Complexes of Ligands derived from 1,8-Dihydroxynaphthalene. Synthesis and Crystal Structures of a Palladium and a Copper Complex*

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A simplified synthesis has been elaborated for 2,7-diacetyl-1,8-dihydroxy-3,6-dimethylnaphthalene, H_2daddn, whose di-Schiff base derivatives in principle offer binuclear metal complexes with potentially useful geometrical features; only mono-Schiff base products, however, are formed upon condensation with the mono-primary amines 2-aminomethylpyridine, 2-aminoethylpyridine or *N,N*-dimethylethylenediamine in either metal-free reactions or in the presence of Pd^{2+} or Cu^{2+}. The X-ray crystal structures of two metal derivatives of H_2daddn have been determined. Crystals of [PdL(N_3)] (in which L is the monoanion formed by proton loss from a phenolic group in the mono-Schiff base from H_2daddn and 2-aminoethylpyridine) are monoclinic, space group $P2_1/c$, with a = 11.220(1), b = 12.910(2), c = 14.521(2) Å and β = 92.540(9)°; at convergence R = 0.030 for 3398 reflections [$I > 2\sigma(I)$]. The Pd is essentially square planar with one N_3^- ligand, L acting as a tridentate chelating ligand which has a pronounced fold. The intact phenolic OH is hydrogen-bonded to the adjacent deprotonated and co-ordinated phenoxy centre. Crystals of [Cu(daddn)(en)]·MeOH (en = ethylenediamine) are orthorhombic, space group *Pbca*, with a = 14.515(2), b = 16.596(3) and c = 16.406(3) Å; at convergence R = 0.046 for 1158 reflections [$I > 3\sigma(I)$]. An approximately square O_2N_2 arrangement around the Cu is provided by a bidentate daddn^{2-} on one side and a bidentate ethylenediamine on the other; the molecules are present in pairs in which a phenoxide atom in one molecule is weakly bonded [Cu ··· O 2.848(12) Å] to the Cu in its neighbour.

Complexes of binucleating ligands which provide an accessible bridging site where a variety of species can be introduced show unusual co-ordination chemistry[1] including catalytic activity.[2] Models of complexes of the general type **1** constructed around the 1,8-dihydroxynaphthalene nucleus reveal a geometry in the region of Y and Z conducive, we believe, to enhanced efficiency in the catalysis of the hydration of nitriles to carboxamides, compared with earlier systems;[2] in particular, we anticipate more facile release of the carboxamide product from the binuclear site, the bottleneck in the earlier catalytic cycle.[2] We have therefore been investigating the chelating ability of various appropriately 2,7-disubstituted-1,8-dihydroxynaphthalenes, some results of which are reported here. Related ligands based on the 2-substituted-1,8-dihydroxynaphthalene nucleus and some of their complexes have been described by Fenton and co-workers.[3]

Results and Discussion

Our work is based on the building block 2,7-diacetyl-1,8-dihydroxy-3,6-dimethylnaphthalene **2**, H_2daddn, which has been reported previously[4] and for which an improved synthesis is described here. The BF_3-catalysed rearrangement of 1,8-diacetoxy-2-acetyl-3,6-dimethylnaphthalene afforded the diboron complex daddn(BF_2)$_2$ **3**. Chelation of both acetyl oxygens, as in **3**, is indicated by the fact that the band of highest frequency in the 1600–1700 cm^{-1} region of the IR spectum is found at 1610 cm^{-1}, significantly lower than the ν(C=O) band for any of the derivatives reported here in which one or both of the acetyl groups are unco-ordinated (1695–1660 cm^{-1}). Hydrolysis of the diboron complex in aqueous acidic methanol gave H_2daddn. Prior isolation of the 1,8-diacetoxy compound proved to be unnecessary and a very convenient route to H_2daddn is provided by the direct reaction of the readily available 2-acetyl-1,8-dihydroxy-3,6-dimethylnaphthalene[5] with BF_3·Et_2O in acetic anhydride followed by hydrolysis with acid in aqueous methanol.

Attempts to isolate solid di-Schiff base ligands related to **1** from the condensation of H_2daddn with two equivalents of either 2-(aminomethyl)pyridine (amp) or 2-(aminoethyl)-pyridine (aep) or *N,N*-dimethylethylenediamine gave only the mono-Schiff bases. Examination by ^1H NMR spectroscopy of the reaction in $CDCl_3$ between H_2daddn and amp (1:2 proportions) revealed that, in solution also, the reaction proceeds only as far as the mono-Schiff base formation. The two CH_3 singlets in the ^1H NMR spectrum of H_2daddn (δ 2.49, 3- and 6-CH_3, δ 2.68, 2- and 7-CH_3CO–) upon addition of two equivalents of amp were replaced within minutes at room temperature by four singlets at δ 2.78, 2.90, 2.99 and 3.06; at the same time the singlet at δ 6.85 due to the 4- and 5-aromatic protons was replaced by two singlets at δ 6.91 and 7.07. Roughly half the amp remained unchanged. Attempts to push the reaction in favour of the di-Schiff base by heating the solution, by adding an excess of amp and/or by adding catalytic amounts of CF_3CO_2D all failed, the above features of the mono-Schiff base remaining essentially unchanged in the ^1H NMR spectrum.

