X-Ray Crystal Structure of {7,8,15,17,18,20-Hexahydrodibenzo[*e*,*m*]pyrazino[2,3-*b*][1,4,8,11]tetra-azacyclotetradecinato(2-)}nickel(II) and of {7,8,15,16,17,18-Hexahydrodibenzo[*e*,*m*][1,4,8,11]tetra-azacyclotetradecinato(2-)}nickel(II)

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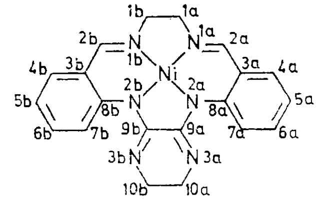
The crystal structures of the title compounds [(I) and the related non-pyrazino-compound (II)] have been determined by Patterson and Fourier methods from single-crystal *X*-ray diffractometer data, and refined by least-squares methods to R 0·058 [(I) 1272] and 0·048 [(II) 995 reflections].

Crystals of (I) are triclinic, space group $P\bar{1}$, a = 12·134(1), b = 9·132(1), c = 8·1994(9) Å, α = 69·10(1), β = 96·58(1), γ = 92·11(1)°, Z = 2; crystals of (II) are orthorhombic, space group $Pbca$, a = 26·775(4), b = 18·980(2), c = 6·0675(7) Å, Z = 8.

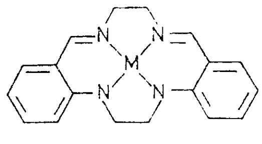
Within the NiN_4 molecular core, Ni–N distances are in both cases as expected [means: (I) 1·857(6), (II) 1·847(6) Å]; both environments have a small distortion from planarity.

RECENT studies [1,2] in the preparation and reactivity of quadridentate macrocyclic derivatives of cobalt(II) and nickel(II) have revealed wide variations in the co-ordinating power and reactivity of the fifth co-ordination site, and have resulted in a number of crystal structure determinations being carried out.[3-5] As an extension of these studies, we intended to carry out a structure determination of (III), the cobalt(II) analogue of (II); however, the nickel(II) compound proved less sensitive to decomposition and since it was isomorphous, but with slightly larger crystals, its structure was determined instead.

The complexes were prepared as described in the literature.[2] The nickel derivative, recrystallized from dimethylformamide, showed the presence of two kinds of crystal. When the cell dimensions were determined the calculated density of the prismatic crystals (I), which were present only in small quantities, was inconsistent with that of the bulk sample, which were needles, (II). Structure determinations of (II) and also of (I), obviously an impurity, were carried out.



(I) Showing the atom numbering system used for both compounds in the analysis



(II) M = Ni
(III) M = Co

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[1] R. Karlsson, L. M. Engelhardt, and M. Green, *J.C.S. Dalton*, 1972, 2463.

[2] M. Green and P. A. Tasker, *Inorg. Chim. Acta*, 1971, **5**, 65 and refs. therein.

[3] S. Bruckner, M. Calligaris, G. Nardin, and L. Randaccio, *Acta Cryst.*, 1969, **B25**, 1671.

[3] (*a*) '*X*-Ray '72' system of programs, University of Maryland Technical Report TR 192, June 1972; (*b*) D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321; (*c*) D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

[4] W. P. Schaeffer and R. E. Marsh, *Acta Cryst.*, 1969, **B25**, 1675.

[5] M. Cesari, C. Neri, G. Derego, E. Perrotti, and A. Zazzetta, *Chem. Comm.*, 1970, 276.

