Compartmental Ligands. Part 9.[1] Crystal and Molecular Structure † of 6,11-Dimethyl-7,10-diazahexadeca-5,11-diene-2,4,13,15-tetraone and of the Related Mononuclear Copper(II) Complex having N_2O_2 Occupancy

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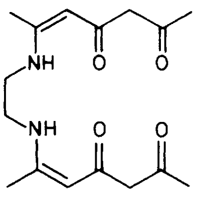
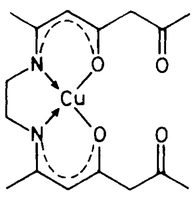
The crystal and molecular structures of 6,11-dimethyl-7,10-diazahexadeca-5,11-diene-2,4,13,15-tetraone and [6,11-dimethyl-7,10-diazahexadeca-5,11-diene-2,4,13,15-tetraonato(2−)-*N,N′,O*^{4}*,O*^{13}]copper(II) are reported, together with a discussion of the changes made on metal incorporation into the free ligand.

The syntheses and properties of acyclic Schiff bases derived from symmetrical 1,3,5-triketones and α,ω-alkanediamines were reported in Part 2 of this series.[2] We now report the crystal and molecular structures of the free acyclic compartmental Schiff base (1) and of the related mononuclear copper(II) complex (2). The availability of the structure of the free ligand enables comment to be made on the changes accompanying metal incorporation into the ligand, to give first mononuclear and then binuclear complexes.


(1)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Results and Discussion

The structures of the two molecules are illustrated in Figures 1 and 2 respectively, in each case with the atom labelling used in the corresponding Tables. Bond lengths and angles (together with estimated standard deviations) and details of planar fragments are given in Tables 1—4.

The free ligand was prepared by the method of ref. 2. The i.r. spectrum (KBr disc) gave a weak band at 3 385 cm^{-1} (O−H···O stretch), a strong, broad band at 3 140 cm^{-1} (N−H···O stretch), and a strong carbonyl band at 1 700 cm^{-1}. The ^{1}H n.m.r. spectrum, in $CDCl_3$, showed that two tautomers were present in solution. Immediately after dissolution the outer-compartment keto-tautomer was present in almost 100% abundance, but after standing for 2—3 weeks this tautomer had diminished to 69.7% abundance and the enol form accounted for the remaining 30.3%.

The molecule (1) possesses crystallographically imposed C_2 symmetry and the terminal β-diketone residue is present in its keto tautomeric form. In the absence of a metal, no constraints are placed on the conformation adopted by the chains and there is no tendency to display the bicompartmental capabilities of the ligand. The β-ketoimine fragment is planar and is stabilised by an internal hydrogen bond. The carbon–carbon torsion angle of the di-iminoethane fragment is, as expected, much larger (−61.1°) than that found in metal complexes having N_2O_2 occupancy. There are close intermolecular contacts across an inversion centre between both the keto-oxygen atom O(2) and the imino-nitrogen atom to a symmetry related O(2) to form an isosceles triangle [O(2)···N(1) 2.69, O(2)···O(2^{II}) 3.00, N(1)···O(2^{II}) 3.01 Å]. Although the position of the hydrogen on the imino-nitrogen H(N1) was clearly detected and successfully refined in a position to form an intramolecular hydrogen bond, it seems likely that its position within the triangle of electronegative atoms helps to stabilise some intermolecular association.

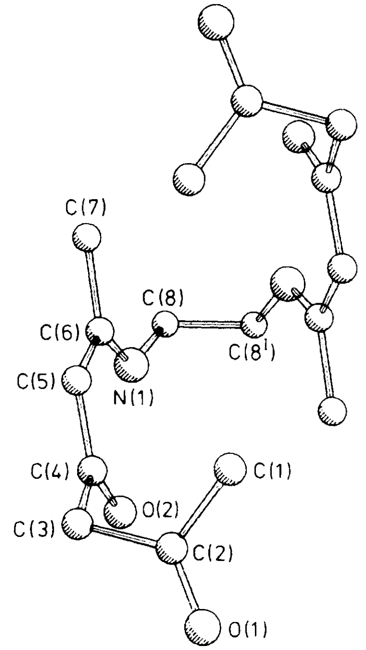

Figure 1. Molecular structure of (1) showing the atom labelling. The view is down the C_2 symmetry axis; atom C(8^1) is related to C(8) by the C_2 symmetry. Hydrogen atoms are omitted for clarity