Attempts to use metal ions to promote formation of di-Schiff base complexes of the type **1** yielded, like the metal-free reactions, only mono-Schiff base products. By condensation of H_2daddn with the appropriate amine in the presence of Pd^{II} and the appropriate anion the complexes represented in **4** were isolated. The structure of **4c**, [PdL(N_3)] {HL = 2-acetyl-1,8-dihydroxy-3,6-dimethyl-7-[2-(2-pyridyl)ethyliminoethyl]-naphthalene} determined by single-crystal X-ray diffraction is described below. We concentrated here mainly on Pd^{II} because this seemed to us the metal of choice for complexes of the type **1** whose potential catalytic properties provided the prime motivation for the work, but IR analysis of solids isolated

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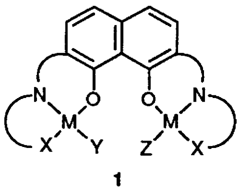
* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

Non-SI unit employed: eV ≈ 1.6 × 10^{-19} J.



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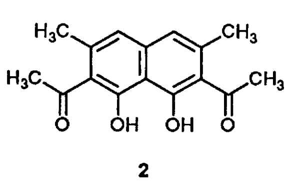

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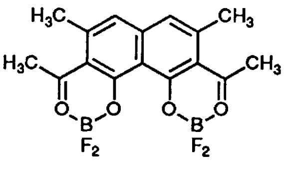

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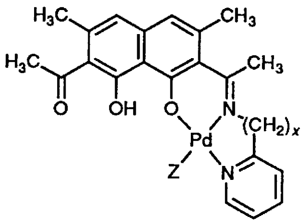
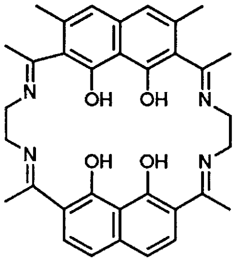


	x	Z
4a	1	Cl
4b	2	Cl
4c	2	N_3



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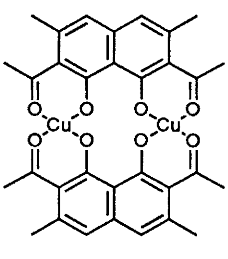

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from similar reactions with Cu^{II} suggested again that only mono-Schiff base complexes were formed. It is not clear to us why these systems are so reluctant to give di-Schiff bases, for the first acetyl group clearly reacts readily with the above primary amines. To add to this mystery the di-primary amines ethylenediamine and propylenediamine condense readily with both acetyl groups of H_2daddn.

Reactions of H_2daddn with ethylenediamine in methanol gives a yellow crystalline solid, for which analytical, IR and mass spectral evidence are consistent with the 2:2 macrocyclic tetra-Schiff base structure **5** (the compound was too insoluble for NMR analysis). The macrocycle **5** and the related acyclic di-Schiff base from one ethylenediamine (en) and two H_2daddn units have been referred to briefly by other workers.[4] Since we were unable to isolate any pure complexes from attempted insertion of Cu^{II} or Pd^{II} into the preformed macrocycle we investigated the alternative approach of a template synthesis of the metal complexes, for which purpose $[Cu_2(daddn)_2]$, presumed to have the structure **6**, was prepared as a precursor from reaction of H_2daddn with $Cu(O_2CMe)_2$ in methanol. X-Ray crystallography would be required to establish the structure of this product with certainty but suitable crystals have eluded us. Reaction of $[Cu_2(daddn)_2]$ with 2 equivalents of ethylenediamine in methanol yielded initially blue-green crystals of the mononuclear complex [Cu(daddn)(en)] in which the diamine and the diketone are present unconnected by Schiff-base links, as was established by the single-crystal X-ray diffraction study described below. After prolonged heating of the reaction mixture the initially formed crystals of [Cu(daddn)(en)] gradually redissolved to give other products none of which was isolated in pure form.

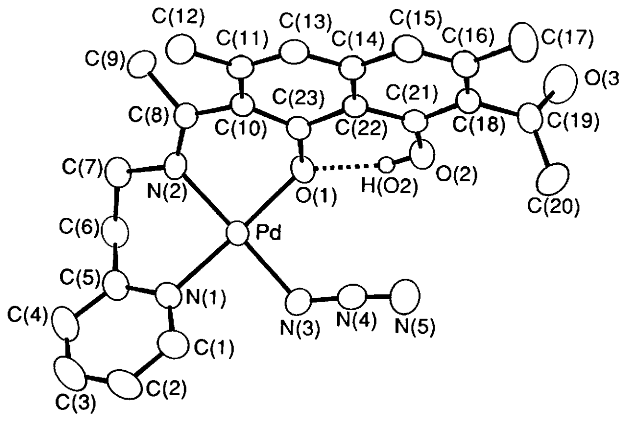

Fig. 1 Molecular structure of $[PdL(N_3)]$ showing atom numbering scheme

Table 1 Fractional atomic coordinates for the non-hydrogen atoms of $[PdL(N_3)]$ with estimated standard deviations (e.s.d.s) of the last significant figure given in parentheses

