and 0.032 (R_N 0.063 and 0.055) for NIFORM 2 and NIFORM 3 respectively. Weighting schemes $w = (3 + F_o + 0.009F_o^2)^{-1}$ and $w = (5.2 + F_o + 0.01F_o^2)^{-1}$ respectively were used. $(\Delta/\sigma)_{\text{max}} = 1.6$ and 1.2 for NIFORM 2 and NIFORM 3 respectively; $(\Delta\rho)_{\text{max}}$ and $(\Delta\rho)_{\text{min}} = 0.7$ and -0.3 e Å⁻³ for NIFORM 2. The anomalous dispersion of Ni was taken

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into account. Scattering factors from *International Tables for X-ray Crystallography* (1974); no correction for secondary extinction. The calculations were performed with XRAY76 system (Stewart, 1976) and a local program for the Patterson minimum function.

Discussion. Final atomic parameters are given in Table 1.* The shape of the molecules and the atomic numbering are indicated in Fig. 1. Selected distances and angles are given in Table 2. In both structures the Ni atom has a planar, approximately square coordination (Fig. 2) as in NIFORM 1 (Renkema *et al.*, 1979). The essential difference between NIFORM 2 on the one hand and NIFORM 1 and 3 on the other is that in NIFORM 2 Ni is coordinated to one terminal and one non-terminal N atom forming a five-membered ring $\text{NiN}(2)\text{C}(1)\text{N}(3)\text{N}(4)$ whilst in the other two complexes Ni is coordinated to two terminal N atoms resulting in a six-membered ring $\text{NiN}(1)\text{N}(2)\text{C}(1)\text{N}(3)\text{N}(4)$. As a result the adjacent ring involving the hydroxyphenyl group is six-membered in NIFORM 2 and five-membered in NIFORM 1 and 3. In Table 2 the bond lengths and angles involving the formazan moiety are compared for NIFORM 1,† 2 and 3 and CUFORM. It can be seen from this table that in NIFORM 1, NIFORM 3 and CUFORM the formazan parts are very similar and show practically complete delocalization of the π electrons in the formazan part [standard bond lengths C–N 1.41, C=N 1.27, N–N 1.41, N=N 1.23 Å (Burke-Laing & Laing, 1976)]. This is what one would expect from the geometry of the complexes in which the entire formazan section is part of a planar six-membered ring including Ni^{2+} . The two principal resonance structures (I) and (II) (Fig. 3) with the formal negative charge N(1) and N(4) respectively will be expected to have equal contributions to the resonance. The formazan part of NIFORM 2 with N(1)–N(2) and C(1)–N(3) shorter and N(2)–C(1) and N(3)–N(4) longer than the corresponding bonds in NIFORM 3 and CUFORM apparently has somewhat less complete delocalization. This also can be understood in terms of the geometry of the complex. Since the two principal resonance structures (III) and (IV)

(Fig. 3) are now different one would expect structure (III), with the formal negative charge nearer to Ni^{2+} , to be favoured above structure (IV).

The formazan part N(1)N(2)C(1)N(3)N(4) and the benzene rings C(2)–C(7), C(8)–C(13), C(14)–C(19) are planar within 0.018, 0.006, 0.020 and 0.005 Å respectively for NIFORM 2 and within 0.018, 0.003, 0.005 and 0.021 Å respectively for NIFORM 3. The angles between the formazan part and the benzene rings in the four complexes NIFORM 1, 2, 3 and CUFORM are given in Table 3.

Table 1. Fractional coordinates and equivalent isotropic thermal parameters with calculated e.s.d.'s in parentheses