The mononuclear copper(II) complex was also prepared as described in Part 2.[2] The i.r. spectrum (KBr disc) gave two strong bands at 1 721 and 1 705 cm^{-1} indicative of the presence of two different orientations for the carbonyl groups of the outer, unco-ordinated compartment. In $CHCl_3$ solution only one carbonyl band, at 1 700 cm^{-1}, was detected. The diffuse reflectance spectra gave a band at 549 nm; this band was also found in the visible spectrum run in $CHCl_3$ and compares with the value of 545 nm found for [Cu(acen)] [acen =

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† *Supplementary data available* (No. SUP 56020, 4 pp.): H-atom co-ordinates, thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

Table 1. Bond lengths (Å) and angles (°), with estimated standard deviations, for the free ligand (1)

C(1)–H(1A)	1.06(5)	C(3)–H(3B)	1.02(4)	C(7)–H(7A)	0.95(4)	C(8)–H(8B)	1.12(4)
C(1)–H(1B)	0.87(6)	C(3)–C(4)	1.535(6)	C(7)–H(7B)	0.98(4)	C(8)–C(8^{I})	1.520(5)
C(1)–H(1C)	0.95(6)	O(2)–C(4)	1.237(5)	C(7)–H(7C)	0.98(5)	O(2) · · · N(1)	2.687(4)
C(1)–C(2)	1.494(8)	C(4)–C(5)	1.402(6)	N(1)–C(6)	1.330(5)	O(2) · · · H(N1)	1.94(3)
O(1)–C(2)	1.203(7)	C(5)–H(5)	0.94(3)	N(1)–H(N1)	0.91(3)	O(2) · · · O(2^{II})	3.000(4)
C(2)–C(3)	1.507(7)	C(5)–C(6)	1.393(6)	N(1)–C(8)	1.453(5)	N(1) · · · O(2^{II})	3.009(4)
C(3)–H(3A)	0.93(4)	C(6)–C(7)	1.511(6)	C(8)–H(8A)	1.00(3)	H(N1) · · · O(2^{II})	2.32(3)

C(2)–C(1)–H(1A)	114(3)	H(3A)–C(3)–H(3B)	111(3)	H(7A)–C(7)–H(7C)	109(3)
C(2)–C(1)–H(1B)	108(4)	O(2)–C(4)–C(3)	116.6(4)	H(7B)–C(7)–H(7C)	108(4)
C(2)–C(1)–H(1C)	99(4)	O(2)–C(4)–C(5)	125.6(4)	C(6)–N(1)–C(8)	126.8(3)
H(1A)–C(1)–H(1B)	104(5)	C(3)–C(4)–C(5)	117.7(4)	C(6)–N(1)–H(N1)	113.6(20)
H(1A)–C(1)–H(1C)	113(5)	C(4)–C(5)–C(6)	122.9(4)	C(8)–N(1)–H(N1)	118.9(20)
H(1B)–C(1)–H(1C)	119(5)	C(4)–C(5)–H(5)	116.6(21)	N(1)–C(8)–C(8^{I})	111.1(3)
O(1)–C(2)–C(1)	120.5(5)	C(6)–C(5)–H(5)	120.4(21)	N(1)–C(8)–H(8A)	108.5(19)
O(1)–C(2)–C(3)	121.7(5)	N(1)–C(6)–C(5)	121.6(4)	N(1)–C(8)–H(8B)	108.5(20)
C(1)–C(2)–C(3)	117.9(5)	N(1)–C(6)–C(7)	119.4(4)	C(8^{I})–C(8)–H(8A)	107.5(19)
C(2)–C(3)–C(4)	108.8(4)	C(5)–C(6)–C(7)	119.0(4)	C(8^{I})–C(8)–H(8B)	111.2(20)
C(2)–C(3)–H(3A)	112.8(26)	C(6)–C(7)–H(7A)	113.9(22)	H(8A)–C(8)–H(8B)	110(3)
C(2)–C(3)–H(3B)	109.1(22)	C(6)–C(7)–H(7B)	102.8(24)	N(1)–H(N1) · · · O(2)	138(3)
C(4)–C(3)–H(3A)	103.5(25)	C(6)–C(7)–H(7C)	113.1(28)	N(1)–H(N1) · · · O(2^{II})	132(3)
C(4)–C(3)–H(3B)	111.5(22)	H(7A)–C(7)–H(7B)	109(3)	O(2) · · · H(N1) · · · O(2^{II})	89.1(12)