Atom	*x*	*y*	*z*
Pd	0.838 16(2)	0.076 21(2)	0.390 45(2)
O(1)	0.798 4(2)	0.086 5(2)	0.523 4(1)
O(2)	0.830 2(2)	−0.006 4(2)	0.681 0(2)
O(3)	0.766 9(5)	−0.076 9(3)	0.899 0(2)
N(1)	0.871 3(3)	0.068 8(2)	0.254 1(2)
N(2)	0.756 0(3)	0.213 7(2)	0.372 8(2)
N(3)	0.921 0(3)	−0.062 5(2)	0.406 3(2)
N(4)	0.913 0(3)	−0.117 8(2)	0.471 7(2)
N(5)	0.910 8(3)	−0.176 6(3)	0.531 3(2)
C(1)	0.856 3(4)	−0.020 6(3)	0.207 7(3)
C(2)	0.864 9(4)	−0.025 0(4)	0.113 1(3)
C(3)	0.889 3(4)	0.063 7(4)	0.066 0(3)
C(4)	0.906 4(4)	0.155 4(4)	0.113 3(3)
C(5)	0.897 6(3)	0.156 0(3)	0.209 0(2)
C(6)	0.917 9(3)	0.251 7(3)	0.266 1(3)
C(7)	0.806 0(4)	0.290 4(3)	0.309 3(3)
C(8)	0.665 3(3)	0.239 7(3)	0.419 2(2)
C(9)	0.618 2(4)	0.348 6(3)	0.412 1(3)
C(10)	0.611 6(3)	0.169 4(3)	0.485 5(2)
C(11)	0.484 7(3)	0.171 2(3)	0.498 2(2)
C(12)	0.396 9(3)	0.225 1(3)	0.432 6(2)
C(13)	0.440 0(3)	0.114 9(3)	0.567 5(2)
C(14)	0.513 3(3)	0.059 6(2)	0.631 5(2)
C(15)	0.464 8(3)	0.005 4(3)	0.705 7(2)
C(16)	0.534 7(4)	−0.049 4(3)	0.767 6(2)
C(17)	0.479 0(5)	−0.104 7(4)	0.846 3(3)
C(18)	0.659 3(3)	−0.051 7(3)	0.757 4(2)
C(19)	0.739 3(4)	−0.110 1(3)	0.824 7(3)
C(20)	0.778 9(4)	−0.215 6(3)	0.796 4(3)
C(21)	0.710 0(3)	−0.002 0(3)	0.684 4(2)
C(22)	0.637 6(3)	0.054 6(2)	0.618 8(2)
C(23)	0.658 2(3)	0.104 0(2)	0.539 8(2)

Crystal Structure of $[PdL(N_3)]$.—The asymmetric unit of $[PdL(N_3)]$ **4c** consists of a single molecule. The atomic arrangement and numbering scheme are presented in Fig. 1, the atomic coordinates in Table 1 and selected interatomic distances and angles in Table 2. Only one of the naphthol groups [O(1)] is deprotonated and this together with the adjacent imine nitrogen [N(2)] and the pyridyl nitrogen [N(1)] chelates the Pd. A roughly square arrangement around the Pd is completed by co-ordination of a terminal nitrogen [N(3)] of the monodentate azide ion. Metal–donor distances are unexceptional in the range 2.005(2) to 2.033(3) Å.

Steric repulsion between the methyl groups C(9) and C(12), which would be extreme if the imine were coplanar with the naphthalene, is most likely responsible for a marked fold in the molecule such that the average metal co-ordination plane is inclined at 54.5° to the average naphthalene plane. The imine carbon atom [C(8)] and the attached methyl carbon [C(9)] are displaced 0.318 and 1.348 Å respectively to the side of the

Table 2 Selected interatomic distances (Å) and angles (°) for [PdL(N$_3$)] with e.s.d.s in parentheses *

Pd–O(1)	2.005(2)	N(3)–N(4)	1.195(4)
Pd–N(1)	2.033(3)	N(4)–N(5)	1.152(4)
Pd–N(2)	2.011(3)	C(5)–C(6)	1.500(5)
Pd–N(3)	2.026(3)	C(6)–C(7)	1.513(6)
O(1)–C(23)	1.322(4)	C(8)–C(9)	1.504(5)
O(2)–C(21)	1.353(4)	C(8)–C(10)	1.471(5)
O(3)–C(19)	1.189(5)	C(11)–C(12)	1.510(5)
N(1)–C(1)	1.343(5)	C(16)–C(17)	1.507(6)
N(1)–C(5)	1.342(5)	C(18)–C(19)	1.500(5)
N(2)–C(7)	1.480(5)	C(19)–C(20)	1.496(6)
N(2)–C(8)	1.290(5)		
O(1)–Pd–N(1)	177.4(1)	N(2)–C(8)–C(10)	122.5(3)
O(1)–Pd–N(2)	86.8(1)	C(9)–C(8)–C(10)	117.9(3)
O(1)–Pd–N(3)	94.0(1)	C(8)–C(10)–C(11)	120.6(3)
N(1)–Pd–N(2)	91.1(1)	C(8)–C(10)–C(23)	119.5(3)
N(1)–Pd–N(3)	88.1(1)	C(10)–C(11)–C(12)	123.1(3)
N(2)–Pd–N(3)	179.2(2)	C(13)–C(14)–C(15)	121.4(2)
Pd–O(1)–C(23)	116.2(2)	C(15)–C(16)–C(17)	120.0(3)
Pd–N(1)–C(1)	120.3(3)	C(15)–C(16)–C(18)	119.0(3)
Pd–N(1)–C(5)	119.3(2)	C(16)–C(18)–C(19)	120.6(3)
Pd–N(2)–C(7)	119.0(2)	C(19)–C(18)–C(21)	118.5(3)
Pd–N(2)–C(8)	122.1(2)	O(3)–C(19)–C(18)	122.3(3)
C(7)–N(2)–C(8)	118.7(3)	O(3)–C(19)–C(20)	120.6(3)
Pd–N(3)–N(4)	124.6(2)	C(18)–C(19)–C(20)	117.1(3)
N(3)–N(4)–N(5)	174.6(3)	O(2)–C(21)–C(18)	116.9(2)
N(1)–C(5)–C(6)	116.9(3)	O(2)–C(21)–C(22)	122.4(2)
C(4)–C(5)–C(6)	122.6(3)	C(21)–C(22)–C(23)	122.7(2)
C(5)–C(6)–C(7)	113.1(3)	O(1)–C(23)–C(10)	123.3(2)
N(2)–C(7)–C(6)	112.4(3)	O(1)–C(23)–C(22)	117.5(2)
N(2)–C(8)–C(9)	119.4(3)		

* Naphthalene and pyridine rings: C–C distances are in the range 1.35–1.44 Å, average e.s.d. *ca.* 0.005 Å, internal bond angles for the naphthalene and pyridine rings are in the range 117.6–122.5°, average e.s.d. *ca.* 0.3°.

