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Stereochemistry of Bis(salicylaldiminato)metal(II) Compounds, Part (II)[a]. Crystal and Molecular Structure of a Binuclear Nickel(II) Compound with a Bridging Water Molecule $[Ni_2(C_{14}H_{11}N_2O_4)_4\cdot H_2O]\cdot 2H_2O$

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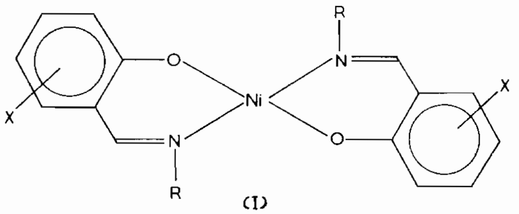
Yellow-green crystals of a 'sesquihydrate' of bis-[N-(4-methoxyphenyl)-5-nitrosalicylideneiminato]-nickel(II) are monoclinic, a = *17.04(3),* b = *20.16(2),* c = *36.44(6) Å, β = 99.42(1)°, space group C2/c. A three-dimensional X-ray analysis of the structure was made with counter data (2803 unique reflexions). The structure was solved by the heavy-atom method and refined by block-diagonal least-squares to a final* R *of 0.081 (*R′ = *0.107). Two octahedral* $[NiN_2O_4]$ *polyhedra are linked facially through two bridging phenolic oxygens and a water molecule. Two other water molecules are hydrogen-bonded to both the bridging water, and to phenolic oxygens of the Schiff base ligands, forming a compact unit* $[Ni_2(Schiff\ base)_4(H_2O)]\cdot 2H_2O$*. The nickel polyhedra are markedly distorted because of ligand constraints: bond angles at the nickels range from 74 to 104°, and the bond lengths from the nickels to the bridging water oxygen are rather long at 2.24(1) and 2.30(1) Å.*

Introduction

Nickel(II) bis-salicylaldiminates (I) are stereochemically versatile, with changes between four-co-planar, tetrahedral, five coordinate and octahedral structures being governed by a complex interplay of steric, electronic and entropy effects [1–5].



(I)

Oligomerisation of the compounds I occurs readily to give octahedral species, which we believe to be tetramers, with a cuboid arrangement of nickels and bridging phenolic oxygens [1]. To prove this point we have been looking for suitable crystals, but they seem rather scarce. Thus we proceeded with the current analysis of compound I for R = *p*-methoxyphenyl and X = 5-nitro although we were aware of the presence of other potential donor molecules (either water or ethanol) in the crystals: space group consideration gave cause for hope that a tetrameric structure would be found.

In the event, we found instead a novel dimeric structure, with a (so-far) unusual bridging water molecule. A preliminary report has appeared [6].

Experimental

Preparation of Compound

A suspension of the yellow Schiff base was prepared in hot ethanol (3.34 g aldehyde and 3.46 g amine in 100 ml). Nickel(II) acetate (2.15 g) in water (~10 ml) was then added, and the mixture was digested on the water-bath until all of the yellow ligand had been replaced by brown crystals of the trihydrate of the nickel compound (3–4 hr). The brown compound was filtered and washed with 95% ethanol. Found: wt. loss of 8.1% at 120 °C. Calc. for $Ni(C_{14}H_{11}N_2O_4)_2\cdot 3H_2O$:$3H_2O$, 8.2%.

Green crystals of the title compound were obtained by dissolving the brown product in hot acetone or butan-2-one, adding an equal volume of hot absolute ethanol, and setting the mixture aside to cool (use of 95% ethanol gives the brown trihydrate again). The most suitable crystals for X-ray work were obtained from butan-2-one. The one used for data collection approximated to an octahedral shape, with dimension 0.3 × 0.4 × 0.3 mm, and gave broad asymmetric diffraction maxima.