Symmetry transformations: I, $\frac{1}{2} - x, \frac{1}{2} - y, z$; II, $-x, -y, 1 - z$

Table 2. Bond lengths (Å) and angles (°), with estimated standard deviations, for (2)

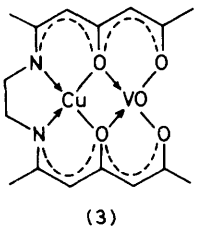
Cu(1)–O(2)	1.911(3)	O(2)–C(4)	1.290(5)	N(1)–C(8)	1.469(6)	O(3)–C(13)	1.290(5)
Cu(1)–O(3)	1.901(3)	C(3)–C(4)	1.523(6)	C(8)–C(9)	1.508(6)	C(12)–C(13)	1.372(6)
Cu(1)–N(1)	1.930(3)	C(4)–C(5)	1.366(6)	N(2)–C(9)	1.462(5)	C(13)–C(14)	1.513(7)
Cu(1)–N(2)	1.926(3)	C(5)–C(6)	1.417(6)	N(2)–C(11)	1.311(5)	C(14)–C(15)	1.450(7)
O(1)–C(2)	1.207(6)	C(6)–C(7)	1.507(6)	C(10)–C(11)	1.511(6)	O(4)–C(15)	1.234(6)
C(1)–C(2)	1.469(8)	N(1)–C(6)	1.301(5)	C(11)–C(12)	1.408(6)	C(15)–C(16)	1.495(8)
C(2)–C(3)	1.506(7)						

O(2)–Cu(1)–O(3)	87.41(12)	O(2)–C(4)–C(5)	126.1(4)	C(9)–N(2)–C(11)	121.4(3)
O(2)–Cu(1)–N(1)	93.40(13)	C(3)–C(4)–C(5)	119.1(4)	N(2)–C(11)–C(10)	120.6(4)
O(2)–Cu(1)–N(2)	171.34(13)	C(4)–C(5)–C(6)	125.9(4)	N(2)–C(11)–C(12)	122.0(4)
O(3)–Cu(1)–N(1)	172.74(13)	N(1)–C(6)–C(5)	122.0(4)	C(10)–C(11)–C(12)	117.3(4)
O(3)–Cu(1)–N(2)	94.01(13)	N(1)–C(6)–C(7)	121.5(4)	C(11)–C(12)–C(13)	126.3(4)
N(1)–Cu(1)–N(2)	86.27(13)	C(5)–C(6)–C(7)	116.5(4)	O(3)–C(13)–C(12)	125.8(4)
Cu(1)–O(2)–C(4)	125.3(3)	Cu(1)–N(1)–C(6)	127.1(3)	O(3)–C(13)–C(14)	114.2(4)
Cu(1)–O(3)–C(13)	125.4(3)	Cu(1)–N(1)–C(8)	110.9(3)	C(12)–C(13)–C(14)	120.0(4)
O(1)–C(2)–C(1)	123.4(5)	C(6)–N(1)–C(8)	121.9(3)	C(13)–C(14)–C(15)	117.1(4)
O(1)–C(2)–C(3)	118.5(4)	N(1)–C(8)–C(9)	109.3(4)	O(4)–C(15)–C(14)	121.8(5)
C(1)–C(2)–C(3)	118.1(4)	N(2)–C(9)–C(8)	109.1(3)	O(4)–C(15)–C(16)	122.4(5)
C(2)–C(3)–C(4)	111.8(4)	Cu(1)–N(2)–C(9)	111.9(3)	C(14)–C(15)–C(16)	115.8(5)
O(2)–C(4)–C(3)	114.8(4)	Cu(1)–N(2)–C(11)	126.5(3)		

N,*N*′-ethylenebis(acetylacetoniminate)], which has a square-planar co-ordinated copper(II) in a N_2O_2 donor site.[3]