$$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$U_{\text{eq}}(\text{\AA}^2)$
NIFORM 2				
Ni	0.14208 (5)	0.13052 (4)	0.02928 (5)	0.0422 (2)
N(1)	0.3520 (3)	0.0893 (3)	0.2365 (3)	0.050 (1)
N(2)	0.3062 (3)	0.1189 (2)	0.1282 (3)	0.044 (1)
N(3)	0.3422 (3)	0.1754 (2)	−0.0385 (3)	0.050 (1)
N(4)	0.2162 (2)	0.1787 (3)	−0.0765 (3)	0.048 (1)
N(5)	−0.0301 (3)	0.1404 (2)	−0.0763 (3)	0.049 (1)
O	0.0757 (2)	0.0762 (2)	0.1351 (2)	0.047 (1)
C(1)	0.3919 (3)	0.1470 (3)	0.0722 (3)	0.047 (2)
C(2)	0.5314 (3)	0.1456 (3)	0.1299 (4)	0.052 (2)
C(3)	0.5890 (4)	0.1880 (3)	0.2396 (4)	0.061 (2)
C(4)	0.7199 (4)	0.1911 (3)	0.2888 (4)	0.074 (2)
C(5)	0.7910 (4)	0.1501 (4)	0.2284 (5)	0.086 (2)
C(6)	0.7370 (4)	0.1070 (4)	0.1206 (5)	0.084 (2)
C(7)	0.6040 (4)	0.1034 (3)	0.0685 (4)	0.069 (2)
C(8)	0.2725 (3)	0.0565 (3)	0.2946 (3)	0.046 (2)
C(9)	0.1391 (3)	0.0484 (3)	0.2432 (3)	0.043 (1)
C(10)	0.0761 (3)	0.0040 (3)	0.3150 (3)	0.052 (2)
C(11)	0.1370 (4)	−0.0264 (3)	0.4274 (4)	0.058 (2)
C(12)	0.2680 (4)	−0.0145 (3)	0.4791 (4)	0.066 (2)
C(13)	0.3320 (4)	0.0266 (3)	0.4122 (4)	0.060 (1)
C(14)	0.1639 (3)	0.2074 (3)	−0.1972 (3)	0.047 (1)
C(15)	0.2044 (4)	0.1693 (3)	−0.2866 (4)	0.060 (2)
C(16)	0.1519 (5)	0.1985 (4)	−0.4030 (4)	0.072 (2)
C(17)	0.0564 (5)	0.2660 (4)	−0.4339 (4)	0.074 (2)
C(18)	0.0150 (5)	0.3036 (4)	−0.3465 (4)	0.075 (2)
C(19)	0.0670 (4)	0.2750 (3)	−0.2299 (4)	0.061 (2)
NIFORM 3				
Ni	−0.06907 (5)	0.40830 (2)	0.50796 (4)	0.0414 (2)
N(1)	0.1143 (3)	0.3708 (1)	0.6152 (2)	0.040 (1)
N(2)	0.2379 (3)	0.3462 (1)	0.5942 (2)	0.042 (1)
N(3)	0.1206 (3)	0.3649 (1)	0.3668 (2)	0.042 (1)
N(4)	−0.0117 (3)	0.3924 (1)	0.3698 (3)	0.041 (1)
N(5)	−0.2795 (3)	0.4457 (1)	0.4136 (2)	0.040 (1)
O	−0.1163 (2)	0.4250 (1)	0.6528 (2)	0.052 (1)
C(1)	0.2375 (3)	0.3450 (1)	0.4741 (3)	0.040 (1)
C(2)	0.3888 (3)	0.3189 (2)	0.4606 (3)	0.040 (1)
C(3)	0.5458 (4)	0.3185 (1)	0.5632 (3)	0.047 (1)
C(4)	0.6898 (4)	0.2957 (2)	0.5502 (3)	0.050 (1)
C(5)	0.6812 (4)	0.2725 (1)	0.4360 (3)	0.049 (1)
C(6)	0.5247 (4)	0.2731 (1)	0.3341 (3)	0.052 (2)
C(7)	0.3803 (3)	0.2958 (1)	0.3456 (3)	0.048 (2)
C(8)	0.1204 (3)	0.3693 (1)	0.7425 (3)	0.040 (1)
C(9)	−0.0110 (4)	0.4001 (1)	0.7561 (3)	0.045 (1)
C(10)	−0.0220 (4)	0.4025 (2)	0.8776 (3)	0.055 (1)
C(11)	0.0922 (4)	0.3746 (2)	0.9784 (3)	0.057 (1)
C(12)	0.2213 (4)	0.3439 (2)	0.9627 (3)	0.061 (1)
C(13)	0.2360 (4)	0.3410 (1)	0.8448 (3)	0.053 (1)
C(14)	−0.1242 (3)	0.4064 (2)	0.2403 (3)	0.043 (1)
C(15)	−0.2158 (4)	0.3660 (1)	0.1592 (3)	0.055 (1)
C(16)	−0.3333 (4)	0.3793 (2)	0.0394 (3)	0.071 (1)
C(17)	−0.3566 (4)	0.4318 (2)	0.0023 (4)	0.080 (2)
C(18)	−0.2615 (5)	0.4715 (2)	0.0800 (4)	0.075 (2)
C(19)	−0.1414 (4)	0.4591 (1)	0.2017 (3)	0.057 (2)
C(20)	−0.4197 (3)	0.4181 (2)	0.3451 (3)	0.046 (1)
C(21)	−0.5779 (4)	0.4422 (2)	0.2891 (3)	0.057 (1)
C(22)	−0.5919 (4)	0.4962 (2)	0.3033 (3)	0.063 (2)
C(23)	−0.4489 (5)	0.5248 (2)	0.3727 (4)	0.065 (1)
C(24)	−0.2952 (4)	0.4984 (2)	0.4277 (4)	0.055 (2)
C(25)	0.8389 (4)	0.2480 (1)	0.4230 (4)	0.067 (1)

