Synthesis and Crystal Structure of Bis-μ-(5-chloro-2-hydroxy-*N*-methyl-α-phenylbenzylideneiminato-*N,O*)-bis[ethanol(nitrato-*O,O′*)nickel(II)]: a New Type of Nickel(II) Dimer

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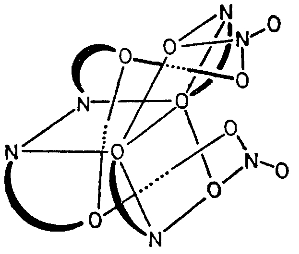
The title complex (4) is formed by reaction of nickel(II) dinitrate hexahydrate and triethoxymethane (tem) with bis(5-chloro-2-hydroxy-*N*-methyl-α-phenylbenzylideneiminato)nickel(II); its crystal and molecular structure were determined by single-crystal *X*-ray diffraction. The two nickel atoms are in distorted octahedral environments with a shared edge formed by the phenolic oxygens of the Schiff-base ligands, each of which bonds to both metal atoms. Like the Schiff-base ligands, the nitrato-groups are bidentate, and an ethanol molecule bonded at oxygen completes the octahedron. The ethanol is formed by the reaction of hydrate water with tem. These results are in contrast with those of related nickel complexes and nickel nitrate which form trinuclear complexes, in which the solvent plays no part. An analogous reaction proceeds in other solvents, *e.g.* ethanol and methanol, but the product is difficult to control because water and solvent molecules compete for the sixth ligand position on the metal.

Crystals of (4) are triclinic, space group $P\bar{1}$, unit-cell parameters: $a = 8.969(7)$, $b = 9.601(3)$, $c = 11.926(7)$ Å, $\alpha = 100.32(5)$, $\beta = 92.12(7)$, $\gamma = 114.01(3)°$, $Z = 1$ dimer. The structure was solved by the heavy-atom method from diffractometer data, and refined by least squares to R 0.029 for 2 090 observed reflections.

THE reaction of nickel nitrate with the nickel complexes of certain bidentate salicylaldimines results in the formation of trinuclear complexes.[1,2] The nature of the product varies with the solvent used, and solvent molecules may occupy co-ordination sites. In one example, where the Schiff base is the condensate of salicylaldehyde and n-propylamine and the solvent triethoxymethane (tem), a trinuclear complex (1) is formed, and the solvent plays no part in the co-ordination. It seems likely that this type of structure can be altered radically, not only by the use of various co-ordinating and non-co-ordinating solvents, but also by chemical alteration of the Schiff base to induce steric constraints. Such modification is most readily made at the nitrogen substituent (R^1) or the adjacent imine carbon substituent (R^2). Reaction with R^2 = Ph and, R^1 = Me, produced the first success and is reported here.



(1)

EXPERIMENTAL

5-*Chloro-2-hydroxy-*N*-methyl-α-phenylbenzylideneimine*, (mcp).—This was prepared by the reaction of methylamine in ethanol with an ethanol solution of 5-chloro-2-hydroxybenzophenone at 80 °C. Concentration of the solution afforded yellow crystals which were characterized by mass spectroscopy.

[Ni(mcp)$_2$].—This was prepared by the reaction of ethanolic nickel acetate with mcp in ethanol at room temperature. The olive green complex, which precipitated, was characterized by mass spectroscopy.

[{Ni(mcp)NO$_3$(EtOH)}$_2$] (4).—Reaction of a 50% excess of nickel nitrate hexahydrate dissolved in a minimum of triethoxymethane (tem), with a fairly saturated hot (*ca.* 100 °C) solution of [Ni(mcp)$_2$] in tem affords pale green crystals, one of which was selected for *X*-ray diffraction.

Electronic spectra were measured on a Zeiss PMQ II spectrophotometer with a RA3 reflectance attachment calibrated with magnesium oxide. I.r. spectra were determined for Nujol mulls as previously described.[2]

Crystal Data for (4) [{Ni(mcp)NO$_3$(EtOH)}$_2$].—$C_{32}H_{34}Cl_2N_4Ni_2O_{10}$, $M = 823.15$, triclinic, $a = 8.969(7)$, $b = 9.601(3)$, $c = 11.926(7)$ Å, $\alpha = 100.32(5)$, $\beta = 98.12(7)$, $\gamma = 114.01(3)°$, $U = 896$ Å^3, $D_c = 1.52$, $Z = 1$ (dimeric molecule), $D_m = 1.47$ g cm^{-3} (by flotation). Mo-K_α radiation, $\lambda = 0.710$ Å; μ(Mo-K_α) = 12.6 cm^{-1}. Space group $P\bar{1}$.

