

Table 4. Comparison of Mo—C distances (Å) with values calculated from the equation

$$l^2 = p^2 + r^2 - 2pr \cos 87^\circ \cos (20 + 72j)^\circ$$

<i>j</i>	<i>l</i> _{obs}	<i>l</i> _{calc}
0	2.311, 2.300	2.317
1	2.386, 2.371	2.370
2	2.407, 2.415	2.419
3	2.395, 2.393	2.398
4	2.366, 2.337	2.335

The different Mo—C distances for each C₅H₅ ring can be treated as a tilt of the ring plane so that the line joining the Mo atom to the C₅H₅ centroid is not perpendicular to the ring. If a metal atom is situated above a planar polygon circumscribed by a circle, the distance *l* from the metal *M* to any point *S* on the circle is given by:

$$l^2 = p^2 + r^2 - 2pr \cos \theta \cos \omega. \quad (1)$$

Here, *p* is the distance from *M* to the ring centre *O*, *r* is the radius of the circle, θ is the angle between *OM* and the plane of the circle, and ω is the angle *SOR*, *R* being the point on the circumference closest to the metal. If the polygon is regular *r* is simply related to the length of the polygon side and the angles ω appropriate to the *n* vertices will be given by $\omega = \Delta + j2\pi/n$, *j* = 0...(*n* - 1), where Δ will be 0° if the vertex *j* = 0 coincides with *R*. For an isolated (η -C₅H₅)Mo(NO) unit with mirror symmetry and longest Mo—C distance *trans* to NO Δ is 36° but when the metal atom is attached to other atoms in an unsymmetrical pattern Δ is expected to depart from this value. In the present case, Δ is *ca* 20° and θ *ca* 87°. For ring C(1...5) *p* is

2.053 and *r* is 1.191 Å, while for ring C(6...10) *p* is 2.051 and *r* is 1.174 Å; the mean values are *p* = 2.052 and *r* = 1.183 Å and with these values (1) reproduces the experimental Mo—C distances with a r.m.s. deviation of 0.013 Å (Table 4). The parameters *p*, *r*, θ and Δ may be of utility for the comparison of metal-cyclopentadienyl systems. Finally, we observe that a notable spread of Mo—C distances in a (η -C₅H₅)Mo system is associated with even a small tilt of the ring, values of $l_{\max} - l_{\min}$ for various values of θ being

θ	90	89	88	87	86	85°
$l_{\max} - l_{\min}$	0.00	0.03	0.07	0.10	0.13	0.16 Å.

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(1,5-Diazacyclooctane)dinitratocopper(II)

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Abstract. C₆H₁₄CuN₄O₆, [Cu(C₆H₁₄N₂)(NO₃)₂], *M_r* = 301.75, monoclinic, *P*2₁/*c*, *a* = 8.56 (2), *b* = 10.39 (5), *c* = 13.38 (5) Å, β = 78.52 (3)°, from diffractometer measurements (Mo *K* α radiation). *V* = 1167.8 Å³, *Z* = 4, *D_m* = 1.73, *D_c* = 1.72 Mg m⁻³, *F*(000) = 592, μ = 1.752 mm⁻¹. The ligand adopts a boat-chair conformation.

Introduction. Systematic absences (from precession photographs) *h*0*l*, *l* odd and 0*k*0, *k* odd indicated space

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group *P*2₁/*c*. Data were collected for *h*0–10*l* with θ_{\max} = 27.5° on a Stoe STADI-2 two-circle diffractometer (graphite-monochromated Mo *K* α radiation). This gave 2136 data of which 1711 unique reflexions with *I* > 3 σ (*I*) were used in subsequent calculations. Lorentz and polarization corrections (but none for extinction or absorption) were applied, and the data scaled by a Wilson plot. The structure was solved by direct methods with *SHELX* 76 (Sheldrick, 1976), which was used for all calculations. Complex neutral scattering © 1980 International Union of Crystallography