EXPERIMENTAL

Single crystals suitable for X-ray work were obtained as a prism $0{\cdot}03 \times 0{\cdot}13 \times 0{\cdot}04$ mm, (I), and a prismatic needle section $0{\cdot}04 \times 0{\cdot}09 \times 0{\cdot}15$ mm, (II). In both cases, cell dimensions were obtained by a least-squares fit of the angular parameters of 15 reflections (2θ *ca.* 20—30°) centred in the counter aperture of a Syntex P$\bar{1}$ diffractometer. Unique data sets in the range $2\theta < 100°$ (Ni filtered Cu-K_α radiation, $\lambda = 1{\cdot}5418$ Å) were collected by a conventional 2θ—θ scan, to give 1600 (I) and 995 (II) reflections; for (I), 1272 reflections with $I > 2\sigma(I)$, and for (II), all reflections were used in the subsequent solution and refinement procedures with unit weights. All data processing and computation was carried out by use of a local adaptation of the 'X-Ray '72' system [3a] for our CDC 6200 machine; all data were corrected for the effects of absorption.

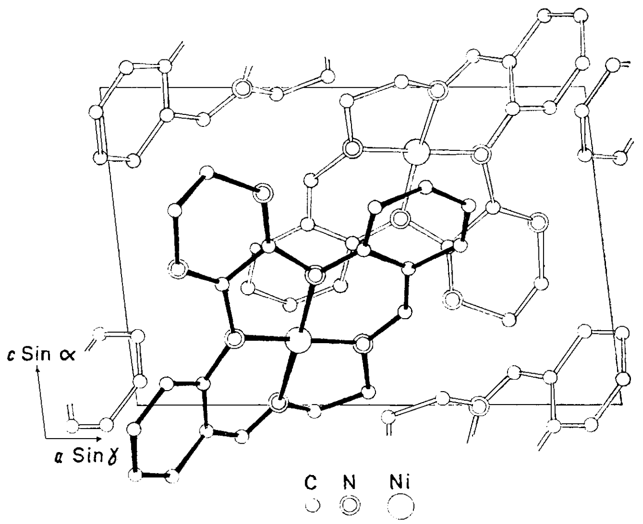

FIGURE 1 Structure of (I), projected down b

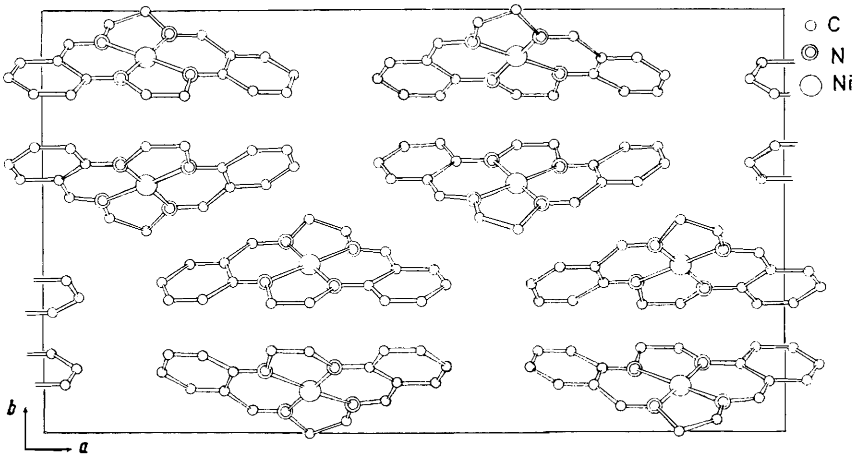

FIGURE 2 Structure of (II), projected down c

Crystal Data.—(I), $C_{20}H_{18}N_6Ni$, $M = 401{\cdot}1$, Triclinic, $a = 12{\cdot}134(1)$, $b = 9{\cdot}132(1)$, $c = 8{\cdot}1994(9)$ Å, $\alpha = 69{\cdot}10(1)$, $\beta = 96{\cdot}58(1)$, $\gamma = 92{\cdot}11(1)°$, $U = 843{\cdot}2(2)$ Å^3, $D_c = 1{\cdot}58$ g cm^{-3}, $Z = 2$, $F(000) = 416$. $\mu(\text{Cu-}K_{\bar{\alpha}}) = 17{\cdot}5\ \text{cm}^{-1}$. Space group $P\bar{1}$ (C_i^1, No. 2).

