Compartmental Ligands. Part 7.[1] The Reactions of 1,2-Diaminobenzene and *cis*-1,2-Diaminocyclohexane with Heptane-2,4,6-trione and 1-(*o*-Hydroxyphenyl)butane-1,3-dione. The Crystal Structures of 1-(*o*-Aminophenyl)-2,6-dimethyl-4-pyridone hemihydrate and {3,3′-(*cis*-1,2-Cyclohexanediyldi-imino)bis[1-(*o*-hydroxyphenyl)but-2-enonato]-(*N*,*N*′,*O*^{1},*O*$^{1\prime}$)}copper(II) †

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The reaction of 1,2-diaminobenzene with heptane-2,4,6-trione yielded either the compound 2-(acetylmethyl)-4-methyl-3*H*-1,5-benzodiazepine or 1-(*o*-aminophenyl)-2,6-dimethyl-4-pyridone (5) depending upon the conditions used. The reaction of 1,2-diaminobenzene with 1-(*o*-hydroxyphenyl)-butane-1,3-dione yielded a diazepine. In contrast the reaction of *cis*-1,2-diaminocyclohexane with heptane-2,4,6-trione yielded a tetramine macrocyclic compound, and with 1-(*o*-hydroxyphenyl)butane-1,3-dione afforded the compartmental Schiff base 3,3′-(*cis*-1,2-cyclohexanediyldi-imino)bis[1-(*o*-hydroxyphenyl)but-2-enone] (10). The metal-complexing properties of this ligand are reported. Three-dimensional *X*-ray crystal-structure analyses have been carried out on compound (5) and on the mononuclear copper(II) derivative of (10), *i.e.* (12). Compound (5) has $Z = 8$ in a monoclinic cell with space group $P2_1/c$, and dimensions $a = 14.984(1)$, $b = 7.475(3)$, $c = 21.173(1)$ Å, and $\beta = 98.71(1)°$; $R = 0.0388$ for 2 392 reflections. Complex (12) has $Z = 4$ in a triclinic cell with space group $P\bar{1}$, and dimensions $a = 13.143(8)$, $b = 14.279(8)$, $c = 14.289(14)$ Å, $\alpha = 67.36(6)$, $\beta = 71.18(7)$, and $\gamma = 91.36(5)°$; $R = 0.0651$ for 2 985 reflections. The structure shows the copper(II) to occupy the inner (N_2O_2) co-ordination site in an environment with a marked (*ca.* 14°) tetrahedral twist.

The reaction of β-diketones with α,ω-diamines leads to a large range of products depending on the experimental conditions used.[2] In reaction (i) (Scheme) it is found that neutral and mildly alkaline media favour bis(oxoenamine) formation whereas reactions at pH < 6 and pH > 10 favour diazepine formation. In reaction (ii) (Scheme) it is the anil that is stabilised if $R = R^1 = R^2 = CH_3$ because of the steric hindrance of the vicinal methyl groups. With β-triketones extra degrees of complexity are offered and it has been found that reactions of heptane-2,4,6-trione with various stoicheiometric proportions of 1,2-diaminoethane (and also 1,2- and 1,3-diaminopropane) give the macrocyclic Schiff bases corresponding to (1).[3] With the related unsymmetrical triketones, 1-phenylhexane-1,3,5-trione and 7,7-dimethyloctane-2,4,6-trione, acyclic Schiff bases such as (2) are formed.[4,5] These reactions parallel the behaviour of the corresponding β-diketones in which condensation occurs at the carbonyl group adjacent to the methyl group.[6,7]

The reaction of pentane-2,4-dione with 1,2-diaminobenzene has been shown to give the diazepine (3).[8] Using similar reaction conditions, 1,2-diaminobenzene in an ethanol–ethanoic acid mixture was treated with heptane-2,4,6-trione to give a red compound, subsequently identified as the diazepine (4). However if the reaction was carried out by adding the components in reverse order, followed by pouring into water and refrigerating, then two products were recovered, (4) together with a white crystalline compound identified as the pyridone (5).

Results and Discussion

The i.r. spectrum of compound (4) (KBr disc) shows bands at 1 658, 1 630, and 1 580 cm^{-1}, assigned to ν(C=O) (hydrogen bonded), ν(C=N), and ν(C=C). There are also weak bands at 3 300 and 3 250 cm^{-1} indicating a hydrogen-bonded amino-function. The ^1H n.m.r. spectrum ($CDCl_3$) showed resonances at δ 2.15 (3 H, $CH_3C=O$), 2.32 (3 H, $CH_3C=N$), 2.90 (2 H, $-CH_2-$), 5.12 (1 H, HC=), 7.1—7.3 (4 H, aromatic), and 10.40 p.p.m. (1 H, NH · · · O). The $^{13}C-\{^1H\}$ n.m.r. spectrum shows, amongst others, three bands at low field, 197.1, 165.6, and 155.8 p.p.m. The last two absorptions were assigned to the $>C=N$ related species and the first to a $>C=O$ group in a delocalised environment. These spectral data indicate that compound (4) is not present in the imine–imine–keto-form but rather in the tautomeric enolic form (6). The intense red colour of (4) is characteristic of an extended π-conjugated chromophore of this type. 1,5-Benzodiazepines are normally colourless but when protonated they become maroon-violet.[2] It is pertinent to note also that the diazepines derived from 1,2-diaminobenzene and the tetraketones $RCOCH_2COCOCH_2COR$ ($R = CH_3$ or C_6H_5) are red and orange in colour.[9]

The two isomeric products (4) and (5) show molecular ions in their mass spectra at *m*/*z* 214; however the fragmentation patterns differ considerably. Both compounds show loss of $\dot{C}H_3$ and $CH_3\dot{C}O$ from the molecular ion, but in the case of (5) this probably arises from a sequential rather than a single-step pathway. The fragmentation pattern of (4) resembles that reported [10] for 2-phenacyl-4-phenyl-1*H*-1,5-benzodiazepine.

The i.r. spectrum of the colourless product (5) (KBr disc) shows a strong band at 1 640 cm^{-1}, assigned to ν(C=O), but no bands assignable to imine groups. There are also strong bands at 3 330 and 3 200 cm^{-1} ascribed to hydrogen-bonded water and amine functions. The ^1H n.m.r. [$(CD_3)_2SO$] shows resonances at δ 1.90 (6 H, $2CH_3$), 4.50 (2 H, NH_2), 6.10 (2 H,