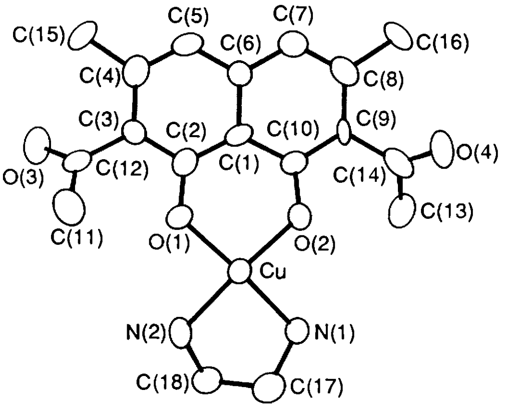

Fig. 2 Molecular structure of [Cu(daddn)(en)] showing atom numbering scheme

Table 3 Fractional atomic coordinates for the non-hydrogen atoms of [Cu(daddn)(en)] with e.s.d.s of the last significant figure given in parentheses *

Atom	*x*	*y*	*z*
Cu	−0.005 15(9)	0.393 30(7)	−0.038 91(6)
N(1)	−0.104 1(5)	0.425 0(5)	−0.117 7(4)
N(2)	0.051 4(6)	0.336 5(5)	−0.134 7(5)
O(1)	0.078 6(5)	0.340 3(4)	0.031 5(4)
O(2)	−0.066 8(4)	0.447 2(4)	0.046 3(4)
O(3)	0.247 4(6)	0.194 6(4)	0.119 5(5)
O(4)	−0.231 0(5)	0.572 7(5)	0.160 3(4)
O(5)	0.035 4(8)	0.184 4(6)	−0.012 2(5)
C(1)	0.016 2(7)	0.387 8(6)	0.158 1(5)
C(2)	0.083 8(7)	0.347 3(6)	0.111 8(7)
C(3)	0.158 7(7)	0.308 6(6)	0.149 5(6)
C(4)	0.166 9(7)	0.309 5(6)	0.236 3(6)
C(5)	0.101 0(8)	0.347 3(6)	0.280 4(6)
C(6)	0.023 3(6)	0.385 3(5)	0.245 7(6)
C(7)	−0.046 2(8)	0.421 1(6)	0.293 9(6)
C(8)	−0.121 0(8)	0.459 5(6)	0.261 6(6)
C(9)	−0.127 4(6)	0.463 4(6)	0.175 3(6)
C(10)	−0.060 9(7)	0.431 5(6)	0.124 5(6)
C(11)	0.274 7(8)	0.303 3(8)	0.030 9(7)
C(12)	0.227 6(0)	0.263 2(8)	0.100 6(6)
C(13)	−0.260 0(7)	0.466 2(7)	0.068 2(7)
C(14)	−0.207 6(8)	0.505 5(7)	0.136 3(6)
C(15)	0.248 6(8)	0.271 9(6)	0.279 9(6)
C(16)	−0.193 1(7)	0.494 4(7)	0.317 3(6)
C(17)	−0.076 3(7)	0.404 2(6)	−0.202 7(6)
C(18)	−0.020 9(7)	0.327 6(6)	−0.198 3(6)
C(19)	0.014 3(13)	0.129 9(9)	0.045 1(9)

* The atoms of the methanol molecule are designated C(19) and O(5).

Table 4 Selected interatomic distances (Å) and angles (°) for [Cu(daddn)(en)] with e.s.d.s in parentheses *

Cu–N(1)	2.003(7)	N(1)–C(17)	1.492(12)
Cu–N(2)	2.008(8)	N(2)–C(18)	1.487(13)
Cu–O(1)	1.894(7)	C(9)–C(14)	1.501(15)
Cu–O(2)	1.886(7)	C(8)–C(16)	1.381(14)
C(2)–O(1)	1.325(13)	C(13)–C(14)	1.501(15)
C(10)–O(2)	1.312(12)	C(3)–C(12)	1.487(15)
C(12)–O(3)	1.214(15)	C(4)–C(15)	1.519(15)
C(14)–O(4)	1.231(14)	C(17)–C(18)	1.506(14)
N(1)–Cu–N(2)	84.9(4)	C(2)–C(3)–C(12)	120.9(8)
N(1)–Cu–O(1)	167.5(3)	C(4)–C(3)–C(12)	119.1(8)
N(1)–Cu–O(2)	90.8(3)	C(3)–C(12)–C(11)	119.8(8)
N(2)–Cu–O(1)	89.8(4)	C(3)–C(12)–O(3)	119.8(8)
N(2)–Cu–O(2)	175.5(4)	C(11)–C(12)–O(3)	120.4(8)
O(1)–Cu–O(2)	94.2(3)	C(3)–C(4)–C(15)	122.0(8)
Cu–N(2)–C(18)	107.9(6)	C(5)–C(6)–C(7)	122.2(7)
Cu–O(1)–C(2)	127.1(6)	C(7)–C(8)–C(16)	119.8(8)
Cu–O(2)–C(10)	126.9(6)	C(9)–C(8)–C(16)	122.8(8)
C(10)–C(9)–C(14)	117.6(7)	C(8)–C(9)–C(14)	119.8(7)
C(2)–C(1)–C(10)	125.0(7)	C(9)–C(14)–C(13)	120.5(8)
C(1)–C(10)–O(2)	121.6(7)	C(9)–C(14)–O(4)	120.0(8)
C(9)–C(10)–O(2)	117.9(7)	C(13)–C(14)–O(4)	119.5(8)
C(1)–C(2)–O(1)	122.5(7)	N(1)–C(17)–C(18)	107.2(7)
C(3)–C(2)–O(1)	116.2(7)	N(2)–C(18)–C(17)	109.1(7)

* Naphthalene rings: C–C distances are in the range 1.35–1.44 Å, average estimated e.s.d. *ca.* 0.01 Å, bond angles are in the range 116–124°, average e.s.d. *ca.* 0.8°.

naphthalene plane remote from the Pd while the imine nitrogen [N(2)] is 0.231 Å on the opposite side. The co-ordinated naphthol oxygen [O(1)] is also displaced from the naphthalene plane in the direction of the Pd by 0.276 Å.

