Metal Complexes as Ligands. Part 12. Synthesis and *X*-Ray Crystal Structure of a Hexanuclear Nickel(II) Complex based on two Isosceles Trinuclear Components with Imidazolate Bridges†

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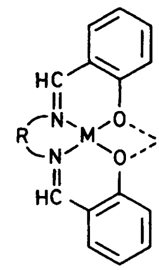
The new ligand H_2L, derived from 5-chloro-2-hydroxybenzophenone, *o*-phenylenediamine, and imidazole-2-carbaldehyde, forms an insoluble, apparently polymeric nickel(II) complex, which can dissociate and act as a monodentate ligand *via* a ring nitrogen donor. It forms a 2:1 adduct with nickel hexafluoroacetylacetonate, Ni(hfacac)$_2$, with a toluene molecule in the hollow of the V-shaped trinuclear fragment. The central nickel is octahedral with two hfacac ligands and two *cis*-bonded NiL complex ligands, to form an isosceles triangle of nickel atoms, of dimensions 5.754 × 5.783 × 6.407 Å. The overall structure is hexanuclear, consisting of two trinuclear subunits joined by two weak (2.908 Å) Ni–O links between NiL complex ligands. $[(NiL)_2Ni(hfacac)_2]_2\cdot 2C_6H_5Me$ crystallizes in space group $P\bar{1}$ with a = 16.044(6), b = 15.939(4), c = 14.971(9) Å, α = 78.33(4), β = 72.09(5), γ = 63.56(6)°, and Z = 1; R = 0.065 for 4 660 reflections.

The possibility of imidazolate (im) bridging between transition metals was invoked in cytochrome oxidase[1,2] to model an active site which is believed to contain strong coupling between iron and copper in this enzyme.[3–9] While im bridging is not required to account for these properties, it has raised interest in im bridges between transition metals.[10–13] Further interest is generated by the known im bridges in native and metal-substituted superoxide dismutase.[14–17]



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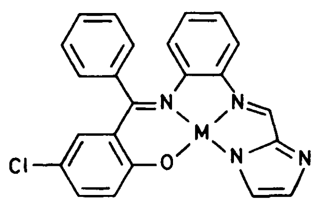

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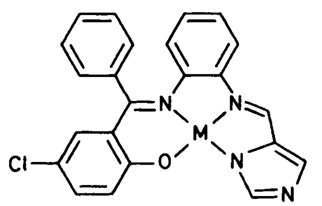

[ML'] (3)

Metal complexes of tetradentate Schiff bases, (1), readily act as bidentate ligands on other complexes which can act as Lewis bases, *e.g.* metal halides, perchlorates, nitrates, hexafluoroacetylacetonates, M(hfacac)$_2$,[18–21] and organometallic clusters.[22] Modification of the ligand to incorporate an im group forms a monodentate complex ligand, (2) or (3), which co-ordinates through the im, thereby enabling the formation of a rich variety of homo- and hetero-binuclear complexes with im bridges.[5,13] One example of this is the bonding of (3) to macrocycles and clusters to give complexes of type (4) (cap = capping organic fragment)[4] and (5).[22] With copper(II), the adducts of (1)—(3) (M = M' = Cu^{II}) are five- or six-co-ordinated complexes, depending on stoicheiometry, choice of substituent, and reaction conditions. Reaction of Ni(hfacac)$_2$ with [NiL] (2; M = Ni) produces a complex which is hexanuclear and is the first member of the new type of im-bridged complex, described here.

Experimental

Synthesis.—The complex [NiL] was synthesized by refluxing 5-chloro-2-hydroxybenzophenone, phenylenediamine (1.68 g, 5.2 mmol),[23] for 1 h with imidazole-2-carbaldehyde (0.50 g, 5.2 mmol) (Aldrich) in anhydrous methanol. To the filtered golden brown solution, Ni(CH$_3$COO)$_2$·4H$_2$O (1.29 g, 5.2 mmol) in anhydrous methanol (80 cm^3) was added dropwise with stirring. The bright red crystalline product which formed gradually was collected and washed with methanol (yield 2.2 g, 92%) (Found: C, 60.25; H, 3.9; N, 12.35. Calc. for $C_{23}H_{15}ClN_4NiO$: C, 60.35; H, 3.30; N, 12.25%). The mass spectrum showed the parent peak at m/e = 459 (M + 1).

The hexanuclear complex was prepared by refluxing [NiL] (0.20 g) and Ni(hfacac)$_2$·2H$_2$O[21,24] (0.22 g) (1:1 mol ratio) in CH$_2$Cl$_2$ (50 cm^3) for 1 h. All the solid dissolved after 5—10 min. The reddish brown product (0.21 g, 70%) was filtered off from the cooled solution, washed with cold n-butanol and diethyl ether and air-dried. Ligand peaks due to hfacac and the Schiff base L^{2-} in the i.r. spectrum verified adduct formation (Found: C, 55.8; H, 2.8; N, 9.10. Calc. for $C_{56}H_{32}Cl_2F_{12}N_8Ni_3O_6$: C, 55.5; H, 2.65; N, 9.25%) Several pure solvents and mixtures were used in an attempt to produce crystals suitable for *X*-ray analysis, but crystals failed to form if toluene was absent. A 4:1 mixture of CH$_2$Cl$_2$ and toluene produced dark red, flattened needles on slow evaporation.