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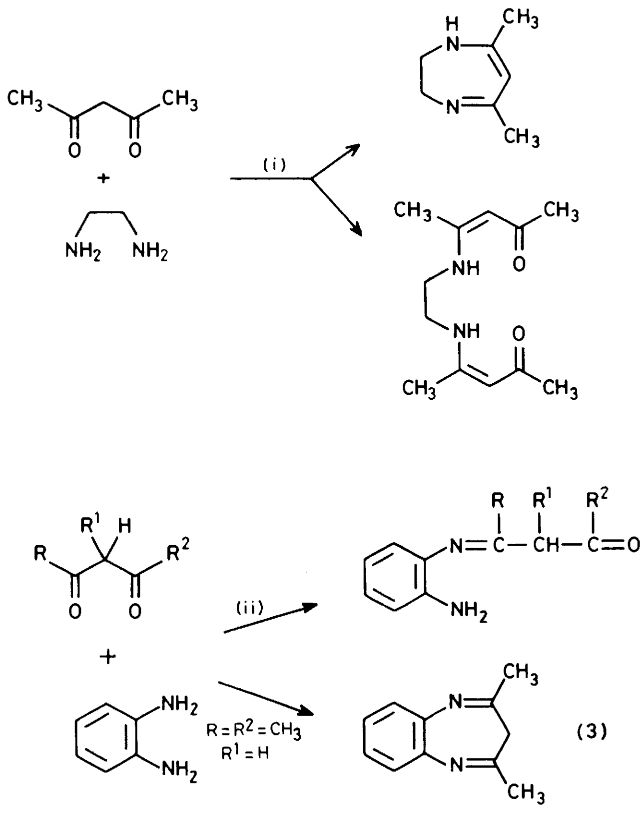
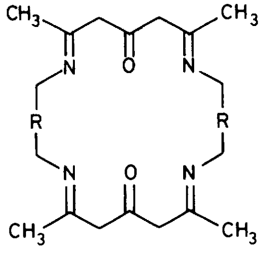
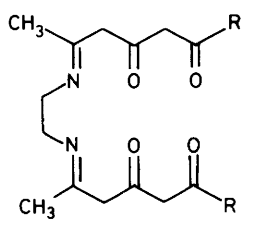
† *Supplementary data available* (No. SUP 23688, 55 pp.): H-atom co-ordinates, thermal parameters, structure factors. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.



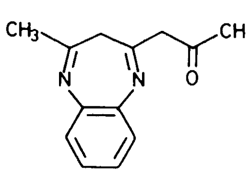
Scheme.



(1) R = CH_2CH_2, $CH_2CH(CH_3)$, or $CH_2CH_2CH_2$



(2) R = C_6H_5 or $(CH_3)_3C$



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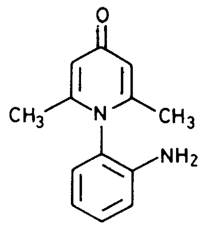

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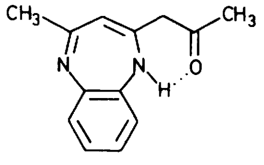

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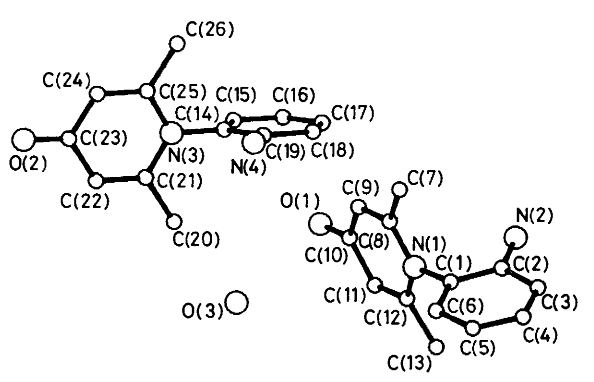


Figure 1. The molecular structure of compound (5)

olefinic), and 6.75—7.30 p.p.m. (4 H, aromatic). These spectral data are in agreement with the structure proposed for compound (5) and this has been confirmed by a single-crystal *X*-ray crystallographic study, which revealed two molecules of the pyridone associated with one molecule of water of crystallisation as the asymmetric unit (Figure 1). There is very little difference in geometry between the two pyridone molecules (Table 1). Furthermore these bond lengths and angles agree for the most part with those determined previously [11] for other 4-pyridones, the only exception being the pyridone N–C bond lengths, mean 1.382(3) Å which lies outside the range 1.34—1.375 Å previously encountered.[10–12] The lengthening of these bonds could perhaps reflect some reduced conjugation of the nitrogen lone pair with the pyridone ring. The pyridone and the phenyl rings are planar, equations to these planes being given in Table 2; the angle of twist between the pyridone-ring plane and the phenyl-ring plane differs slightly between the two molecules, being 89.7 and 84.9°. Finally the crystal structure shows a considerable degree of intermolecular hydrogen bonding associated with the water of crystallisation, the amino, and the carbonyl groups; these hydrogen bonds are listed in Table 3.

Pyridones have been synthesised previously by the reaction of 1-phenylhexane-1,3,5-trione, and related triones, with ammonia [13] and with aniline.[14] The mechanism proposed is initial attack by the amine at carbonyl 1 or 5 of the triketone to give a diketo-enamine. This is followed by an intramolecular addition reaction at the remaining terminal carbonyl group; subsequent dehydration gives the pyridone. The reaction with aniline [14] requires hot polyphosphoric acid to effect cyclisation; this is in marked contrast to the conditions used in the present synthesis of the pyridone (5). It is probable that the formation of (5) follows a similar course to that outlined above, but that formation of the diazepine (4) occurs as an alternative cyclisation involving attack at the central carbonyl carbon atom. The factors governing the mechanistic paths are perhaps complex as there is not only a possible pH control but also the presence of various conformers and tautomers of heptane-2,4,6-trione in solution. Steric effects arising from the potential close proximity of the methyl groups in heptane-2,4,6-trione and the 3,6 protons in 1,2-diaminobenzene could also be important. It is presumably this latter effect which prevents formation of either macrocyclic or acyclic Schiff bases similar to (1) or (2) in the reaction under discussion.

The reaction of 1,2-diaminobenzene with the β-keto-phenolic compound 1-(*o*-hydroxyphenyl)butane-1,3-dione (7) gave only the diazepine (8) [15] and this is presumably for steric reasons similar to those outlined above. The compound (7) has been found to react with 1,2-diaminoethane to give (9) which acts as a compartmental ligand.[16] By introducing a

Table 1. Interatomic distances (Å) and angles (°), with estimated standard deviations in parentheses, for compound (5)

Molecule 1				Molecule 2			
C(1)–C(2)	1.392(4)	C(8)–C(7)	1.496(4)	C(14)–C(19)	1.397(4)	C(21)–C(20)	1.493(4)
C(2)–C(3)	1.402(4)	C(8)–C(9)	1.351(4)	C(19)–C(18)	1.403(4)	C(21)–C(22)	1.360(4)
C(2)–N(2)	1.384(4)	C(9)–C(10)	1.424(4)	C(19)–N(4)	1.375(3)	C(22)–C(23)	1.420(4)
C(3)–C(4)	1.374(4)	C(10)–O(1)	1.272(3)	C(18)–C(17)	1.381(4)	C(23)–O(2)	1.268(3)
C(4)–C(5)	1.383(5)	C(10)–C(11)	1.429(4)	C(17)–C(16)	1.379(4)	C(23)–C(24)	1.429(4)
C(5)–C(6)	1.384(4)	C(11)–C(12)	1.353(4)	C(16)–C(15)	1.384(4)	C(24)–C(25)	1.355(4)
C(6)–C(1)	1.389(4)	C(12)–N(1)	1.382(3)	C(15)–C(14)	1.386(4)	C(25)–N(3)	1.382(3)
C(1)–N(1)	1.449(3)	C(12)–C(13)	1.497(4)	C(14)–N(3)	1.452(3)	C(25)–C(26)	1.498(4)
N(1)–C(8)	1.382(3)			N(3)–C(21)	1.381(3)		