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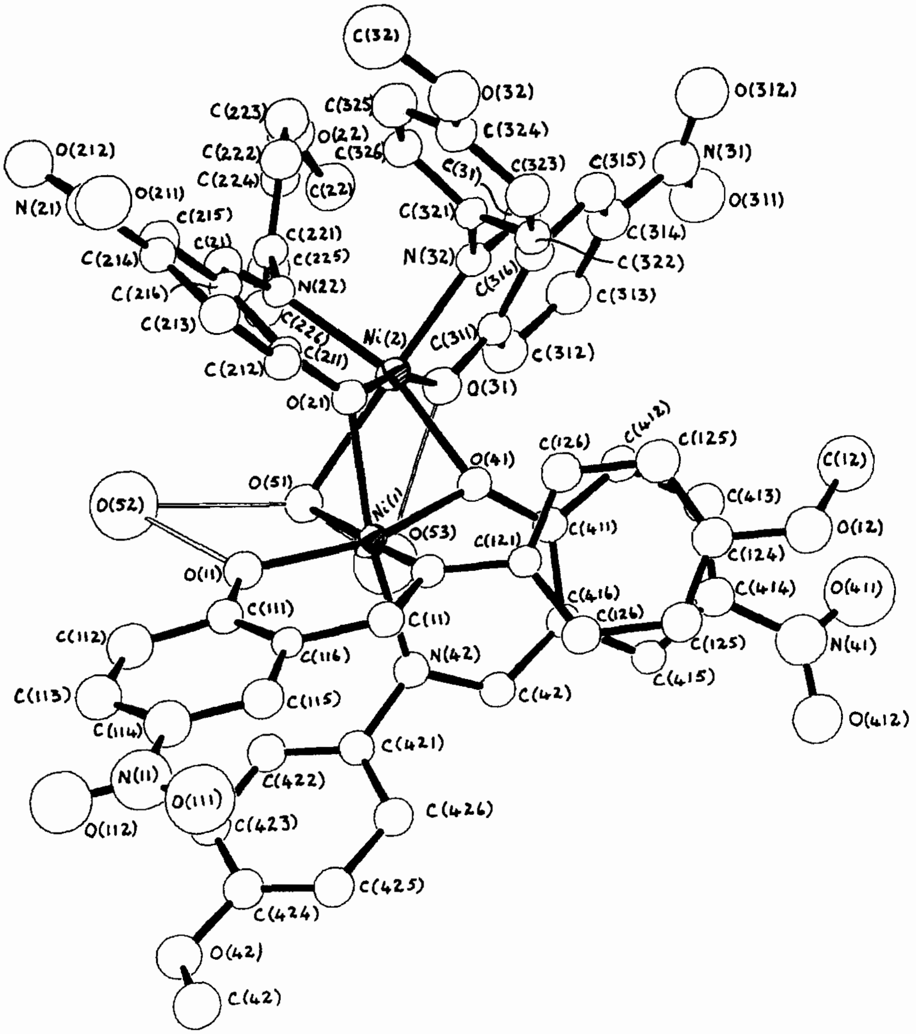

Figure 1. A perspective drawing of the asymmetric unit and the labelling of the atoms. Thermal ellipsoids are scaled to include 35% probability. Hydrogen bonds are indicated by open lines.

Crystal Data

$C_{56}H_{50}N_8Ni_2O_{19}$, M = 1256.5, monoclinic, a = 17.04(3), b = 20.16(2), c = 36.44(6) Å, β = 99.42(1)°, U = 12349 Å^3, D_m = 1.38 g cm^{-3} (by flotation), Z = 8, D_c = 1.35 g cm^{-3}, $F(000)$ = 3232, μ(Mo-K$_\alpha$) = 6.8 cm^{-1}. Systematic absences $h\ k\ l$ if $h + k \neq 2n$, $h\ 0\ l$ if $l \neq 2n$, space group $Cc(C_s^4$, No. 9) or $C2/c(C_{2h}^6$, No. 15).

X-ray data with $6.5 < 2\theta < 50°$ were collected from a crystal mounted along b on a Stoe Stadi-2 automatic diffractometer in stationary-counter-moving-crystal mode, using graphite-monochromated Mo-K$_\alpha$ radiation. Angular step-scan ranges were systematically varied to allow for variations in peak-width of the different reflexions and a counting-time of 0.5 sec was used for each 0.02° increment of scan. Background counts were accumulated for 10 sec at each extremity of the scan. The collection procedure was programmed to ignore reflexions with count-rates <20 counts/sec at the calculated peak centre. Reflexions with intensity $I < 3\sigma(I)$ were ignored, as were those with background difference $\Delta > 4\sigma(I)$. Lorentz and polarisation corrections were applied, but no allowance was made for absorption or extinction. A data set of 2803 unique reflexions was obtained.

Scattering factors were taken from International Tables for X-ray Crystallography [7]. Data processing used programmes from the Sheffield X-ray system on the Sheffield University ICL 1907 computer. Solution and refinement calculations were carried out on a UNIVAC 1106 computer at Macquarie University with programmes written by one of us (F.S.S.).

A three-dimensional Patterson synthesis indicated the centrosymmetric space group to be correct, and the structure was solved by the heavy-atom method. Refinement was by least-squares in which $\Sigma\omega\Delta^2$ was