Spectroscopy and Physical Data.—Optical spectra were recorded in solution and in the solid state using a Varian 634 Series u.v.–visible spectrophotometer at room temperature. Infrared spectra were recorded on a Perkin-Elmer 1430 Ratio

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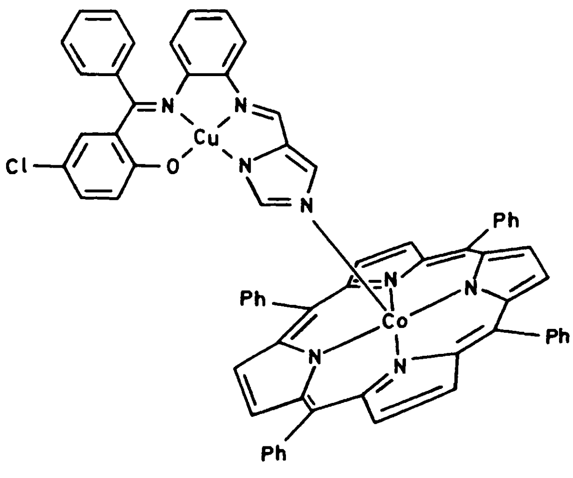
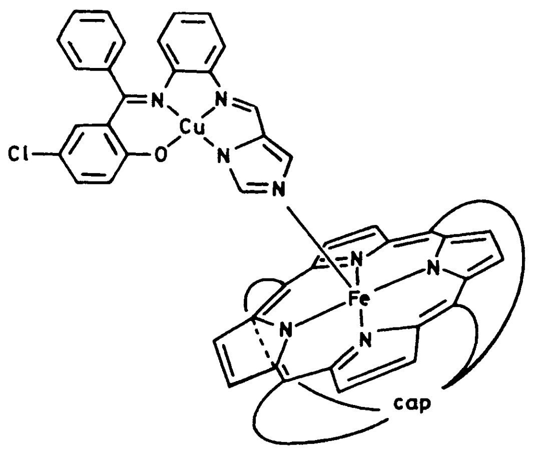
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

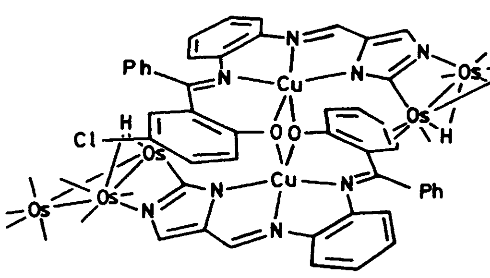
Non-S.I. unit employed: B.M. = 0.9247 × 10^{-23} J T^{-1}.



(4a)



(4b)



(5)

Recording Spectrophotometer. Magnetic data (5—350 K) were collected on a SQUID magnetometer. The calibration and method of operation were as described previously.[25,26]

X-Ray Crystallography.—*Crystal data for* [(NiL)$_2$Ni(hfacac)$_2$]$_2$·2C$_6$H$_5$Me. C$_{126}$H$_{80}$Cl$_4$F$_{24}$N$_{16}$Ni$_6$O$_{12}$, M = 2 960, space group $P\bar{1}$, $Z = 1$, a = 16.044(6), b = 15.939(4), c = 14.971(9) Å, α = 78.33(4), β = 72.09(5), γ = 63.56(6)°, U = 3 251 Å^3, D_c = 1.51 g cm^{-3}, D_m = 1.47 g cm^{-3}, μ(Mo-K_α) = 10.33 cm^{-1}; dark red crystal, dimensions (mm): 0.52 × 0.26 × 0.14.

Data collection. Cell dimensions and space group data were obtained by standard methods on a Nicolet P3 four circle diffractometer using Mo-K_α radiation (λ = 0.7107 Å). The θ—2θ scan technique was used at 293 K, as described previously,[27] to record the intensities of non-equivalent reflections in the range $2 < 2\theta < 53°$.

The intensities of three standard reflections showed no greater fluctuations (4%) during data collection than those expected from Poisson statistics. The raw intensity data were corrected for Lorentz-polarization effects and absorption. Of the 12 314 independent intensities, there were 4 660 with $F_o^2 > 3\sigma(F_o^2)$, where $\sigma(F_o^2)$ was estimated from counting statistics.[28] These data were used in the final refinement of the structural parameters.