Molecule 1				Molecule 2			
C(1)–C(2)–C(3)	117.8(3)	C(8)–N(1)–C(12)	119.9(2)	C(14)–C(19)–C(18)	116.6(2)	C(21)–N(3)–C(25)	120.0(2)
C(1)–C(2)–N(2)	121.0(3)	N(1)–C(8)–C(7)	116.9(2)	C(14)–C(19)–N(4)	122.0(2)	N(3)–C(21)–C(20)	117.5(3)
N(2)–C(2)–C(3)	121.2(3)	N(1)–C(8)–C(9)	120.4(3)	N(4)–C(19)–C(18)	121.4(3)	N(3)–C(21)–C(22)	120.5(3)
C(2)–C(3)–C(4)	120.2(3)	C(7)–C(8)–C(9)	122.7(3)	C(19)–C(18)–C(17)	121.3(3)	C(20)–C(21)–C(22)	122.0(3)
C(3)–C(4)–C(5)	121.4(3)	C(8)–C(9)–C(10)	122.4(3)	C(18)–C(17)–C(16)	121.0(3)	C(21)–C(22)–C(23)	121.8(3)
C(4)–C(5)–C(6)	119.5(3)	C(9)–C(10)–O(1)	123.0(3)	C(17)–C(16)–C(15)	119.0(3)	C(22)–C(23)–O(2)	122.6(3)
C(5)–C(6)–C(1)	119.3(3)	C(9)–C(10)–C(11)	114.7(2)	C(16)–C(15)–C(14)	120.1(3)	C(22)–C(23)–C(24)	115.5(3)
C(6)–C(1)–C(2)	121.8(3)	O(1)–C(10)–C(11)	122.3(3)	C(15)–C(14)–C(19)	122.1(3)	O(2)–C(23)–C(24)	122.0(3)
C(6)–C(1)–N(1)	119.6(3)	C(10)–C(11)–C(12)	122.6(3)	C(15)–C(14)–N(3)	118.3(2)	C(23)–C(24)–C(25)	121.8(3)
C(2)–C(1)–N(1)	118.5(2)	C(11)–C(12)–N(1)	120.0(3)	C(19)–C(14)–N(3)	119.6(2)	C(24)–C(25)–N(3)	120.5(3)
C(1)–N(1)–C(12)	118.6(2)	C(11)–C(12)–C(13)	122.4(3)	C(14)–N(3)–C(25)	119.9(2)	C(24)–C(25)–C(26)	122.0(3)
C(1)–N(1)–C(8)	121.3(2)	N(1)–C(12)–C(13)	117.7(3)	C(14)–N(3)–C(21)	120.2(2)	N(3)–C(25)–C(26)	117.6(2)

Table 2. Equations to planes, $PX + QY + RZ = W$, for compound (5)

	P	Q	R	W	Mean deviation from plane (Å)	Angle between (°)
(*a*) Molecule 1						
Phenylene C(1)—C(6)	−0.697	0.671	0.252	−8.249	0.014	89.7
Pyridone N(1)—C(12)	−0.292	−0.581	0.759	−2.584	0.007	
(*b*) Molecule 2						
Phenylene C(14)—C(19)	0.707	−0.683	0.183	5.202	0.003	84.9
Pyridone N(3)—C(25)	0.293	0.404	0.866	9.191	0.005	

Table 3. Intermolecular hydrogen-bond lengths and angles for compound (5)

Bond type A–H ··· B	Distance (Å) A ··· B	Angle (°) A–H ··· B
N(2)–H ··· $O(3^{I})$	2.91	151.0
N(4)–H ··· $O(1^{II})$	3.04	171.9
N(4)–H ··· $O(2^{III})$	2.93	150.7
O(3)–H ··· $O(2^{III})$	2.91	159.3
O(3)–H ··· $O(1^{II})$	2.81	168.4

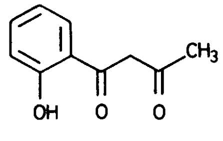
Symmetry operations: I $-x, 0.5 + y, 0.5 - z$; II $x, 0.5 - y, 0.5 + z$; III $-x, -y, -z$.

more flexible bridging unit the steric inhibition to Schiff-base formation is reduced or removed.

cis-1,2-Diaminocyclohexane (*cis*-dach) reacts readily with (7) to give the compartmental ligand (10). The compound *cis*-dach was separated from a commercially available mixture of isomers by means of selective complex formation with nickel(II).[17] It was chosen for Schiff-base formation as in Schiff bases derived from *trans*-dach the bite sizes limit complex formation because of the strain introduced by an unfavourable overlap between the cyclohexane bridge protons and the methyl groups adjacent to the nitrogen of the Schiff base.

The ligand (10) was prepared by reaction of (7) with *cis*-dach in ethanol and recovered as a yellow solid. The dioxouranium(VI) and copper(II) complexes (11) and (12) were prepared by reaction of (10) with the corresponding metal ethanoate in $CHCl_3$–C_2H_5OH and $CHCl_3$–H_2O respectively as representative examples of O_2O_2 and N_2O_2 site occupancies.[18] The dioxouranium(VI) cation has been found to occupy only the outer, O_2O_2, compartment of this class of ligands and retains a molecule of solvent in order to achieve seven-co-ordination.[18] The i.r. spectrum of complex (11) shows bands at 909 (ν_3, O–U–O), 1 350 [ν(C–O), phenolic], 1 560, 1 580, 1 600 [ν(C=O) and ν(C=C)], 1 620 [ν(C=N)], and 3 450 cm^{-1} [ν(O–H)] and these are directly comparable to the bands observed for complex (13).[16] The i.r. spectrum of complex (12) resembles that of (14) having bands at 1 290 [ν(C–O), phenolic], 1 515 and 1 590 cm^{-1} [ν(C=C), ν(C=O), and ν(C=N)].[16] Its diffuse reflectance spectrum shows a band at 649 nm; a red shift has occurred relative to (14) which might be interpreted as a movement towards a more tetrahedral occupancy of the N_2O_2 compartment.[19]

The crystal structure of the heterobinuclear complexes (15) and (16) have generated interest due to the different geometries determined for the inner compartmental occupancy.[20,21] In these structures the nickel [in (15)] has a distorted geometry described either as severely distorted tetrahedral or trigonal bipyramidal with an equatorial site vacancy, and the copper atom [in (16)] is square pyramidally co-ordinated with a molecule of dmso (dimethyl sulphoxide) occupying the apical position. There is conjecture concerning the origin of these geometries and it has been proposed that either the dioxo-



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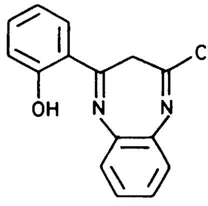

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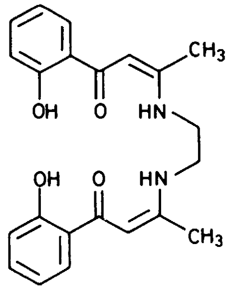

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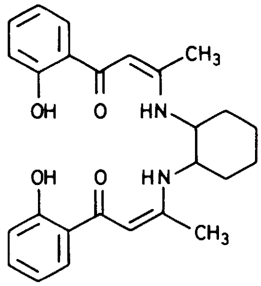

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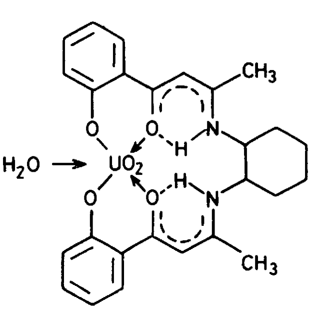

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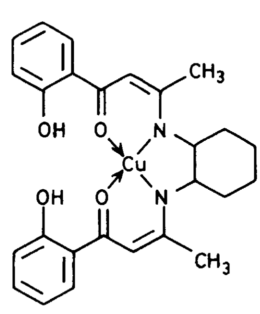