(II), $C_{16}H_{18}N_4Ni$, $M = 347{\cdot}1$, Orthorhombic, $a = 26{\cdot}775(4)$, $b = 18{\cdot}980(2)$, $c = 6{\cdot}0675(7)$ Å, $U = 3083{\cdot}5(6)$ Å^3, $D_m = 1{\cdot}49$, $Z = 8$, $D_c = 1{\cdot}50$ g cm^{-3}, $F(000) = 1360$. $\mu(\text{Cu-}K_{\bar{\alpha}}) = 17{\cdot}7\ \text{cm}^{-1}$. Space group, *Pbca* ($D_{2h}^{15}$, No. 61).

For (III): $a = 27{\cdot}76(1)$, $b = 19{\cdot}188(9)$, $c = 5{\cdot}989(2)$ Å, $U = 3075(2)$ Å^3; intensity statistics and systematic absences indicate the space group to be the same.

Both structures were solved by the heavy-atom method. Block diagonal (9×9) least-squares refinements of the structures were carried out for the non-hydrogen atoms with anisotropic thermal parameters of the form: exp-$[-2\pi^2 . (U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$. Hydrogen atoms were located from geometrical considerations and their positional parameters refined, thermal parameters being constrained isotropically at $U = 0{\cdot}09$ Å^2. At convergence, no parameter shifts in the final least-squares cycles were $>0{\cdot}06\sigma$ and final difference maps showed no significant features. Final residuals, $\{R' = [\Sigma(|F_o| - |F_c|)^2/\Sigma|F_o|^2]^{\frac{1}{2}}\}$, were (I) R 0·058 and R' 0·060 and (II) R 0·048 and R' 0·051. Scattering factors used were for the neutral atoms, that for Ni being corrected for the effects of anomalous dispersion ($\Delta f'$, $\Delta f''$)[3b,c].

Structure factors and hydrogen atom parameters for both compounds are given in Supplementary Publication No SUP 21034 (18 pp., 1 microfiche).* Final positional and thermal parameters for non-hydrogen atoms are listed in Table 1.

DISCUSSION

The structures of both complexes comprise discrete molecular units; in neither case is there an intermolecular Ni · · · N distance <6 Å so that the nickel atoms are four-co-ordinate. The similarity of the cell dimensions and space group of (III) makes it seem likely that the metal is also four-co-ordinate. The nickel–nitrogen distances are similar in both structures (Table 2); the mean of 1·85 Å is similar to that found in *NN'*-ethylenebis-(salicylaldiminato)nickel(II) [6] and bis(dimethylglyoxim-

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* For details see Notice Authors No. 7 in *J.C.S. Dalton*, 1973, Index issue.

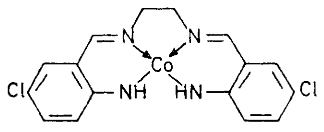
[6] L. M. Shkol'nikova, E. M. Yutal, E. A. Shugam, and V. A. Voblikova, *Zhur. strukt. Khim.*, 1970, **11**, 886.

TABLE 1

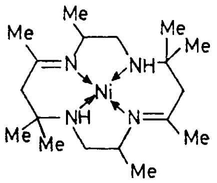
Final atomic fractional cell and thermal (× 10^3) parameters, with least squares estimated standard deviations in parentheses. Values for (II) are given below those for (I). A decimal point precedes (x, y, z)