Structure determination. A three-dimensional Patterson function was used to determine the metal positions, which phased the intensity data sufficiently well to permit location of the other atoms from Fourier synthesis. The asymmetric unit contains a disordered occluded toluene molecule. The disorder prevents location of the methyl group. Because of the large number of parameters, anisotropic thermal parameters were introduced only for atoms heavier than carbon. Hydrogen atoms were included at their calculated positions. The models converged with $R = 0.065$ and $R' = 0.072$. The principal programs used are as described previously.[7]

Final atomic co-ordinates are given in Table 1; bond lengths and angles are in Table 2. Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

Results and Discussion

The parent complex, [NiL], was found to be insoluble in common organic solvents and very sparingly soluble in boiling CH$_2$Cl$_2$, dimethylformamide, and dimethyl sulphoxide. In this way, it behaves like its even more insoluble copper analogue, [CuL].[29] These properties indicate a probable polynuclear structure in both complexes, and bridging *via* im nitrogens is likely. This contrasts with the behaviour of the isomeric ligand L′, which forms soluble complexes with copper(II) and nickel.[13,23,29]

In the synthesis of the Ni(hfacac)$_2$ adduct it is neither necessary nor possible to dissolve the [NiL] before mixing the components. As the formation of the adduct proceeds, [NiL] is taken up into solution until no solid remains. This behaviour is also consistent with a polymeric structure which dissociates gradually and passes into solution as it does so. The 2:1 adduct forms preferentially, even when the two components, [NiL] and Ni(hfacac)$_2$, are reacted in other proportions. In contrast to its parent complex, the Ni(hfacac)$_2$ adduct is soluble in most organic solvents.

Structure.—The overall structure of the molecule (Figure 1) has the nickel atoms in planar and octahedral environments linked by im bridges. The NiL groups bridge through im to form *cis*-bonded ligands on the 'central' nickel. This is made possible by the roughly planar nature of NiL which allows the complex ligands to orient such as to minimize steric crowding. The complex was crystallized from dichloromethane–toluene and contains a toluene molecule of crystallization per trinuclear fragment. The toluene occupies the V-shaped trough formed by the two NiL fragments bonded to the octahedral central nickel. Two weak (2.908 Å) Ni–O links across an inversion centre join one of the NiL units to its equivalent in the adjacent trinuclear fragment.

The hexanuclear complex is soluble in a variety of organic solvents, but attempts to form single crystals failed unless toluene was present. Evidently the solvent molecule is necessary to fill the crystallographic hole which would otherwise occur in the hollow of the 'V' formed by the trinuclear subunits. While

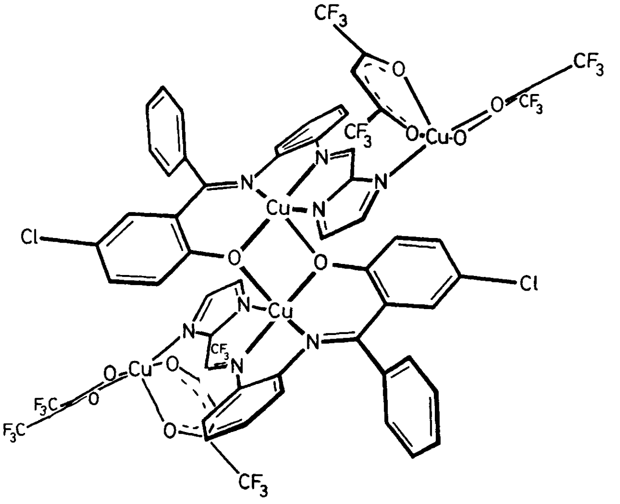
Table 1. Atomic co-ordinates for $[(NiL)_2Ni(hfacac)_2]_2 \cdot 2C_6H_5Me$