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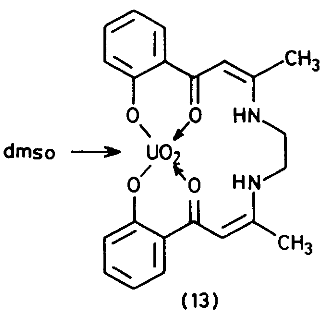

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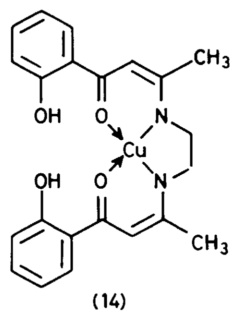
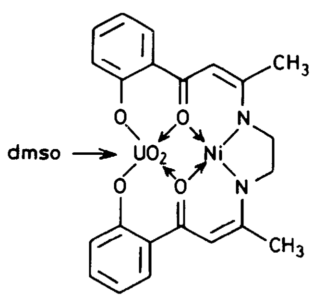


(14)

uranium(VI) cation imposes a steric constraint on the inner compartment occupancy or that there is an inherent tetradral twist in the inner donor set. The crystal structure of complex (12) was determined in order to investigate the geometry available at the inner site as crystals of (14) suitable for *X*-ray structure determination were not available despite attempts to obtain them from different solvent media. The structure of complex (12) clearly demonstrates the inner compartment occupancy and confirms the assignment of *cis*-dach.

The structures of the two crystallographically independent molecules are illustrated in Figures 2 and 3, in each case with the atom labelling used in the corresponding Tables. Bond lengths and angles (together with estimated standard deviations) are compared in Table 4 and details of planar fragments are given in Table 5.



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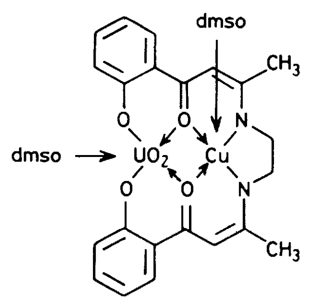

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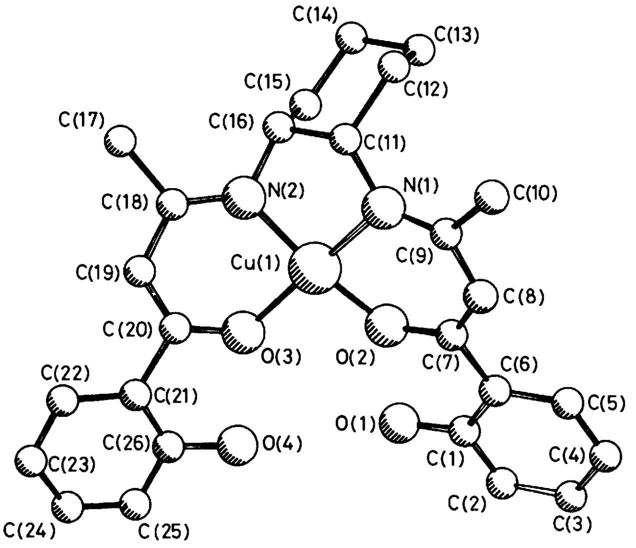


Figure 2. The molecular structure of complex (12), molecule 1

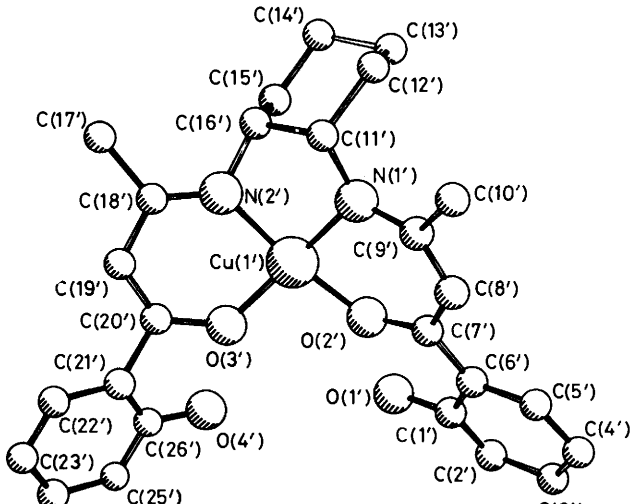


Figure 3. The molecular structure of complex (12), molecule 2

The two crystallographically independent molecules are essentially identical, except for minor conformational differences which reflect their different intermolecular environ-

Table 4. Bond lengths (Å) and angles (°) with estimated standard deviations for the two crystallographically independent molecules of complex (12)

	Molecule 1	Molecule 2
Cu(1)–O(2)	1.869(9)	1.890(10)
Cu(1)–O(3)	1.950(9)	1.905(9)
Cu(1)–N(1)	1.950(11)	1.951(10)
Cu(1)–N(2)	1.887(11)	1.900(10)
O(1)–C(1)	1.315(17)	1.368(18)
C(1)–C(2)	1.376(19)	1.350(22)
C(2)–C(3)	1.383(21)	1.358(24)
C(3)–C(4)	1.382(21)	1.412(23)
C(4)–C(5)	1.370(20)	1.380(22)
C(5)–C(6)	1.389(18)	1.382(19)
C(6)–C(1)	1.431(18)	1.414(19)
C(6)–C(7)	1.478(18)	1.454(18)
O(2)–C(7)	1.342(15)	1.334(16)
C(7)–C(8)	1.362(18)	1.402(18)
C(8)–C(9)	1.407(19)	1.383(18)
C(9)–C(10)	1.533(21)	1.521(19)
N(1)–C(9)	1.286(18)	1.356(16)
N(1)–C(11)	1.501(17)	1.420(16)

	Molecule 1	Molecule 2
C(11)–C(12)	1.543(20)	1.530(20)
C(12)–C(13)	1.501(22)	1.518(23)
C(13)–C(14)	1.514(22)	1.526(23)
C(14)–C(15)	1.503(21)	1.510(22)
C(15)–C(16)	1.546(20)	1.523(20)
C(16)–C(11)	1.518(19)	1.548(19)
N(2)–C(16)	1.450(18)	1.461(17)
N(2)–C(18)	1.316(18)	1.292(16)
C(17)–C(18)	1.507(22)	1.505(20)
C(18)–C(19)	1.444(20)	1.410(19)
C(19)–C(20)	1.346(19)	1.331(19)
O(3)–C(20)	1.309(16)	1.341(15)
C(20)–C(21)	1.503(18)	1.506(18)
C(21)–C(26)	1.382(20)	1.356(19)
C(21)–C(22)	1.378(21)	1.393(19)
C(22)–C(23)	1.389(24)	1.367(21)
C(23)–C(24)	1.361(24)	1.373(23)
C(24)–C(25)	1.363(25)	1.365(22)
C(25)–C(26)	1.397(23)	1.399(20)
O(4)–C(26)	1.355(20)	1.344(16)