Preliminary cell dimensions were obtained by use of the Enraf–Nonius program SEARCH to locate 15 independent reflections. Refined cell dimensions and their estimated standard deviations were obtained from a least-squares refinement of the preliminary values against the observed values of $\pm\theta$ for 24 strong reflections, centred on the diffractometer for Mo-$K_{\alpha1}$ and Mo-$K_{\alpha2}$ wavelengths. The mosaicity of the crystal was examined by the ω-scan technique and judged to be satisfactory. Diffraction data were collected at 292 K on an Enraf–Nonius four-circle CAD 4 diffractometer controlled by a PDP8 M computer. The θ—2θ scan technique was used to record the intensities of all reflections for which $0° < 2\theta < 50°$, and the symmetric scans were centred on calculated peak positions. Reflection data were considered insignificant if intensities registered <10 counts above background on a rapid prescan, and were rejected automatically by the computer. The intensities of four standard reflections, monitored at 100 reflection intervals, showed no greater fluctuations than those expected from Poisson statistics during data collection. The raw intensity data were corrected for Lorentz and polarization effects, but not for absorption. After averaging the intensities of equivalent reflections, data were

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[1] R. J. Butcher, E. J. Cukauskas, B. S. Deaver, jun., and E. Sinn, unpublished work.

[2] J. O. Miners, E. Sinn, R. B. Coles, and C. M. Harris, *J.C.S. Dalton*, 1972, 1149, and refs. therein.

reduced to 2 812 independent reflections, of which 2 090, having $F_o^2 > 3\sigma(F_o^2)$, were used in the final refinement of the structure parameters.

Refinement of the Structure.—Full-matrix least-squares refinement was based on F, and the function minimized was $\Sigma\omega(|F_o| - |F_c|)^2$, with weights w taken as $[2F_o/\sigma(F_o)^2]^2$. Atomic scattering factors for non-hydrogen atoms were taken from ref. 3, and for hydrogen from ref. 4. The effects of anomalous dispersion were included taking values for $\Delta f'$ and $\Delta f''$ from ref. 5. To minimize computer time, initial calculations were carried out on the first 800 reflections.