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni	3521(1)	4471(2)	2042(2)	58(1)	53(1)	57(1)	−4(1)	13(1)	−14(1)
	3597(1)	3985(1)	3846(2)	89(1)	58(1)	68(1)	2(1)	14(1)	−1(1)
N(1a)	2974(6)	6130(7)	0056(9)	50(5)	31(4)	40(4)	−4(3)	17(3)	−9(3)
	3278(3)	4517(3)	175(1)	79(5)	42(4)	57(5)	15(4)	7(4)	12(4)
N(1b)	4839(6)	5567(7)	1917(8)	51(4)	30(4)	39(4)	−9(3)	24(3)	−11(3)
	4178(3)	4370(3)	270(1)	75(5)	36(4)	47(4)	−4(4)	26(4)	3(4)
N(2a)	2203(5)	3355(7)	2107(8)	24(4)	38(4)	41(4)	1(3)	7(3)	−6(3)
	3013(2)	3566(3)	482(1)	53(4)	36(4)	44(4)	2(4)	1(4)	3(3)
N(2b)	4015(5)	2866(7)	4119(8)	32(4)	34(4)	39(4)	−7(3)	8(3)	−14(3)
	3928(2)	3486(3)	601(1)	51(4)	41(4)	39(4)	−4(3)	5(4)	4(4)
C(1a)	3646(8)	757(1)	−019(1)	69(7)	37(5)	52(6)	−3(5)	15(5)	−12(5)
	3606(4)	5056(5)	069(2)	115(8)	66(6)	84(8)	12(7)	21(8)	24(6)
C(1b)	4823(8)	708(1)	043(1)	62(6)	45(6)	60(6)	−17(5)	27(5)	−19(5)
	4101(4)	4767(5)	065(2)	99(8)	55(6)	76(8)	−2(6)	34(7)	10(6)
C(2a)	2092(7)	613(1)	−099(1)	61(6)	55(6)	23(5)	13(5)	15(4)	−7(4)
	2828(4)	4470(4)	110(2)	114(8)	60(6)	57(6)	27(6)	−10(7)	0(6)
C(2b)	5755(7)	511(1)	289(1)	42(5)	54(6)	55(6)	−24(4)	23(4)	−32(5)
	4623(3)	4264(4)	340(2)	71(6)	50(5)	84(8)	−8(5)	40(6)	−15(5)
C(3a)	1367(7)	483(1)	−082(1)	36(5)	42(5)	51(6)	2(4)	14(4)	−12(4)
	2457(3)	4004(5)	202(1)	66(6)	55(5)	70(6)	18(5)	0(6)	−11(6)
C(3b)	5948(7)	361(1)	429(1)	44(5)	57(6)	44(5)	−10(4)	9(4)	−33(5)
	4771(3)	3862(4)	526(1)	54(5)	52(6)	67(6)	9(5)	8(5)	−7(5)
C(4a)	0545(7)	501(1)	−224(1)	46(6)	64(6)	39(5)	18(5)	7(4)	−6(5)
	1989(4)	3978(5)	099(2)	97(2)	77(6)	73(7)	27(6)	−15(7)	3(7)
C(4b)	7052(7)	321(1)	505(1)	36(5)	86(8)	61(7)	−23(5)	14(5)	−32(6)
	5283(3)	3832(5)	581(2)	72(6)	59(6)	98(8)	−7(5)	30(7)	1(6)
C(5a)	−0181(7)	382(1)	−219(1)	32(5)	91(8)	44(6)	12(5)	−11(4)	−24(5)
	1617(3)	3566(5)	173(2)	61(6)	88(7)	102(9)	28(6)	−20(6)	−22(7)
C(5b)	7323(7)	177(1)	627(1)	30(6)	93(8)	73(7)	5(5)	0(5)	−31(6)
	5453(4)	3477(5)	758(2)	58(6)	84(7)	123(9)	−10(6)	−5(7)	−2(8)
C(6a)	−0107(7)	247(1)	−078(1)	45(6)	75(7)	43(6)	4(5)	−4(4)	−23(5)
	1708(3)	3163(4)	359(2)	71(6)	53(6)	109(9)	7(5)	11(7)	−13(7)
C(6b)	6512(7)	073(1)	683(1)	37(5)	80(7)	57(6)	6(5)	−9(5)	−39(6)
	5120(3)	3114(5)	881(2)	69(7)	74(7)	83(7)	−3(5)	−11(7)	6(7)
C(7a)	0660(7)	229(1)	063(1)	42(5)	50(6)	51(6)	−1(4)	14(5)	−10(5)
	2153(3)	3170(4)	460(2)	46(5)	61(6)	79(7)	9(5)	−4(5)	−14(6)
C(7b)	5420(7)	108(1)	621(1)	49(6)	39(5)	49(6)	−4(4)	6(4)	−20(4)
	4621(3)	3118(4)	838(2)	65(6)	58(6)	74(7)	0(5)	−4(6)	6(6)
C(8a)	1424(6)	348(1)	069(1)	27(5)	42(5)	39(5)	6(4)	12(4)	−9(4)
	2561(3)	3573(4)	386(1)	61(5)	34(4)	49(5)	9(4)	16(6)	−8(5)
C(8b)	5094(6)	253(1)	491(1)	22(4)	47(5)	53(6)	−9(4)	12(4)	−28(4)
	4414(3)	3481(4)	656(1)	56(5)	28(4)	54(6)	−2(4)	12)5)	−6(5)
C(9a)	2079(7)	236(1)	380(1)	37(5)	29(5)	35(5)	−7(4)	11(4)	0(4)
	3076(3)	3085(4)	667(1)	51(5)	62(6)	52(6)	2(5)	11(5)	5(5)
C(9b)	3124(6)	219(1)	502(1)	23(4)	22(4)	43(5)	0(3)	3(4)	−17(4)
	3600(3)	3102(4)	750(1)	63(6)	53(5)	53(5)	−6(5)	−3(5)	3(5)
N(3a)	1183(6)	1628(8)	4291(9)	40(4)	52(5)	42(5)	−8(4)	5(4)	11(4)
N(3b)	3141(5)	1599(8)	6691(9)	37(4)	40(4)	37(4)	−3(3)	5(3)	0(3)
C(10a)	1261(8)	063(1)	615(1)	53(6)	64(7)	51(6)	−21(5)	11(5)	−6(6)
C(10b)	2029(8)	122(1)	728(1)	57(6)	49(6)	53(6)	−7(5)	17(5)	−4(5)

