Structure and Redox Properties of Some Planar [M^{II}N$_4$] Chelate Compounds of Cobalt and Nickel.
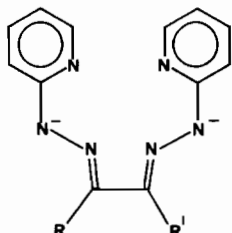# Part III*. Crystal and Molecular Structure of Bis[cyclohexane-1,2-bis-2'-pyridylhydrazonato]-dinickel(II), 2-benzene

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The structure of the title compound has been determined by a three-dimensional X-ray structural analysis. Crystals were monoclinic with a = 9.97(1), b = 21.77(1), c = 19.74(2) Å, β = 102.0(1)°, space group P2₁/c, and Z = 4. The structure was solved by conventional Patterson and Fourier techniques, and was refined anisotropically by block-diagonal least-squares methods using 2979 independent reflections, obtained by visual estimation of photographs, to a final R of 0.085. The analysis shows an unusual dimeric structure in which two nickel atoms share the two quadridentate ligands. Each nickel atom has an essentially four co-planar coordination polyhedron made up from three nitrogens from one ligand and a pyridyl nitrogen of the other ligand {pyridyl N–C–N–N–C–C–N–N–C–N }.

The Ni–N distances are (a) (terminal pyridyl) 1.89(1) Å; (b) (bridging pyridyl) 1.94(1) Å; and (c) (hydrazone) 1.84(1) Å. There are two N–C–N groups bridging the two nickel atoms. The coordination planes of the nickels are inclined at 34° to one another. The relatively short Ni–Ni distance of 2.809(2) Å is indicative of a significant metal–metal bond. Some disorder was evident in the positions of some of the atoms of the cyclohexyl moieties, and there was only partial occupancy of one of the three independent sites for benzene molecules.

Introduction

Reactions of the dianionic ligands I with nickel-(II) or palladium(II) compounds were found [1] to give a novel

series of dimeric compounds [M₂(L)₂] in addition to the previously described [2–4] monomeric species. The dimers were characterised by their ¹H NMR, electronic, and mass spectra [1], and an X-ray structural analysis was undertaken to determine the structure. For the latter, the first available compound was chosen – the nickel(II) species of the ligand I, for which R + R' = (CH₂)₄ – and here we report the final details of our analysis of this structure.

Experimental

Opaque red crystals of the solvate, obtained from benzene, rapidly lost solvent on exposure to air, and thus were mounted in sealed Lindemann glass capillaries which also contained some of the mother liquor. Although the crystals were not in contact with the solution phase, they had limited life for data collection. Decay of crystallinity, characterised by a deterioration in the quality of the photographic data, was accompanied by the appearance of small holes in the surface of the crystals.

Crystal Data

[Ni₂(C₁₆H₁₆N₆)₂], 1.91(2). C₆H₆; *M* = 852.9. Monoclinic, *a* = 9.97(1), *b* = 21.77(1), *c* = 19.74(2) Å, β = 102.0(1)°, *U* = 4185 Å³, *D_m* = 1.37 g cm⁻³ (by flotation), *Z* = 4, *D_c* = 1.36 g cm⁻³, *F*(000) = 1780. Space group *P2₁/c* [*C₂ₕ⁵*, No. 14] from systematic absences. Ni-filtered CuK_α radiation, λ = 1.5418 Å, μ(CuK_α) = 14.4 cm⁻¹.

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*Part II. E. D. McKenzie, R. D. Moore and J. M. Worthington, *Inorg. Chim. Acta, 14,* 37 (1975).
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Photographic X-ray data were collected by the Weissenberg equi-inclination method using multiple film packs. Layers {*h, k,* 0 → 6}, {*h, k,* 7 → 9}, and {*h, k,* 10 → 17} were collected from three separate crystals (dimensions were approx. 0.78 × 0.14 × 0.12, 0.49 × 0.20 × 0.09, and 0.60 × 0.14 × 0.11 mm, respectively).

The visually estimated intensities were corrected for Lorentz, polarisation, spot-shape, and absorption effects, and, at an advanced state of refinement, the reflections {0, 2 1}, {0, 3, 1}, {$\bar{1}$, 0, 2}, and {1, 0, 0} were removed from the data set because of probable extinction effects. Initial layer scaling used precession {*h,* 0, *l*} and {0, *k, l*} data (MoK$_\alpha$ radiation), but these were removed from the data set before allowance was made for absorption and anomalous scattering. Layer scales were subsequently refined by correlation with calculated structure factors before the introduction of anisotropic temperature parameters. The final data set comprised 2979 independent reflections.