The crystal structure of the copper complex shows the metal to be co-ordinated in the inner N_2O_2 site, the β-diketone chains which define the outer compartment again adopt keto tautomeric forms with the keto-groups twisted about the single carbon–carbon bond away from the potential co-ordination site. This conformation is in contrast to that found in copper complexes of related ligands in which the donor atoms which would form the outer compartment derive from phenolic [1,4] or pyrrole [5] residues. In these complexes, no such tautomerism is possible and the N_2O_2 monometallic complex adopts a conformation in which the shape of the outer compartment is essentially retained, but is empty. There is a small tetrahedral distortion (10.9°) in the co-ordination polyhedron of the copper (similar to that found in the complexes cited above [1,4,5]) and a reduction in the carbon–carbon torsion angle of the di-iminoethane fragments. The sites above and below the copper atom are blocked by atoms H(9A) and H(16B) of symmetry related molecules at distances of 3.18 and 3.19 Å respectively. There is no dimerisation as has been found in the mononuclear copper(II) complex [5,10-dimethyl-1,14-diphenyl-6,9-diazatetradeca-4,10-diene-1,3,12,14-tetraonato(2−)-O^1,O^3,O^{12},O^{14}]copper(II), in which the copper(II) is in the outer compartment.[6]

A particularly illuminating feature of these two molecules, when taken together, and particularly when compared also with the structure of a related bimetallic complex (3),[7] is



(3)

the conformational change which occurs in a potentially binucleating ligand on progressive complexation. The change

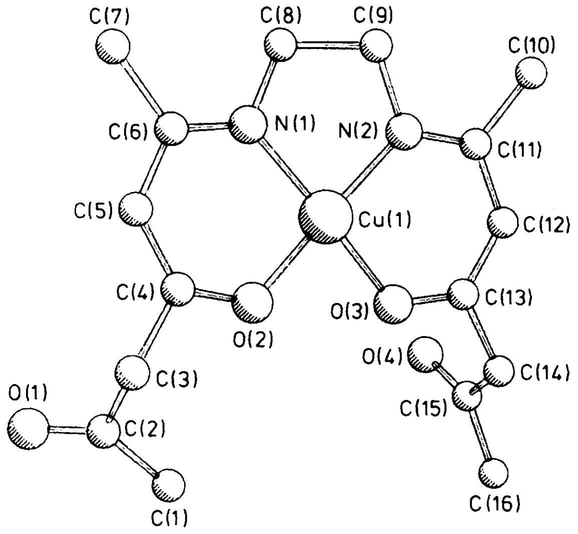


Figure 2. Molecular Structure of (2) showing the atom labelling

Table 3. Details of planar fragments of (1). Equations of least-squares planes are in the form $pX + qY + rZ = d$, where p, q, and r are direction cosines referred to orthogonal crystal axes a, b, and c. Deviations (Å) of atoms from mean planes are given in square brackets

		p	q	r	d
Plane A:	O(2), N(1),C(4)—C(6)				r.m.s. deviation 0.018 Å
		0.4510	−0.8363	0.3118	3.5001
	[O(2) 0.014, N(1) −0.001, C(4) −0.027, C(5) 0.024, C(6) −0.010, C(3) −0.235, C(7) −0.055, C(8) −0.239]				
Plane B:	O(1),C(1)—C(3)				r.m.s. deviation 0.002 Å
		0.1388	−0.3644	−0.9209	−6.3889
	[O(1) −0.002, C(1) −0.001, C(2) 0.004, C(3) −0.001, C(4) −1.392]				

Angle (°) between planes	A—B	85.4
Torsion angles (°)	N(1)–C(8)–C(8^1)–N(1^1)	−61.1
	C(2)–C(3)–C(4)–C(5)	−105.4
	C(2)–C(3)–C(4)–O(2)	+71.1

Table 4. Details of planar fragments of (2). Equations of least-squares planes are in 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 mean planes are given in square brackets

		p	q	r	d
Plane A:	O(2),O(3),N(1),N(2)				r.m.s. deviation 0.133 Å
		0.1945	−0.6821	0.7049	−0.8389
	[O(2) 0.133, O(3) −0.133, N(1) −0.133, N(2) 0.133, Cu(1) −0.011, O(1) −1.419, O(4) −2.574]				
Plane B:	Cu(1),O(2),N(1)				
		0.2872	−0.6668	0.6877	−0.4593
	[O(3) −0.239, N(2) 0.290, C(4) 0.074, C(5) 0.039, C(6) 0.003]				
Plane C:	Cu(1),O(3),N(2)				
		0.1004	−0.6926	0.7143	−1.2303
	[O(2) 0.284, N(1) −0.244, C(11) 0.064, C(12) 0.064, C(13) 0.023]				
Plane D:	O(2),N(1),C(4)—C(6)				r.m.s. deviation 0.018 Å
		0.3011	−0.6796	0.6689	−0.4105
	[O(2) −0.020, N(1) 0.015, C(4) 0.026, C(5) −0.008, C(6) −0.014, Cu(1) 0.029, C(3) 0.154, C(7) −0.029, C(8) −0.042]				
Plane E:	O(3),N(2),C(11)—C(13)				r.m.s. deviation 0.010 Å
		0.0903	−0.6694	0.7374	−1.3388
	[O(3) 0.010, N(2) −0.010, C(11) 0.011, C(12) −0.000, C(13) −0.011, Cu(1) 0.044, C(9) 0.062, C(10) 0.057, C(14) −0.066]				
Plane F:	O(1),C(1)—C(3)				r.m.s. deviation 0.002 Å
		−0.6107	−0.2159	0.7619	−0.2602
	[O(1) −0.001, C(1) −0.001, C(2) 0.003, C(3) −0.001, C(4) −1.398]				
Plane G:	O(4),C(14)—C(16)				r.m.s. deviation 0.009 Å
		−0.4787	0.5661	0.6711	−4.7257
	[O(4) −0.006, C(14) −0.005, C(15) 0.015, C(16) −0.005, C(13) 0.215]				