ato)nickel(II),[7] in spite of many differences in, *e.g.* occupancy of fifth and sixth co-ordination sites, distortions imposed by ligand constraints, and differing crystal-field strengths. In (IV), a related cobalt(II) derivative[1] [*NN'*-ethylenebis-(2-amino-5-chlorobenzylideneiminato)]cobalt(II), the metal atom is at the apex of a square pyramid, and is displaced from the four basal nitrogen atoms by 0·14 Å; (I) and (II), however, both exhibit slight alternate up-and-down out-of-plane distortions (Table 3). In this they resemble such derivatives as [(1*RS*, 3*SR*, 8*RS*, 10*SR*)-3,5,7,7,10,12,14,14-octamethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene]-nickel(II), (V),[8-10] which display similar distortions, probably as a consequence of the constraints imposed by a pair of $-CH_2-CH_2-$ bridges rather than the single



(IV)



(V)

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[7] D. E. Williams, G. Wahlaben, and R. E. Rundle, *J. Amer. Chem. Soc.*, 1959, **81**, 755.

[8] D. A. Sann, T. N. Waters, and N. F. Curtis, *J.C.S. Dalton*, 1972, 1115.

[9] M. F. Bailey and I. E. Maxwell, *J.C.S. Dalton*, 1972, 938.