The structure was solved by conventional Patterson and Fourier techniques and refined by block-diagonal least-squares methods.

An early difference Fourier showed that one of the non-aromatic carbocyclic residues was probably subject to disorder. Three of the four carbon atoms of this moiety were found to show either conformational disorder or highly anisotropic thermal motion. However, whereas an ordered isotropic model gave *divergence* of thermal parameters in refinement, a disorder model with two components and isotropic thermal parameters gave adequate convergence. The remaining carbon atoms of this aliphatic carbocyclic moiety and those of the other aliphatic carbocyclic group showed a similar, but smaller, tendency to disorder. However, isotropic thermal parameters refined successfully for all these atoms, and the quality of the data was not considered adequate for a further elaboration of the disorder model in refinement.

Benzene molecules were located in three independent sites. One was in a general position and behaved normally on refinement. The atoms of the two others, which occur about the inversion centres at (0, ½, 0), and (½, ½, 0), had high isotropic vibrational parameters in refinement, suggesting partial occupation of the sites.

A final refinement scheme was adopted as follows:

(*i*) For the nickel atoms, positional and anisotropic thermal parameters were refined and anomalous dispersion corrections (both Δ*f'* and Δ*f''*) were applied to the scattering factors.

(*ii*) {C(7), C(8), C(9)} and {C(71), C(81), C(91)} (Fig. 1) were refined as rigid groups with coupled (sum = 1.0) but different populations. The bond lengths were fixed at 1.54 Å and the C–C–C angle at 112° {as found in the residue C(23)–C(26)}.

(*iii*) The atoms C(6), C(10), C(11) and C(22)–C(27) were refined independently with isotropic thermal parameters.

(*iv*) The remaining carbon and nitrogen atoms of the quadridentate ligands were refined independently with anisotropic thermal parameters. (Hamilton's *R*-factor ratio test [5] indicated that the inclusion of the latter gave an improvement with a probability in excess of 95%).

(*v*) Hydrogen atoms of the pyridyl residues (located from a low-angle difference Fourier synthesis) were included, but not refined, at calculated positions (C–H = 0.95 Å, ref. 6) and with fixed isotropic thermal parameters of 5.5 Å^2.

(*vi*) The benzene molecules were refined as rigid planar groups with C–C = 1.39 Å. Isotropic thermal parameters were allowed for the atoms: those of the molecules centred at (½, ½, 0) were varied as a single parameter with simultaneous refinement of a population parameter for the molecule.

(*vii*) A weighting scheme was used which set $w_{hkl} = 36/|F_{hkl}|$ for $|F_{hkl}| > 36$, but unity for the remainder. This gave no systematic variation of mean $w\{|F_o| - |F_c|\}^2$ with change in $|F_o|$.

Parameter shifts were reduced to less than one-sixth of their e.s.d.'s with $R = 0.085$.

The final atomic positional and vibrational parameters are given in Table I.

Scattering factors and correction parameters were taken from International Tables [7]. Programmes used were part of the Sheffield X-ray system. Calculations were performed on the Sheffield University ICL1907 computer.

Observed and calculated structure factors are listed in a Table available from the Editor.

Results and Discussion

Each asymmetric unit of the full cell contains one [Ni$_2$(L)$_2$] molecule, one benzene molecule in a general position, and halves of two other benzene molecules which are located across centres of symmetry at (0, ½, 0) and (½, ½, 0). The latter appears to be the most readily lost from the solid, since the present analysis of these unstable crystals suggested only ~80% occupancy of the site.

The geometry of the binuclear nickel(II) compound is given in Fig. 1(a), and the atom labelling scheme in Fig. 1(b). Bond-lengths and angles within the dimer are listed in Table II.

Each nickel is bonded to four nitrogen atoms which are in an essentially planar array, as expected from the diamagnetism of the compound. Each quadridentate ligand is bonded by three of its nitrogen atoms to one nickel and by a fourth (from a pyridyl moiety) to the second nickel. The ligands form two N–C–N bridges between the two nickels

TABLE I. Atomic Positional and Thermal Parameters with Estimated Standard Deviations (from Block-diagonal least-squares Refinement) in Parentheses.