TABLE 1

Positonal parameters with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Ni	0.157 26(6)	−0.001 47(6)	−0.032 91(5)
Cl	0.270 8(1)	−0.036 9(1)	0.569 32(9)
O(1)	0.002 0(3)	−0.084 5(2)	0.076 2(2)
O(2)	0.346 5(3)	−0.049 2(3)	0.054 0(2)
O(3)	0.353 4(3)	0.179 6(3)	0.115 3(2)
O(4)	0.552 4(3)	0.128 6(4)	0.198 0(3)
O(5)	0.316 1(3)	0.094 0(3)	−0.140 2(2)
N(1)	0.022 4(3)	−0.197 7(3)	−0.165 9(3)
N(2)	0.420 8(3)	0.088 5(4)	0.124 6(3)
C(1)	0.095 0(4)	0.065 6(4)	0.281 0(3)
C(2)	0.062 6(4)	−0.068 8(4)	0.189 9(3)
C(3)	0.099 2(5)	−0.187 6(4)	0.220 0(3)
C(4)	0.162 6(5)	−0.180 7(4)	0.334 9(4)
C(5)	0.190 5(4)	−0.050 2(4)	0.423 4(3)
C(6)	0.159 3(4)	0.069 8(4)	0.397 4(3)
C(7)	−0.076 0(4)	−0.205 4(4)	−0.259 3(3)
C(8)	−0.182 9(4)	−0.360 4(4)	−0.351 2(3)
C(9)	−0.334 8(4)	−0.460 9(4)	−0.332 3(4)
C(10)	−0.437 5(5)	−0.603 5(5)	−0.414 2(4)
C(11)	−0.391 0(5)	−0.647 2(4)	−0.514 2(4)
C(12)	−0.242 0(5)	−0.549 0(4)	−0.533 8(4)
C(13)	−0.135 8(4)	−0.406 2(4)	−0.452 7(4)
C(14)	0.034 7(5)	−0.339 8(4)	−0.147 4(4)
C(15)	0.438 7(9)	0.249 9(9)	−0.133 6(6)
C(15′)	0.394 5(15)	0.266 7(12)	−0.129 2(11)
C(16)	0.348 4(10)	0.344 3(9)	−0.146 5(8)
C(16′)	0.575 0(17)	0.355 3(19)	−0.088 9(17)
H(3) *	0.077 4(6)	−0.283 5(6)	0.154 9(5)
H(4)	0.186 3(7)	−0.268 1(6)	0.354 1(5)
H(6)	0.180 9(6)	0.162 3(6)	0.461 7(4)
H(9)	−0.370 1(6)	−0.430 4(6)	−0.259 8(5)
H(10)	−0.545 8(7)	−0.675 8(6)	−0.399 9(5)
H(11)	−0.465 9(7)	−0.751 1(6)	−0.572 7(5)
H(12)	−0.209 6(7)	−0.579 4(6)	−0.607 7(5)
H(13)	−0.025 5(6)	−0.336 1(6)	0.466 7(5)
H(151)	0.519 2(9)	0.293 3(9)	−0.055 5(6)
H(152)	0.495 7(9)	0.246 5(9)	−0.197 6(6)
H(153)	0.358 8(15)	0.281 2(11)	−0.212 4(11)
H(154)	0.341 0(15)	0.317 2(11)	−0.077 0(11)
H(0)	0.362 5(46)	0.026 2(44)	−0.152 8(38)
H(141)	0.138 4(37)	−0.330 0(35)	−0.125 9(29)
H(142)	−0.024 4(39)	−0.432 4(36)	−0.204 4(30)
H(143)	0.002 3(38)	−0.339 6(36)	−0.068 5(29)
H(161)	0.271 2(57)	0.306 1(54)	−0.219 8(43)
H(162)	0.426 7(57)	0.453 3(54)	−0.138 4(43)
H(163)	0.286 7(57)	0.349 4(53)	−0.085 5(44)

* B 5.0 Å^2.

The co-ordinates of the two nickel atoms and the bridging oxygens were determined from a three-dimensional Patterson synthesis and used to phase subsequent electron-density maps. All non-hydrogen atoms were located on Fourier-difference syntheses (R 0.011). The remaining diffraction data were added to the calculations, anisotropic temperature factors were introduced for all but the co-ordinated ethanol ligand, which showed disorder, and non-methyl hydrogen atoms were inserted (except on ethanol) as fixed atoms in calculated positions (assuming C–H 1.00 Å) with fixed temperature factors B 5.0 Å^2. Refinement of this model showed that the ethyl group of the co-ordinated ethanol was disordered between two alternative positions, with an occupancy ratio of precisely 2 : 1 (to three significant figures). This model converged with R 0.035. A Fourier-difference map located all remaining hydrogen atoms, except those on C(16′) which has occupancy 1/3. The observed hydrogen atoms were subjected to one cycle of full-matrix least-squares refinement, with fixed temperature factors (B 5.0 Å^2). With all hydrogens subsequently fixed, the model converged with R 0.029 and R' 0.031 $\{R' = [\Sigma\omega(|F_o| - |F_c|)^2/\Sigma\omega|F_o|^2]^{\frac{1}{2}}\}$. A structure-factor calculation with all observed and unobserved reflections included (no refinement) gave R 0.037; on this basis, it was decided that careful measurement of reflections rejected automatically during data collection would not significantly improve the results.

A final Fourier-difference map was featureless except for poorly resolved peaks near C(16′), presumably the missing H atoms. These were not included.