	Molecule 1	Molecule 2
O(2)–Cu(1)–O(3)	90.6(4)	90.2(4)
O(2)–Cu(1)–N(1)	93.3(4)	93.5(4)
O(2)–Cu(1)–N(2)	168.5(4)	170.4(4)
O(3)–Cu(1)–N(1)	169.4(4)	169.2(4)
O(3)–Cu(1)–N(2)	92.3(4)	93.3(4)
N(1)–Cu(1)–N(2)	85.9(5)	84.6(4)
O(1)–C(1)–C(2)	117.4(12)	118.0(13)
O(1)–C(1)–C(6)	123.9(12)	120.7(12)
C(6)–C(1)–C(2)	118.6(12)	121.0(13)
C(1)–C(2)–C(3)	122.4(13)	122.3(15)
C(2)–C(3)–C(4)	118.7(14)	119.6(15)
C(3)–C(4)–C(5)	120.5(13)	116.8(14)
C(4)–C(5)–C(6)	121.8(12)	124.6(14)
C(5)–C(6)–C(1)	117.9(11)	115.3(12)
C(5)–C(6)–C(7)	122.5(11)	122.7(12)
C(1)–C(6)–C(7)	119.5(11)	121.8(12)
Cu(1)–O(2)–C(7)	125.1(8)	125.3(8)
O(2)–C(7)–C(6)	116.4(11)	117.5(11)
O(2)–C(7)–C(8)	121.6(11)	121.1(11)
C(6)–C(7)–C(8)	122.0(11)	121.5(12)
C(7)–C(8)–C(9)	127.7(12)	126.5(12)
C(8)–C(9)–C(10)	114.2(12)	115.4(11)
N(1)–C(9)–C(8)	122.9(13)	125.0(12)
N(1)–C(9)–C(10)	123.0(13)	119.6(11)
Cu(1)–N(1)–C(9)	121.4(9)	116.6(8)
Cu(1)–N(1)–C(11)	110.3(8)	113.6(8)
C(9)–N(1)–C(11)	125.2(11)	124.4(10)
N(1)–C(11)–C(12)	115.9(11)	114.8(11)
N(1)–C(11)–C(16)	107.2(11)	107.3(10)

	Molecule 1	Molecule 2
C(12)–C(11)–C(16)	107.9(11)	109.2(11)
C(11)–C(12)–C(13)	114.3(13)	113.7(12)
C(12)–C(13)–C(14)	108.3(13)	109.5(13)
C(13)–C(14)–C(15)	110.3(13)	109.8(13)
C(14)–C(15)–C(16)	113.3(12)	111.7(12)
C(11)–C(16)–C(15)	111.3(11)	113.6(11)
N(2)–C(16)–C(11)	106.9(11)	106.8(10)
N(2)–C(16)–C(15)	108.9(11)	107.6(11)
C(16)–N(2)–C(18)	122.7(11)	122.6(11)
Cu(1)–N(2)–C(16)	109.9(8)	109.0(8)
Cu(1)–N(2)–C(18)	127.2(10)	127.6(9)
N(2)–C(18)–C(17)	121.9(13)	122.8(12)
N(2)–C(18)–C(19)	122.3(13)	122.0(12)
C(17)–C(18)–C(19)	115.7(13)	115.2(12)
C(18)–C(19)–C(20)	125.8(13)	125.1(13)
C(19)–C(20)–C(21)	121.9(12)	121.5(12)
O(3)–C(20)–C(19)	123.6(12)	126.3(12)
O(3)–C(20)–C(21)	114.5(11)	112.0(10)
Cu(1)–O(3)–C(20)	125.3(8)	122.1(8)
C(20)–C(21)–C(26)	121.4(12)	120.9(12)
C(20)–C(21)–C(22)	120.5(12)	120.4(12)
C(26)–C(21)–C(22)	117.9(13)	118.7(12)
C(21)–C(22)–C(23)	121.4(15)	122.1(13)
C(22)–C(23)–C(24)	118.9(16)	118.1(15)
C(23)–C(24)–C(25)	121.8(16)	121.4(15)
C(24)–C(25)–C(26)	118.6(16)	119.5(14)
C(25)–C(26)–C(21)	121.2(14)	120.2(13)
O(4)–C(26)–C(21)	123.5(14)	124.6(12)
O(4)–C(26)–C(25)	115.2(14)	115.2(12)

Selected intramolecular contacts

	Molecule 1	Molecule 2
O(1) ··· O(2)	2.511(14)	2.513(14)
O(3) ··· O(4)	2.526(16)	2.559(13)
O(2) ··· H(O1)	1.79	1.70
O(3) ··· H(O4)	1.88	1.76

Selected short intermolecular contacts (all involving molecule 1)

Cu(1) ··· C(4^{IV})	3.40	C(1) ··· C(9^{IV})	3.37
Cu(1) ··· C(5^{IV})	3.26	C(7) ··· C(7^{IV})	3.36

Symmetry operation: IV $1 - x, 1 - y, -z$.

Table 5. Details of planar fragments of the two crystallographically independent molecules of complex (12). Equations of the least-squares planes are of the form $pX + qY + rZ = d$, where p, q, and r are direction cosines referred to orthogonal crystal axes a, b^*, c'. Deviations (Å) of atoms from the mean planes are given in parentheses

	Molecule 1						
		p	*q*	*r*	*d*		
Plane A:	Cu(1), O(2), N(1)	−0.3948	−0.9111	−0.1186	−6.7337		[O(3) −0.334, N(2) 0.376, C(7) −0.429, C(8) −0.762, C(9) −0.561]
Plane B:	Cu(1), O(3), N(2)	−0.1521	−0.9698	−0.1910	−6.2177		[O(2) 0.363, N(1) −0.352, C(18) −0.195, C(19) −0.471, C(20) −0.376]
Plane C:	O(2), N(1), C(7)—C(9)	−0.4590	−0.7484	−0.4787	−7.6242	r.m.s. deviation 0.041 Å	[O(2) −0.045, N(1) 0.038, C(7) 0.059, C(8) −0.019, C(9) −0.033, Cu(1) −0.518, C(6) 0.207, C(10) −0.151]
Plane D:	O(3), N(2), C(18)—C(20)	−0.0829	−0.9959	0.0355	−4.5231	r.m.s. deviation 0.046 Å	[O(3) 0.041, N(2) −0.052, C(18) 0.067, C(19) −0.021, C(20) −0.036, Cu(1) −0.318, C(17) 0.225, C(21) −0.170]
Plane E:	C(1)—C(6)	−0.4680	−0.8143	−0.3433	−7.5946	r.m.s. deviation 0.014 Å	[C(1) 0.019, C(2) −0.002, C(3) −0.013, C(4) 0.010, C(5) 0.008, C(6) −0.022, O(1) 0.011, C(7) −0.028]
Plane F:	C(21)—C(26)	−0.1162	−0.9624	0.2455	−3.1266	r.m.s. deviation 0.018 Å	[C(21) 0.001, C(22) 0.021, C(23) −0.030, C(24) 0.019, C(25) 0.003, C(26) −0.013, O(4) −0.099, C(20) 0.073]
Plane G:	C(11), C(13), C(14), C(16)	0.7713	−0.3878	−0.5048	−3.1301	r.m.s. deviation 0.014 Å	[C(11) −0.014, C(13) 0.014, C(14) −0.014, C(16) 0.014, N(1) 1.393, N(2) 0.833, C(12) −0.672, C(15) 0.642]