Atom	*x*	*y*	*z*
Ni	−0.073 5(1)	0.255 8(1)	0.247 6(2)
Ni(a)	0.340 7(1)	0.116 1(1)	0.128 6(2)
Ni(b)	0.074 8(1)	0.437 1(1)	0.415 8(1)
Cl(a)	0.807 0(4)	0.068 7(4)	−0.147 1(4)
Cl(b)	0.433 4(3)	0.373 4(4)	0.634 7(4)
F(1)	−0.454 6(9)	0.392 8(12)	0.341(1)
F(2)	−0.374 5(10)	0.253 2(14)	0.361(2)
F(3)	−0.383 6(12)	0.329 4(20)	0.449(1)
F(4)	−0.316 7(12)	0.577 6(13)	0.121(1)
F(5)	−0.189 2(14)	0.570 0(11)	0.127(1)
F(6)	−0.190 5(14)	0.500 7(11)	0.029(1)
F(7)	−0.008 4(12)	−0.104 1(9)	0.327(1)
F(8)	0.054 1(10)	−0.052 0(10)	0.381(1)
F(9)	−0.086 3(12)	−0.016 0(12)	0.435(1)
F(10)	−0.145(1)	0.044(1)	0.075(1)
F(11)	−0.077(1)	0.125(1)	−0.011(1)
F(12)	−0.227(1)	0.187(1)	0.072(2)
O(a)	0.399 2(7)	0.151 3(7)	0.014 1(8)
O(b)	0.102 2(7)	0.397 7(7)	0.529 1(8)
O(1f)	−0.211 5(7)	0.277 5(8)	0.325 3(9)
O(2f)	−0.128 0(8)	0.389 3(8)	0.185 6(8)
O(3f)	−0.030 2(7)	0.121 4(6)	0.308 2(8)
O(4f)	−0.103 2(8)	0.210 7(8)	0.145 2(8)
N(1a)	0.447 8(9)	0.040 5(9)	0.176 1(9)
N(2a)	0.270 0(8)	0.083 1(9)	0.241 3(9)
N(1ia)	0.319 8(8)	0.191 0(8)	0.102 9(9)
N(3ia)	0.059 4(8)	0.237 8(8)	0.161 0(9)
N(1b)	0.137 6(8)	0.517 6(8)	0.375 4(9)
N(2b)	0.042 8(8)	0.474 8(8)	0.300 4(9)
N(1ib)	0.016 4(9)	0.254 1(8)	0.428 4(9)
N(3ib)	−0.046 4(8)	0.294 6(8)	0.356 5(9)
C(1a)	0.558(1)	0.075(1)	0.039(1)
C(2a)	0.493(1)	0.129(1)	−0.014(1)
C(3a)	0.523(1)	0.163(1)	−0.110(1)
C(4a)	0.619(1)	0.146(1)	−0.150(1)
C(5a)	0.681(1)	0.094(1)	−0.095(1)
C(6a)	0.657(1)	0.060(1)	−0.005(1)
C(7a)	0.536(1)	0.034(1)	0.132(1)
C(8a)	0.616(1)	−0.016(1)	0.179(1)
C(9a)	0.690(1)	−0.104(1)	0.151(1)
C(10a)	0.766(1)	−0.149(1)	0.192(1)
C(11a)	0.773(2)	−0.108(2)	0.256(2)
C(12a)	0.704(2)	−0.021(2)	0.285(2)
C(13a)	0.625(1)	0.025(1)	0.245(1)
C(14a)	0.422(1)	−0.006(1)	0.266(1)
C(15a)	0.323(1)	0.021(1)	0.301(1)
C(16a)	0.286(1)	−0.020(1)	0.386(1)
C(17a)	0.344(1)	−0.089(1)	0.438(1)
C(18a)	0.444(1)	−0.116(1)	0.403(2)
C(19a)	0.482(1)	−0.077(1)	0.320(1)
C(2ia)	0.149(1)	0.181(1)	0.175(1)
C(4ia)	0.079(1)	0.284(1)	0.075(1)
C(5ia)	0.177(1)	0.255(1)	0.040(1)
C(6ia)	0.177(1)	0.119(1)	0.253(1)
C(1b)	0.229(1)	0.451(1)	0.494(1)
C(2b)	0.174(1)	0.402(1)	0.551(1)
C(3b)	0.197(1)	0.351(1)	0.635(1)
C(4b)	0.274(1)	0.345(1)	0.660(1)
C(5b)	0.331(1)	0.387(1)	0.602(1)
C(6b)	0.312(1)	0.438(1)	0.523(1)
C(7b)	0.210(1)	0.508(1)	0.410(1)
C(8b)	0.274(1)	0.555(1)	0.357(1)
C(9b)	0.281(1)	0.626(1)	0.392(1)
C(10b)	0.347(1)	0.665(1)	0.337(1)
C(11b)	0.401(1)	0.634(1)	0.254(2)
C(12b)	0.399(1)	0.563(2)	0.220(2)
C(13b)	0.336(1)	0.523(1)	0.272(1)
C(14b)	0.109(1)	0.579(1)	0.298(1)
C(15b)	0.062(1)	0.550(1)	0.252(1)
C(16b)	0.033(1)	0.599(1)	0.174(1)
C(17b)	0.048(1)	0.681(1)	0.137(1)
C(18b)	0.090(1)	0.711(1)	0.186(1)
C(19b)	0.120(1)	0.663(1)	0.263(1)
C(2ib)	−0.012(1)	0.360(1)	0.350(1)
C(4ib)	−0.039(1)	0.247(1)	0.441(1)
C(5ib)	0.000(1)	0.283(1)	0.485(1)
C(6ib)	0.001(1)	0.429(1)	0.282(1)
C(1f)	−0.378(2)	0.334(2)	0.361(2)
C(2f)	−0.285(1)	0.343(1)	0.303(1)
C(3f)	−0.292(1)	0.416(1)	0.238(1)
C(4f)	−0.215(1)	0.434(1)	0.184(1)
C(5f)	−0.229(2)	0.515(2)	0.114(2)
C(6f)	−0.027(1)	−0.025(1)	0.359(1)
C(7f)	−0.046(1)	0.059(1)	0.289(1)
C(8f)	−0.082(1)	0.059(1)	0.216(1)
C(9f)	−0.107(1)	0.134(1)	0.151(1)
C(10f)	−0.151(2)	0.135(2)	0.063(2)
C(1t)	0.294(2)	0.298(2)	0.243(2)
C(2t)	0.338(2)	0.330(2)	0.151(3)
C(3t)	0.448(3)	0.316(3)	0.129(3)
C(4t)	0.444(2)	0.274(2)	0.242(2)
C(5t)	0.402(2)	0.247(2)	0.328(2)
C(6t)	0.305(3)	0.254(3)	0.333(3)