[10] B. T. Kilbourn, R. R. Ryan, and J. D. Dunitz, *J. Chem. Soc.* (*A*), 1969, 2407.

bridge in (IV) and in ethylenebis(salicylaldimine) derivatives. Although the effects of a lack of correction for thermal motion are apparent in the shortened peripheral aromatic C–C distances in the present structure, the inner distances within the ligand are close to the usual values and it is likely that the metal–nitrogen distances are good approximations to the correct values. In all totally saturated macrocyclic derivatives of nickel(II) for which structural data are available,[11,12] the nickel–

TABLE 2

Interatomic distances (Å) and angles (°), with least-squares estimated standard deviations in parentheses. Values for (II) are given below these for (I) *

(*a*) Distances	
Ni–N(1a,b)	1·859(6), 1·847(7) 1·836(7), 1·851(7)
Ni–N(2a,b)	1·861(6), 1·859(6) 1·851(6), 1·848(6)
C(1a)–C(1b)	1·49(1) 1·44(1)
C(1a,b)–N(1a,b)	1·48(1), 1·48(1) 1·49(1), 1·47(1)
N(1a,b)–C(2a,b)	1·29(1), 1·28(1) 1·27(1), 1·28(1)
C(2a,b)–C(3a,b)	1·43(1), 1·45(1) 1·44(1), 1·42(1)
C(3a,b)–C(4a,b)	1·41(1), 1·41(1) 1·42(1), 1·42(1)
C(3a,b)–C(8a,b)	1·40(1), 1·41(1) 1·42(1), 1·43(1)
C(4a,b)–C(5a,b)	1·37(1), 1·36(1) 1·34(1), 1·35(1)
C(5a,b)–C(6a,b)	1·36(1), 1·35(1) 1·39(1), 1·35(1)
C(6a,b)–C(7a,b)	1·36(1), 1·37(1) 1·34(1), 1·36(1)
C(7a,b)–C(8a,b)	1·41(1), 1·40(1) 1·41(1), 1·42(1)
C(8a,b)–N(2a,b)	1·39(1), 1·39(1) 1·34(1), 1·34(1)
N(2a,b)–C(9a,b)	1·38(1), 1·38(1) 1·46(2), 1·46(1)
C(9a)–C(9b)	1·50(1) 1·49(1)
C(9a,b)–N(3a,b)	1·28(1), 1·28(1)
N(3a,b)–C(10a,b)	1·47(1), 1·47(1)
C(10a)–C(10b)	1·46(1)
(*b*) Angles	
N(1,2a)–Ni–N(1,2b)	86·5(3), 86·3(3) 85·1(3), 87·6(3)
N(1a,b)–Ni–N(2a,b)	92·9(3), 94·4(3) 93·7(3), 93·8(3)
C(1b,a)–C(1a,b)–N(1a,b)	108·0(7), 108·2(7) 106·8(7), 108·1(8)
C(1a,b)–M(a,b)–Ni	111·9(5), 114·5(5) 113·6(6), 113·7(6)
C(1a,b)–N(1a,b)	121·2(6), 118·3(7) 118·3(7), 119·3(7)
C(1a,b)–C(2a,b)–C(3a,b)	125·6(7), 125·7(8) 125·4(8), 127·3(8)
C(2a,b)–C(3a,b)–C(4a,b)	116·3(7), 117·7(8) 117·9(8), 118·6(8)
C(2a,b)–C(3a,b)–C(8a,b)	122·6(8), 123·4(7) 121·5(8), 121·4(7)
C(3a,b)–C(4a,b)–C(5a,b)	119·9(7), 121·7(8) 122·5(9), 122·3(9)
C(4a,b)–C(5a,b)–C(6a,b)	119·9(8), 119·2(8) 117·6(9), 118·3(9)
C(5a,b)–C(6a,b)–C(7a,b)	121·3(9), 121·6(8) 121·6(9), 122·5(9)
C(6a,b)–C(7a,b)–C(8a,b)	122·1(7), 121·7(8) 123·3(9), 122·6(8)
C(7a,b)–C(a,b)–C(3a,b)	115·6(6), 116·7(7) 114·4(8), 114·3(7)
C(7a,b)–C(8a,b)–Ni	124·3(7), 123·5(7) 123·9(7), 125·2(7)