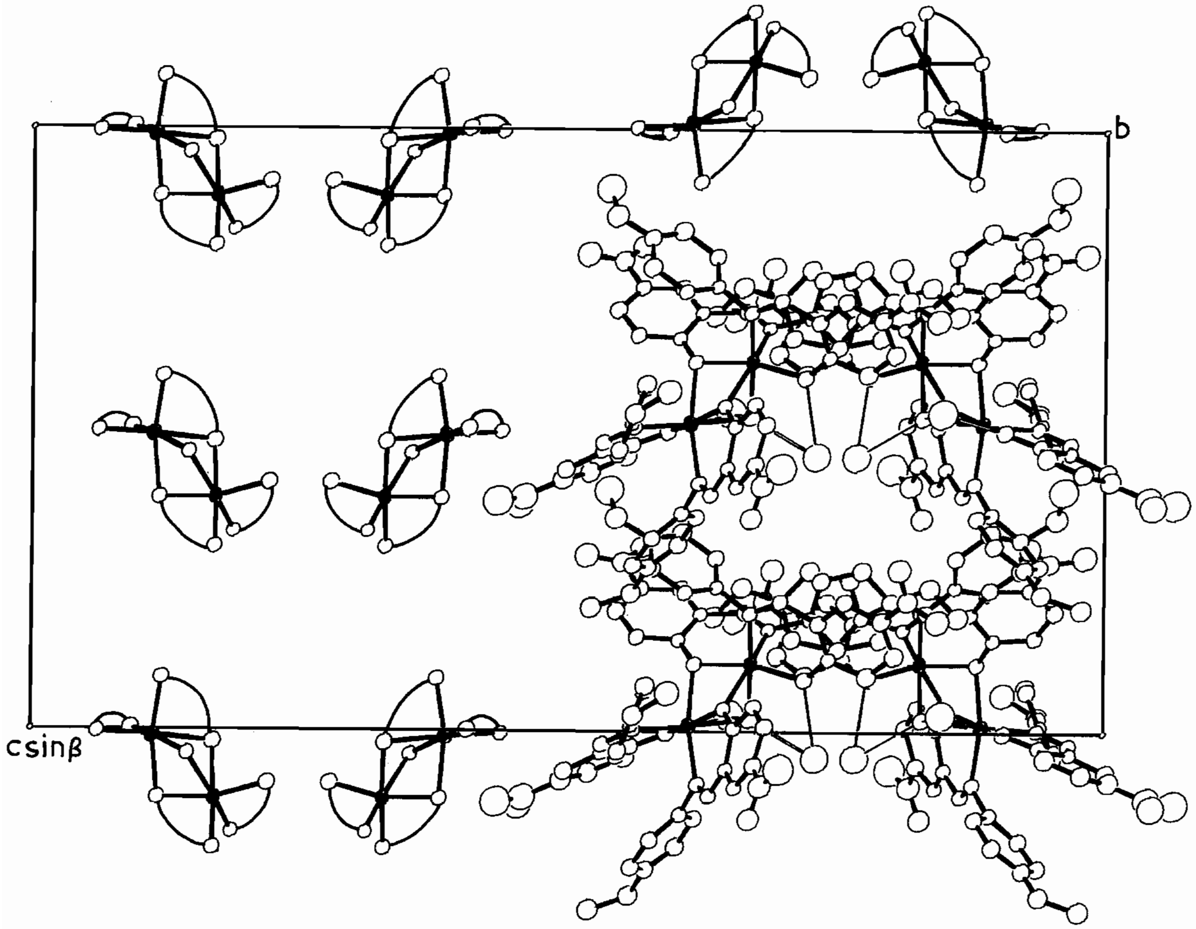

Figure 2. The contents of the unit cell projected down *a*. For clarity in some molecules only the coordination polyhedra are shown.

minimised. The weight for each reflexion was initially unity, but in the final stages $\omega = (100 - |F_o| + 0.0055|F_o|^2)^{-1}$. Reflexions for which $|F_c| < 1/3|F_o|$ were omitted. The large number of parameters (351) necessitated the use of block matrices and seven were employed: (1) overall scale and thermal parameters; (2) Ni atoms and the nine donor oxygen and nitrogen atoms; (3)–(6) the remaining atoms of the four ligand molecules; and (7) the lattice water molecules. Refinement was terminated when the maximum shift in any parameter was $<0.1\sigma$. 2799 reflexions were included in the final cycle. The final R, based on 2803 reflexions, was 0.081 and R' ($= [\Sigma\omega\Delta^2/\Sigma\omega|F_o|^2]^{1/2}$) was 0.107. A final difference map showed no features $>|0.8|$ eÅ^{-3}.

The final atomic parameters are given in Table I. A list of observed and calculated structure factors has been deposited with the Editor.

Results and Discussion

The molecular species observed and the atom-labelling scheme are in Figure 1 [8]. Figure 2 shows the contents of the unit-cell projected down *a* [8].

Two octahedral bis(salicylaldiminato)nickel(II) moieties are joined facially through one each of their phenolic oxygens and a water molecule. The $[NiN_2O_4]$ coordination polyhedra are markedly distorted at least in part due to ligand constraints. Bond lengths (Table II) are within the usually observed ranges, except for the rather long bonds to the bridging water molecule {O(51)}. In the few other known examples of water bridges in nickel(II) structures [9, 10] the Ni–OH_2 lengths are close to 2.10 Å, yet the observed lengths here are 2.24(1) and 2.30(1) Å. Perhaps some of this bond-lengthening can be accounted for by the involvement of the water molecule in hydrogen-bonds to two other waters [O(52) and O(53) – Figure 1]. The latter are themselves hydrogen-bonded also to phenolic oxygens of the ligands (Figure 1 and Table III), so that the three waters and the two nickel polyhedra make up a compact unit. The Ni...Ni distance is 2.969 Å.

