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Folding onto Copper(II) of a Flexible Bis-Chelating 4-Acyl-pyrazol-5-olate

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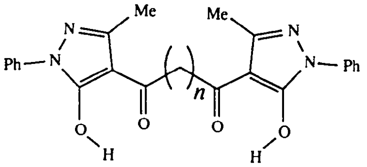
Abstract

The structure of {1,10-bis[5-(hydroxy-κ*O*)-3-methyl-1-phenyl-4-pyrazolyl]decane-1,10-dionato(2−)-$\kappa^2O^{1,10}$}-copper(II), $[Cu(C_{30}H_{32}N_4O_4)]$, has been determined. It consists of two types of $[Cu\{L-(CH_2)_8-L\}]$ mononuclear unit (H*L* = 5-hydroxy-3-methyl-1-phenyl-4-pyrazoloyl functional group), characterized by different conformations of the polymethylene chain. Both molecules contain a Cu atom in an almost square-planar environment of O atoms [1.907 (8) < Cu—O < 1.939 (8) Å]. All acylpyrazolonate moieties are planar within experimental error. The phenyl rings make angles in the range 2–28° with the corresponding pyrazole planes. In the first type of $[Cu\{L-(CH_2)_8-L\}]$ moiety (1), the two chelating subunits and the metal plane adopt a stepped conformation, whereas in the second $[Cu\{L-(CH_2)_8-L\}]$ moiety (2), one of the two chelating subunits and the metal plane are coplanar. The mononuclear units form centrosymmetric dimers (1,1′) and (2,2′), in which the Cu atoms may be viewed as five-coordinate [Cu···O′ = 2.546 (8) and 2.463 (9) Å, respectively, in (1,1′) and (2,2′)].

Comment

4-Acylpyrazol-5-ones are dissymmetric β-diketones which have been used extensively as metal extractants (see, *e.g.* Zolotov & Kuz'min, 1977; Lakkis, Lakkis, Goetz-Grandmont & Brunette, 1991, and references therein). Bis(acylpyrazolones) in which the chelating subunits are separated by polymethylene spacers, $HL-(CH_2)_n-LH$, are currently being investigated in view of their coordination and extracting properties (see, *e.g.* Li & Yang, 1992; Miyazaki, Mukai, Umetani, Kihara & Matsui, 1989; Diantouba, Guiguemde, Tayeb, Goetz-Grandmont & Brunette, 1994, and references therein). They may act as bis-chelating ligands folded onto a metallic centre, as bridging bis-chelatants or as mono-chelatants. From the study of copper extraction by a series of such extractants with various polymethylene chain lengths (n = 0–8, 10, 20), Miyazaki *et al.* (1992) showed that monomeric $[Cu\{L-(CH_2)_n-L\}]$ complexes were extracted for $n \geq 8$, while dimeric ones were extracted for $n < 8$. It was assumed that the octamethylene chain was just long enough to allow the ligand to fold onto the metal without significant strain. In this paper, the first X-ray structural characterization of such a $[Cu\{L-(CH_2)_n-L\}]$ complex is reported.



$HL-(CH_2)_n-LH$

The X-ray study reveals that the solid-state structure consists of the juxtaposition of two isomers, (1) and (2), mainly differing in the conformation of the C_8 chains. Isomers (1) and (2) are shown in Figs. 1 and 2, respectively. In each isomer the environment of the Cu atom deviates slightly from an ideal square-planar geometry: the CuO_4 units are bent along O1–O3 [O2—Cu1—O4 = 172.5 (3)°] in (1) and along O12–O14 [O11—Cu2—O13 = 172.4 (6)°] in (2). The Cu—O distances and ligand bite angles lie in the range usually found for copper β-diketonate complexes (see, *e.g.* Mehrotra, Bohra & Gaur, 1978, and references therein; Tobon-Cervantes, Toscano, Rosales, Fernandez-G. & Bernal-Uruchurtu, 1988; Baxter, Blake, Gould, Heath & Stephenson, 1993). In molecule (1) both metallacycles are folded along a line through the O atoms, corresponding to a stepped geometry, while in molecule (2) only one chelate unit is folded, so that a 'deck chair'-shaped structure is observed (Fig. 3). All pyrazole rings are planar within experimental error and the bond lengths in these heterocycles are consistent with their aromaticity. The O atoms of the acyl fragments do not lie significantly out of the corresponding pyrazole planes. Three of the *N*-phenyl rings are almost parallel to the corresponding pyrazole plane (dihedral angles < 9°). For the fourth phenyl group [C47–C52, belonging to (2)], the conjugation with the pyrazole ring appears to be lower (dihedral angle *ca* 28°). The particular orientation of this latter phenyl group is likely to favour a weak offset face-to-face stacking interaction with the pyrazole ring (N1,N2...C16) of a neighbouring molecule of type (1) (distance between the barycentres/angle between the rings: 3.74 Å/14°).