Angles (°) between planes	B–C	10.9
	B–D	1.5
	C–E	2.0
	D–F	61.8
	E–G	85.8
Torsion angles (°)	N(1)–C(8)–C(9)–N(2)	+38.7
	C(2)–C(3)–C(4)–C(5)	+110.9
	C(2)–C(3)–C(4)–O(2)	−70.0
	C(15)–C(14)–C(13)–C(12)	−98.5
	C(15)–C(14)–C(13)–O(3)	+81.0

can be most graphically described as a 'zipping up' of the ligand by the introduction of metal atoms, first in the inner (N_2O_2), then in the outer (O_2O_2) compartment, progressively reducing its degrees of freedom to permit the thermodynamic advantage of increased metal–ligand bond formation.

Experimental

The Schiff base and copper(II) complex were prepared by methods described in the literature.[2,8]

Crystal Data for (1).—$C_{16}H_{24}N_2O_4$, M = 308.38, orthorhombic, a = 7.627(4), b = 10.158(3), c = 22.099(8) Å, U = 1 712(1) Å^3, D_m = 1.21, Z = 4, D_c = 1.196 g cm^{-3}, space group *Pccn* (D_{2h}^{10}, no. 56), Mo-K_α radiation (λ = 0.710 69 Å), μ(Mo-K_α) = 0.81 cm^{-1}, F(000) = 664.

The ligand (1) crystallizes from ethanol–methanol as colourless bricks; a crystal of dimensions 0.15 × 0.23 × 0.55 mm was used for data collection. The data were collected and processed (666 independent reflections, absorption corrections not applied) as for the copper complex below. The structure was solved by multiple-solution direct methods and difference-Fourier techniques (hydrogen atoms). All atoms were refined by block-diagonal least-squares methods, with allowance for thermal anisotropy of non-hydrogen atoms to a final R = 0.0487. Table 5 lists atomic co-ordinates and estimated standard deviations.

Crystal Data for (2).—$C_{16}H_{22}CuN_2O_4$, M = 369.90, triclinic, a = 10.915(11), b = 8.689(10), c = 9.593(8) Å, α = 104.87(7), β = 89.66(3), γ = 106.342(11)°, U = 841.7(14) Å^3, D_m = 1.49, Z = 2, D_c = 1.460 g cm^{-3}, space group $P\bar{1}$

Table 5. Atomic co-ordinates with estimated standard deviations for (1) *

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
O(1)	−0.190 8(6)	−0.015 9(6)	0.307 0(2)	H(1A)	−0.091 2(72)	0.214 0(55)	0.276 8(24)
O(2)	0.054 4(4)	−0.037 2(3)	0.437 1(1)	H(1B)	0.068 1(85)	0.189 3(60)	0.317 2(27)
N(1)	0.283 1(4)	0.108 8(3)	0.500 7(2)	H(1C)	0.080 8(78)	0.125 4(58)	0.252 6(28)
C(1)	0.015 0(8)	0.150 3(6)	0.287 5(3)	H(3A)	0.059 9(55)	−0.157 8(39)	0.340 7(18)
C(2)	−0.039 3(7)	0.016 7(6)	0.308 7(2)	H(3B)	0.202 9(54)	−0.076 1(37)	0.302 8(17)
C(3)	0.101 1(7)	−0.073 7(5)	0.332 7(2)	H(5)	0.392 5(45)	0.038 8(34)	0.363 8(15)
C(4)	0.160 0(5)	−0.023 7(4)	0.395 0(2)	H(7A)	0.537 6(48)	0.274 2(35)	0.448 3(15)
C(5)	0.323 0(5)	0.039 5(4)	0.398 8(2)	H(7B)	0.600 7(56)	0.153 2(39)	0.409 4(19)
C(6)	0.378 1(5)	0.107 3(4)	0.450 2(2)	H(7C)	0.630 8(61)	0.154 8(46)	0.480 7(21)
C(7)	0.550 2(5)	0.180 9(4)	0.448 4(2)	H(8A)	0.285 5(47)	0.138 0(31)	0.590 7(15)
C(8)	0.311 7(5)	0.191 2(4)	0.553 5(2)	H(8B)	0.451 5(52)	0.223 4(37)	0.553 8(16)
H(N1)	0.182 1(41)	0.061 5(29)	0.498 0(15)				