A) *Fractional coordinates* $(\times 10^4)$ *of the non-hydrogen atoms with isotropic thermal parameters where appropriate*

Atom	x/a	y/b	z/c	B (Å^2)
Ni(1)	402.2(16)	1681.5(7)	1018.4(9)	
Ni(2)	2986.0(16)	2246.9(7)	1204.2(8)	
N(1)	847(8)	1025(4)	1651(4)	
N(2)	−329(9)	1663(4)	2290(4)	
N(3)	−518(8)	1985(4)	1660(4)	
N(4)	−1018(9)	2809(4)	479(5)	
N(5)	302(8)	2394(3)	500(4)	
N(6)	2193(9)	2495(4)	262(4)	
N(7)	2546(8)	2980(4)	1613(4)	
N(8)	3606(9)	2450(4)	2604(5)	
N(9)	3900(8)	2073(4)	2094(4)	
N(10)	4450(8)	1091(4)	1183(4)	
N(11)	3362(8)	1472(4)	913(4)	
N(12)	1137(8)	1290(3)	294(4)	
C(1)	1591(11)	488(5)	1616(7)	
C(2)	1926(13)	87(5)	2162(7)	
C(3)	1454(14)	220(6)	2768(7)	
C(4)	678(14)	730(6)	2812(6)	
C(5)	375(11)	1147(5)	2246(6)	
C(6)	−1366(10)	2456(5)	1603(5)	3.47(3)
C(7) ⎫	−2172(32)	2580(15)	2178(16)	4.4(3) ⎫
C(8) ⎬ a,d	−3095(30)	3154(11)	2060(13)	5.4(3) ⎪
C(9) ⎭	−3930(32)	3192(15)	1311(16)	5.9(3) ⎬ b
C(71) ⎫	−1672(56)	2664(19)	2330(25)	4.4(3) ⎪
C(81) ⎬ a,e	−2454(52)	3272(18)	2347(18)	5.4(3) ⎪
C(91) ⎭	−2969(56)	3538(19)	1616(25)	5.9(3) ⎭
C(10)	−2802(14)	3320(6)	863(7)	5.73(5)
C(11)	−1669(11)	2819(5)	984(6)	3.84(3)
C(12)	817(10)	2557(5)	23(5)	
C(13)	263(12)	2753(6)	−651(6)	
C(14)	1136(13)	2860(5)	−1086(6)	
C(15)	2556(14)	2772(6)	−852(6)	
C(16)	3066(12)	2594(5)	−191(6)	
C(17)	1878(12)	3504(5)	1308(6)	
C(18)	1441(14)	3961(5)	1684(6)	
C(19)	1738(15)	3901(6)	2406(7)	
C(20)	2419(14)	3393(5)	2722(6)	
C(21)	2858(10)	2930(5)	2300(5)	
C(22)	4841(10)	1632(5)	2292(5)	3.45(3)
C(23)	5490(12)	1581(6)	3051(6)	4.83(4)
C(24)	6772(13)	1155(6)	3222(7)	5.49(4)
C(25)	6546(14)	572(6)	2786(7)	6.01(5)
C(26)	6398(13)	757(6)	2024(7)	5.16(4)
C(27)	5170(10)	1184(5)	1812(5)	3.38(3)
C(28)	2486(10)	1203(4)	332(5)	
C(29)	2979(11)	879(5)	−184(6)	
C(30)	2051(13)	678(5)	−738(6)	
C(31)	652(13)	773(6)	−801(6)	
C(32)	225(11)	1083(5)	−293(6)	
C(33) ⎫	−3201(11)	1459(5)	68(5)	5.8(4)
C(34) ⎪	−3649(12)	1853(4)	−488(6)	5.6(4)
C(35) ⎪	−4163(11)	1614(5)	−1144(5)	6.5(4)
C(36) ⎬ a	−4229(11)	981(5)	−1244(5)	6.9(5)
C(37) ⎪	−3781(12)	588(4)	−688(6)	5.3(4)
C(38) ⎭	−3267(11)	827(5)	−32(5)	5.1(4)

(continued overleaf)

TABLE I. *(continued)*

Atom		x/a	y/b	z/c	B (Å^2)
C(39)	a	1238(7)	5163(6)	−169(7)	6.2(4)
C(40)		474(12)	5601(2)	98(7)	5.6(4)
C(41)		−764(11)	5438(4)	266(6)	5.6(4)
C(42)	a,f	4906(16)	4848(7)	672(3)	
C(43)		5407(16)	5420(5)	534(5)	5.85^c
C(44)		5501(16)	5572(3)	−139(8)	

B) *Calculated fractional coordinates of hydrogen atoms ($\times 10^3$). Estimated overall isotropic thermal parameter 5.5* Å^2

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
H[C(1)]	190	398	117	H[C(17)]	173	354	79
H[C(2)]	248	−29	211	H[C(18)]	95	432	144
H[C(3)]	171	−6	317	H[C(19)]	143	423	270
H[C(4)]	29	81	324	H[C(20)]	259	335	324
H[C(13)]	−76	280	−81	H[C(29)]	400	81	−14
H[C(14)]	80	301	−156	H[C(30)]	238	44	−111
H[C(15)]	316	283	−118	H[C(31)]	−2	62	−122
H[C(16)]	407	253	−3	H[C(32)]	−78	117	−33