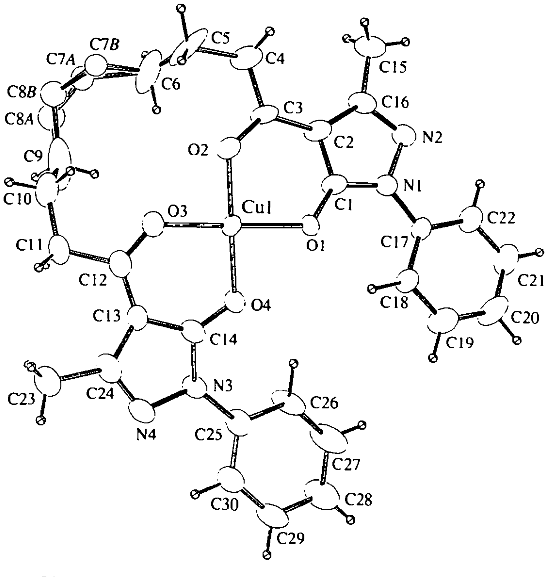


Fig. 1. *ORTEP* (Johnson, 1965) diagram of the mononuclear unit (1).

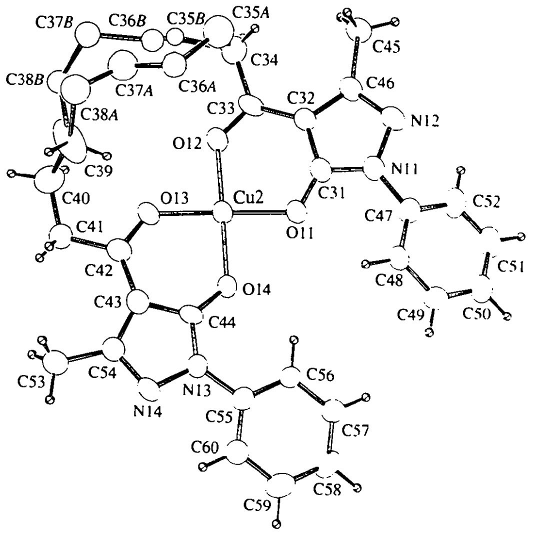
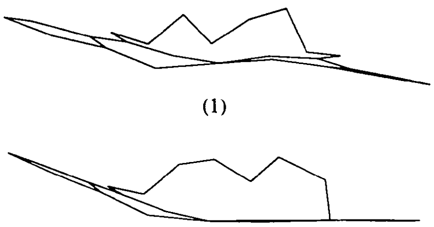
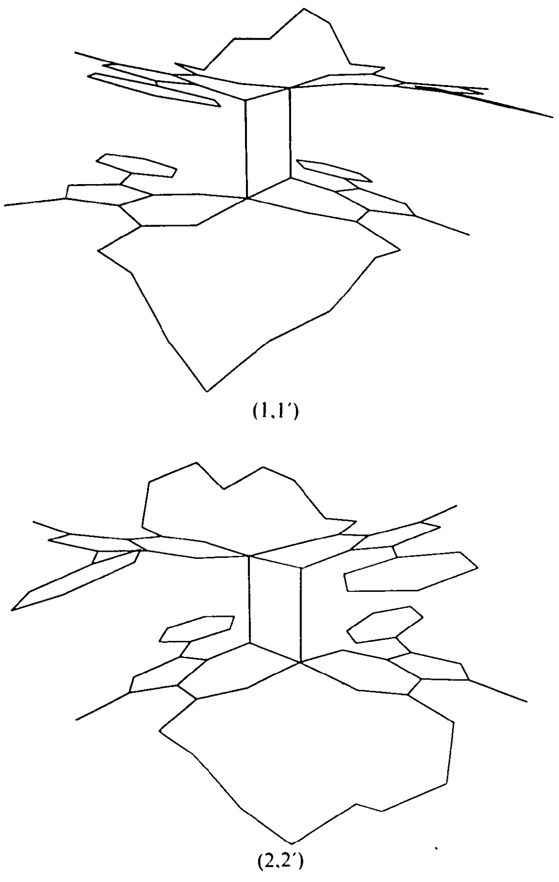


