

(Albano, Braga, Martinengo, Chini, Sansoni & Strumolo, 1980). The mean Cu—Ru distance for the four Cu atoms in the two independent clusters is 2.66 (6) Å compared with 2.65 (9) Å in  $(CH_3CN)_2Cu_2Ru_6C(CO)_{16}$ . The Ru—Ru bonds in the octahedral core fall into two groups. Those on the opposite copper-capped trigonal faces [Ru(1)—Ru(2), Ru(1)—Ru(3), Ru(2)—Ru(3) and Ru(4)—Ru(5), Ru(4)—Ru(6), Ru(5)—Ru(6)] have significantly longer bond lengths than the Ru—Ru distances between these faces [2.93 (2) Å as compared to 2.87 (2) Å]. This effect was difficult to identify in  $(CH_3CN)_2Cu_2Ru_6C(CO)_{16}$  because of the asymmetry of the cluster, where the range of Ru—Ru distances was wide (2.798–3.072 Å), with the long Ru—Ru bond (3.072 Å) associated with both Cu atoms. All 18 carbonyls on each cluster are essentially terminal with Ru—C—O angles ranging from 150–170°. This contrasts with the geometry of the starting material  $[Ru_6(CO)_{18}]^{2-}$  (Jackson, Johnson, Lewis, McPartlin & Nelson, 1979) which contains two  $\mu_2$ -bridging carbonyls and two  $\mu_3$ -bridging carbonyls. The toluene molecules on each of the four Cu atoms are disordered to some degree. This results in only Cu(1) and Cu(4) with the expected  $\mu_2$ -bonding mode usable in the refinement.

The difference between the structures of the two bimetallic clusters  $(CH_3CN)_2Cu_2Ru_6C(CO)_{16}$  and  $(C_6H_5CH_3)_2Cu_2Ru_6(CO)_{18}$  is striking. In both cases, the Ru atoms form an octahedral core. In the former

carbide-containing cluster the Cu atoms occupy adjacent positions on the  $Ru_6$  core, and are directly bonded to one another (Bradley *et al.*, 1982), whereas in the non-carbide analog, the two Cu atoms are found on opposite faces of the  $Ru_6$  octahedron. This may reflect the spatial constraints imposed by the presence of 18 carbonyls in the latter case, in comparison to the relatively flexible carbonyl configuration allowed in the former, where the local perturbation caused by the presence of two adjacent heterometal atoms is more easily accommodated.

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## Bis(2,6-dimethyl-4H-pyran-4-one)dinitratozinc, $[Zn(NO_3)_2(C_7H_8O_2)_2]$

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**Abstract.**  $M_r = 437.66$ , monoclinic,  $A2/a$ ,  $a = 16.786$  (8),  $b = 12.922$  (8),  $c = 9.089$  (4) Å,  $\beta = 106.80$  (4)°,  $V = 1887.34$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.540$ ,  $D_m = 1.536$  Mg m<sup>-3</sup>,  $\lambda(Cu K\alpha) = 1.5418$  Å,  $\mu = 2.38$  mm<sup>-1</sup>,  $F(000) = 896$ ,  $T = 293$  K. Final  $R = 0.043$  for 1500 observed visually estimated reflexions. The Zn atom lies on a twofold axis and coordinates tetrahedrally to two O atoms of the dimethyl-4-pyrone ligands, and to two O atoms of nitrate groups.

**Introduction.** The synthesis of the title compound was described originally by Hill (1971). Its properties have been studied by spectroscopic and other physical

methods (Briggs & Hill, 1969, 1970) and this work was undertaken to provide conclusive structural information particularly concerning the Zn coordination. Similar determinations have been concluded for the corresponding Cu and Cd complexes.

**Experimental.** Sample prepared by Dr A. E. Hill of this Polytechnic; slightly unstable crystals  $ca 0.5 \times 0.5 \times 0.1$  mm, m.p. 421 K, which decompose in air within a few weeks.  $D_m$  by flotation in organic liquids. Lattice parameters from high-angle reflexions on Weissenberg photographs; intensity data from  $0kl$ ,  $h0l \rightarrow h1l$ , and  $hk0$  levels on a Stoe integrating Weissenberg camera

using multiple films; visual estimation using calibrated scale: inter-layer scaling by common reflexions and comparison of Wilson plots; 1737 measured reflexions, 1500 considered observed with  $I > 3\sigma(I)$ , index range  $h -20 \rightarrow 20$ ,  $k 0 \rightarrow 11$ ,  $l 0 \rightarrow 11$ . Corrections made for  $L_p$  effects and an empirical absorption correction following the theory of Wells (1937), transmission factors 0.65–0.95. Structure solved from Patterson synthesis which gave Zn; Fourier synthesis using Zn phases gave all non-H atoms; refinement by least squares using initially  $B_{iso}$  and  $\sqrt{w} = 1/F_o$  and then  $B_{ij}$  until shifts  $< 0.5\sigma$ ; H atoms derived from difference Fourier map, but included in structure-factor calculations in calculated positions with  $B_{iso} = 7.0 \text{ \AA}^2$  without refining;  $R = 0.043$ ,  $wR = 0.053$ . Residual electron density in final difference map within  $\pm 0.2 e \text{ \AA}^{-3}$ . Atomic scattering factors from *International Tables for X-ray Crystallography* (1962). NRC programs (Ahmed, Hall, Pippy & Huber, 1970) implemented on the ICL 1905E computer at the London Polytechnics Computer Unit.