C) *Anisotropic thermal parameters ($\times 10^5$). The expression for the temperature factors is:* $exp[-(h^2 b_{11} + k^2 b_{22} + l^2 b_{33} + klb_{23} + hlb_{13} + hkb_{12})]$

Atom	b_{11}	b_{22}	b_{33}	b_{23}	b_{13}	b_{12}
Ni(1)	770(3)	160(1)	205(1)	−30(1)	223(3)	4(2)
Ni(2)	783(3)	156(1)	167(1)	−23(1)	148(2)	5(2)
N(1)	1052(17)	145(3)	226(5)	12(6)	226(15)	42(12)
N(2)	1259(20)	256(4)	155(5)	−1(7)	131(15)	−18(14)
N(3)	815(15)	175(3)	222(8)	−40(6)	393(14)	117(12)
N(4)	975(17)	176(3)	328(5)	72(7)	251(16)	132(12)
N(5)	735(15)	161(3)	224(5)	2(6)	64(14)	163(11)
N(6)	1080(17)	159(3)	200(5)	1(6)	254(15)	29(12)
N(7)	804(15)	152(3)	173(4)	−21(6)	73(13)	71(11)
N(8)	1182(18)	212(4)	208(5)	−103(7)	191(16)	93(13)
N(9)	956(16)	165(3)	154(4)	−47(6)	193(13)	−140(11)
N(10)	776(16)	185(3)	265(5)	75(6)	461(14)	97(11)
N(11)	677(15)	175(3)	264(5)	−133(6)	179(14)	125(11)
N(12)	785(15)	135(3)	240(4)	−3(6)	233(14)	85(11)
C(1)	972(22)	174(4)	421(7)	−3(9)	377(21)	−18(15)
C(2)	1716(30)	202(5)	376(8)	141(10)	462(25)	355(19)
C(3)	1531(29)	274(5)	363(8)	48(11)	112(24)	126(20)
C(4)	1876(32)	286(5)	211(6)	111(10)	235(23)	152(21)
C(5)	1051(22)	205(4)	235(6)	−102(8)	54(19)	22(16)
C(12)	717(17)	194(4)	144(5)	−4(7)	36(16)	−20(14)
C(13)	1124(23)	255(5)	264(6)	55(10)	23(20)	163(18)
C(14)	1609(28)	244(5)	212(6)	−5(9)	351(21)	106(19)
C(15)	2007(32)	237(5)	270(7)	57(10)	774(23)	−98(21)
C(16)	1316(24)	214(5)	275(7)	−20(9)	727(21)	−199(16)
C(17)	1385(25)	176(4)	209(6)	−68(8)	117(20)	−74(16)
C(18)	2021(32)	209(5)	258(6)	−86(9)	−35(24)	290(20)
C(19)	2379(37)	214(5)	293(7)	−313(10)	153(26)	491(22)
C(20)	1826(31)	220(5)	227(6)	−135(9)	136(22)	397(19)

TABLE I. *(continued)*

Atom	b_{11}	b_{22}	b_{33}	b_{23}	b_{13}	b_{12}
C(21)	874(19)	199(4)	170(5)	−53(7)	87(17)	85(14)
C(28)	927(20)	141(3)	197(5)	−2(7)	286(17)	−78(13)
C(29)	1126(23)	204(4)	272(6)	−49(9)	437(20)	159(16)
C(30)	1653(28)	234(5)	194(6)	−160(9)	278(21)	62(19)
C(31)	1470(27)	257(5)	230(6)	−134(9)	243(21)	−19(19)
C(32)	977(21)	229(4)	240(6)	−45(9)	47(19)	−142(16)