The flexible N(2)–C(7)–C(6)–C(5) chain allows the pyridine ring to be inclined at 36.6° to the metal co-ordination plane and to be approximately perpendicular (89.4°) to the naphthalene plane.

The intact hydroxy group, O(2)–H(O2), is hydrogen bonded to the adjacent deprotonated and co-ordinated naphthoxide atom O(1) with an O(1)···O(2) separation of 2.594 Å [O(2)–H(O2) 0.83(4) Å, O(1)···H(O2) 1.88(4) Å]; this is very similar to the N···N separation of 2.60 Å in protonated proton sponge,[6] 1,8-bis(dimethylamino)naphthalene, which corresponds to a very strong hydrogen bond.*

The acetyl group which failed to form a Schiff base is twisted around the C(18)–C(19) bond so that the C(20)–C(19)–O(3)

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* We are indebted to one of the referees for suggesting that the apparent strength of this hydrogen bond could be responsible for restricting the template condensation to mono-Schiff base formation.

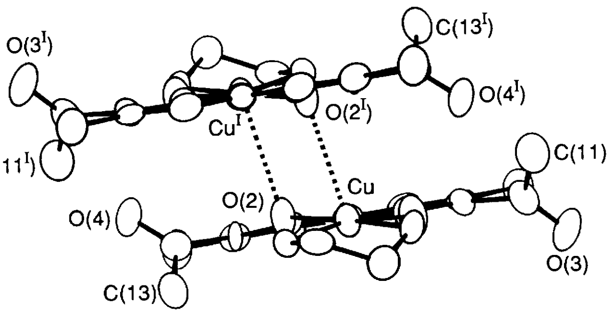

Fig. 3 Dimeric association in [Cu(daddn)(en)]. Broken lines correspond to the Cu–O(2^I) and Cu^I · · · O(2) bonds of length 2.85 Å

plane is almost perpendicular to the naphthalene unit; steric repulsion from the adjacent methyl group C(17) is probably largely responsible for this twisting.

Crystal Structure of [Cu(daddn)(en)]·MeOH.—The molecular geometry and atom numbering scheme for [Cu(daddn)(en)] are shown in Fig. 2. Tables 3 and 4 provide atomic coordinates and selected interatomic distances/angles respectively. The asymmetric unit contains one molecule of the complex and one molecule of solvation. A daddn^{2-} ion chelates the Cu through O(1) and O(2) on one side of the metal and ethylenediamine is chelated on the other side so that N(1), N(2), O(1) and O(2) are close to coplanar. Copper–donor distances are normal and in the range 1.886(7) to 2.008(8) Å. Angles at Cu range from 84.9(4) to 94.2(3)°.

The complex molecules appear in centrosymmetric pairs [centre of symmetry at (0,0,0)], a phenoxide atom in one molecule [O(2)] providing a long 'axial' bond of 2.848(12) Å to the Cu in the other so that the co-ordination geometry is essentially square pyramidal as shown in Fig. 3. The Cu is displaced 0.110 Å from the average plane of N(1),N(2),O(1),O(2) towards the attached phenoxide in the associated molecule. The mean donor atom plane is inclined at 9.5° to the mean naphthalene plane.

The two acetyl groups are oriented so that their oxygens are on opposite sides of the naphthalene; O(3) and C(13) are located 0.974 and 0.932 Å respectively on the side of the naphthalene remote from the associated molecule and O(4) and C(11) are 0.771 and 0.798 Å respectively on the opposite side. Again, steric repulsion by the adjacent methyl groups is probably responsible for this twisting.

Atom O(2) is displaced 0.155 Å from the mean naphthalene plane towards the Cu of the associated molecule while O(1) is displaced 0.261 Å on the opposite side to produce an O(1) · · · O(2) bite distance of 2.768(13) Å.

The methanol of solvation is hydrogen bonded to the non-bridging phenoxide, O(1) with an O · · · O separation of 2.757(12) Å.

Experimental

NMR spectra were recorded on JEOL FX-100 or FX-90Q spectrometers, IR spectra as KBr discs on a JASCO A302 spectrophotometer and electron impact (EI), positive-ion mass spectra on VG Micromass 7070F and JEOL AX 505H GC-MS instruments. Elemental analyses were performed by the Microanalytical Service, University of Queensland, St. Lucia, Australia and by the Microanalytical Service, University of Otago, Dunedin, New Zealand.