	Molecule 2						
		p	*q*	*r*	*d*		
Plane A:	Cu(1′), O(2′), N(1′)	−0.5820	0.6018	0.5470	2.1909		[O(3′) −0.336, N(2′) 0.311, C(7′) −0.516, C(8′) −0.916, C(9′) −0.721]
Plane B:	Cu(1′), O(3′), N(2′)	−0.5600	0.7454	0.3617	2.0933		[O(2′) 0.294, N(1′) −0.359, C(18′) −0.115, C(19′) −0.398, C(20′) −0.355]
Plane C:	O(2′), N(1′), C(7′)—C(9′)	−0.1387	0.6705	0.7289	1.7848	r.m.s. deviation 0.053 Å	[O(2′) −0.057, N(1′) 0.055, C(7′) 0.065, C(8′) −0.002, C(9′) −0.061, Cu(1′) −0.618, C(6′) 0.316, C(10′) −0.225]
Plane D:	O(3′), N(2′), C(18′)—C(20′)	−0.7007	0.6752	0.2305	2.6142	r.m.s. deviation 0.058 Å	[O(3′) 0.053, N(2′) −0.065, C(18′) 0.083, C(19′) −0.021, C(20′) −0.050, Cu(1′) −0.266, C(17′) 0.409, C(21′) −0.123]
Plane E:	C(1′)—C(6′)	−0.1740	0.5119	0.8413	1.5731	r.m.s. deviation 0.021 Å	[C(1′) −0.033, C(2′) 0.022, C(3′) −0.006, C(4′) 0.004, C(5′) −0.016, C(6′) 0.029, O(1′) −0.002, C(7′) 0.038]
Plane F:	C(21′)—C(26′)	−0.9614	0.2220	0.1624	3.8382	r.m.s. deviation 0.008 Å	[C(21′) 0.000, C(22′) 0.006, C(23′) −0.002, C(24′) −0.008, C(25′) 0.013, C(26′) −0.009, O(4′) −0.012, C(20′) 0.011]
Plane G:	C(11′), C(13′), C(14′), C(16′)	0.1529	0.8472	−0.5088	−2.7030	r.m.s. deviation 0.034 Å	[C(11′) −0.034, C(13′) 0.034, C(14′) −0.035, C(16′) 0.035, N(1′) 1.277, N(2′) 0.882, C(12′) −0.645, C(15′) 0.654]

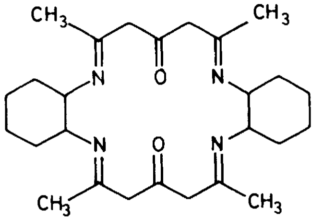
Selected angles (°) between planes

	Molecule 1	Molecule 2
A–B	14.9	13.5
A–C	23.1	28.0
B–D	13.7	11.8
C–D	40.0	44.1
C–E	8.7	11.3
D–F	12.4	30.6
E–F	41.1	65.3

Selected torsion angles (°) associated with the di-iminocyclohexyl fragment

	Molecule 1	Molecule 2
N(1)–C(11)–C(16)–N(2)	+45.0	+42.6
C(11)–C(12)–C(13)–C(14)	+60.4	+58.5
C(12)–C(13)–C(14)–C(15)	−57.3	−59.6
C(13)–C(14)–C(15)–C(16)	+56.1	+57.9
C(14)–C(15)–C(16)–C(11)	−54.1	−53.7
C(15)–C(16)–C(11)–C(12)	+51.7	+49.2
C(16)–C(11)–C(12)–C(13)	−57.7	−52.3

ments. In each molecule the copper atom occupies the inner (N_2O_2) site with a co-ordination geometry which has a marked tetrahedral twist (14.9 and 13.5°) away from the anticipated square-plane. Although the patterns of copper–ligand bond lengths are fairly similar in the two molecules, the Cu(1)–N(1) bond is markedly longer than the other three bonds. In the bridging di-iminocyclohexyl fragment, the ring adopts a fairly regular chair conformation but the N–C–C–N torsion angles are somewhat reduced (45.0 and 42.6°) from the ideal value. Whilst this is clearly a result of the co-ordination of the copper atom in the inner site, the torsion angle is much greater than has been observed with the more flexible di-iminoethane bridge.[22] The β-ketoimino-fragments are not particularly planar [root mean square (r.m.s.) deviations 0.041, 0.046, 0.053, and 0.058 Å] and the copper atoms lie substantially (up to 0.62 Å) out of their mean planes. There is some evidence for slight π-bond localisation within these chelate chains, bonds C(7)–C(8) and C(19)–C(20) being, on average, shorter than



(17)

bonds C(8)–C(9) and C(18)–C(19). The progressive deviations from coplanarity of the skeletal atoms forming the inner compartment give a ' twisted butterfly ' shape to the quadridentate ligand. The phenyl rings of the non-co-ordinating phenol substituents are each closely planar and the bonds to the keto-carbon atom are long and essentially single. There are substantial out-of-plane twists of these phenyl rings, greater in the case of molecule 2, but the contacts between phenolic and ketonic oxygens are all very short, indicating strong hydrogen bonding and the hydrogen atoms were clearly detected in such positions. The bond angles O(1)–C(1)–C(6), *etc.* are all significantly greater than the other exocyclic trigonal angle at C(1), *etc.*, thus hydrogen bonding seems to be optimised if the two oxygen atoms are moved slightly apart.

There are few significant intermolecular interactions, the most noteworthy (*ca.* 3.3 Å) being between Cu(1) and a phenyl ring of a symmetry-related molecule.

The reaction of *cis*-dach with heptane-2,4,6-trione gives the macrocycle (17) as yellow crystals, further indicating the facile formation of Schiff bases when the steric constraint is lifted. The macrocycle has been treated with copper(II) ethanoate under the conditions used for the reaction of (1) with copper(II) ethanoate. Mixtures of products were recovered, but were not separated due to their insolubility. The mass spectra of these mixtures indicate that they include copper(II) complexes of (17), together with the corresponding complexes of an acyclic ligand analogous to (2; R = CH_3) but having a 1,2-diaminocyclohexyl bridge.

Experimental

I.r. spectra of KBr discs were measured using a Perkin-Elmer 297 instrument. Mass spectra were obtained using KRATOS MS25 and MS80 mass spectrometers coupled to a DS55 data system. ^1H N.m.r. spectra were recorded at 220 MHz using a Perkin-Elmer R34 spectrometer at ambient temperature, ^{13}C n.m.r. spectra on a JEOL PFT-100 spectrometer at 25.15 MHz (^1H noise decoupled).

cis-1,2-Diaminocyclohexane was separated from a mixture of isomers using the method of Saito and Kidani.[17] *o*-Acetoacetylphenol and heptane-2,4,6-trione were prepared according to literature procedures.[16]

2-(*Acetylmethyl*)-4-*methyl*-3H-1,5-*benzodiazepine* (4).—1,2-Diaminobenzene (6.49 g) was added to a warm solution of ethanol (24 cm^3) containing ethanoic acid (9 cm^3) and then treated with heptane-2,4,6-trione (8.4 g). The resulting solution was added to ice–water (120 cm^3), left for 3 h, and then refrigerated overnight. The *diazepine* (4) was collected by filtration and dried *in vacuo* over silica gel, m.p. 172—174 °C, yield 2.6 g (20.5% from trione) (Found: N, 12.9%; *m/z* 214.1107. $C_{13}H_{14}N_2O$ requires N, 13.05%; *M* 214.1106); $\nu_{max.}$ at 1 658, 1 530, and 1 580 cm^{-1}. ^{13}C-{^1H} N.m.r. ($CDCl_3$): 197.1 [C(11)], 165.6 [C(9)], 155.8 [C(7)], 140.4 [C(6)], 130.8 [C(5)], 128.1 [C(1)], 125.9 [C(4)], 124.5 [C(2)], 122.5 [C(3)], 94.5 [C(8)], 40.3 [C(10)], 29.1 [C(12)], and 27.3 [C(13)] p.p.m.