Bond-angles in the nickel polyhedra vary over a wide range from 74 to 104° (Table II). These distor-

TABLE I. Final Atomic Parameters with Estimated Standard Deviations in Parentheses. Fractional coordinates ($\times 10^4$) and anisotropic thermal parameters ($\times 10^5$) in the form $\exp-(h^2b_{11} + k^2b_{22} + l^2b_{33} + 2hkb_{12} + 2hlb_{13} + 2klb_{23})$.

	x/a	y/b	z/c	B (Å^2)
Ni(1)	2408.7(1.3)	100.0(1.0)	3863.7(0.6)	–
Ni(2)	2434.0(1.3)	1135.2(1.0)	3286.3(0.6)	–
O(11)	1403(6)	−22(5)	4069(3)	3.8(2)
C(111)	1352(10)	−251(8)	4398(5)	3.2(4)
C(112)	565(13)	−432(10)	4461(6)	5.4(5)
C(113)	406(13)	−692(10)	4799(6)	5.3(5)
C(114)	1073(14)	−818(10)	5052(6)	5.6(5)
C(115)	1875(11)	−660(9)	5024(5)	4.3(4)
C(116)	1979(9)	−363(7)	4684(4)	2.5(3)
N(11)	965(17)	−1110(12)	5411(7)	9.3(6)
O(111)	1540(14)	−1183(11)	5656(7)	12.2(6)
O(112)	291(12)	−1245(9)	5454(5)	9.7(5)
C(11)	2813(10)	−212(8)	4675(5)	3.4(4)
N(12)	3079(7)	36(6)	4380(3)	2.9(3)
C(121)	3910(9)	98(8)	4408(4)	2.8(3)
C(122)	4421(11)	−405(9)	4538(5)	3.8(4)
C(123)	5274(11)	−331(9)	4527(5)	4.1(4)
C(124)	5504(11)	231(9)	4386(5)	4.2(4)
C(125)	5022(12)	760(10)	4276(6)	4.9(4)
C(126)	4200(11)	695(9)	4286(5)	4.1(4)
O(12)	6320(8)	271(7)	4383(4)	5.5(3)
C(12)	6550(15)	638(13)	4064(7)	8.1(7)
O(21)	2248(6)	1134(5)	3815(3)	3.1(2)
C(211)	1765(9)	1523(8)	3965(4)	2.7(3)
C(212)	1878(10)	1573(8)	4353(5)	3.4(4)
C(213)	1420(11)	1995(9)	4542(5)	4.1(4)
C(214)	828(10)	2363(8)	4314(5)	3.3(4)
C(215)	716(11)	2357(9)	3938(5)	4.0(4)
C(216)	1205(10)	1941(8)	3758(4)	2.7(3)
N(21)	322(11)	2809(8)	4494(5)	5.1(4)
O(211)	558(10)	2916(8)	4822(5)	7.8(4)
O(212)	−241(9)	3054(7)	4312(4)	5.9(3)
C(21)	1042(10)	1974(8)	3340(5)	3.5(4)
N(22)	1431(7)	1695(6)	3126(3)	2.5(3)
C(221)	1229(10)	1872(8)	2738(4)	3.0(3)
C(222)	1304(11)	2508(9)	2633(5)	4.4(4)
C(223)	1227(12)	2676(10)	2255(6)	4.8(4)
C(224)	1061(11)	2167(9)	1988(5)	3.8(4)
C(225)	983(11)	1531(9)	2089(5)	4.4(4)
C(226)	1065(11)	1375(9)	2480(5)	3.8(4)
O(22)	1038(8)	2385(7)	1623(4)	5.6(3)
C(22)	1268(13)	1903(11)	1363(6)	5.9(5)
O(31)	2674(7)	877(5)	2790(3)	3.7(2)
C(311)	3052(9)	1214(8)	2567(4)	2.8(3)
C(312)	3013(12)	937(10)	2209(5)	5.1(5)
C(313)	3476(12)	1269(10)	1955(5)	4.8(4)
C(314)	3876(12)	1838(10)	2075(5)	4.6(4)
C(315)	3885(11)	2146(9)	2417(5)	4.2(4)
C(316)	3442(11)	1796(9)	2663(5)	3.8(4)
N(31)	4380(10)	2162(9)	1832(5)	5.3(4)
O(311)	4453(10)	1830(8)	1554(5)	7.7(4)
O(312)	4642(9)	2687(8)	1908(4)	7.0(4)
C(31)	3477(10)	2156(8)	3019(5)	3.3(4)
N(32)	3146(8)	1952(6)	3297(4)	3.0(3)
C(321)	3252(10)	2393(8)	3612(4)	2.6(3)
C(322)	3874(10)	2304(8)	3909(5)	3.3(4)
C(323)	3946(12)	2706(10)	4225(5)	4.8(4)

(continued on facing page)