[a]Atoms bracketed thus are members of the same group (with fixed internal geometry). Estimated standard deviations in fractional coordinates are calculated from those of the positional and orientational parameters of these rigid groups; [b]Shifts of these thermal parameters all correlated, relative values fixed; [c]Isotropic thermal parameter fixed at this value; [d]Group population parameter $p_1 = 0.62(2)$; [e]Group population parameter $p_2 = 1.0 - p_1 = 0.38(2)$; [f]Group population parameter 0.82(2).
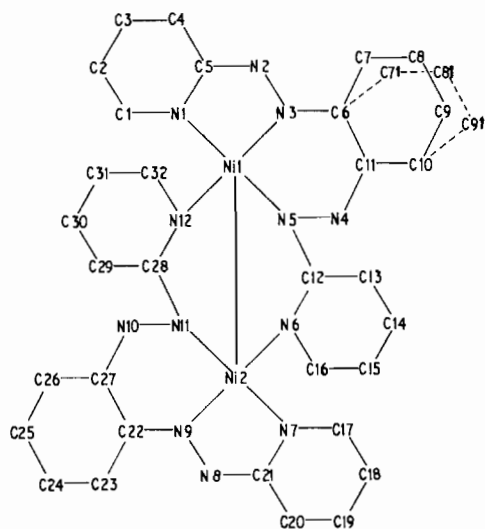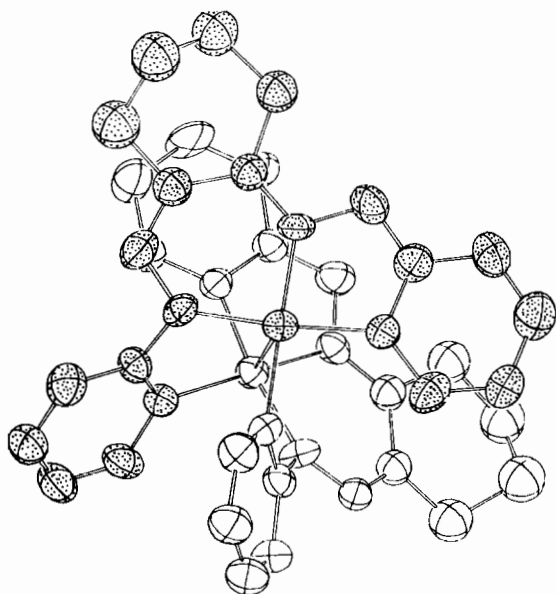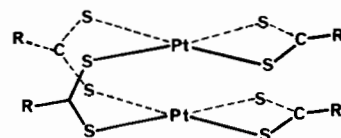

Fig. 1. (a) The molecular geometry of Bis[cyclohexane-1,2-bis-2'-pyridylhydrazonato]-dinickel. (b) The atom labelling for Bis[cyclohexane-1,2-bis-2'-pyridylhydrazonato]-dinickel.

in a structure that has a direct parallel in a bis-μ-dithiocarbamato-diplatinum(II) species [8] II.

II

The angle between the two nickel co-ordination planes is ~34°.

There are small tetrahedral twists in the [NiN₄] coordination polyhedra: the angles between the two three-atom planes such as {Ni(1), N(1), N(3)} and {Ni(1), N(5), N(12)} being ~9° (Table III).

The Ni–N *bond-lengths* are significantly different for the different donor atom types: (a) (terminal pyridyl) = 1.89(1) Å; (b) (bridging pyridyl) = 1.94(1) Å; and (c) (hydrazone) = 1.84(1) Å. Both the (a) and the (c) type bond-lengths are normal for diamagnetic four-coplanar nickel(II), but the (b) type bonds are at the upper limits for known diamagnetic Ni^{II}–N bond lengths [9]. The long (b)-type bonds reflect a steric strain in the bridging system, which is also manifested in other distortions discussed below.

The Ni–Ni distance of 2.809(2) Å, although longer than the distances observed in some compounds which have a copper(II) acetate structure {2.50 [10], 2.56 [11] and 2.40 [12]}, is comparable with those of several oligomeric μ-thiolato nickel(II) species [13] (observed values of 2.73, 2.76 and 2.72 Å), and with the Pt–Pt distance [8] of 2.87 Å for II. But it is much less than in other Ni–Ni bonded species such as [Ni(dmg)₂] [14], [Ni(salen)] [15], and [Ni(saltn)] [16], where the observed distances are 3.2 → 3.3 Å. Further, the nickels here are not constrained to the shorter distance: framework molecular models suggest that the Ni–Ni distance in the hydrazone dimer could expand beyond 3 Å without significant distortion of ligand bond angles. The evidence strongly suggests a significant metal–

TABLE II. Interatomic Distances (A) and Angles (°) with Estimated Standard Deviations in Parentheses.