1-(o-*Aminophenyl*)-2,6-*dimethyl*-4-*pyridone* (5).—A solution of heptane-2,4,6-trione (2.84 g) in ethanol (80 cm^3) was added to a hot solution of 1,2-diaminobenzene (2.16 g) in ethanol (8 cm^3) and ethanoic acid (4 cm^3). The resulting brown-red solution was diluted with water (*ca.* 1 000 cm^3) and after heating under reflux for 3 h the colour changed to pale yellow. The mixture was evaporated to half volume and then kept at 0 °C overnight. The *pyridone* (5) was collected and dried *in vacuo* over silica gel, yield 2.34 g (54.6% based on the trione). Recrystallisation from a large volume of water gave the pyridone as colourless needles, m.p. 238—240 °C (decomp.) (Found: N, 12.3%; *m/z* 214.1105. $C_{13}H_{14}N_2O{\cdot}0.5H_2O$ requires N, 12.55%; *M* – H_2O 214.258); $\nu_{max.}$ at 1 640, 1 600, 1 590, and 1 550 cm^{-1}. ^{13}C-{^1H} N.m.r. ($CDCl_3$): 149.3, 130.8, 128.3, 119.1, 117.9, 116.5, 63.7, and 20.4 p.p.m.

Crystal data. $C_{13}H_{14}N_2O{\cdot}0.5H_2O$, $M = 223.266$, Monoclinic, $a = 14.984(1)$, $b = 7.475(3)$, $c = 21.173(1)$ Å, $\beta = 98.71(1)°$, $U = 2\ 344.1$ Å^3, $Z = 8$, $D_c = 1.31$ g cm^{-3}, Cu-K_α radiation ($\lambda = 1.5418$ Å), μ(Mo-K_α) = 6.40 cm^{-1}, $F(000) = 952$, space group $P2_1/c$.

Three-dimensional *X*-ray data were collected using an Enraf–Nonius CAD 4 diffractometer. Intensities were measured out to $\theta = 66°$; 4 090 reflections were scanned and of these 2 392 had $I > 3\sigma(I)$ and were used in the refinement. The structure was solved by direct methods and the co-ordinates of all the non-hydrogen atoms comprising the two molecules of the asymmetric unit were refined. A Fourier-difference map revealed the oxygen atom associated with the water of crystallisation. Routine full-matrix refinement using isotropic and then anisotropic thermal parameters gave a final *R* value of 0.0388. At a late stage in the refinement all the hydrogen atoms were located from a difference map; they were included in the structure but were not refined. Table 6 reports atomic positional parameters with estimated standard deviations.

3,3′-(cis-1,2-*Cyclohexanediyldi-imino*)*bis*[1-(o-*hydroxyphenyl*)*but*-2-*enone*] (10).—*o*-Acetoacetylphenol (2 g) in hot ethanol (50 cm^3) was added to a hot solution of *cis*-1,2-diaminocyclohexane (0.64 g) in ethanol (20 cm^3). A bright yellow precipitate formed rapidly, and was collected by filtration, washed with cold ethanol, and dried under vacuum. The filtrate was concentrated and yielded further yellow solid after storing at 0 °C overnight (Found: C, 71.6; H, 7.65; N, 6.25%; *M* 434. $C_{26}H_{30}N_2O_4$ requires C, 71.9; H, 6.90; N, 6.45%; *M* 434); $\nu_{max.}$ (KBr disc) at 1 600, 1 575, 1 550, 1 519, 1 337, and 1 258 cm^{-1}.

{3,3′-(cis-1,2-*Cyclohexanediyldi-imino*)*bis*[1-(o-*hydroxyphenyl*)*but*-2-*enonato*]-(N,N′,O^1,O$^{1\prime}$)}*copper*(II) (12).—Compound (10) (0.2 g) was dissolved in the minimum amount of $CHCl_3$ and to this was added an aqueous solution of copper(II) ethanoate. The mixture was shaken overnight and a slight brown colour appeared in the organic layer, the aqueous layer remaining dark blue. The mixture was heated under reflux with stirring (48 h), and the organic layer darkened considerably. The organic layer was separated, dried ($MgSO_4$), and evaporated; the resulting solid was recrystallised from ethanol to give the *copper complex* (12) (Found: C, 63.0; H, 5.45; N, 5.65%; *M* 496. $C_{26}H_{28}CuN_2O_4$ requires C, 62.95; H, 5.65; N, 5.65%; *M* 496); $\nu_{max.}$ (KBr disc) at 1 590br, 1 515, and 1 290 cm^{-1}.

Crystal data. $C_{26}H_{28}CuN_2O_4$, $M = 496.06$, thin, plate-shaped, green crystals from chloroform, 0.35 × 0.21 × 0.04 mm, triclinic, $a = 13.143(8)$, $b = 14.279(8)$, $c = 14.289\ (14)$ Å, $\alpha = 67.36(6)$, $\beta = 71.18(7)$, $\gamma = 91.36(5)°$, $U = 2\ 308(8)$ Å^3, $D_m = 1.44$, $Z = 4$, $D_c = 1.43$ g cm^{-3}, space group $P\bar{1}$ (assumed and confirmed by the analysis), Mo-K_α radiation ($\lambda = 0.710\ 69$ Å), μ(Mo-K_α) = 9.26 cm^{-1}, $F(000) = 1\ 036$.

Table 6. Fractional atomic co-ordinates ($\times 10^4$), with standard deviations in parentheses, for compound (5)

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
N(1)	9 604(1)	1 320(3)	1 296(1)	N(4)	6 303(2)	4 287(3)	4 345(1)
N(2)	10 405(2)	4 222(4)	762(1)	O(2)	3 510(1)	1 451(3)	4 696(1)
O(1)	7 799(1)	−1 558(3)	61(1)	C(14)	5 690(2)	2 654(4)	3 389(1)
C(1)	10 272(2)	2 406(4)	1 686(1)	C(15)	5 631(2)	2 348(4)	2 739(1)
C(2)	10 687(2)	3 778(4)	1 394(1)	C(16)	6 160(2)	3 321(5)	2 381(1)
C(3)	11 407(2)	4 676(4)	1 761(2)	C(17)	6 734(2)	4 603(4)	2 681(1)
C(4)	11 659(2)	4 246(5)	2 393(2)	C(18)	6 788(2)	4 920(4)	3 328(1)
C(5)	11 215(2)	2 936(5)	2 684(1)	C(19)	6 269(2)	3 938(4)	3 704(1)
C(6)	10 516(2)	2 003(4)	2 329(1)	C(20)	6 323(2)	−681(4)	3 857(2)
C(7)	8 443(2)	3 401(5)	1 545(2)	C(21)	5 414(2)	−70(4)	3 974(1)
C(8)	8 704(2)	1 797(4)	1 194(1)	C(22)	4 878(2)	1 099(4)	4 288(1)
C(9)	8 102(2)	845(4)	789(1)	C(23)	4 017(2)	−509(4)	4 402(1)
C(10)	8 355(2)	−677(4)	455(1)	C(24)	3 758(2)	1 232(4)	4 167(1)
C(11)	9 290(2)	−1 129(4)	591(1)	C(25)	4 300(2)	2 237(4)	3 853(1)
C(12)	9 893(2)	−142(4)	984(2)	C(26)	4 030(2)	4 059(4)	3 604(2)
C(13)	10 879(2)	−565(5)	1 098(1)	O(3)	8 218(2)	201(3)	5 005(1)
N(3)	5 129(1)	1 594(3)	3 747(1)				

Table 7. Atomic positional parameters, with estimated standard deviations, for complex (12). Primed atoms comprise molecule 2