2-Acetyl-1,8-dihydroxy-3,6-dimethylnaphthalene was prepared from 3-acetyl-6-methyl-1-oxacyclohex-5-ene-2,4-dione (Aldrich) by the method of Bethell and Maitland.[5] δ_H(CDCl$_3$) 2.41 (3 H, s, CH$_3$ of aryl), 2.61 (3 H, s, CH$_3$ of aryl), 2.72 (3 H, s, COCH$_3$), 6.67 (1 H, s, aryl H), 6.86 (2 H, s, aryl H), 10.18 (1 H, br s, OH) and 17.46 (1 H, br s, OH). δ_C(CDCl$_3$) 22.0, 25.3 (CH$_3$ of aryl), 32.0 (COCH$_3$), 111.0, 112.6, 113.0, 117.4, 121.3, 133.4, 138.4, 143.9, 158.0, 168.9 (10 × aryl C) and 204.4 (C=O). 1,8-Diacetoxy-2-acetyl-3,6-dimethylnaphthalene was prepared as described in the literature.[7] δ_H(CDCl$_3$) 2.12 (3 H, s, CH$_3$), 2.17 (3 H, s, CH$_3$), 2.19 (3 H, s, CH$_3$), 2.32 (3 H, s, CH$_3$), 2.77 (3 H, s, CH$_3$), 6.31 (2 H, s, aryl H) and 6.77 (1 H, s, aryl H).

Preparations.—*2,7-Diacetyl-1,8-dihydroxy-3,6-dimethylnaphthalene* (H$_2$daddn) **2**. Addition of BF$_3$·Et$_2$O (48%, 7.4 g, 52 mmol) to a solution of 2-acetyl-1,8-dihydroxy-3,6-dimethylnaphthalene (2.96 g, 12.9 mmol) gave a bright red solution which was stirred at *ca.* 120 °C for 10 min. After the mixture had cooled to room temperature the yellow crystals of the diboron complex **3** which had separated were collected, washed with glacial acetic acid and could be recrystallised from chloroform, although this step was unnecessary (2.58 g, 54%), m.p. 192–194 °C (Found: C, 52.5; H, 3.9; F, 20.5. C$_{16}$H$_{14}$B$_2$F$_4$O$_4$ requires C, 52.2; H, 3.8; F, 20.6%). *m/z* (+EI, 15 eV) 348 (*M* – F, 5), 328 (*M* – 2F, 5), 300 (100), 285 (43), 258 (34), 243 (14) and 216 (40%).

The diboron complex **3** was converted to H$_2$daddn, **2**, in essentially quantitative yield by heating for 1 h in suspension in boiling methanol–aqueous hydrochloric acid (10%) (10:3) giving a yellow crystalline solid which could be recrystallised from ethyl acetate although this was not necessary (Found: C, 70.6; H, 6.0%; accurate mass, *m/z* 272.1048 (M^+). C$_{16}$H$_{16}$O$_4$ requires C, 70.6; H, 5.9%; M^+ 272.1048). δ_H(CDCl$_3$) 2.49 (6 H, s, CH$_3$), 2.68 (6 H, s, COCH$_3$), 6.85 (2 H, s, aryl H) and 14.13 (2 H, s, OH of aryl). δ_C(CDCl$_3$) 20.6 (CH$_3$ of aryl), 31.5 (COCH$_3$), 111.0, 119.1, 121.2, 135.8, 136.7, 157.2 (aryl C) and 203.6 (C=O). *m/z* (+EI, 70 eV) 272 (M^+, 85), 257 (100), 239 (95), 115 (10) and 43 (22%).

2-Acetyl-1,8-dihydroxy-3,6-dimethyl-7-[(2-dimethylamino)-ethyliminoethyl]naphthalene. A solution of H$_2$daddn (0.0562 g, 0.21 mmol), *N,N*-dimethylethylenediamine (0.0424 g, 0.48 mmol) and toluene-*p*-sulfonic acid (0.0118 g, 0.06 mmol) in ethanol (4 cm^3) was heated under reflux for 15 h, after which time the volume was reduced at atmospheric pressure until yellow crystals started to separate. After the mixture had cooled and had been standing for several hours the crystals were collected and washed with ethanol (0.059 g, 82%), m.p. 162–164 °C (Found: C, 70.0; H, 7.7; N, 8.0%; accurate mass, *m/z* 342.1945 (M^+). C$_{20}$H$_{26}$N$_2$O$_3$ requires C, 70.2; H, 7.7; N, 8.2%; M^+, 342.1943). δ_H(CDCl$_3$) 2.33 [6 H, s, N(CH$_3$)$_2$], 2.45 (3 H, s, CH$_3$), 2.50 (3 H, s, CH$_3$), 2.62 (3 H, s, CH$_3$), 2.66 (3 H, s, CH$_3$), 3.59 (2 H, t, *J*, 5.9, CH$_2$), 3.66 (2 H, t, *J*, 5.9, Hz, CH$_2$), 6.44 (1 H, s, aryl H) and 6.61 (1 H, s, aryl H). δ_C(CDCl$_3$) 20.0 (CH$_3$), 20.9 (CH$_3$), 26.0 (CH$_3$), 32.4 (CH$_3$), 43.1 (CH$_2$), 45.4 [N(CH$_3$)$_2$], 57.5 (CH$_2$), 109.8, 113.8, 117.0, 117.3, 122.7, 136.1, 138.5, 140.0, 161.5, 171.6 (aryl C), 180.2 and 204.6 (C=O/C=N). *m/z* (+EI, 70 eV) 342 (M^+, 1), 220 (26), 205 (100), 145 (11) and 57 (39%).

