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A Novel Binuclear Nickel(II) Salicylaldiminate with Bridging Water Molecule (X-ray Analysis)

E. DONALD McKENZIE*

Chemistry Department, The University, Sheffield, S3 7HF, U.K.

FREDERICK S. STEPHENS

School of Chemistry, Macquarie University, North Ryde, N.S.W. 2113, Australia

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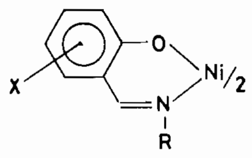
As part of our interest in the nature of the oligomerisation [1] of the nickel(II) bissalicylaldiminates I, we have carried out an X-ray analysis of the structure of the compound I for X = 5-nitro and R = 4-methoxyphenyl. Although the crystals contained potential donor molecules (either H_2O or EtOH, as evidenced by the i.r. spectra), space group considerations suggested that this compound might be an example of the tetrameric cubanoid structure which we think [2] should be characteristic of the oligomers of I.



I

Green crystals of the sesquihydrate form are obtained by adding hot absolute ethanol to a hot methylethylketone solution of the compound. If aqueous ethanol is used a brown tetrahydrate forms.

Crystal Data: $[Ni_2(C_{14}H_{11}N_2O_4)_4(H_2O)]\cdot 2H_2O$, $M = 1256.5$, monoclinic, $a = 17.04(3)$, $b = 20.16(2)$, $c = 36.44(6)$ Å, $\beta = 99.42(1)^\circ$, $D_m = 1.38$ g cm^{-3} (by flotation), $Z = 8$, $D_c = 1.35$, space group $C_{2/c}$.

The intensities of 2803 unique reflexions were measured on a Stoë 'Stadi-2' automatic diffractometer (Mo-K_α with a graphite monochromator). The structure was solved by the heavy atom method and refined by block-matrix least-squares methods to a final R of 0.081 ($R' = [\Sigma w\Delta^2/\Sigma w/F_o/^2]^{1/2} = 0.107$). Only the nickel atoms were allowed to vibrate anisotropically.

The analysis reveals a bridging water molecule.

Two octahedral $[NiN_2O_4]$ polyhedra are linked facially through bridging phenolic oxygen atoms and a water molecule. The remaining two waters are H-bonded to the dimer as shown in the figure.

Few examples of water molecules bridging two metals have been structurally characterised. Turpeinen has recently described examples in a class of nickel–diamine–haloacetates [3] and halopropio-

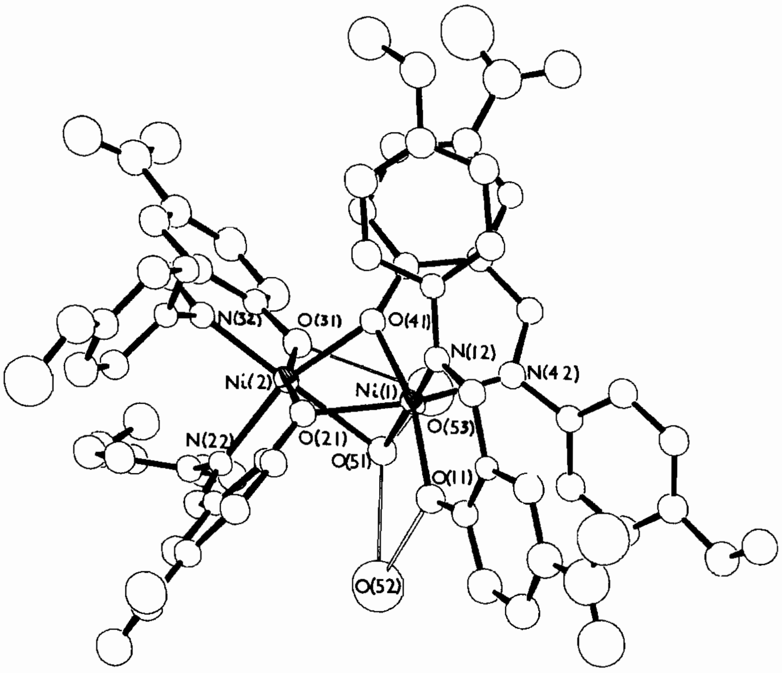


Figure. Perspective drawing of the molecule. Hydrogen bonding is indicated by open lines.

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*Present address: Chemistry Department, University of Queensland, Brisbane, 4067, Australia.

TABLE. Selected Bond Lengths and Angles.

(a) Bond lengths (Å)			
Ni(1).....Ni(2)		2.969(3)	
Ni(1)–O(11)	1.99(1)	Ni(2)–O(31)	1.99(1)
Ni(1)–N(12)	2.04(1)	Ni(2)–N(32)	2.04(1)
Ni(1)–N(42)	2.06(1)	Ni(2)–N(22)	2.05(1)
Ni(1)–O(41)	2.01(1)	Ni(2)–O(21)	2.00(1)
Ni(1)–O(21)	2.11(1)	Ni(2)–O(41)	2.10(1)
Ni(1)–O(51)	2.24(1)	Ni(2)–O(51)	2.30(1)
(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(41)–Ni(2)	92.5(4)		
Ni(1)–O(21)–Ni(2)	92.5(4)		
Ni(1)–O(51)–Ni(2)	81.8(4)		

nates [4]. A recent description [5] of another binuclear compound [Ni$_2$(acac)$_4$(Ph$_3$AsO)] gives an example closely paralleling the present structure.

The coordination polyhedra of the present Ni Schiff base compound are markedly distorted – a necessary result of the various ligand constraints within the molecule. The angle at the bridging water molecule (81.8°) is particularly acute but is a consequence of the long Ni–OH$_2$ lengths.

This structure shows the need for scrupulously dry conditions in any study of the oligomerisation of the compounds I in non-donor solvents. Very low concentrations of water could give significant amounts of octahedral dimers of the present type, and these would be indistinguishable magnetically and spectroscopically from oligomers made up purely of compounds I.

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