TABLE 2

Bond distances (Å)

Ni–O(1)	2.061(3)	C(1)–C(2)	1.427(5)
Ni–O(1′)	1.973(2)	C(1)–C(6)	1.412(5)
Ni–O(2)	2.115(2)	C(2)–C(3)	1.398(5)
Ni–O(3)	2.185(3)	C(3)–C(4)	1.387(5)
Ni–O(5)	2.093(3)	C(4)–C(5)	1.395(5)
Ni–N(1)	2.015(3)	C(5)–C(6)	1.367(5)
Cl–C(5)	1.748(4)	C(7)–C(8)	1.515(5)
O(1)–C(2)	1.345(4)	C(8)–C(9)	1.390(5)
O(2)–N(2)	1.275(4)	C(8)–C(13)	1.393(5)
O(3)–N(2)	1.261(4)	C(9)–C(10)	1.385(5)
O(4)–N(2)	1.235(4)	C(10)–C(11)	1.369(6)
O(5)–C(15)	1.43(3)	C(11)–C(12)	1.368(6)
O(5)–C(15′)	1.49(3)	C(12)–C(13)	1.388(5)
N(1)–C(7)	1.291(4)	C(15)–C(16)	1.45(2)
N(1)–C(14)	1.465(5)	C(15′)–C(16′)	1.45(5)

TABLE 3

Bond angles (°)

O(1)–Ni–O(1′)	82.1(1)	C(7)–N(1)–C(14)	120.3(3)
O(1)–Ni–O(2)	92.8(1)	O(2)–N(2)–O(3)	116.8(3)
O(1)–Ni–O(3)	91.4(1)	O(2)–N(2)–O(4)	120.8(4)
O(1)–Ni–O(5)	177.2(1)	O(3)–N(2)–O(4)	122.4(4)
O(1)–Ni–N(1)	93.0(1)	C(2)–C(1)–C(6)	118.0(3)
O(1′)–Ni–O(2)	165.4(1)	O(1)–C(2)–C(1)	122.8(3)
O(1′)–Ni–O(3)	106.0(1)	O(1)–C(2)–C(3)	118.7(3)
O(1′)–Ni–O(5)	96.2(1)	C(1)–C(2)–C(3)	118.5(3)
O(1′)–Ni–N(1)	90.7(1)	C(2)–C(3)–C(4)	122.5(4)
O(2)–Ni–O(3)	60.3(1)	C(3)–C(4)–C(5)	118.5(4)
O(2)–Ni–O(5)	88.4(1)	Cl–C(5)–C(4)	119.8(3)
O(2)–Ni–N(1)	103.3(1)	Cl–C(5)–C(6)	119.4(3)
O(3)–Ni–O(5)	86.9(1)	C(4)–C(5)–C(6)	120.8(4)
O(3)–Ni–N(1)	163.3(1)	C(1)–C(6)–C(5)	121.8(3)
O(5)–Ni–N(1)	89.3(1)	N(1)–C(7)–C(8)	121.3(3)
Ni–O(1)–Ni′	97.9(1)	C(7)–C(8)–C(9)	117.9(3)
Ni–O(1)–C(2)	122.1(1)	C(7)–C(8)–C(13)	123.1(4)
Ni–O(1)–C(2′)	119.9(2)	C(9)–C(8)–C(13)	119.0(4)
Ni–O(2)–N(2)	92.9(2)	C(8)–C(9)–C(10)	120.0(4)
Ni–O(3)–N(2)	90.0(2)	C(9)–C(10)–C(11)	120.7(4)
Ni–O(5)–C(15)	133.8(10)	C(10)–C(11)–C(12)	119.8(4)
Ni–O(5)–C(15′)	120.7(15)	C(11)–C(12)–C(13)	120.8(4)
C(15)–O(5)–C(15′)	19.2(20)	C(8)–C(13)–C(12)	119.7(4)
Ni–N(1)–C(7)	124.6(3)	O(5)–C(15)–C(16)	106.8(18)
Ni–N(1)–C(14)	115.1(2)	O(5)–C(15′)–C(16′)	119(3)

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[3] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 511.

[4] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[5] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

RESULTS AND DISCUSSION

Table 1 contains the atomic parameters defining the crystal structure of the molecule and their standard deviations, Tables 2 and 3 bond distances and angles, and Table 4 closest intermolecular contacts. Final observed and calculated structure factors and anisotropic thermal parameters are listed in Supplementary Publication No. SUP 21701 (11 pp., 1 microfiche),* as $|F_c| \cos \alpha$.