2-Acetyl-1,8-dihydroxy-3,6-dimethyl-7-[2-(2-pyridyl)ethyliminoethyl]naphthalene, HL. The procedure used was closely analogous to that above for the preparation of the *N,N*-dimethylethylenediamine mono-Schiff base. δ_H(CDCl$_3$) 2.78 (3 H, s, CH$_3$), 2.90 (3 H, s, CH$_3$), 2.99 (3 H, s, CH$_3$), 3.06 (3 H, s, CH$_3$), 5.33 (2 H, s, CH$_2$), 6.91 (1 H, s, aryl H), 7.07 (1 H, s, aryl H), 7.50–8.99 (m, CH of pyridyl). δ_C(CDCl$_3$) 20.2 (CH$_3$), 20.9 (CH$_3$), 26.1 (CH$_3$), 32.4 (CH$_3$), 50.0 (CH$_2$), 110.2, 113.7, 117.2, 119.9, 121.4, 122.9, 136.1, 137.2, 138.5, 140.3, 149.8, 154.8, 161.2, 172.2 (aryl C), 180.8 and 204.6 (C=O/C=N). *m/z* (+EI, 70 eV) 320 (M^+, 100), 285 (46), 214 (51), 133 (46), 93 (60) and 92 (53%).

H$_2$daddn–*ethylenediamine macrocycle* **5**. Ethylenediamine (0.0287 g, 0.48 mmol) was added to a suspension of H$_2$daddn (0.1031 g, 0.38 mmol) in methanol (7 cm^3) heated under reflux. The suspended solid dissolved over a period of 15 min to produce a clear orange solution. After several further min at the boiling point compound **5** started to precipitate as a microcrystalline yellow solid. The mixture was heated under reflux for 1 h and was then allowed to cool. The solid was

Table 5 Crystal data and details of crystal structure determinations

Compound	[Cu(daddn)(en)]	$[PdL(N_3)]$
Formula	$C_{18}H_{22}CuN_2O_4 \cdot CH_3OH$	$C_{23}H_{23}N_5O_3Pd$
M	426.0	522.0
Crystal system	Orthorhombic	Monoclinic
Space group	*Pbca* (no. 61)	$P2_1/c$ (no. 14)
a/Å	14.515(2)	11.220(1)
b/Å	16.596(3)	12.910(2)
c/Å	16.406(3)	14.521(2)
β/°		92.540(9)
U/Å^3	3952(2)	2101.3(8)
Z	8	4
D_c/g cm^{-3}	1.432	1.656
D_m/g cm^{-3}	1.433(5)	1.653(5)
Crystal dimensions (distance in mm from the centroid)	±(−1 1 1) 0.064 ±(1 −1 1) 0.050 ±(1 1 −1) 0.050 ±(1 1 1) 0.057	±(1 0 0) 0.093 ±(0 1 1) 0.093 ±(0 −1 1) 0.010
F(000)	1752	1064
μ(Mo-Kα)/cm^{-1}	10.99	8.75
Absorption correction (min., max. transmission coefficients)	0.8764, 0.9451	0.8484, 0.8875
2θ range/°	2.0–40.0	2.0–55.0
Range of h, k, l	$0 \leqslant h \leqslant 15, -2 \leqslant k \leqslant 17, -2 \leqslant l \leqslant 17$	$-1 \leqslant h \leqslant 14, -1 \leqslant k \leqslant 16, -18 \leqslant l \leqslant 18$
Total no. of reflections	4956	6278
No. of unique reflections	2579	4812
R_{int}	0.0193	0.0141
No. of unique reflections used in refinement	1158 $[I \geqslant 3\sigma(I)]$	3398 $[I \geqslant 2\sigma(I)]$
Function minimized	$\Sigma w(\lvert F_o \rvert - \lvert F_c \rvert)^2$	$\Sigma w(\lvert F_o \rvert - \lvert F_c \rvert)^2$
Weighting scheme parameters g, k in $w = k/[\sigma^2(F_o) + gF_o^2]$	0.001, 1.2034	0.000 23, 1.0575
No. of variables	264	305
Final R	0.046	0.030
Final R'	0.047	0.030
Max. shift/e.s.d. for non-hydrogen atom	0.011	0.001
Goodness of fit, S	1.139	1.363
Maximum residual electron density/e Å^{-3}	0.32	0.53

collected and washed with methanol (0.0420 g, 37%) (Found: C, 72.6; H, 6.9; N, 9.6. $C_{36}H_{40}N_4O_4$ requires C, 72.9; H, 6.8; N, 9.5%). *m/z* (+EI, 15 eV) 592 (M^+, 100), 296 (10), 230 (30), 188 (6), 84 (54) and 55 (18%).

Metal Complexes.—[PdL′Cl] **4a** {HL′ = *2-acetyl-*1,8-*dihydroxy-*3,6-*dimethyl-*7-[(2-*pyridyl*)*methyliminoethyl*]*naphthalene*}. A solution of 2-(aminomethyl)pyridine (0.0560 g, 0.52 mmol) and H_2daddn (0.0652 g, 0.24 mmol) in methanol (5 cm^3) was heated under reflux 0.5 h and then 1,8-diazabicyclo[5.4.0]-undec-7-ene (0.0390 g, 0.26 mmol) in methanol (*ca.* 1 cm^3) was added. The resulting solution was added to a boiling solution of $PdCl_2$ (0.0453 g, 0.26 mmol) and LiCl (0.0311 g, 0.74 mmol) in methanol. Yellow crystals of [PdL′Cl] **4a** formed immediately and were collected and washed with methanol (0.0690 g, 57%) (Found: C, 52.6; H, 4.2; N, 6.0. $C_{22}H_{21}ClN_2O_3Pd$ requires C, 52.5; H, 4.2; N, 5.6%). ν(C=O) 1682 and ν(C=N) 1615 cm^{-1}.