Table 1. Fractional atomic coordinates ($\times 10^4$) with e.s.d.'s in parentheses

	x	y	z
Cu(1)	-534 (1)	8662 (1)	2506 (0)
C(2)	-3373 (10)	7103 (9)	2844 (10)
C(3)	-3885 (16)	7971 (13)	3587 (8)
C(4)	-3679 (7)	9378 (10)	3603 (5)
C(6)	-2757 (10)	10330 (10)	1856 (8)
C(8)	-2520 (9)	8150 (14)	1077 (6)
C(7)	6612 (12)	9406 (12)	1309 (8)
N(1)	-2023 (6)	7483 (5)	2014 (5)
N(3)	2177 (6)	8285 (7)	1183 (4)
N(4)	1046 (6)	9096 (6)	4017 (4)
N(5)	-2327 (5)	9893 (5)	2819 (4)
O(1)	1342 (4)	7602 (4)	1891 (3)
O(2)	1577 (7)	9316 (6)	985 (4)
O(3)	3499 (5)	7884 (8)	770 (4)
O(4)	841 (5)	9723 (4)	3234 (3)
O(5)	299 (6)	8077 (6)	4199 (4)
O(6)	1908 (7)	9547 (7)	4554 (4)

Table 2. Anisotropic thermal parameters ($\times 10^3$, for Cu $\times 10^4$) with e.s.d.'s in parentheses

The expression for the temperature factor is

$$\exp[-2\pi^2(h^2 a^{*2} U_{11} + \dots + 2klb^* c^* U_{23} + \dots)].$$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cu(1)	257 (3)	284 (4)	394 (4)	13 (3)	-32 (2)	-6 (3)
C(2)	69 (5)	75 (6)	212 (11)	6 (7)	18 (6)	-29 (4)
C(3)	181 (11)	138 (10)	103 (7)	30 (7)	57 (7)	-64 (9)
C(4)	45 (3)	136 (7)	71 (4)	-44 (5)	9 (3)	-6 (4)
C(6)	100 (6)	89 (6)	129 (8)	19 (6)	-36 (6)	33 (5)
C(8)	68 (4)	290 (13)	65 (4)	-92 (6)	-36 (3)	68 (6)
C(7)	139 (8)	139 (9)	102 (7)	61 (7)	-52 (6)	-21 (7)
N(1)	48 (3)	68 (4)	110 (5)	-38 (3)	-12 (13)	-2 (3)
N(3)	49 (3)	88 (4)	69 (3)	-8 (3)	9 (2)	-10 (3)
N(4)	62 (3)	72 (4)	66 (3)	-3 (3)	-24 (2)	5 (3)
N(5)	41 (2)	57 (3)	87 (3)	-18 (3)	-7 (2)	7 (2)
O(1)	49 (2)	57 (3)	76 (3)	-2 (2)	5 (2)	11 (2)
O(2)	107 (4)	79 (4)	87 (4)	28 (3)	14 (3)	-5 (3)
O(3)	48 (3)	179 (7)	120 (4)	-35 (5)	26 (3)	-6 (3)
O(4)	61 (2)	55 (3)	70 (3)	3 (2)	-21 (2)	-8 (2)
O(5)	95 (4)	76 (3)	78 (3)	23 (3)	-11 (3)	-6 (3)
O(6)	100 (4)	138 (5)	113 (4)	-18 (4)	-66 (4)	1 (4)

factors were taken from *International Tables for X-ray Crystallography* (1974). Weighted full-matrix least-squares refinement (excluding H atoms) converged at $R = 0.0517$ for 1711 observed reflexions ($R = \sum |F_o| - |F_c| / \sum |F_o|$); $R_w = 0.0577$ ($R_w = \sum (|F_o| - |F_c|) w^{1/2} / \sum (|F_o| w^{1/2})$, $w = 2.689 / [\sigma^2(F_o) + 0.000866F_o^2]$). In the final cycle all shifts in parameters were less than their e.s.d.'s. Positional parameters are given in Table 1, anisotropic thermal parameters in Table 2, bond distances and angles in Table 3,* and selected torsion angles in Table 4. Fig. 1 shows a general view of the molecule.