TABLE 2 (*Continued*)

(*b*) Angles (*contd.*)	
C(8a,b)–N(2a,b)–Ni	126·3(5), 128·2(5) 128·4(5), 130·1(5)
N(2a,b)–C(9a,b)–C(9b,a)	112·4(6), 111·4(6) 110·9(7), 111·6(7)
C(9a,b)–N(2a,b)–Ni	110·9(5), 109·9(4) 114·6(5), 114·1(5)
C(9a,b)–N(3a,b)C–(10b,c)	114·4(7), 113·3(6)
N(3a,b)–C(10a,b)–C(10b,a)	113·8(7), 114·3(9)
N(2a,b)–C(9a,b)–(Ca,b)	124·8(7), 125·7(7)
N(3a,b)–C(9a,b)–C(9b,a)	122·8(7), 122·8(7)

* The quantity C(3a,b)–C(4a,b) denotes the pair of distances C(3a)–C(4a) and C(3b)–C(4a); likewise C(3a,b)–C(4a,b)–C(5a,b) denotes the pair of angles C(3a)–C(4a)–C(5a) and C(3b)–C(4b)–C(5b).

TABLE 3

Equations of best least-squares planes in the form: $lX + mY + nZ = p$, where X, Y, and Z are orthogonal co-ordinates in Å, with X parallel to a, and Z in the ac plane. Atomic deviations (Å) of relevant atoms are given in square brackets; σ/Å is the standard deviation. Equations and deviations for (II) follow those for (I) except for plane (IV)

	10^4l	10^4m	10^4n	p	σ
Plane (I) NiN_4 ‘ plane ’					
	−4226	4745	7722	2·566	0·045
	−1065	7577	6439	6·198	0·047

[Ni −0·01, 0·01; N(1a) 0·05, 0·05; N(1b) −0·04, −0·05; N(2a) −0·04, −0·05; N(2b) 0·05, 0·04; C(1a) 0·50, 0·32; C(1b) −0·01, −0·26; C(9a) 0·48, −0·03; C(9b) 0·66, 0·17; C(2a) −0·19, −0·15; C(2b) −0·17, −0·05; C(8a) −0·51, −0·28; C(8b) −0·20, 0·11]

	10^4l	10^4m	10^4n	p	σ
Plane (II): C(2a)—(8a), N(1a), N(2a)					
	6943	−4135	−5891	−1·122	0·062
	−3003	7424	5989	4·382	0·026

[N(2a) −0·07, −0·03; C(8a) −0·02, 0·00; C(7a) 0·04, 0·03; C(6a) 0·06, 0·01; C(5a) 0·00, −0·03; C(4a) −0·04, −0·02; C(3a) −0·02, 0·02; C(2a) −0·06, 0·04; N(1a) 0·12, −0·02; Ni 0·44, −0·26; C(1a) 0·01, 0·10; C(9a) −0·53, −0·08]

	10^4l	10^4m	10^4n	p	σ
Plane (III): C(2b)—C(8b), N(1b), N(2b)					
	−2334	4109	8813	3·750	0·066
	−1227	7995	5880	6·180	0·025

[N(2b) 0·01, 0·04; C(8b) 0·07, −0·01; C(7b) 0·01, 0·02; C(6b) −0·07, 0·02; C(5b) −0·05, 0·01; C(4b) 0·05, −0·03; C(3b) 0·06, −0·01; C(2b) 0·04, −0·01; N(1b) −0·12, 0·04; Ni −0·36, 0·06; C(9b) 0·49, 0·02; C(1b) −0·24, −0·07]

	10^4l	10^4m	10^4n	p	σ
Plane (IV): plane through N(2a,b), N(3a,b), C(9a,b), C(10a,b)					
	−3215	8498	4177	2·625	0·203