Fig. 2. *ORTEP* (Johnson, 1965) diagram of the mononuclear unit (2).


(1)

(2)

Fig. 3. A side-view of the [Cu{*L*–(CH$_2$)$_8$–*L*}] units; the methyl and phenyl substituents have been omitted to show the polymethylene chains and chelate conformations.

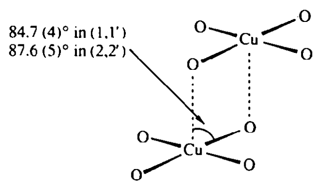

(1,1′)

(2,2′)

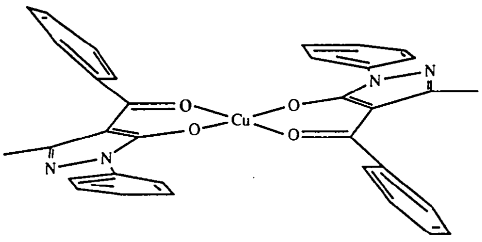
Fig. 4. The dimers (1,1′) and (2,2′).

The other phenyl [C55–C60 in (2)] and pyrazole [N3,N4...C14 in (1)] groups of the same molecules interact in the same manner (3.72 Å/12°). In molecule (1), the C7 and C8 atoms are disordered over two positions, while in molecule (2) a similar disorder is observed for the four methylene groups C35–C38.

Molecules (1) and (2) each interact with their centrosymmetric counterpart to form a weakly bound pair of monomers involving two O (pyrazolone) bridging atoms, O1, O1′ in (1,1′) and O14, O14′ in (2,2′) (Fig. 4). These O atoms lie almost apically to the Cu atoms, so that the latter may be regarded as having a square-pyramidal environment.



The Cu···O′ distances are 2.546 (8) Å in (1,1′) and 2.463 (9) Å in (2,2′). Dimerization of this type, with comparable Cu···O′ distances (2.38–2.94 Å), has been observed frequently in Cu^{II} complexes with Schiff bases (Maslen & Waters, 1975). Interestingly, to our knowledge, it has not yet been observed for copper β-diketonates, and it particularly does not occur for the related complex *trans*-Cu(PMBP)$_2$ (Miao, Liu & Li, 1991).



Cu(PMBP)$_2$

The tendency of the Cu atoms to adopt five-coordinate geometries in acylpyrazolonates could arise from the presence of the pyrazole groups, which act as very strong electron-withdrawing moieties thus making the metal centre somewhat electron deficient. It is likely that the formation of (1,1′) and (2,2′) dimers is made possible by the presence of sterically non-demanding acyl substituents, allowing the approach of two CuO$_4$ monomers. Moreover, the *cis* arrangement of the two chelating moieties might favour some stacking interaction in the dimers [distances between the barycentres of the interacting pyrazole rings: *ca* 2.96 and 3.96 Å, in (1,1′) and (2,2′), respectively]. These two criteria cannot be implemented for Cu(PMBP)$_2$.