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Cu(1)	0.294 64(13)	0.357 71(12)	0.224 49(13)	C(20)	0.356 8(10)	0.331 6(8)	0.409 7(10)
Cu(1′)	−0.210 04(13)	0.040 17(12)	0.028 07(13)	C(21)	0.451 3(10)	0.334 4(9)	0.446 6(9)
O(1)	0.583 8(8)	0.274 1(7)	0.085 3(7)	C(22)	0.440 3(12)	0.356 4(12)	0.534 8(11)
O(2)	0.406 5(7)	0.341 2(6)	0.114 7(7)	C(23)	0.526 4(13)	0.358 2(12)	0.570 8(13)
O(3)	0.381 2(7)	0.322 7(6)	0.317 5(7)	C(24)	0.620 0(12)	0.328 8(12)	0.523 6(13)
O(4)	0.572 1(8)	0.291 4(10)	0.307 1(9)	C(25)	0.634 7(12)	0.306 1(13)	0.436 3(13)
O(1′)	−0.016 1(7)	0.319 9(8)	−0.208 5(8)	C(26)	0.549 4(11)	0.309 6(11)	0.397 5(11)
O(2′)	−0.091 9(7)	0.151 0(7)	−0.044 9(7)	C(1′)	0.078 9(10)	0.317 7(10)	−0.188 4(10)
O(3′)	−0.222 1(6)	0.058 7(6)	−0.107 0(6)	C(2′)	0.161 0(12)	0.398 0(11)	−0.254 3(13)
O(4′)	−0.188 2(8)	0.184 8(7)	−0.302 8(7)	C(3′)	0.258 4(12)	0.402 6(12)	−0.241 0(13)
N(1)	0.212 5(8)	0.418 0(7)	0.130 4(8)	C(4′)	0.273 0(11)	0.324 8(11)	−0.150 9(13)
N(2)	0.168 0(8)	0.348 5(8)	0.339 9(8)	C(5′)	0.186 7(10)	0.245 0(10)	−0.083 2(11)
N(1′)	−0.187 9(7)	−0.002 7(7)	0.166 3(7)	C(6′)	0.086 3(9)	0.239 3(9)	−0.094 3(10)
N(2′)	−0.341 8(7)	−0.056 5(7)	0.111 0(8)	C(7′)	−0.003 3(8)	0.154 7(9)	−0.019 4(10)
C(1)	0.603 6(9)	0.320 9(9)	−0.019 5(10)	C(8′)	0.001 5(9)	0.081 7(9)	0.077 8(10)
C(2)	0.700 3(10)	0.312 6(10)	−0.088 7(11)	C(9′)	−0.083 1(9)	0.006 6(9)	0.161 2(9)
C(3)	0.730 3(10)	0.359 8(10)	−0.200 5(12)	C(10′)	−0.053 2(11)	−0.067 4(11)	0.254 2(11)
C(4)	0.660 0(11)	0.416 4(10)	−0.244 0(11)	C(11′)	−0.275 4(9)	−0.076 2(9)	0.255 6(10)
C(5)	0.564 0(10)	0.427 7(9)	−0.177 5(10)	C(12′)	−0.301 4(11)	−0.063 7(11)	0.362 1(11)
C(6)	0.533 7(9)	0.383 7(8)	−0.065 2(10)	C(13′)	−0.348 9(12)	0.032 5(13)	0.360 3(12)
C(7)	0.430 5(9)	0.395 3(9)	0.007 7(10)	C(14′)	−0.453 3(11)	0.031 0(11)	0.335 6(13)
C(8)	0.365 1(9)	0.460 3(9)	−0.031 1(10)	C(15′)	−0.428 6(10)	0.026 7(10)	0.226 6(11)
C(9)	0.260 9(11)	0.471 4(10)	0.027 7(10)	C(16′)	−0.377 4(9)	−0.067 0(9)	0.223 1(10)
C(10)	0.210 4(11)	0.553 3(11)	−0.041 3(11)	C(17′)	−0.512 3(10)	−0.161 9(10)	0.147 8(12)
C(11)	0.100 1(9)	0.424 2(10)	0.196 5(10)	C(18′)	−0.402 2(10)	−0.096 3(9)	0.075 6(10)
C(12)	0.008 3(10)	0.407 2(11)	0.156 4(12)	C(19′)	−0.370 2(10)	−0.079 1(9)	−0.034 6(10)
C(13)	−0.009 3(11)	0.302 5(11)	0.157 5(12)	C(20′)	−0.287 2(9)	−0.009 0(9)	−0.115 4(9)
C(14)	−0.039 8(11)	0.222 9(11)	0.273 2(12)	C(21′)	−0.260 8(9)	0.006 1(9)	−0.231 5(10)
C(15)	0.047 6(10)	0.233 3(10)	0.317 0(11)	C(22′)	−0.284 1(10)	−0.076 0(9)	−0.255 3(10)
C(16)	0.072 7(9)	0.342 2(10)	0.311 1(11)	C(23′)	−0.261 5(12)	−0.065 1(11)	−0.359 6(12)
C(17)	0.055 1(12)	0.337 8(13)	0.520 4(12)	C(24′)	−0.214 9(11)	0.030 3(12)	−0.442 4(12)
C(18)	0.161 5(10)	0.340 5(10)	0.436 6(10)	C(25′)	−0.192 8(11)	0.112 9(11)	−0.422 0(11)
C(19)	0.256 2(10)	0.339 5(10)	0.467 1(10)	C(26′)	−0.214 5(9)	0.099 6(9)	−0.314 7(9)

Three-dimensional *X*-ray diffraction data were collected in the range $3.5 < 2\theta > 50^\circ$ on a Nicolet/Syntex P3 four-circle diffractometer by the θ—2θ scan method. 2 985 Independent reflections for which $I/\sigma(I) > 3.0$ were corrected for Lorentz and polarisation effects. The structure was solved by standard Patterson and Fourier methods and refined by block-diagonal least squares. Hydrogen atoms were placed in calculated positions [C–H 0.97, O–H 0.92 Å; C–O–H 109, C–C–H (methyl) 112°]; their contributions were included in structure-factor calculations ($B = 7.0$ Å^2) but no refinement of positional parameters was permitted. Refinement converged at *R* 0.0651 with allowance for anisotropic thermal motion of all non-hydrogen atoms and for the anomalous scattering of copper. Table 7 lists the atomic positional parameters with estimated standard deviations.

Scattering factors were taken from ref. 23; unit weights were used throughout the refinements. Computer programs used were SHELX, CRYSTALS, and those of the Sheffield *X*-ray system.

6,10,17,21-*Tetramethyl*-1,2,3,4,4a,7,9,11a,12,13,14,15,15a,18,20,22a-*hexadecahydrodibenzo*[*b*,*k*][1,4,10,13]*tetra-azacyclo-*

octadecine-8,19-*dione* (17).—*cis*-1,2-Diaminocyclohexane (1.68 g) in ethanol (20 cm^3) was added to heptane-2,4,6-trione (2.1 g) in ethanol (40 cm^3) and stirred under reflux for 2 h. The solution was evaporated to dryness under diminished pressure and then triturated with light petroleum (b.p. 40—60 °C) to give the *product* (17) (Found: C, 67.5; H, 9.20; N, 12.0%; M 440. $C_{26}H_{40}N_4O_2{\cdot}H_2O$ requires C, 68.1; H, 9.15; N, 12.2%; $M - H_2O$ 440); $\nu_{max.}$ (KBr disc) at 2 925, 2 850, 1 635, 1 570, 1 480, 1 440, 1 300, 1 100, and 800 cm^{-1}.

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