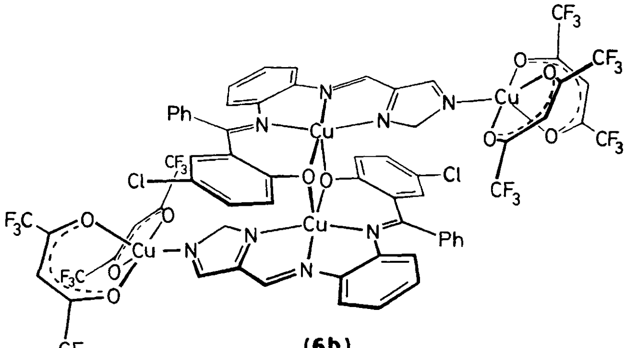
there are indications from the solubility behaviour, as well as from the spectra (below) that the trinuclear subunit remains intact in solution, there is no clear indication of how strongly the hexanuclear structure holds together. Attempts at freezing-point depression measurements produced only negative evidence: the temperature change was too small to measure and for the high-molecular-weight hexanuclear molecule a very low depression is expected.

The ligand L forms a variety of complexes which can bridge *via* imidazole. The [ML] and [ML′] complexes can act as ligands to form a variety of adducts with $M'(hfacac)_2$. With copper(II), the parent complex $[(CuL')_2] \cdot 2H_2O$ is binuclear with oxygen bridges. The 1:1 adducts $[(CuL)Cu(hfacac)_2]$ (**6**) link *via* imidazole, but have additional, weaker, links *via* oxygen, to form tetranuclear units.[13-18]

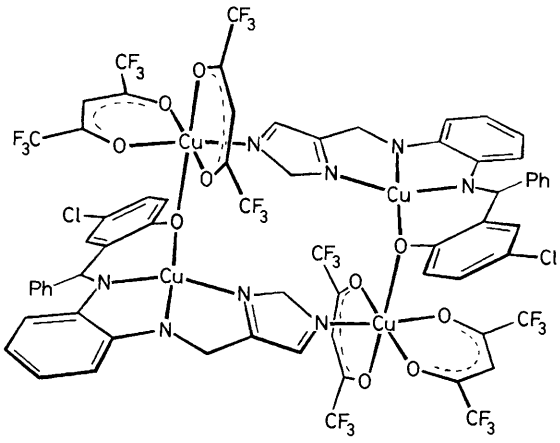
The trinuclear structure is shown in Figure 1, which illustrates the 2:1 combination of the adducts, with bridging through the imidazolate fragments. Figure 2 shows this schematically. Unlike the [CuL] and [CuL′] complexes, there is no strong linkage of the nickel atoms *via* the oxygens of the Schiff base. Nickel atom Ni(a) is strictly four-co-ordinated with shorter average metal–ligand bonds than in the octahedral nickel atom. The other NiL units, designated (b), are essentially four-co-ordinated, but there is a weak link to the oxygen atom, O(b′), of the adjacent NiL fragment (b). This forms weak bridges between pairs of Ni_3 molecules to form an overall Ni_6 molecule (Figure 3). However, these bridging bonds are marginal: Ni(b)–O(b′) 2.908(5) Å. This compares with a non-bonded distance of 3.17 Å, based on van der Waals radii for nickel and oxygen of 1.63[30] and 1.54 Å[31] respectively. Molecular distortions discussed below also indicate that these distances should be considered as bonding. The distance between the nickel atoms Ni(b)–Ni(b′) is 3.190(2) Å, through a crystallographic inversion centre. By contrast, the next nearest intermolecular approach of nickel atoms is between neighbouring Ni(a) atoms at 5.609 Å.



(6a)



(6b)



(6c)

The nickel atoms of the Ni_3 subunit form a near-isosceles triangle. The distances through the im bridges are 5.783(3) and 5.754(3) Å for Ni–Ni(a) and Ni–Ni(b) respectively. The triangular base, formed by the chemically unlinked Ni(a) and Ni(b), is of dimensions 6.407(3) Å.