The existence of [Cu{*L*–(CH$_2$)$_8$–*L*}] molecules in which one ligand acts as a tetradentate bis-chelatant, folded onto the Cu atom, agrees with the conclusions drawn from studies of liquid–liquid extraction processes. This structural study obviously shows that the octamethylene chain is not strained and that, in organic solution, it might induce some hindrance to further axial coordination of bulky electron donors. This might explain why tri-*n*-octylphosphine (TOPO) acts as a synergist for the extraction of copper with HPMBP, through the formation of a Cu(PMBP)$_2$.TOPO complex, while it has no effect upon the extraction of the same metal with H*L*–(CH$_2$)$_8$–*L*H.

Experimental

100 ml of a chloroform solution of H*L*–(CH$_2$)$_8$–*L*H (0.515 g, 1.0 mmol) was added to 100 ml of an aqueous nitric acid solution of copper [Cu(NO$_3$)$_2$.3H$_2$O: 0.483 g, 2.0 mmol; HNO$_3$, pH *ca* 1.5] under vigorous stirring. The pH of the solution was controlled with a glass electrode. Small aliquots of an aqueous NaOH (0.1 *M*) solution were added. After each addition, the system was left under stirring to allow cation exchange to occur, until the pH remained unchanged. Care was taken that the pH never exceeded 3.5 to prevent any precipitation of Cu(OH)$_2$. The final pH was 3.3. The phases were separated by gravity and the chloroformic extract was collected. 25 ml of hexane was added to this solution and the complex was allowed to precipitate in a refrigerator (*ca* 278 K). The complex was filtered off, washed with a chloroform–hexane mixture and then dried at 313 K *in vacuo*. Recrystallization from CHCl$_3$–hexane gave the complex as green microcrystals (0.270 g, 47%). Suitable crystals for X-ray analysis were obtained by slow evaporation of a CHCl$_3$ solution of the complex; m.p. > 493 K. Analysis for CuC$_{23}$H$_{32}$N$_4$O$_4$ (calculated/found %): C 62.59/61.67, H 5.61/5.65, N 9.74/9.70. MS (CI), *m*/*z* (%): 575 (100) M^-. IR (KBr) (cm^{-1}): 1604 [$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{O})$, chelate], 1592 [$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{C})$, phenyl], 1577 and 1492 [$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N})$, pyrazole, and $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{C}\overset{\cdots}{-}\mathrm{C})$, chelate]. A single air-stable crystal was used for data collection.

Crystal data

[Cu(C$_{30}$H$_{32}$N$_4$O$_4$)]
$M_r = 576.2$
Triclinic
$P\overline{1}$
$a = 12.955$ (4) Å
$b = 14.217$ (6) Å
$c = 16.494$ (9) Å
$\alpha = 98.82$ (5)°
$\beta = 112.57$ (5)°
$\gamma = 101.15$ (3)°
$V = 2664$ (2) Å^3
$Z = 4$
$D_x = 1.436$ Mg m^{-3}

Mo *Kα* radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 1$–25°
$\mu = 0.862$ mm^{-1}
$T = 120$ K
Plate
0.35 × 0.25 × 0.05 mm
Dark green

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
8749 measured reflections
4218 independent reflections
4218 observed reflections [$I > 3\sigma(I)$]

$R_{\rm int} = 0.037$
$\theta_{\rm max} = 25°$
$h = 0 \rightarrow 14$
$k = -15 \rightarrow 15$
$l = -17 \rightarrow 17$
3 standard reflections
frequency: 60 min
intensity variation: 0.4%

Refinement

Refinement on *F*
$R = 0.082$
$wR = 0.072$
$S = 2.841$
4218 reflections
698 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(I) + (0.04F_o^2)^2]$

$(\Delta/\sigma)_{\rm max} = 0.21$
$\Delta\rho_{\rm max} = 0.36$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.10$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters* (Å^2)

$B_{\rm iso}$ for disordered atoms*; $B_{\rm eq} = (4/3)\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j$ for others.