TABLE I. *(continued)*

	x/a	*y/b*	*z/c*	*B* (Å^2)
C(324)	3357(12)	3183(9)	4227(5)	4.2(4)
C(325)	2739(12)	3298(10)	3938(6)	5.2(5)
C(326)	2687(11)	2881(9)	3619(5)	3.7(4)
O(32)	3464(9)	3549(7)	4555(4)	6.5(3)
C(32)	2842(20)	4013(16)	4619(9)	11.0(9)
O(41)	3197(6)	392(5)	3541(3)	2.9(2)
C(411)	3796(9)	56(8)	3449(4)	3.0(3)
C(412)	4338(10)	422(8)	3262(5)	3.4(4)
C(413)	5009(11)	89(9)	3157(5)	4.0(4)
C(414)	5116(11)	−561(9)	3259(5)	3.9(4)
C(415)	4605(10)	−931(8)	3436(4)	3.0(3)
C(416)	3911(10)	−625(8)	3518(4)	2.9(3)
N(41)	5819(12)	−909(10)	3193(5)	6.7(5)
O(411)	6268(14)	−624(12)	3016(7)	12.6(7)
O(412)	5978(8)	−1455(8)	3295(4)	6.1(3)
C(41)	3394(10)	−1066(8)	3674(4)	3.2(3)
N(42)	2705(8)	−872(6)	3782(4)	3.2(3)
C(421)	2281(10)	−1379(8)	3941(5)	3.2(3)
C(422)	1472(11)	−1445(9)	3807(5)	3.8(4)
C(423)	1030(11)	−1906(9)	3974(5)	4.3(4)
C(424)	1404(11)	−2286(9)	4257(5)	4.1(4)
C(425)	2216(11)	−2244(9)	4394(5)	4.1(4)
C(426)	2673(11)	−1798(9)	4218(5)	3.8(4)
O(42)	894(8)	−2718(6)	4413(4)	5.2(3)
C(42)	1169(13)	−2961(10)	4786(6)	5.7(5)
O(51)	1661(7)	206(5)	3301(3)	3.7(2)
O(52)	202(12)	283(11)	3486(6)	11.6(6)
O(53)	2120(21)	−433(17)	2684(10)	20.2(11)

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Ni(1)	256(9)	189(6)	48(2)	56(7)	45(3)	18(3)
Ni(2)	284(10)	181(6)	40(2)	45(7)	46(3)	6(3)

TABLE II. Bond Lengths and Angles with Estimated Standard Deviations in Parentheses.

(a) Distances (Å)

	Ni(1)...Ni(2)	2.969(3)	
Ni(1)–O(11)	1.994(11)	Ni(2)–O(31)	1.987(11)
Ni(1)–N(12)	2.040(12)	Ni(2)–N(32)	2.041(13)
Ni(1)–N(42)	2.058(13)	Ni(2)–N(22)	2.051(13)
Ni(1)–O(41)	2.012(10)	Ni(2)–O(21)	2.004(10)
Ni(1)–O(21)	2.106(10)	Ni(2)–O(41)	2.097(10)
Ni(1)–O(51)	2.238(11)	Ni(2)–O(51)	2.296(11)

	n = 1	n = 2	n = 3	n = 4
O(n1)–C(n11)	1.30(2)	1.32(2)	1.31(2)	1.32(2)
C(n11)–C(n12)	1.44(2)	1.40(2)	1.41(2)	1.44(2)
C(n12)–C(n13)	1.41(3)	1.41(2)	1.47(2)	1.43(2)
C(n13)–C(n14)	1.37(3)	1.41(2)	1.37(2)	1.36(2)
C(n14)–C(n15)	1.42(3)	1.35(2)	1.39(2)	1.38(2)
C(n15)–C(n16)	1.41(2)	1.42(2)	1.45(2)	1.41(2)
C(n16)–C(n11)	1.38(2)	1.40(2)	1.37(2)	1.40(2)
C(n14)–N(n1)	1.47(3)	1.47(2)	1.48(2)	1.44(2)
N(n1)–O(n11)	1.22(3)	1.21(2)	1.24(2)	1.22(2)

(continued overleaf)

TABLE II. *(continued)*

N(n1)–O(n12)	1.22(2)	1.18(2)	1.16(2)	1.18(2)
C(n16)–C(n1)	1.46(2)	1.51(2)	1.48(2)	1.44(2)
C(n1)–N(n2)	1.33(2)	1.24(2)	1.31(2)	1.35(2)
N(n2)–C(n21)	1.41(2)	1.45(2)	1.44(2)	1.43(2)
C(n21)–C(n22)	1.37(2)	1.35(2)	1.40(2)	1.39(2)
C(n22)–C(n23)	1.47(2)	1.41(2)	1.40(2)	1.40(2)
C(n23)–C(n24)	1.33(2)	1.41(2)	1.39(2)	1.36(2)
C(n24)–C(n25)	1.37(2)	1.35(2)	1.38(2)	1.39(2)
C(n25)–C(n26)	1.41(2)	1.44(2)	1.43(2)	1.41(2)
C(n26)–C(n21)	1.40(2)	1.37(2)	1.38(2)	1.40(2)
C(n24)–O(n2)	1.39(2)	1.39(2)	1.39(2)	1.41(2)
O(n2)–C(n2)	1.48(3)	1.46(2)	1.46(3)	1.45(2)

(b) Angles (°)