A) *The Nickel(II) Coordination Polyhedra*

i) Bond-lengths

	Ni(1)–Ni(2)	2.809(2)	
Ni(1)–N(1)	1.888(8)	Ni(2)–N(6)	1.940(9)
Ni(1)–N(3)	1.835(8)	Ni(2)–N(7)	1.881(8)
Ni(1)–N(5)	1.853(8)	Ni(2)–N(9)	1.842(8)
Ni(1)–N(12)	1.936(8)	Ni(2)–N(11)	1.845(8)

ii) Bond-angles

N(1)–Ni(1)–N(3)	84.1(4)	N(7)–Ni(2)–N(9)	83.1(4)
N(3)–Ni(1)–N(5)	90.5(4)	N(9)–Ni(2)–N(11)	91.0(4)
N(5)–Ni(1)–N(12)	91.3(4)	N(11)–Ni(2)–N(6)	91.4(4)
N(12)–Ni(1)–N(1)	94.7(4)	N(6)–Ni(2)–N(7)	95.2(4)
N(1)–Ni(1)–Ni(2)	99.4(3)	N(7)–Ni(2)–Ni(1)	97.9(3)
N(3)–Ni(1)–Ni(2)	109.2(3)	N(9)–Ni(2)–Ni(1)	107.0(3)
N(5)–Ni(1)–Ni(2)	77.2(3)	N(11)–Ni(2)–Ni(1)	78.4(3)
N(12)–Ni(1)–Ni(2)	79.1(2)	N(6)–Ni(2)–Ni(1)	79.5(3)
N(1)–Ni(1)–N(5)	172.4(4)	N(7)–Ni(2)–N(11)	171.8(4)
N(3)–Ni(1)–N(12)	171.7(4)	N(6)–Ni(2)–N(9)	173.5(4)

B) *The Hydrazone Ligands* (Corresponding distances and angles from each ligand are listed in parallel in the two columns)

i) Bond-lengths

N(1)–C(1)	1.39(1)	N(7)–C(17)	1.39(1)
N(1)–C(5)	1.38(1)	N(7)–C(21)	1.33(1)
C(1)–C(2)	1.37(2)	C(17)–C(18)	1.37(2)
C(2)–C(3)	1.40(2)	C(18)–C(19)	1.40(2)
C(3)–C(4)	1.37(2)	C(19)–C(20)	1.38(2)
C(4)–C(5)	1.42(2)	C(20)–C(21)	1.43(2)
C(5)–N(2)	1.34(1)	C(21)–N(8)	1.35(1)
N(2)–N(3)	1.40(1)	N(8)–N(9)	1.38(1)
N(3)–C(6)	1.32(1)	N(9)–C(22)	1.34(1)
C(6)–C(11)	1.43(2)	C(22)–C(27)	1.44(1)
C(6)–C(7)	1.55(3)	C(22)–C(23)	1.51(2)
C(7)–C(8)	1.54[a]	C(23)–C(24)	1.56(2)
C(8)–C(9)	1.54[a]	C(24)–C(25)	1.52(2)
C(9)–C(10)	1.59(3)	C(25)–C(26)	1.53(2)
C(10)–C(11)	1.55(2)	C(26)–C(27)	1.52(2)
C(6)–C(71)	1.59(5)		
C(71)–C(81)	1.54[a]		
C(81)–C(91)	1.54[a]		
C(91)–C(10)	1.60(5)		
C(11)–N(4)	1.30(1)	C(27)–N(10)	1.31(1)
N(4)–N(5)	1.38(1)	N(10)–N(11)	1.38(1)
N(5)–C(12)	1.39(1)	N(11)–C(28)	1.41(1)
C(12)–N(6)	1.36(1)	C(28)–N(12)	1.35(1)
C(12)–C(13)	1.40(2)	C(28)–C(29)	1.41(1)
C(13)–C(14)	1.36(2)	C(29)–C(30)	1.35(2)
C(14)–C(15)	1.41(2)	C(30)–C(31)	1.39(2)
C(15)–C(16)	1.36(2)	C(31)–C(32)	1.35(2)
C(16)–N(6)	1.39(1)	C(32)–N(12)	1.39(1)

ii) Bond-angles

Ni(1)–N(1)–C(1)	131.0(7)	Ni(2)–N(7)–C(17)	130.0(7)
Ni(1)–N(1)–C(5)	110.1(7)	Ni(2)–N(7)–C(21)	110.0(6)
Ni(1)–N(3)–N(2)	115.9(6)	Ni(2)–N(9)–N(8)	115.8(6)
Ni(1)–N(3)–C(6)	128.6(7)	Ni(2)–N(9)–C(22)	127.0(7)