	x	*y*	*z*	$B_{\rm iso}/B_{\rm eq}$
Cu1	−0.07878 (9)	−0.08622 (8)	−0.09760 (8)	1.79 (2)
O1	−0.1210 (5)	0.0161 (5)	−0.0355 (4)	2.0 (1)
O2	−0.1261 (5)	−0.1805 (5)	−0.0387 (4)	2.3 (2)
O3	−0.0430 (5)	−0.1918 (5)	−0.1621 (4)	2.6 (2)
O4	−0.0520 (5)	0.0021 (5)	−0.1680 (4)	2.4 (2)
N1	−0.2486 (6)	0.0562 (2)	0.0226 (5)	2.1 (2)

N2	−0.3193 (6)	0.0137 (6)	0.0610 (5)	2.3 (2)
N3	0.0430 (6)	0.0534 (6)	−0.2551 (5)	2.2 (2)
N4	0.1031 (6)	0.0170 (7)	−0.3031 (5)	2.7 (2)
C1	−0.1941 (7)	−0.0080 (7)	−0.0036 (6)	1.8 (2)
C2	−0.2321 (7)	−0.0970 (7)	0.0186 (6)	1.8 (2)
C3	−0.1957 (7)	−0.1814 (7)	−0.0007 (7)	2.4 (2)
C4	−0.2374 (9)	−0.2763 (8)	0.0209 (8)	3.7 (3)
C5	−0.1771 (9)	−0.3542 (8)	0.003 (1)	6.6 (4)
C6	−0.215 (1)	−0.403 (1)	−0.092 (1)	7.3 (5)
C7*A**	−0.161 (2)	−0.479 (2)	−0.142 (1)	2.9 (4)
C7*B**	−0.112 (2)	−0.452 (1)	−0.081 (1)	2.5 (4)
C8*A**	−0.193 (2)	−0.502 (2)	−0.246 (2)	3.8 (5)
C8*B**	−0.140 (2)	−0.500 (2)	−0.181 (1)	3.4 (5)
C9	−0.129 (1)	−0.420 (1)	−0.253 (1)	9.3 (5)
C10	−0.001 (1)	−0.3674 (9)	−0.2133 (9)	5.0 (3)
C11	0.0303 (9)	−0.2817 (8)	−0.2515 (7)	3.6 (3)
C12	0.0051 (8)	−0.1861 (8)	−0.2160 (7)	2.6 (3)
C13	0.0369 (8)	−0.0997 (7)	−0.2402 (7)	2.5 (2)
C14	0.0035 (8)	−0.0149 (8)	−0.2157 (6)	2.3 (2)
C15	−0.3704 (9)	−0.1409 (9)	0.0986 (7)	3.7 (3)
C16	−0.3070 (8)	−0.0782 (8)	0.0593 (7)	2.5 (2)
C17	−0.2478 (8)	0.1530 (7)	0.0106 (7)	2.3 (2)
C18	−0.1815 (8)	0.2003 (7)	−0.0283 (7)	2.9 (3)
C19	−0.187 (1)	0.2927 (9)	−0.0380 (9)	5.4 (3)
C20	−0.255 (1)	0.3425 (9)	−0.010 (1)	5.5 (4)
C21	−0.3207 (9)	0.2955 (9)	0.0283 (9)	4.3 (3)
C22	−0.3178 (8)	0.2007 (8)	0.0383 (7)	3.1 (3)
C23	0.157 (1)	−0.1313 (9)	−0.3362 (8)	4.3 (3)
C24	0.0981 (8)	−0.0735 (8)	−0.2921 (7)	2.8 (3)
C25	0.0301 (9)	0.1503 (8)	−0.2560 (7)	3.1 (3)
C26	−0.0397 (9)	0.1864 (8)	−0.2213 (7)	5.0 (3)
C27	−0.052 (1)	0.280 (1)	−0.226 (1)	9.3 (4)
C28	0.007 (1)	0.3381 (9)	−0.2624 (9)	7.9 (4)
C29	0.079 (1)	0.3031 (9)	−0.2955 (8)	4.8 (3)
C30	0.0894 (9)	0.2092 (8)	−0.2931 (7)	3.4 (3)
Cu2	−0.4367 (1)	−0.5424 (1)	−0.4156 (1)	6.09 (4)
O11	−0.4521 (7)	−0.4379 (6)	−0.3367 (5)	6.3 (2)
O12	−0.4927 (7)	−0.6438 (6)	−0.3664 (5)	5.9 (2)