TABLE 4

Closest intermolecular contacts (Å) and hydrogen bonds

$\mathrm{Cl}\cdots\mathrm{O}(5^{\mathrm{I}})$	3.372	$\mathrm{O}(4)\cdots\mathrm{H}(0^{\mathrm{IV}})$	1.959
$\mathrm{Cl}\cdots\mathrm{O}(4^{\mathrm{II}})$	3.429	$\mathrm{O}(4)\cdots\mathrm{O}(5^{\mathrm{IV}})$	2.862 *
$\mathrm{Cl}\cdots\mathrm{C}(11^{\mathrm{III}})$	3.598	$\mathrm{O}(4)\cdots\mathrm{C}(11^{\mathrm{V}})$	3.556
$\mathrm{O}(2)\cdots\mathrm{O}(2^{\mathrm{IV}})$	3.074	$\mathrm{O}(5)\cdots\mathrm{N}(2^{\mathrm{IV}})$	3.469
$\mathrm{O}(2)\cdots\mathrm{N}(2^{\mathrm{IV}})$	3.263	$\mathrm{C}(9)\cdots\mathrm{C}(11^{\mathrm{VI}})$	3.458
$\mathrm{O}(2)\cdots\mathrm{O}(5^{\mathrm{IV}})$	3.278	$\mathrm{C}(10)\cdots\mathrm{C}(10^{\mathrm{VI}})$	3.466
$\mathrm{O}(2)\cdots\mathrm{O}(4^{\mathrm{IV}})$	3.309	$\mathrm{C}(10)\cdots\mathrm{C}(11^{\mathrm{VI}})$	3.502
$\mathrm{O}(2)\cdots\mathrm{C}(16'^{\mathrm{IV}})$	3.369	$\mathrm{C}(16)\cdots\mathrm{C}(16'^{\mathrm{VII}})$	3.408
$\mathrm{O}(2)\cdots\mathrm{C}(15^{\mathrm{IV}})$	3.390		

Roman numerals denote the following equivalent positions:

I $x, y, 1 + z$
II $1 - x, -y, 1 - z$
III $-x, -1 - y, -z$
IV $1 - x, -y, -z$
V $1 + x, 1 + y, 1 + z$
VI $-1 - x, -1 - y, -1 - z$
VII $1 - x, 1 - y, -z$

* Hydrogen bond.

TABLE 5

Coefficients of least-squares planes, $AX + BY + CZ = D$, and distances (Å) of relevant atoms from planes

	A	B	C	D
Plane (I): Ni, Ni′, O(1), O(1′)	−0.1435	−0.6758	−0.7230	0
[Ni 0, Ni′ 0, O(1) 0, O(1′) 0]				
Plane (II): C(1)—(6)	−0.8516	0.5125	−0.1106	−0.4055
[C(1) 0.0051, C(2) −0.0090, C(3) −0.0037, C(4) 0.0058, C(5) −0.0098, C(6) 0.0042]				
Plane (III): O(2), O(3), N(2), O(4)	0.5372	0.5289	−0.6570	1.0029
[O(2) 0.001, O(3) 0.001, N(2) −0.0005, O(4) 0.0002]				
Plane (IV): Ni, O(2)—(4), N(2)	0.5527	0.5317	−0.6417	1.0802
[Ni 0.0211, O(2) −0.0199, O(3) −0.0185, N(2) −0.0052, O(4) 0.0224]				
Plane (V): C(8)—(13)	−0.6533	0.5919	−0.4721	0.4224
[C(8) 0.0029, C(9) 0.007, C(10) −0.014, C(11) −0.0017, C(12) 0.0054, C(13) −0.0060]				
Plane (VI): O(1), O(1′), O(2), O(5)	−0.0338	−0.7270	−0.6859	0
[O(1) 0.1063, O(1′) −0.1063, O(2) −0.0961, O(5) 0.0962]				
Plane (VII): O(5), N(1), O(3), O(1)	−0.7604	0.6110	−0.2200	−1.1136
[O(5) 0.1688, N(1) −0.1683, O(3) −0.1600, O(1) 0.1594]				
Plane (VIII): O(2), N(1), O(1′), O(3)	0.5292	0.5879	−0.6119	1.0439
[O(2) −0.0741, N(1) 0.0565, O(1′) −0.0546, O(3) 0.0721]				

Interplanar angles (°): (I)–(II) 67.1, (I)–(III) 87.7, (I)–(IV) 88.6, (I)–(V) 88.0, (I)–(VI) 7.3, (II)–(VI) 71.0, (III)–(VIII) 4.3, (VI)–(VII) 74.5, (VI)–(VIII) 88.5, (VII)–(VIII) 84.8.