TABLE II. *(continued)*

Ni(1)–N(5)–N(4)	129.0(6)	Ni(2)–N(11)–N(10)	128.5(6)
Ni(1)–N(5)–C(12)	120.7(6)	Ni(2)–N(11)–C(28)	120.1(7)
Ni(2)–N(6)–C(12)	122.6(7)	Ni(1)–N(12)–C(28)	123.3(7)
Ni(2)–N(6)–C(16)	118.4(7)	Ni(1)–N(12)–C(32)	118.4(8)
C(1)–N(1)–C(5)	118.8(9)	C(17)–N(7)–C(21)	119.7(8)
N(1)–C(1)–C(2)	123(1)	N(7)–C(17)–C(18)	123(1)
C(1)–C(2)–C(3)	118(1)	C(17)–C(18)–C(19)	118(1)
C(2)–C(3)–C(4)	121(1)	C(18)–C(19)–C(20)	121(1)
C(3)–C(4)–C(5)	120(1)	C(19)–C(20)–C(21)	119(1)
N(1)–C(5)–N(2)	119.5(9)	N(7)–C(21)–N(8)	120.4(9)
C(4)–C(5)–N(1)	119(1)	C(20)–C(21)–N(7)	120.0(9)
C(4)–C(5)–N(2)	121(1)	C(20)–C(21)–N(8)	120(1)
C(5)–N(2)–N(3)	109.8(8)	C(21)–N(8)–N(9)	108.7(8)
N(3)–C(6)–C(11)	121.3(9)	N(9)–C(22)–C(27)	122.2(9)
N(2)–N(3)–C(6)	115.5(8)	N(8)–N(9)–C(22)	117.1(8)
N(3)–C(6)–C(7)	120(1)	N(9)–C(22)–C(23)	118.1(9)
N(3)–C(6)–C(71)	112(2)		
C(7)–C(6)–C(11)	119(1)	C(23)–C(22)–C(27)	119.5(9)
C(71)–C(6)–C(11)	124(2)		
C(6)–C(7)–C(8)	115(2)	C(22)–C(23)–C(24)	115(1)
C(6)–C(71)–C(81)	117(4)		
C(7)–C(8)–C(9)	112[a]	C(23)–C(24)–C(25)	111(1)
C(71)–C(81)–C(91)	112[a]		
C(8)–C(9)–C(10)	104(2)	C(24)–C(25)–C(26)	108(1)
C(81)–C(91)–C(10)	133(4)		
C(9)–C(10)–C(11)	112(1)	C(25)–C(26)–C(27)	110(1)
C(91)–C(10)–C(11)	106(2)		
C(6)–C(11)–N(4)	127(1)	C(22)–C(27)–N(10)	124.7(9)
C(6)–C(11)–C(10)	122(1)	C(26)–C(27)–C(22)	120.7(9)
C(10)–C(11)–N(4)	111(1)	C(26)–C(27)–N(10)	114.6(9)
C(11)–N(4)–N(5)	119.1(9)	C(27)–N(10)–N(11)	120.3(8)
N(4)–N(5)–C(12)	110.2(8)	N(10)–N(11)–C(28)	111.5(8)
N(5)–C(12)–C(13)	123.8(9)	N(11)–C(28)–C(29)	123.0(9)
N(5)–C(12)–N(6)	114.3(8)	N(11)–C(28)–N(12)	115.3(8)
N(6)–C(12)–C(13)	122.0(9)	N(12)–C(28)–C(29)	121.7(9)
C(12)–C(13)–C(14)	118(1)	C(28)–C(29)–C(30)	118(1)
C(13)–C(14)–C(15)	120(1)	C(29)–C(30)–C(31)	122(1)
C(14)–C(15)–C(16)	120(1)	C(30)–C(31)–C(32)	118(1)
C(15)–C(16)–N(6)	120(1)	C(31)–C(32)–N(12)	122(1)
C(16)–N(6)–C(12)	118.9(9)	C(32)–N(12)–C(28)	118.3(8)

[a]Fixed parameter of a rigid group.

TABLE III. Equations of Some Least-squares Planes Given in the Form $lX + mY + nZ = d$ (where X, Y and Z are A Coordinates referred to the Axes a, b and c^*). The Deviations of Various Atoms from these Planes are given in Square Brackets. Angles between Some of the Planes are given at the End of the Table.

	l	m	n	d
Plane (1)				
N(1), N(3), N(5), N(12)	−0.8029	−0.4123	−0.4305	−2.3145
[N(1) −0.109, N(3) 0.117, N(5) −0.108, N(12) 0.100, Ni(1) −0.026, C(5) −0.139, N(2) −0.060, C(6) 0.401, C(11) 0.628, N(4) 0.369]				
Plane (2)				
N(6), N(7), N(9), N(11)	−0.9184	−0.3677	0.1460	−3.7460
[N(6) −0.086, N(7) 0.094, N(9) −0.101, N(11) 0.092, Ni(2) 0.009, C(21) 0.302, N(8) 0.202, C(22) −0.480, C(27) −0.739, N(10) −0.420]				