The ligand environment about the central nickel atom is an octahedron formed by two imidazole nitrogen atoms and the four hfacac oxygens. The equatorial planes are inclined at 88.3, 89.6, and 88.1° to each other, compared with the 90° values required of a regular octahedron. The nickel atom is 0.01 Å from the centre of the plane containing the two imidazole nitrogens and 0.06 and 0.05 Å from the centres of the other two equatorial planes. The O–C–C–C–O planes of the hfacac ligands bend

Table 2. Selected interatomic distances (Å) and angles (°) for $[(NiL)_2Ni(hfacac)_2]_2{\cdot}2C_6H_5Me$ *

Ni–Ni(a)	5.783(3)	Ni–N(3ia)	2.053(5)
Ni–Ni(b)	5.754(3)	Ni–N(3ib)	2.077(5)
Ni(a)–Ni(b)	6.407(3)	Ni(a)–O(a)	1.796(5)
Ni(b)–Ni(b′)	3.190(2)	Ni(a)–N(1a)	1.862(5)
Ni(b)–O(b′)	2.908(5)	Ni(a)–N(2a)	1.845(5)
Ni(a)–Ni(a″)	5.609(3)	Ni(a)–N(1ia)	1.883(5)
Ni–O(1f)	2.067(5)	Ni(b)–O(b)	1.802(5)
Ni–O(2f)	2.049(5)	Ni(b)–N(1b)	1.868(5)
Ni–O(3f)	2.042(5)	Ni(b)–N(2b)	1.860(5)
Ni–O(4f)	2.072(5)	Ni(b)–N(1ib)	1.886(5)
O(1f)–Ni–O(2f)	88.46(4)	O(4f)–Ni–N(3ib)	176.22(5)
O(1f)–Ni–O(3f)	87.48(4)	N(3ia)–Ni–N(3ib)	92.59(6)
O(1f)–Ni–O(4f)	86.61(4)	O(a)–Ni(a)–N(1a)	99.59(5)
O(1f)–Ni–N(3ia)	175.46(5)	O(a)–Ni(a)–N(2a)	174.16(5)
O(1f)–Ni–N(3ib)	91.19(5)	O(a)–Ni(a)–N(1ia)	90.38(5)
O(2f)–Ni–O(3f)	174.56(4)	N(1a)–Ni(a)–N(2a)	85.90(5)
O(2f)–Ni–O(4f)	87.82(4)	N(1a)–Ni(a)–N(1ia)	169.80(5)
O(2f)–Ni–N(3ia)	88.70(5)	N(2a)–Ni(a)–N(1ia)	84.22(5)
O(2f)–Ni–N(3ib)	95.21(5)	O(b)–Ni(b)–N(1b)	97.85(5)
O(3f)–Ni–O(4f)	88.34(4)	O(b)–Ni(b)–N(1ib)	93.38(5)
O(3f)–Ni–N(3ia)	95.12(5)	O(b)–Ni(b)–N(2b)	177.33(5)
O(3f)–Ni–N(3ib)	88.49(5)	N(1b)–Ni(b)–N(2b)	84.79(5)
O(4f)–Ni–N(3ia)	89.75(5)	N(1b)–Ni(b)–N(1ib)	167.52(5)
N(2b)–Ni(b)–N(1ib)	84.02(5)	O(b′)–Ni(b)–N(1b)	87.33(4)
Ni(b)–O(b)–Ni(b′)	81.62(3)	O(b′)–Ni(b)–N(2b)	81.32(4)
O(b)–Ni(b)–O(b′)	98.38(4)	O(b′)–Ni(b)–N(1ib)	96.44(4)

* Primes denote atoms at positions $-x$, $1-y$, $1-z$; double primes those at $1-x$, $-y$, $-z$.

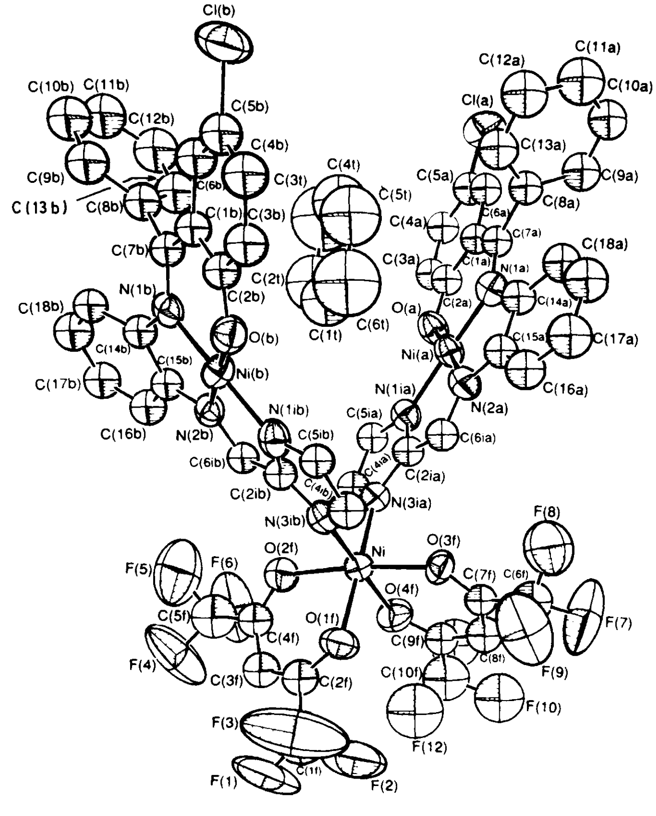


Figure 1. ORTEP Diagram of the trinuclear fragment $[(NiL)_2Ni(hfacac)_2]{\cdot}C_6H_5Me$