Figure 1 is a view of the molecule, and Figure 2 a packing diagram. The molecules are discrete, neutral, dimeric units with a crystallographic centre of symmetry which requires the two nickel and the two phenolic oxygens to lie in a plane. The complex is clearly analogous to the well-established copper(II) dimers of type (2),[6-8] and is the first such complex with nickel. However, all the copper complexes (2) are four-co-ordinated approximately square planar distorted towards tetrahedral, with the exception of (3) the nitrato-form [9] of (2) with $X = NO_3$, $R^1 = Et$, $R^2 = R^3 = H$ while [$\{Ni(mcp)NO_3(EtOH)\}_2$] (4) contains six-co-ordinated nickel atoms. This copper(II) nitrato-complex (3) is formed in the same solvent system as (4) and is its closest copper(II) analogue, although the differences between the two are dramatic. Complex (3) resembles the others of type (2) except that it has a weak fifth bond to a second nitrato-oxygen, presumably more because of the nearness of this oxygen than any strong tendency to form such a bond. In this way, the fifth bond in (3) is analogous to the weak fifth bonds occasionally formed to ligand oxygens of neighbouring molecules in copper(II) Schiff-base complexes.[10] By contrast, the nickel complex contains six nearly equal nickel–ligand bonds, the strongest of which is the Ni–O(1′) bond, which links the two monomeric units. The nitrato-group is bonded *via* approximately equal metal–oxygen links. The main deviation from octahedral geometry arises from the narrow bite angle of the

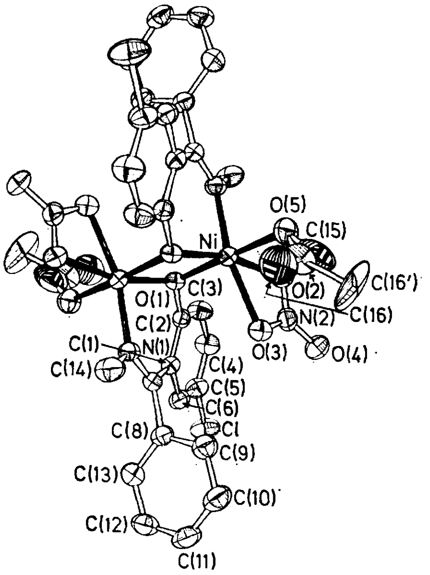

FIGURE 1 View of a single molecule of (4)

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* For details of Supplementary Publications, see Notice to Authors No. 7 in *J.C.S. Dalton*, 1975, Index issue.

[6] W. T. Robinson and E. Sinn, *J.C.S. Chem. Comm.*, 1972, 359.

[7] R. M. Countryman, W. T. Robinson, and E. Sinn, *Inorg. Chem.*, 1974, **13**, 2013.

[8] P. Gluvchinsky, G. M. Mockler, P. C. Healy, and E. Sinn, *J.C.S. Dalton*, 1974, 1156.

[9] E. Sinn, unpublished work.

[10] C. A. Bear, J. M. Waters, and T. N. Waters, *Chem. Comm.*, 1971, 703.

nitrato-group and of the two oxygen atoms of the Ni_2O_2 bridge (Table 3). These two planes are tilted at 88° to each other. The various equatorial planes [(VI)–(VIII)], made up of sets of four ligand atoms, are reasonably close to coplanar and orthogonal although some further distortion from octahedral symmetry is indicated by the deviation of the interplanar angles from 90° (Table 5), and by the deviation of nickel from planes (VI)–(VIII) by 0.14, 0.13, and 0.02 Å respectively.