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34888 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Bond distances (Å) and angles ($^\circ$) with e.s.d.'s in parentheses

Cu(1)-N(1)	1.975 (5)	C(6)-C(7)	1.381 (14)
Cu(1)-N(5)	1.979 (4)	C(6)-N(5)	1.480 (9)
Cu(1)-O(1)	1.987 (4)	C(7)-C(8)	1.504 (16)
Cu(1)-O(2)	2.532 (4)	C(8)-N(1)	1.565 (11)
Cu(1)-O(4)	2.003 (4)	N(3)-O(1)	1.282 (6)
Cu(1)-O(5)	2.579 (4)	N(3)-O(2)	1.240 (8)
C(2)-C(3)	1.350 (14)	N(3)-O(3)	1.230 (7)
C(2)-N(1)	1.488 (10)	N(4)-O(4)	1.276 (6)
C(3)-C(4)	1.473 (15)	N(4)-O(5)	1.236 (7)
C(4)-N(5)	1.498 (8)	N(4)-O(6)	1.222 (6)
N(5)-Cu(1)-N(1)	86.9 (2)	N(5)-C(6)-C(7)	116.1 (8)
O(1)-Cu(1)-N(1)	92.3 (2)	N(1)-C(8)-C(7)	114.9 (5)
O(1)-Cu(1)-N(5)	167.4 (2)	C(8)-C(7)-C(6)	118.9 (8)
O(2)-Cu(1)-N(1)	107.7 (2)	C(2)-N(1)-Cu(1)	111.9 (5)
O(2)-Cu(1)-N(5)	113.4 (2)	C(8)-N(1)-Cu(1)	106.8 (6)
O(2)-Cu(1)-O(1)	55.0 (2)	C(8)-N(1)-C(2)	114.9 (6)
O(4)-Cu(1)-N(1)	170.4 (2)	O(2)-N(3)-O(1)	116.3 (5)
O(4)-Cu(1)-N(5)	92.8 (2)	O(3)-N(3)-O(1)	118.2 (7)
O(4)-Cu(1)-O(1)	90.1 (2)	O(3)-N(3)-O(2)	125.5 (6)
O(4)-Cu(1)-O(2)	81.3 (2)	O(5)-N(4)-O(4)	116.7 (5)
O(4)-Cu(1)-O(5)	53.9 (2)	O(6)-N(4)-O(4)	119.0 (6)
O(5)-Cu(1)-O(1)	83.7 (2)	O(6)-N(4)-O(5)	124.3 (6)
O(5)-Cu(1)-O(2)	119.4 (2)	C(4)-N(5)-Cu(1)	112.2 (5)
O(5)-Cu(1)-N(1)	117.2 (2)	C(6)-N(5)-Cu(1)	109.4 (4)
O(5)-Cu(1)-N(5)	107.8 (2)	C(6)-N(5)-C(4)	115.3 (5)
N(1)-C(2)-C(3)	117.6 (7)	N(3)-O(1)-Cu(1)	106.6 (4)
C(4)-C(3)-C(2)	130.7 (7)	N(3)-O(2)-Cu(1)	81.8 (3)
N(5)-C(4)-C(3)	115.0 (6)	N(4)-O(4)-Cu(1)	108.0 (3)

Table 4. Torsion angles ($^\circ$) in the bicyclic system (e.s.d.'s ca 0.7 $^\circ$)

N(5)-Cu(1)-N(1)-C(2)	-62.9
N(5)-Cu(1)-N(1)-C(7)	63.6
N(1)-Cu(1)-N(5)-C(4)	62.3
N(1)-Cu(1)-N(5)-C(6)	-66.8
N(1)-C(2)-C(3)-C(4)	20.1
C(3)-C(2)-N(1)-Cu(1)	32.0
C(3)-C(2)-N(1)-C(8)	-89.9
C(2)-C(3)-C(4)-N(5)	-20.3
C(3)-C(4)-N(5)-Cu(1)	-31.7
C(3)-C(4)-N(5)-C(6)	94.2
N(5)-C(6)-C(7)-C(8)	-50.7
C(7)-C(6)-N(5)-Cu(1)	66.5
C(7)-C(6)-N(5)-C(4)	-60.9
N(1)-C(8)-C(7)-C(6)	49.3
C(7)-C(8)-N(1)-Cu(1)	-62.3
C(7)-C(8)-N(1)-C(2)	62.4

Discussion. The structure determination was undertaken as part of a study of the structures of macrocyclic ligands and their complexes (Clay, Murray-Rust & Murray-Rust, 1979). The intention was to prepare a Cu^{II} complex of the sixteen-membered tetradentate macrocycle (I) which had been prepared by a variant of a published method (Richman & Atkins, 1967). A complex of Cu^{II} with what was presumed to be (I) was made but the present structure analysis has shown this to be (II), where the ligand is only half the size. [Sub-