Table 3. Effective magnetic moments*

Unsolvated complex														
T/K	5.09	5.20	5.60	5.80	6.20	6.60	7.49	8.00	8.50	9.0	10.0	10.9	12.0	14.7
$\mu_{eff.}$	2.974	2.983	3.000	3.007	3.021	3.033	3.043	3.051	3.056	3.06	3.069	3.070	3.079	3.086
T/K	17.0	21.2	24.5	27.6	33.0	39.5	43.2	51.9	59.9	64.1	72.3	79.1	86.6	94.1
$\mu_{eff.}$	3.090	3.091	3.090	3.102	3.111	3.112	3.116	3.126	3.132	3.133	3.146	3.151	3.156	3.165
T/K	100.0	125.15	150.2	175	200.2	220	240.4	260.3	282.3	300.5	321.7			
$\mu_{eff.}$	3.175	3.206	3.224	3.240	3.27	3.295	3.328	3.346	3.363	3.367	3.371			
Toluene solvate														
T/K	10.9	21.2	51.9	99.9	199.5	300.2	352.1							
$\mu_{eff.}$	3.222	3.153	3.179	3.193	3.246	3.315	3.384							

* Although absolute values of $\mu_{eff.}$ are accurate to *ca.* ±0.03, the estimated accuracy of relative values is considered to be better than ±0.004.

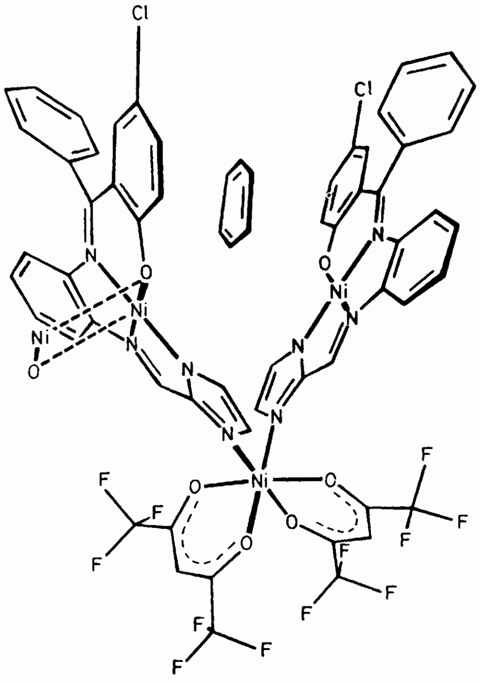


Figure 2. Scale drawing of the $[(NiL)_2Ni(hfacac)_2]$ fragment

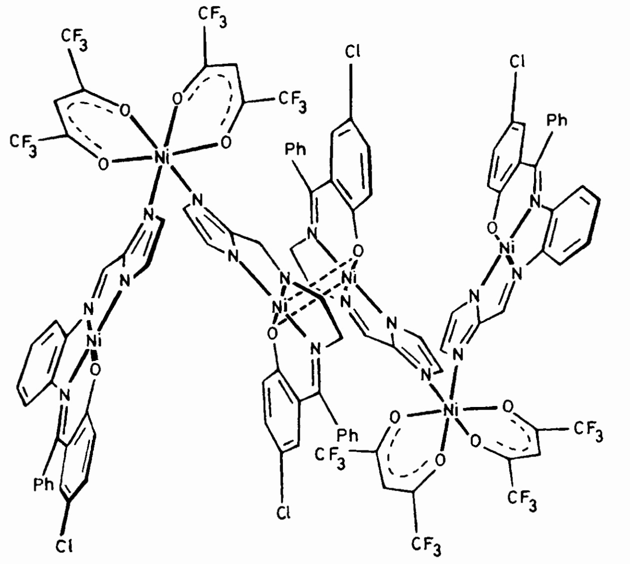


Figure 3. Scale drawing showing the linkage between the two trinuclear fragments

away from the adjoining equatorial planes with angles of 18.8 and 13.1° for the two ligands.