[N(2a) 0·22, C(9a) 0·02, N(3a) −0·08, C(10a) −0·29, C(10b) 0·34, N(3b) 0·02, C(9b) −0·07, N(2b) −0·17, Ni 0·65, C(8a) 0·10, C(8b) −0·59]

Interplanar angles (°):

(I)–(II)	19·2, 11·4	(II)–(III)	31·7, 10·7
(I)–(III)	13·1, 4·1	(II)–(IV)	34·8
(I)–(IV)	30·5	(III)–(IV)	37·6

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[11] Ref. 75 in ref. 15.

[12] B. Bosnich, R. Mason, P. J. Pauling, G. B. Robertson, and M. L. Tobe, *Chem. Comm.*, 1965, 97.

nitrogen distance is close to the value of 2·12 Å, typical of nitrogen σ-donors in octahedral configuration, *e.g.* $[Ni(NH_2OH)_6]SO_4$, $[Ni(en)_3]^{2+}$ (refs. 13, 14) and the fifth and sixth co-ordination positions are occupied by anions. In the planar four-co-ordinate complexes, Curtis has pointed out[15] that the bond length generally decreases as the nitrogen atoms become trigonal in character; calculations appear to confirm this as a real electronic effect.[9] There are exceptions, primarily where the ring system is very highly conjugated and rigid, as in porphyrin[15,16] and corrin[17] derivatives. Thus the values observed in (I) and (II) generally agree with those observed in highly conjugated systems with trigonal nitrogen atoms and ' open ' ring systems, such as the ethylenebis(salicylaldimine)[6] and dimethylglyoxime derivatives;[7] the shorter N–Ni distance may be rationalized in terms of increased σ donor capacity and/or increased π-bonding between the nitrogen and metal as the nitrogen changes from tetrahedral to trigonal.

Although the molecular cores of (I) and (II) are similar, the disposition of the aromatic ligand systems differs widely, presumably as a consequence of the introduction of the third ligand ring in (I). The best description of this is given by the interplanar angles (Table 3) of the NiN_4 systems and the ligand aromatic fragments where it is found that in (II), the maximum interplanar angle is 11·4° between the NiN_4 core and the ligand; whereas, in (I), the angles are generally of the order of 30°. In both derivatives the $-CH_2-CH_2-$ bridges are somewhat affected by thermal motion or possibly disorder. The introduction of the new ring system in (I) changes the conjugation pattern considerably; whereas in (II) it is restricted to the Ni,N(1),N(2),C(2)—(8) bicyclic system, in (I) N(2a,b)–C(9a,b) become considerably shortened [(I) 1·38(1), (II) 1·46(1) Å] and it is apparent that the conjugation now extends through this bond to N(3a,b)–C(9a,b), the length of which is rather greater than a true carbon–nitrogen double bond [(I) 1·28(1) Å]. In spite of this extended conjugation the C(9a,b), N(3a,b) plane is grossly deflected from the remaining molecular planes; this may be partly due to H(7a,b) · · · N(3a,b) interactions, but a more likely explanation is to be found in the bridge distortion evident in 9(a,b) and 1(a,b) which has parallels in other related molecules. It is remarkable, however, that the relatively small changes occurring in the C(9a,b) bridge geometry exert such a large influence on the disposition of all cyclic systems in (I).

A further question arises as to the mode of formation of (I), which is obviously an impurity. The ligand is prepared in the presence of the metal by a template synthesis involving ethylenediamine and the dialdehyde;[2] since the former is present in excess, it may be that prolonged heating of the reaction mixture in air causes oxidation and subsequent condensation of a further mole. It has also been observed that prolonged heating of the dimethylformamide reaction mixture in air rather than in inert atmosphere leads to a low yield of (II) and a substantial quantity of tar.

[3/2310 *Received, 12th November*, 1973]

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