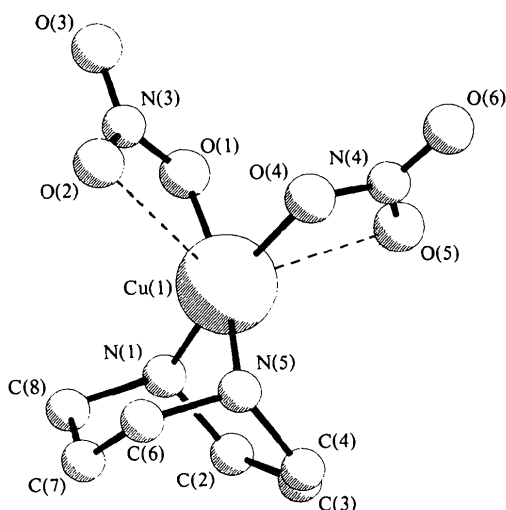
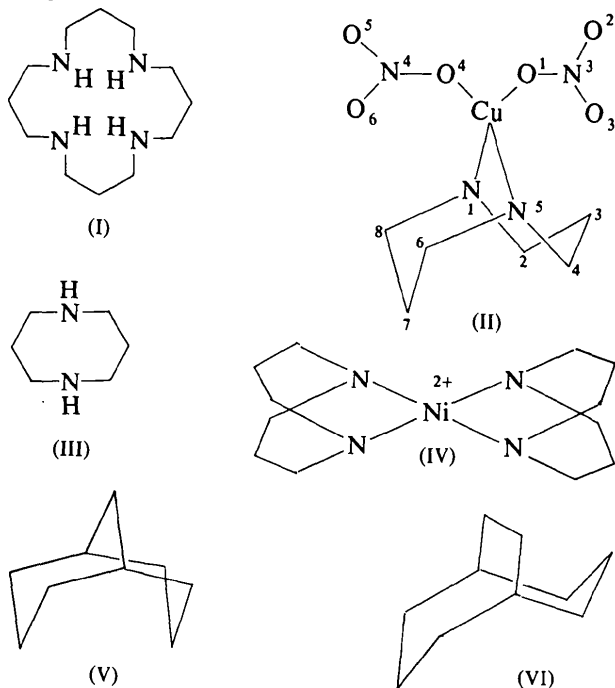


Fig. 1. General view of the molecule.

sequent analysis of the starting material showed it to be 1,5-diazacyclooctane (III) (daco) and that an unexpected ring contraction had taken place in the attempted preparation of (I). Full details of this and the subsequent preparation of metal complexes of (I) will be given elsewhere.]



The structure shows interesting features of the coordination geometry of daco. Formally the Cu(daco) fragment is a bicyclo[3.3.1]nonane system and, like the parent hydrocarbon (V), might be expected to take up a twin-chair conformation (Osing, Mastyukov, Vilkov & Belikova, 1976). In (II), however, the C(3) ring is a shallow boat (see torsion angles, Table 4) whilst the C(7) ring is a somewhat flattened chair. A better analogy may thus be bicyclo[3.3.2]-decane (VI), where the boat-chair arrangement has been found (Murray-Rust & Murray-Rust, 1975) and where the distance between the bridgehead atoms is closer to that in (II). However, the temperature factors of most of the bridge atoms in (II) are markedly anisotropic, suggesting disorder and probably some flexibility in the ligand. In a related structure (IV), the propylene bridges were apparently planar [*i.e.* the rings had sofa conformations (Royer, Schievelbein, Kalyanaraman & Bertrand, 1972)] but the temperature factors were high and the atomic positions were of low accuracy. [In both (II) and (IV) bond angles of over 130° at C(3) were found and these are probably partly crystallographic artefacts since the degree of angle strain suggested would be considerable. It is more likely that one or both rings flap considerably or that (IV) contains two disordered boat-chairs.]

The four major ligand atoms around Cu form a rough square plane [N(1), N(5), O(1), O(4)] with slight distortion towards a tetrahedral arrangement; weak bidentate coordination of the nitrate groups [O(2), O(5)] completes a distorted octahedron.

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