O(11)–Ni(1)–N(12)	91.8(5)	O(31)–Ni(2)–N(32)	91.1(5)
O(41)–Ni(1)–N(42)	89.5(5)	O(21)–Ni(2)–N(22)	91.1(4)
O(11)–Ni(1)–O(41)	162.2(4)	O(31)–Ni(2)–O(21)	164.4(4)
N(12)–Ni(1)–O(51)	178.0(5)	N(32)–Ni(2)–O(51)	177.4(5)
O(21)–Ni(1)–N(42)	164.2(5)	O(41)–Ni(2)–N(22)	161.0(4)
O(11)–Ni(1)–O(21)	92.6(4)	O(31)–Ni(2)–O(41)	90.6(4)
O(11)–Ni(1)–N(42)	100.5(5)	O(31)–Ni(2)–N(22)	99.9(5)
O(11)–Ni(1)–O(51)	87.7(4)	O(31)–Ni(2)–O(51)	90.7(4)
N(12)–Ni(1)–O(21)	100.7(5)	N(32)–Ni(2)–O(41)	104.1(5)
N(12)–Ni(1)–O(41)	103.4(5)	N(32)–Ni(2)–O(21)	99.7(5)
N(12)–Ni(1)–N(42)	87.7(5)	N(32)–Ni(2)–N(22)	91.6(5)
O(41)–Ni(1)–O(21)	75.6(4)	O(21)–Ni(2)–O(41)	76.0(4)
O(41)–Ni(1)–O(51)	76.8(4)	O(21)–Ni(2)–O(51)	78.1(4)
N(42)–Ni(1)–O(51)	94.3(5)	N(22)–Ni(2)–O(51)	90.1(4)
O(21)–Ni(1)–O(51)	77.4(4)	O(41)–Ni(2)–O(51)	73.9(4)
Ni(1)–O(11)–C(111)	126(1)	Ni(2)–O(31)–C(311)	129(1)
Ni(1)–N(12)–C(11)	124(1)	Ni(2)–N(32)–C(31)	125(1)
Ni(1)–N(12)–C(121)	118(1)	Ni(2)–N(32)–C(321)	121(1)
Ni(1)–N(42)–C(41)	124(1)	Ni(2)–N(22)–C(21)	125(1)
Ni(1)–N(42)–C(421)	118(1)	Ni(2)–N(22)–C(221)	118(1)
Ni(1)–O(41)–C(411)	128(1)	Ni(2)–O(21)–C(211)	127(1)
Ni(2)–O(41)–C(411)	135(1)	Ni(1)–O(21)–C(211)	129(1)
Ni(1)–O(41)–Ni(2)	92.5(4)	Ni(2)–O(21)–Ni(1)	92.5(4)
Ni(1)–O(51)–Ni(2)	81.8(4)		

	n = 1	n = 2	n = 3	n = 4
O(n1)–C(n11)–C(n12)	116(2)	118(1)	115(1)	116(1)
O(n1)–C(n11)–C(n16)	126(1)	123(1)	124(1)	123(1)
C(n16)–C(n11)–C(n12)	118(2)	118(1)	122(2)	120(1)
C(n11)–C(n12)–C(n13)	123(2)	123(2)	117(2)	119(2)
C(n12)–C(n13)–C(n14)	114(2)	116(2)	118(2)	117(2)
C(n13)–C(n14)–C(n15)	128(2)	124(2)	126(2)	125(2)
C(n13)–C(n14)–N(n1)	118(2)	118(2)	119(2)	120(2)
C(n15)–C(n14)–N(n1)	115(2)	118(2)	115(2)	115(2)
C(n14)–C(n15)–C(n16)	115(2)	119(2)	114(2)	118(2)
C(n15)–C(n16)–C(n11)	122(2)	121(1)	123(2)	119(1)
C(n15)–C(n16)–C(n1)	112(1)	115(1)	111(2)	114(1)
C(n11)–C(n16)–C(n1)	126(1)	125(1)	127(2)	127(1)
C(n16)–C(n1)–N(n2)	124(1)	126(2)	124(2)	124(1)
C(n1)–N(n2)–C(n21)	117(1)	116(1)	114(1)	116(1)
N(n2)–C(n21)–C(n22)	122(1)	120(1)	121(1)	117(1)
N(n2)–C(n21)–C(n26)	117(1)	119(1)	117(1)	121(2)
C(n26)–C(n21)–C(n22)	121(2)	121(2)	121(1)	122(2)
C(n21)–C(n22)–C(n23)	119(2)	121(2)	121(2)	119(2)

(continued on facing page)

TABLE II. *(continued)*

C(n22)–C(n23)–C(n24)	117(2)	118(2)	116(2)	119(2)
C(n23)–C(n24)–C(n25)	125(2)	121(2)	125(2)	123(2)
C(n23)–C(n24)–O(n2)	114(2)	113(2)	112(2)	114(2)
C(n25)–C(n24)–O(n2)	120(2)	125(2)	123(2)	122(2)
C(n24)–C(n25)–C(n26)	118(2)	119(2)	117(2)	118(2)
C(n25)–C(n26)–C(n21)	119(2)	120(2)	119(2)	119(2)
C(n24)–O(n2)–C(n2)	115(2)	116(1)	119(2)	117(2)
C(n14)–N(n1)–O(n11)	120(3)	115(2)	113(2)	118(2)
C(n14)–N(n1)–O(n12)	118(3)	119(2)	120(2)	124(2)
O(n11)–N(n1)–O(n12)	123(3)	126(2)	127(2)	118(2)

TABLE III. Hydrogen Bond Distances and Close Intermolecular Contacts <3.4 Å.