O13	−0.4001 (7)	−0.6438 (6)	−0.4835 (5)	5.0 (2)
O14	−0.3721 (6)	−0.4409 (6)	−0.4616 (5)	5.1 (2)
N11	−0.4993 (8)	−0.3817 (7)	−0.2196 (6)	3.7 (2)
N12	−0.5415 (7)	−0.4189 (7)	−0.1605 (6)	3.2 (2)
N13	−0.2318 (9)	−0.3770 (7)	−0.5084 (7)	5.2 (3)
N14	−0.1631 (9)	−0.4119 (8)	−0.5486 (7)	5.9 (3)
C31	−0.488 (1)	−0.4556 (9)	−0.2781 (8)	4.1 (3)
C32	−0.5251 (9)	−0.5440 (8)	−0.2567 (7)	3.5 (3)
C33	−0.526 (1)	−0.6383 (9)	−0.3036 (7)	4.4 (3)
C34	−0.564 (1)	−0.7330 (9)	−0.2801 (8)	4.3 (3)
C35*A**	−0.472 (2)	−0.760 (2)	−0.232 (2)	5.2 (6)
C35*B**	−0.538 (1)	−0.829 (1)	−0.323 (1)	1.5 (3)
C36*A**	−0.376 (2)	−0.770 (2)	−0.269 (1)	3.1 (5)
C36*B**	−0.414 (2)	−0.834 (1)	−0.286 (1)	2.6 (4)
C37*A**	−0.427 (2)	−0.851 (2)	−0.354 (2)	4.7 (6)
C37*B**	−0.399 (2)	−0.927 (2)	−0.344 (1)	3.3 (5)
C38*A**	−0.333 (2)	−0.872 (2)	−0.382 (2)	4.6 (6)
C38*B**	−0.423 (2)	−0.924 (2)	−0.444 (1)	3.0 (4)
C39	−0.313 (1)	−0.821 (1)	−0.4361 (9)	8.2 (4)
C40	−0.362 (1)	−0.8181 (9)	−0.5351 (8)	4.1 (3)
C41	−0.306 (1)	−0.7284 (9)	−0.5555 (8)	4.7 (3)
C42	−0.331 (1)	−0.6340 (9)	−0.5201 (8)	4.9 (3)
C43	−0.276 (1)	−0.5409 (9)	−0.5268 (8)	5.5 (3)
C44	−0.300 (1)	−0.4523 (9)	−0.4954 (8)	5.3 (3)
C45	−0.5978 (8)	−0.5786 (8)	−0.1294 (7)	2.9 (3)
C46	−0.5573 (8)	−0.5167 (8)	−0.1840 (7)	2.9 (3)
C47	−0.4731 (8)	−0.2776 (8)	−0.2133 (7)	2.8 (3)
C48	−0.3902 (8)	−0.2316 (8)	−0.2375 (7)	2.8 (3)
C49	−0.3653 (9)	−0.1293 (8)	−0.2274 (7)	2.9 (3)
C50	−0.4272 (9)	−0.0757 (8)	−0.1951 (7)	3.2 (3)
C51	−0.5110 (9)	−0.1226 (8)	−0.1728 (7)	3.3 (3)
C52	−0.5344 (9)	−0.2234 (9)	−0.1810 (8)	3.8 (3)
C53	−0.133 (1)	−0.568 (1)	−0.603 (1)	7.9 (4)
C54	−0.194 (1)	−0.510 (1)	−0.5603 (9)	6.3 (3)
C55	−0.220 (1)	−0.2722 (8)	−0.4864 (7)	3.1 (3)
C56	−0.2765 (9)	−0.2336 (8)	−0.4399 (7)	3.1 (3)
C57	−0.2628 (8)	−0.1308 (8)	−0.4220 (7)	2.7 (3)
C58	−0.1950 (9)	−0.0710 (7)	−0.4513 (7)	2.9 (3)
C59	−0.137 (1)	−0.1121 (9)	−0.4965 (8)	3.7 (3)
C60	−0.149 (1)	−0.2127 (8)	−0.5139 (8)	3.8 (3)

Table 2. *Selected geometric parameters* (Å, °)

Atoms labelled with a prime (′) belong to the centrosymmetric counterpart in the (1,1′) or (2,2′) dimeric units.