The other two nickel atoms are each in a slightly distorted planar environment, Ni(b) consistently being distorted somewhat more than Ni(a). The principal distortion about Ni(a) is a very slight trend towards tetrahedral. For Ni(b), the distortion is more due to the weak linkage (2.908 Å) with the symmetry-related neighbouring O(b′). In addition, the entire NiL fragment (b) curves away from the long Ni(b)–O(b′) linkages such that at opposite ends the phenoxy and imidazole rings make angles of 148.2° to each other, 31.8° away from the 180° required for planarity. By contrast, the same angle for the NiL fragment (a) is 169.3°, 10.7° away from planarity. The nickel atoms are essentially central in the ligand planes [0.0 Å for Ni(a) and 0.04 Å for Ni(b)] and these planes are inclined at 55.7° to each other. The two imidazole fragments are inclined at 64.8° to each other. Co-ordination planes N(1i)–C(2i)–C(6i)–N(2) are bent away from these planes by a small angle of 2.3° for (a) and a larger one of 5.1° for (b). The imidazole rings are bent away from the latter co-ordination planes by 3.5° for (a) and 2.7° for (b). The principal ligand planes for the two planar nickel atoms incline slightly (3.3°) to the adjacent phenylenediamine ligand plane N(1)–C(14)–C(15)–N(2) for (a), and with a sharper angle (11.8°) in (b). These phenylenediamine ligand planes bend away somewhat further with inclinations at the phenyl ring of 4.6° for (a) and 5.3° for (b). The inclination of the principal co-ordination planes to the adjacent Schiff base ligand planes O–C(2)–C(1)–C(7)–N(1) are 5.6° for (a) and 21.0° for (b). This makes the overall geometry of the NiL fragment (a) much closer to planar overall than the corresponding fragment (b). The plane made by the three nickel atoms is inclined at 76.7° and 80.8° respectively with the principal planes of the planar nickel atoms (a) and (b).

Magnetism.—The magnetic moments of the pure hexanuclear adduct in the 10—350 K temperature range show a gradual rise from 2.97 B.M. at 5 K and 3.07 B.M. at 10.9 K up to 3.37 B.M. over the temperature range (Table 3). The values are much the same for the toluene solvate, with a smaller drop in value at low temperatures (3.22 B.M. at 10.9 K). This indicates that the complex contains just two paramagnetic nickel atoms, those in the octahedral sites. The other four are diamagnetic. The weak fifth bond to the NiL fragment (b) does not distort it sufficiently from planarity to make it paramagnetic. The temperature dependence is consistent with a very slight intermolecular magnetic interaction present in the unsolvated complex but disrupted and somewhat reduced by toluene in the lattice.

Spectra.—Solution (toluene) and solid-state spectra of the hexanuclear complex are similar, suggesting similar structures in the two phases. Two peaks and two shoulders are observed in the range 300—600 nm in both solution and solid state. The positions of the peaks are the same in both solid and solution, but there is a slight shift (30 nm) in the positions of the shoulders that appear at the tail of the u.v. charge-transfer peaks. The much lower apparent intensity of the u.v. bands in the solid state leads to considerable inaccuracy in the position of transitions seen as shoulders. Thus, the shift in the shoulder positions may be more apparent than real. The absorption bands (nm) are as follows [intensities as log (ε/dm^3 mol^{-1} cm^{-1}) in parentheses]. Solution: 499 (sh) (4.55), 436 (4.84), 381 (sh) (4.70), and 322 (4.98); solid state: 531 (sh) (4.51), 436 (4.76), 381 (sh) (4.75), and 326 (4.85).

Conclusions

We have characterized a new type of imidazolate-bridged complex. It is now clear that a wide variety of complexes based on L and L′ are all derived from three basic co-ordination modes: (i) co-ordination as monodentate ligands to another metal atom; (ii) weak bridging *via* the phenolic oxygen alone, to form binuclear complexes; (iii) orthometallation.

As in structures (**4**) and (**6**) mode (i) linkage is predominant in the Ni_6 complex, both in the strength of the bridging bond and in the influence on magnetic and electronic properties. The physical limitations of the potential bridging directions, with respect to the orientation of the optimal overlapping orbital, determines this priority. The external imidazole (sp^2-type) nitrogen best bonds to a second metal situated coplanar with the imidazole ring, and this is sterically permitted in the complexes studied to date. However, for the phenolic oxygen, the very similar electronic predisposition is frustrated sterically within the molecular plane of the [ML] or [ML′] complex ligands. The weak mode (ii) linking occurs simultaneously in many such complexes. In $[(CuL')_2]\cdot 2H_2O$, mode (i) is eliminated by hydrogen bonding of a water molecule to the external imidazole nitrogen and the residual intermolecular linkage due to mode (ii) is weak, as is the effect on the magnetism. Here, mode (i) is effectively eliminated by hydrogen bonding of a solvent water molecule to the external imidazole nitrogen. For the copper tetranuclear complexes, imidazole-bridged binuclear subunits are linked by weak Cu–O bonds to form tetranuclear molecules. In the present nickel complex, the same basic principles operate. Bis-monodentate co-ordination of [NiL] or [NiL′] complex ligands, through imidazole, to a central nickel produces trinuclear subunits. Pairs of trinuclear subunits are then linked by weak Ni–O bonds of mode (ii) to form the hexanuclear molecules.

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