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, and bond lengths and angles for NIFORM 2 and NIFORM 3, and the final parameters from a redetermination of NIFORM 1 have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38751 (36 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

† The bond distances in the formazan part of NIFORM 1 (Renkema *et al.*, 1979) showed two significant differences from the corresponding values in NIFORM 2 and CUFORM. A redetermination of NIFORM 1 with intensity data from a new crystal removed the discrepancies which were due to deviations in the coordinates of one atom. The final parameters from the redetermination have been deposited (see previous footnote). In Table 2 the redetermined values have been used.

Comparison of NIFORM 3 with NIFORM 1 shows that substitution of NH₃ by pyridine has very little effect on the geometry of the complex. The NH₃ molecule in NIFORM 2 is involved in two hydrogen bonds: N(5)···O($\bar{x}, \bar{y}, \bar{z}$) 3.11 and N(5)···N(3)($-\frac{1}{2} + x, \frac{1}{2} - y, z$) 3.01 Å.

Table 2. Selected distances (Å) and angles (°) in NIFORM 2 and NIFORM 3 and comparison with NIFORM 1 and CUFORM (e.s.d.'s in parentheses).

	NIFORM 2	NIFORM 3	NIFORM 1	CUFORM†
Ni—O	1.825 (3)	1.860 (3)	1.871 (5)	...
Ni—N(1)	...	1.824 (2)	1.827 (6)	...
Ni—N(2)	1.843 (3)	...	...	...
Ni—N(4)	1.851 (4)	1.832 (4)	1.821 (6)	...
Ni—N(5)	1.937 (3)	1.932 (3)	1.938 (6)	...
N(1)—N(2)	1.286 (5)	1.302 (4)	1.281 (9)	1.294 (7)
N(2)—C(1)	1.396 (6)	1.348 (5)	1.347 (8)	1.348 (7)
C(1)—N(3)	1.309 (5)	1.337 (3)	1.340 (9)	1.338 (7)
N(3)—N(4)	1.341 (4)	1.318 (4)	1.312 (9)	1.318 (6)
N(1)—C(8)	1.376 (6)	1.413 (5)	1.413 (8)	1.394 (7)
C(1)—C(2)	1.493 (5)	1.486 (5)	1.481 (11)	1.486 (7)
N(4)—C(14)	1.413 (5)	1.454 (5)	1.475 (9)	1.439 (7)
C(8)—C(9)	1.428 (4)	1.400 (1)	1.386 (11)	1.416 (7)
C(9)—O	1.306 (4)	1.325 (4)	1.348 (9)	1.315 (7)
N(1)N(2)C(1)	117.0 (3)	119.1 (2)	119.8 (6)	119.0 (5)
N(2)C(1)N(3)	115.4 (3)	128.5 (3)	127.8 (7)	130.1 (5)
C(1)N(3)N(4)	114.0 (4)	121.0 (3)	121.3 (6)	123.0 (5)
N(2)N(1)C(8)	119.7 (3)	116.1 (2)	116.0 (5)	116.7 (5)
N(1)C(8)C(9)	125.3 (4)	111.2 (3)	111.8 (6)	112.0 (4)
C(8)C(9)O	123.7 (4)	117.4 (3)	117.6 (6)	119.7 (5)
N(3)N(4)C(14)	113.3 (3)	110.0 (3)	111.2 (5)	110.4 (4)

* Redetermined, see footnote on p. 1537.

† Renkema *et al.* (1979).

Fig. 1. Shape of the molecule and atomic numbering. (a) NIFORM 2. (b) NIFORM 3.

Fig. 2. Coordination of Ni. (a) NIFORM 2. (b) NIFORM 3. The underlined numbers are the distances from the best plane through the four coordinating atoms. (Distances in Å, angles in deg.)

Fig. 3. Resonance forms of (a) NIFORM 1 and 3 and (b) NIFORM 2.

Table 3. Angles (°) between the Ni-formazan ring (I) and the benzene rings (II) C(2)—C(7), (III) C(8)—C(13) and (IV) C(14)—C(19) (e.s.d.'s about 0.3°)

	NIFORM 1*	NIFORM 2	NIFORM 3	CUFORM†
(I)—(II)	1.7	50.3	28.0	6.4
(I)—(III)	3.7	9.3	6.2	3.5
(I)—(IV)	79.5	48.2	72.2	32.1

* Redetermined, see footnote on p. 1537.

† Renkema *et al.* (1979).

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