Molecule (1)			
Cu1—O1	1.936 (7)	N1—C17	1.42 (1)
Cu1—O2	1.912 (8)	O3—C12	1.27 (1)
Cu1—O3	1.939 (8)	C12—C13	1.38 (2)
Cu1—O4	1.907 (8)	C13—C14	1.41 (2)
O1—C1	1.27 (1)	C14—O4	1.28 (1)
C1—C2	1.42 (1)	C14—N3	1.37 (1)
C2—C3	1.41 (2)	N3—N4	1.42 (1)
C3—O2	1.28 (1)	N4—C24	1.32 (1)
C1—N1	1.37 (1)	C24—C13	1.42 (2)
N1—N2	1.40 (1)	C24—C23	1.51 (2)
N2—C16	1.34 (1)	N3—C25	1.42 (2)
C16—C2	1.42 (2)	Cu1···O1′	2.546 (8)
C15—C16	1.48 (2)		
O1—Cu1—O2	92.3 (3)	C1—C2—C3	122 (1)
O2—Cu1—O3	86.6 (3)	Cu1—O4—C14	120.4 (7)
O3—Cu1—O4	93.3 (3)	Cu1—O3—C12	127.7 (8)
O4—Cu1—O1	87.5 (3)	O4—C14—C13	131 (1)
Cu1—O1—C1	119.5 (7)	O3—C12—C13	123 (1)
Cu1—O2—C3	129.5 (7)	C12—C13—C14	121 (1)
O1—C1—C2	131 (1)	O1—Cu1···O1′	84.7 (4)
O2—C3—C2	121 (1)		
O1—Cu1—O2—C3	21.0 (9)	N2—N1—C17—C22	0 (2)
O4—Cu1—O3—C12	13.0 (9)	N4—N3—C25—C30	−8 (2)
Molecule (2)			
Cu2—O11	1.914 (9)	N11—C47	1.43 (2)
Cu2—O12	1.91 (1)	O13—C42	1.25 (2)
Cu2—O13	1.932 (9)	C42—C43	1.42 (2)
Cu2—O14	1.928 (9)	C43—C44	1.42 (2)
O11—C31	1.26 (2)	C44—O14	1.28 (2)
C31—C32	1.40 (2)	C44—N13	1.35 (2)
C32—C33	1.44 (2)	N13—N14	1.41 (2)
C33—O12	1.26 (1)	N14—C54	1.34 (2)
C31—N11	1.38 (2)	C54—C43	1.41 (2)
N11—N12	1.41 (1)	C53—C54	1.51 (2)
N12—C46	1.34 (2)	N13—C55	1.44 (2)
C46—C32	1.44 (2)	Cu2···O14′	2.463 (9)
C45—C46	1.51 (2)		
O11—Cu2—O12	94.1 (4)	C31—C32—C33	122 (1)
O12—Cu2—O13	86.5 (4)	Cu2—O14—C44	121.5 (9)
O13—Cu2—O14	92.4 (4)	Cu2—O13—C42	128.8 (9)
O14—Cu2—O11	86.7 (4)	O14—C44—C43	129 (1)
Cu2—O11—C31	120.8 (9)	O13—C42—C43	123 (1)
Cu2—O12—C33	130.6 (9)	C42—C43—C44	122 (1)
O11—C31—C32	132 (1)	O14—Cu2···O14′	87.6 (5)
O12—C33—C32	120 (1)		
O11—Cu2—O12—C33	0 (2)	N12—N11—C47—C52	−28 (2)
O14—Cu2—O13—C42	17 (1)	N14—N13—C55—C60	6 (2)