* The hydrogen atoms are labelled according to the carbon atom to which they are attached; where several hydrogen atoms are attached to the same carbon atom, they are distinguished alphabetically. H(N1) is the hydrogen attached to the imino-nitrogen atom N(1).

Table 6. Atomic co-ordinates with estimated standard deviations for (2)

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Cu(1)	0.365 39(4)	0.071 15(6)	−0.161 06(5)	C(6)	0.515 1(4)	0.339 2(5)	0.075 9(4)
O(1)	0.093 7(4)	0.488 5(5)	0.179 6(5)	C(7)	0.638 5(4)	0.458 6(6)	0.153 1(5)
O(2)	0.248 7(2)	0.139 9(3)	−0.026 9(3)	C(8)	0.630 8(4)	0.226 5(5)	−0.122 1(5)
O(3)	0.220 3(3)	−0.066 9(4)	−0.286 8(3)	C(9)	0.615 7(4)	0.051 9(5)	−0.213 1(5)
O(4)	0.115 4(3)	−0.058 8(5)	−0.605 2(4)	C(10)	0.559 8(5)	−0.209 5(6)	−0.473 2(5)
N(1)	0.513 6(3)	0.231 6(4)	−0.047 2(3)	C(11)	0.456 4(4)	−0.142 9(5)	−0.397 1(4)
N(2)	0.484 7(3)	−0.020 3(4)	−0.278 8(3)	C(12)	0.329 9(4)	−0.218 3(5)	−0.458 1(4)
C(1)	−0.014 0(5)	0.233 9(7)	0.013 4(7)	C(13)	0.222 7(4)	−0.178 5(5)	−0.404 2(4)
C(2)	0.081 9(4)	0.342 1(5)	0.130 4(5)	C(14)	0.093 3(5)	−0.267 8(6)	−0.485 0(5)
C(3)	0.170 4(4)	0.266 3(6)	0.190 9(5)	C(15)	0.046 0(4)	−0.183 8(6)	−0.575 9(5)
C(4)	0.280 7(4)	0.250 3(5)	0.095 7(4)	C(16)	−0.089 4(5)	−0.262 9(8)	−0.637 2(7)
C(5)	0.401 7(4)	0.348 4(5)	0.145 7(4)				

(assumed and confirmed by the analysis), Mo-K_α radiation (λ = 0.710 69 Å), μ(Mo-K_α) = 13.19 cm^{-1}, F(000) = 386.

The complex (2) crystallises from chloroform as mauve, elongated plates; a crystal of dimensions 0.108 × 0.269 × 0.439 mm was used for data collection. Three-dimensional X-ray diffraction data were collected in the range $6.5 < 2\theta < 50°$ on a Stoe Stadi-2 diffractometer by the omega-scan method. 2 492 Independent reflections for which $I/\sigma(I) > 3.0$ were corrected for Lorentz and polarisation effects and for absorption. The structure was solved by standard Patterson and Fourier techniques and refined by block-diagonal least-squares methods. Hydrogen atoms were placed in calculated positions [C–H 0.96 Å, C–C–H(methyl) 111°]; their contributions were included in structure factor calculations (B = 6.0 Å^2) but no refinement of positional parameters was permitted. Refinement converged at R = 0.0395 with allowance for anisotropic thermal motion of all non-hydrogen atoms and for the anomalous scattering of copper. Table 6 lists the atomic co-ordinates with estimated standard deviations.

Scattering factors were taken from ref. 9; unit weights were used throughout the refinement. Computer programs used were MULTAN [10] and those of the Sheffield X-ray system.

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