(a) Hydrogen Bonds (Å)

Donor Acceptor	
O(52)....O(11)	2.77(2)
O(53)....O(31)	2.81(4)
O(51)....O(52)	2.69(2)
O(51)....O(53)	2.81(4)

(b) Contact Distances (Å)[a]

O(111)...C(22)^{I}	3.06	O(312)...C(31)^{V}	3.35
O(112)...C(214)^{II}	3.16	...C(315)^{V}	3.39
...C(213)^{II}	3.29	...C(423)^{IV}	3.33
...N(21)^{II}	3.34	O(412)...C(21)^{VI}	3.17
O(212)...C(122)^{III}	3.29	...C(226)^{VI}	3.31
O(311)...C(423)^{IV}	3.22	...C(322)^{VI}	3.25
O(22) ...C(215)^{VII}	3.33	O(42) ...C(325)^{VI}	3.39

[a] Roman numerals as superscripts refer to the following equivalent positions, relative to the molecule x, y, z:

I	$x, -y, \frac{1}{2}+z$	V	$1-x, y, \frac{1}{2}-z$
II	$-x, -y, 1-z$	VI	$\frac{1}{2}+x, y-\frac{1}{2}, z$
III	$x-\frac{1}{2}, \frac{1}{2}+y, z$	VII	$-x, y, \frac{1}{2}-z$
IV	$\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$		

tions are larger than commonly observed for Ni^{II}, but can be readily rationalised as resulting from the various ligand constraints in the molecule – particularly in the bridging system.

A closely related structure of a bis(acetylacetonato)nickel(II) species, with an arsine-oxide and two acetylacetonato oxygens bridging two nickels, has been recently described by Binks *et al.* [11]. They found marked asymmetry in the Ni–O lengths in the bridge system, but here such asymmetry is found only in the bonds to the bridging water. The two halves of the present molecule are in different crystalline environments and this is probably sufficient to account for the bridge asymmetry.

The observed bond lengths in the methoxy substituents (Table II) are within the usually observed range, as recently summarised by Ashida *et al.* [12], but the C–O–Me fragments are far from the usual co-planarity with the phenylenes: observed dihedral angles (Table IV) are 36.0, 28.6, 8.2 and 21.1°. The nitro groups are closer to coplanarity with their carbocyclic ring, but the deviations are still significant; observed dihedral angles are 0.7, 15.3, 10.2 and 9.0°. Also the dihedral angles between the 4-methoxyphenyl groups and the salicylaldiminato

TABLE IV. Least-squares Planes and Their Equations Given by $lX' + mY' + nZ' - p = 0$ where X', Y' and Z' are orthogonal coordinates related to X, Y and Z by $X' = X \sin \beta$, $Y' = Y$, $Z' = Z + X \cos \beta$. Deviations (Å) of most relevant atoms from the planes are given in square brackets. Dihedral angles between some of the planes are listed at the end of the Table.

(a) Four Donor-atom Planes within the Ni Polyhedra

	l	m	n	p
Plane (1): O(11), N(42), O(41), O(21)	.6102	.0698	.7892	12.8791
[O(11)–.05, N(42).05, O(41)–.07, O(21).06, Ni(1).19, N(12) 2.20, O(51)–2.02]				
Plane (2): O(31), N(22), O(21), O(41)	.6560	.7544	.0232	4.4562
[O(31).05, N(22)–.05, O(21).06, O(41)–.06, Ni(2).22, N(32) 2.24, O(51)–2.04]				
Plane (3): O(51), O(21), N(42), N(12)	–.8233	–.1904	.5347	3.6782
[O(51).13, O(21)–.13, N(42)–.12, N(12).12, Ni(1).12, O(11)2.11, O(41)–1.83]				
Plane (4): O(51), O(21), O(31), N(32)	.8084	–.5442	.2245	4.7101
[O(51)–.08, O(21).08, O(31).08, N(32)–.08, Ni(2)–.11, O(41)1.90, N(22)–2.16]				

(continued overleaf)

TABLE IV. *(continued)*

Plane (5): O(51), O(41), O(11), N(12)	–.1248	.9755	.1810	2.2151
[O(51)–.07, O(41).06, O(11).06, N(12)–.06, Ni(1)–.10, O(21)1.95, N(42)–2.14]				
Plane (6): O(51), O(41), N(22), N(32)	–.1374	.2182	.9662	10.9631
[O(51)–.08, O(41).08, N(22).07, N(32)–.07, Ni(2)–.11, O(31)–2.09, O(21)1.84]				

Dihedral Angles (°) between Planes

(1)–(2) 61.9, (3)–(4) 116.2, (5)–(6) 66.1

(b) Planes within Ligands (for atoms defining planes see key at end of Table)