Data collection was carried out using a scan width of $(1 + 0.35\tan\theta)^\circ$ and a variable scan rate with a maximum scan time of 60 s per reflection. After Lorentz and polarization corrections, the crystal structure was solved by direct methods (*MULTAN*11/82; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982), which revealed many non-H atoms of the molecule. The remaining atoms, in particular the C atoms of the disordered CH_2 chains of the two molecules of the asymmetric unit, were found after successive scale-factor and difference Fourier calculations. After isotropic (R = 0.12) then anisotropic refinement (R = 0.095), many H atoms were found with a difference Fourier synthesis (between 0.61 and 0.26 e Å^{-3}). The whole structure was refined by full-matrix least-squares techniques (use of F magnitude; x, y, z, β_{ij} for Cu, O, N and non-disordered C atoms; x, y, z, $B_{\rm iso}$ for disordered C atoms and fixed H atoms). The *MolEN* (Fair, 1990) package was used for all computations. The somewhat high final R value is mainly due to the disorder of the polymethylene chain.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HR1021). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Triruthenium Alkylidyne Cluster Complexes $[H_2Ru_3(CO)_9(\mu_3\text{-}CX)]$ (X = Pyridine, 4-Ethylpyridine)

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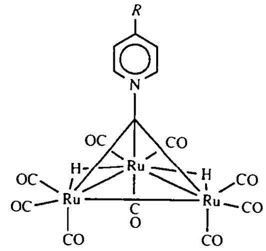
Abstract

Crystal structure analyses of nonacarbonyl-1κ^3C,2κ^3C,3κ^3C-di-μ-hydrido-1:2κ^2H;2:3κ^2H-μ_3-(pyrid-1-ylmethylidyne)-*triangulo*-triruthenium, $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-}C_6H_5N)(CO)_9]$, (I), and nonacarbonyl-1κ^3C,2κ^3C,3κ^3C-μ_3-[(4-ethylpyrid-1-yl)methylidyne]-di-μ-hydrido-1:2κ^2H;2:3κ^2H-*triangulo*-triruthenium, $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-}C_8H_9N)(CO)_9]$, (II), reveal that both compounds consist of a triruthenium alkylidyne core with the nucleophiles [pyridine in (I) and 4-ethylpyridine in (II)] bonded to the μ_3-bridging alkylidyne C atom.

Comment

This work is part of our structural and reactivity studies of triruthenium and triosmium alkylidyne carbonyl clusters. Several triosmium alkylidynes with the formula $[H_2Os_3(CO)_9(\mu_3\text{-}CY)]$ (Y = pyridine, quinoline or trimethyl phosphite) have been synthesized and fully characterized (Johnson, Lahoz, Lewis, Prior, Raithby & Wong, 1992). The title compounds, (I) and (II), have been prepared by a similar route.



(I) R = H
(II) R = Et

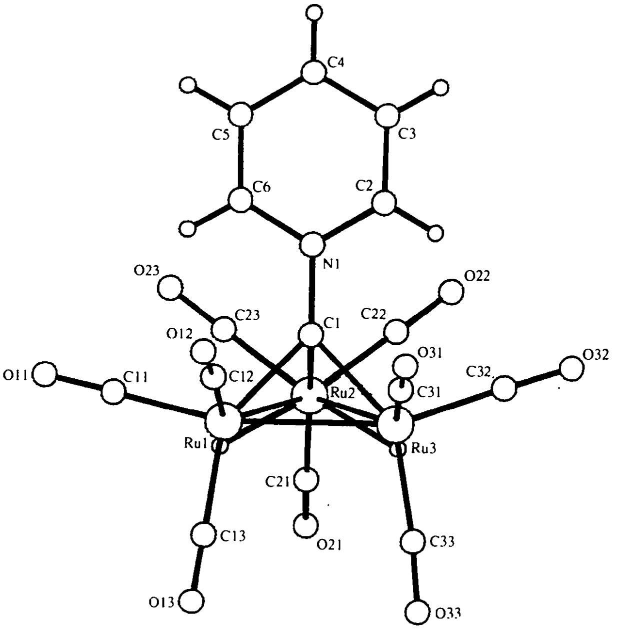


Fig. 1. The molecular structure of $[H_2Ru_3(CO)_9(\mu_3\text{-}Cpy)]$ (I).