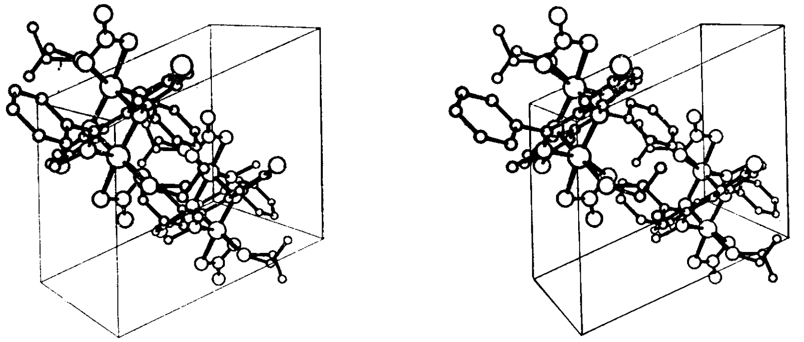
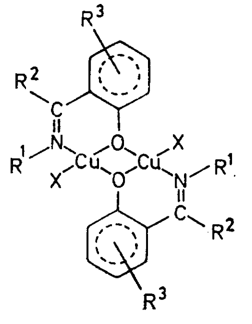


FIGURE 2 Packing in the unit cell



(2)

The difference between (3) and the present nickel dimer (4) reflects the much greater tendency for nickel(II) to become octahedral with these ligands. No ethanol was added to the reaction mixture, and the ethanol in (4) must therefore have been formed from the reaction of tem with water of hydration from nickel(II) nitrate. By contrast, the copper atoms in (3) show no tendency to combine with ethanol in the same solvent system, even when excess of ethanol is added.

The hydroxy-hydrogen of the co-ordinated ethanol is hydrogen-bonded to the un-co-ordinated oxygen of the nitrato-group of a neighbouring molecule. This results in an infinite chain of molecules along the *a* axis, each linked to the next by a pair of such bonds. The location of the ethanol hydrogens unequivocally confirms the hydrogen bonding. The linkage between the individual molecules appears to be significant in determining the magnetic behaviour. The complex is high spin (3.2 B.M. at room temperature) with a moment that rises to a maximum (4.0 B.M.) at 7 K and falls rapidly as temperature is lowered further.[11] This is indicative of the ferromagnetic interactions expected[12] from the observed dimeric structure together with an interdimer antiferromagnetic interaction which presumably acts *via* the intermolecular hydrogen-bonding links. Further magnetic data, obtained by use of a superconducting magnetometer,[13] will be given subsequently.

The i.r. spectrum shows some significant differences between the monomeric [Ni(mcp)$_2$] and the dimeric (4): new bands at 807, 1 032, 1 280—1 300, and 1 480—1 500 cm^{-1} are typical for NO_3, and provide good evidence for the assignment of such absorptions to vibrations of co-ordinated nitrato-groups.[2] The band at 1 532 cm^{-1} in [Ni(mcp)$_2$] shifts to 1 540 cm^{-1} in (4), and is attributed principally to phenolic C–O stretch. A shift of 10—20 cm^{-1} (from *ca.* 1 520 cm^{-1}) to higher frequency is characteristic of the formation of bi- or tri-nuclear complexes *via* phenolic oxygen bridges. The observed shift is smaller than usual, and could be explained if some phenolic oxygen bridging already existed in the parent complex, producing octahedral nickel. This appears to be the case, for [Ni(mcp)$_2$] exhibits electronic reflectance spectra in the solid state typical of octahedral nickel, with absorption peaks matching those of nickel Schiff-base complexes believed to show such phenolic oxygen bridging to neighbouring molecules:[2,14] peaks at 10 500 and 16 500 cm^{-1} (and charge transfer at 22 000—23 000 cm^{-1}). [Ni(mcp)$_2$] is paramagnetic, as expected, and attempts are being made to grow crystals suitable for crystallography to further elucidate the molecular association in this complex.

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[11] R. J. Butcher and E. Sinn, *J.C.S. Chem. Comm.*, 1975, 832.

[12] E. Sinn, *Co-ordination Chem. Rev.*, 1970, **5**, 313; R. L. Martin, in ' New Pathways in Inorganic Chemistry,' eds. E. V. Ebsworth, A. Maddock, and A. G. Sharpe, Cambridge University Press, Cambridge, 1968.

[13] E. J. Cukauskas, B. S. Deaver, and E. Sinn, *J.C.S. Chem. Comm.*, 1974, 698.

[14] A. H. Ewald and E. Sinn, *Inorg. Chem.*, 1967, **6**. 40; G. M. Mockler, G. W. Chaffey, E. Sinn, and H. Wong, *ibid.*, 1972, **11**, 1308.