	l	m	*n*	*p*
Plane (7):	–.1034	.9557	.2754	3.5877
[Ni(1)–.12, O(11).10, C(111) < .01, C(116)–.08, C(11)–.01, N(12).11, C(121).05]				
Plane (8):	.5893	.1363	.7963	12.9502
[Ni(1).14, O(41)–.11, C(411)–.01, C(416).09, C(41).03, N(42)–.14, C(421)–.14]				
Plane (9):	.6210	.7838	–.0022	4.2103
[Ni(2).10, O(21)–.10, C(211).01, C(216).09, C(21)–.03, N(22)–.06, C(221).01]				
Plane (10):	.8171	–.5131	.2629	5.1890
[Ni(2)–.05, O(31).05, C(311)–.02, C(316)–.02, C(31)–.01, N(32).04, C(321).02]				
Plane (11):	–.1159	.9166	.3826	5.2464
[C(111).01, C(112).01, C(113).04, C(114)–.04, C(115)–.03, C(116).01, O(11)–.04, C(11).03, N(12) < $\lvert .01 \rvert$, Ni(1)–.40, C(121)–.10]				
Plane (12):	.6731	.7343	–.0873	3.0895
[C(211)–.06, C(212).02, C(213).06, C(214)–.01, C(215)–.03, C(216)–.02, O(21)–.03, C(21)–.03, N(22).08, Ni(2).36, C(221).23]				
Plane (13):	.8244	–.5155	.2335	4.9442
[C(311).01, C(312)–.06, C(313)–.01, C(314).03, C(315).01, C(316) < .01, O(31).05, C(31)–.02, N(32)–.01, Ni(2)–.11, C(321)–.06]				
Plane (14):	.5142	.2143	.8305	12.8369
[C(411).03, C(412)–.04, C(413)–.07, C(414).02, C(415).07, C(416).01, O(41).07, C(41)–.03, N(42)–.06, Ni(1).42, C(421)–.06]				
Plane (15):	.1403	.3778	.9152	14.7269
[C(121)–.03, C(122).01, C(123).02, C(124)–.03, C(125).01, C(126).01, O(12)–.03, C(12)–.81, N(12)–.15]				
Plane (16):	.9806	–.1440	–.1329	0.1979
[C(221) < .01, C(222) < $\lvert .01 \rvert$, C(223) < .01, C(224) < $\lvert .01 \rvert$, C(225) < .01, C(226) < $\lvert .01 \rvert$, O(22).07, C(22).73, N(22).21]				
Plane (17):	–.5627	–.6470	.5146	0.1044
[C(321).01, C(322) < .01, C(323)–.01, C(324).01, C(325)–.01, C(326) < $\lvert .01 \rvert$, O(32).03, C(32).23, N(32).11]				
Plane (18):	–.1730	.6909	.7019	7.0179
[C(421).03, C(422)–.01, C(423)–.01, C(424).01, C(425).02, C(426)–.04, O(42).05, C(42).53, N(42).12]				
Plane (19):	–.1237	.9190	.3743	5.0364
[N(11)–.01, O(111).01, O(112).01, C(114) < .01]				
Plane (20):	–.5470	–.7742	.3184	0.4868
[N(21).02, O(211)–.01, O(212)–.01, C(214)–.01]				
Plane (21):	.8159	–.4283	.3884	6.2481
[N(31).01, O(311) < $\lvert .01 \rvert$, O(312) < $\lvert .01 \rvert$, C(314) < $\lvert .01 \rvert$]				
Plane (22):	.5091	.3634	.7802	12.1208
[N(41).01, O(411) < $\lvert .01 \rvert$, O(412) < $\lvert .01 \rvert$, O(414) < $\lvert .01 \rvert$]				
Plane (23):	.0417	.8491	.5266	8.3890
Plane (24):	.9501	.3034	.0728	3.5254
Plane (25):	–.4427	–.7248	.5271	0.4720
Plane (26):	–.4241	.7847	.4521	2.2213

(continued on facing page)

rings are different in each case: three are close to 60° and the other is nearly 90° (Table IV). These interplanar angles illustrate the lack of symmetry of the molecule about the bridging system. They can readily be accounted for by the close contacts <3.4 Å which are listed in Table III. All involve either a methoxy or a nitro substituent of the Schiff base ligand. So this is clearly a case of crystal packing effects influencing the conformation adopted by the molecule.

As noted in the Experimental, we have characterised another brown crystalline hydrate of the compound described here. This compound $Ni(C_{14}H_{11}N_2O_4)_2 \cdot 3H_2O$ crystallises in the triclinic unit cell of dimensions a = 11.92, b = 14.53, c = 10.57 Å, α = 101.0, β = 109.0, γ = 112.9° with two formula units per cell (D_m = 1.51 g cm^{-3}). Both the brown and the green forms showed diffuse reflectance electronic spectra typical of octahedral compounds of this type, with bands centred at ~9.5 and 16.5 10^3 cm^{-1}, with relative intensities of ~4:3. The brown trihydrate is likely to be a diaqua monomeric species of well-characterised type *trans*-$[Ni(L)_2(H_2O)_2] \cdot H_2O$, with the brown colour arising from lower energy transitions largely within the Schiff base ligand, which now have mutual orientations different from those in the green μ-aqua dimer.

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TABLE IV. *(continued)*

Key to definition of planes:

	Definiting Atoms	Plane No. n = 1	2	3	4
(A) chelate ring	Ni(n), O(n1), C(n11), C(n16), C(n1), N(n2)	7	8	9	10
(B) salicylaldimine	O(n1), C(n1), N(n2), C(n11)–C(n16)	11	12	13	14
(C) phenyl	C(n21)–C(n26)	15	16	17	18
(D) nitro group	N(n1), O(n11), O(n12), C(n14)	19	20	21	22
(E) methoxy group	C(n24), O(n2), C(n2)	23	24	25	26

Dihedral Angles (°)

n =	1	2	3	4
A–B	6.6	6.4	1.7	6.5
A–C	53.2	60.2	89.6	56.6
B–C	47.1	55.5	90.6	50.1
C–E	36.0	28.6	8.2	21.1
B–D	0.7	164.7	10.2	9.0

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