[PdLCl] **4b**. A mixture of $PdCl_2$ (0.0456 g, 0.257 mmol), lithium chloride (0.0253 g, 0.597 mmol) and H_2daddn (0.0339 g, 0.124 mmol) suspended in methanol (10 cm^3) was heated under reflux until all the solid had dissolved and then 2-(aminoethyl)-pyridine (0.0325 g, 0.266 mmol) was added. The volume was reduced by boiling at atmospheric pressure until crystallisation commenced. The yellow needles of **4b** were collected after the mixture had been allowed to cool and were washed with methanol (0.0632 g, 98%). ν(C=O) 1685 and ν(C=N) 1625 cm^{-1}.

$[PdL(N_3)]$ **4c**. A solution of 2-(aminoethyl)pyridine (0.0183 g, 0.15 mmol) and H_2daddn (0.0176 g, 0.065 mmol) in acetonitrile (5 cm^3) was heated to boiling for 5 min. The resultant orange solution was added to a boiling solution of $Pd(MeCO_2)_2$ (0.0293 g, 0.13 mmol) dissolved in the minimum of acetonitrile. The mixture was heated gently for a further 10 min, cooled to room temperature and sodium azide (0.0142 g, 0.218 mmol) dissolved in methanol (5 cm^3) was added. The clear orange solution upon cooling and standing yielded red prisms suitable for X-ray diffraction studies. The crystals of **4c** were collected and washed with methanol (0.0313 g, 92%). $\delta_H[(CD_3)_2SO]$ 2.23 (3 H, s, CH_3), 2.33 (3 H, s, CH_3), 2.41 (3 H, s, CH_3), 2.49 (3 H, s, CH_3), 3.59 (2 H, br t, CH_2), 3.84 (2 H, br t, CH_2), 6.86 (1 H, s, aryl H) and 7.48–8.38 (4 H, m, aryl H). ν(C=O) 1695, ν(C=N) 1625 and ν(N_3) 2050 cm^{-1}.

[Cu(daddn)(en)]. Copper(II) acetate monohydrate (0.4463 g, 2.34 mmol) in boiling methanol (10 cm^3) was added to H_2daddn (0.5816 g, 2.13 mmol) in boiling methanol (10 cm^3) whereupon a brown microcrystalline solid separated. The mixture was maintained at the boiling point for 30 min and the suspended solid presumed to be **6** was collected and washed with methanol (0.5910 g, 83%) (Found: C, 58.6; H, 4.5. $C_{32}H_{28}Cu_2O_8$ requires C, 57.6; H, 4.2%). ν(C_{aryl}–O) 1550 and ν(C=O) 1660 cm^{-1}. When ethylenediamine (0.0085 g, 0.14 mmol) was added to a suspension of **6** (0.0422 g, 0.063 mmol) in boiling methanol (3 cm^3) the solid dissolved to produce a dark green solution. The volume of the solution was reduced to *ca.* 50% by boiling at atmospheric pressure whereupon dark blue-black octahedral crystals of [Cu(daddn)(en)] separated. The crystals were collected and washed with methanol after the mixture had been allowed to cool (0.0235 g, 47%) (Found: C, 54.3; H, 5.8; N, 6.7. $C_{18}H_{22}CuN_2O_4$ requires C, 54.9; H, 5.6; N, 7.1%).

Crystal Structure Analyses.—Blue-black crystals of [Cu(daddn)(en)] suitable for diffraction studies were obtained by suspending $[Cu_2(daddn)_2]$ **6** in a methanolic solution containing an approximately equimolar amount of ethylenediamine in a glass tube of diameter 0.4 cm and maintaining the mixture at 45 °C in a water-bath for 24 h. The crystals were approximately octahedral in shape.

Cubic red crystals of [PdL(N_3)] **4c** were grown directly from a reaction mixture which was allowed to stand for 24 h.

Intensity data were measured at 294 °C using an Enraf-Nonius CAD-4F single-crystal, automatic diffractometer with monochromated Mo-Kα radiation (λ = 0.710 69 Å) and ω–2θ scan technique. Accurate cell dimensions and the orientation matrix were determined by a least-squares procedure using the angular settings of 25 carefully centred reflections. Crystal data and details of the data collections are listed in Table 5. Neither set of data showed any significant variation in intensity during the course of data collection. Corrections for Lorentz, polarization and absorption effects were applied,[8a,9] but no correction was made for extinction. The scattering factors used for atomic C, H, N and O were those incorporated into the SHELX 76 program,[9] while those for atomic palladium and copper were taken from ref. 8*b* and corrected for both real and imaginary anomalous dispersion effects.[8c]

The positions of the majority of the non-hydrogen atoms for both structures were indicated by the SHELXS 86 program[10] using the direct method routine. The remaining non-hydrogen atoms were indicated in subsequent difference maps produced by the SHELX 76 program.[9] The structures were refined using a full-matrix least-squares procedure with anisotropic thermal parameters applied to all non-hydrogen atoms. The difference maps indicated the positions of all hydrogen atoms. The positions of all the hydrogen atoms bonded to carbon and nitrogen atoms were constrained at geometrically estimated positions with C–H and N–H bond lengths of 1.08 and 1.01 Å, respectively. The hydrogen atom bonded to the unco-ordinated naphthol oxygen atoms, H(O2), in the complex, [PdL(N_3)] was included in the model at the position indicated by the difference map. Isotropic thermal parameters were applied to the hydrogen atoms of the copper complex such that a common thermal parameter was applied to all methyl hydrogen atoms. A similar procedure was used for all the methylene, aromatic and amine hydrogen atoms. In the case of the palladium complex, an isotropic thermal parameter was applied to each aromatic hydrogen atom and a common thermal parameter was applied to the hydrogen atoms of each of the methylene and methyl groups. The refinement was continued until convergence to yield the values of *R*, *R'*, *g* and *k* listed in Table 5, together with the values of the maximum residual electron densities. Crystallographic diagrams were prepared using the ORTEP program.[11]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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