TABLE III. *(continued)*

	l	*m*	*n*	*d*
Plane (3)				
Ni(1), N(1), N(3)	0.7476	0.4841	0.4548	2.6521
[C(5) 0.116, N(2) 0.160]				
Plane (4)				
Ni(1), N(5), N(12)	0.8433	0.3493	0.4085	2.0660
Plane (5)				
Ni(2), N(7), N(9)	0.8844	0.4282	−0.1856	3.8568
[C(21) −0.268, N(8) −0.276]				
Plane (6)				
Ni(2), N(6), N(11)	0.9422	0.3147	−0.1151	3.6090
Plane (7)				
N(5), C(12), N(6), Ni(2)	0.0342	−0.9526	−0.3022	−5.2697
[N(5) 0.009, C(12) −0.017, N(6) 0.015, Ni(2) −0.007, Ni(1) 1.189]				
Plane (8)				
N(11), C(28), N(12), Ni(1)	−0.1086	−0.8715	0.4783	−2.2584
[N(11) −0.014, C(28) 0.030, N(12) −0.027, Ni(1) 0.011, Ni(2) −1.161]				
Plane (9)				
N(1), C(1)–C(5)	0.7818	0.5091	0.3600	2.3991
[N(1) 0.012, C(1) −0.015, C(2) 0.004, C(3) 0.010, C(4) −0.013, C(5) 0.002, N(2) 0.040, Ni(1) 0.157]				
Plane (10)				
N(7), C(17)–C(21)	0.8808	0.4711	0.0479	4.8751
[N(7) −0.020, C(17) 0.013, C(18) −0.004, C(19) 0.001, C(20) −0.008, C(21) 0.017, N(8) 0.099, Ni(2) 0.275]				
Plane (11)				
N(6), C(12)–C(16)	−0.0247	−0.9564	−0.2910	−5.3733
[N(6) −0.018, C(12) 0.019, C(13) −0.004, C(14) −0.009, C(15) 0.009, C(16) 0.004, N(5) 0.114, Ni(2) −0.0242]				
Plane (12)				
N(12), C(28)–C(32)	0.1730	0.8655	−0.4702	2.3548
[N(12) −0.017, C(28) 0.014, C(29) −0.005, C(30) −0.001, C(31) −0.002, C(32) 0.010, N(11) 0.105, Ni(1) −0.115]				

Angles between planes (°)

(1)–(2)	34.3	(5)–(6)	8.3
(1)–(12)	107.1	(7)–(8)	47.0
(1)–(9)	173.0	(8)–(12)	176.3
(2)–(10)	167.2	(7)–(11)	3.4
(2)–(11)	70.6	(11)–(12)	134.0
(3)–(4)	9.8		

metal–metal bond, and adds a further example to the growing list of weak (?) homonuclear bonds between low-spin d^8 metal atoms.

Bond-angles and bond-lengths within the ligands are, within experimental error, in close agreement with those in related compounds [4, 17].

Unfortunately, the accuracy of the present analysis is insufficient to allow any useful comments on the interesting problem of bond-orders of the alternating C–C, N–N, and C–N bonds, and the probable delocalisation of the negative charge of the de-protonated ligand I.

Within the accuracy of the analysis, however, some distortions are apparent in the overall ligand geometries:

(*a*) The N–C–N bridges between the two nickels are not symmetrical: whereas Ni(2) is co-planar with the N(5)–C(12)–N(6) moiety, it is 1.2 Å out of the plane of the N(11)–C(28)–N(12) moiety, and *vice versa* for Ni(1).

(*b*) The pyridyl moieties are not co-planar with the appropriate {Ni, N, C, N} moieties: compare planes (11) and (12) in Table III; and

(*c*) The two five-membered chelate rings are not co-planar with the metal {planes (3) and (5) of Table III}.

The dimeric structure is an almost inevitable result of the use of nitrogens (5) and (11) as donor atoms rather than N(2) and N(10) as in the monomer [4], and the driving force for this expansion of a five-membered chelate ring (in the monomer) to a six-membered one (in the dimer) appears to be the relief of some of the cumulative ring strain in the monomer. The latter is particularly evident [4] in the N–Ni–N bond angles and in the long Ni–N (terminal pyridyl) bond-lengths [4] of 1.94 Å (av). As noted above, we observe significantly shorter bonds (1.89 Å) to our relatively unstrained terminal pyridyls, and equally long bonds (1.94 Å) to the bridging pyridyls, which appear from other (angular) distortions to be in a strained situation.

The results of our preparation [1] of a wide variety of compounds of Ni^{II}, and Pd^{II} of the ligands I also lend support to the contention that this dimeric structure is formed largely because of steric strain inherent in the monomer.

Acknowledgements

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