**Discussion.** The final positional and equivalent isotropic temperature parameters are given in Table 1.\* Numbering of the atoms and the arrangement of the molecules in the unit cell appear in Fig. 1. Bond lengths and inter-bond angles are given in Table 2.

Tetrahedral coordination is not common in Zn compounds. In this structure the tetrahedron is distorted as evinced by the angles subtended at Zn, two of which are  $118.81(9)$  and  $86.98(9)^\circ$ . The size of the coordination sphere is shown in Table 3 along with those of other tetrahedral Zn complexes.

The 2,6-dimethyl-4-pyrone ligands and the nitrate groups are both almost exactly planar, the mean distance of atoms out of the plane of atoms C(1)–C(7), O(1), O(2) being  $0.012(3) \text{ \AA}$ , and that for atoms N(1), O(3)–O(5) being  $0.002(2) \text{ \AA}$ . The angle between these two planes is  $76.89(5)^\circ$ .

\* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and the results of mean-plane calculations have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38992 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

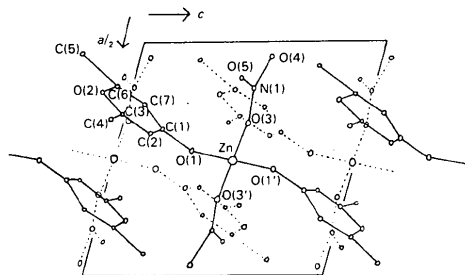


Fig. 1. Packing arrangement of molecules in the unit cell, showing the atomic numbering.

It is noteworthy that although the nitrate group appears to be unidentate with O(3)–Zn =  $2.037(2) \text{ \AA}$ , O(5) is  $2.684(3) \text{ \AA}$  from another Zn. This may be rather long for a bonded interaction but a similar distance has been observed in the pyridine complex (Cameron *et al.*, 1971) where O–Zn =  $2.75 \text{ \AA}$ .

Table 1. Final atomic parameters for the non-H atoms with e.s.d.'s in parentheses

Zn	x	y	z	$B_{eq}^*(\text{Å}^2)$
Zn	0.2500	0.6446 (<1)	0.5000	2.72 (<1)
C(1)	0.1862 (2)	0.5925 (2)	0.1762 (3)	2.67 (5)
C(2)	0.1763 (2)	0.7007 (3)	0.1322 (4)	3.84 (7)
C(3)	0.1409 (2)	0.7255 (2)	−0.0120 (3)	2.72 (6)
C(4)	0.1283 (2)	0.8349 (3)	−0.0714 (4)	4.07 (7)
C(5)	0.0758 (2)	0.4855 (3)	−0.2203 (4)	4.76 (8)
C(6)	0.1145 (2)	0.5524 (2)	−0.0857 (3)	3.07 (6)
C(7)	0.1515 (2)	0.5192 (3)	0.0595 (4)	3.43 (7)
N(1)	0.0985 (2)	0.7178 (2)	0.4996 (3)	4.26 (6)
O(1)	0.2221 (1)	0.5586 (2)	0.3118 (2)	3.05 (4)
O(2)	0.1087 (1)	0.6550 (2)	−0.1202 (2)	3.24 (4)
O(3)	0.1700 (1)	0.7590 (2)	0.5186 (2)	3.72 (5)
O(4)	0.0411 (2)	0.7776 (2)	0.5153 (3)	5.96 (6)
O(5)	0.0868 (2)	0.6269 (2)	0.4702 (3)	6.28 (7)

$$* B_{eq} = \frac{1}{3}(\beta_{11}/a^{*2} + \beta_{22}/b^{*2} + \beta_{33}/c^{*2}).$$

Table 2. Bond lengths (Å) and angles ( $^\circ$ )

Zn–O(1)	1.979 (2)	C(3)–C(4)	1.505 (4)
Zn–O(3)	2.037 (2)	C(3)–O(2)	1.336 (4)
O(1)–C(1)	1.282 (3)	C(5)–C(6)	1.486 (5)
C(1)–C(2)	1.450 (5)	C(6)–O(2)	1.359 (4)
C(1)–C(7)	1.417 (4)	N(1)–O(3)	1.277 (4)
C(2)–C(3)	1.312 (4)	N(1)–O(4)	1.276 (4)
C(7)–C(6)	1.355 (4)	N(1)–O(5)	1.208 (4)
O(1)–Zn–O(3)	118.8 (1)	C(5)–C(6)–C(7)	125.8 (3)
O(1)–Zn–O(1')	111.7 (1)	C(5)–C(6)–O(2)	113.1 (3)
O(1)–Zn–O(3')	109.4 (1)	C(7)–C(6)–O(2)	121.1 (3)
O(3)–Zn–O(3')	87.0 (1)	C(1)–C(7)–C(6)	119.4 (3)
C(2)–C(1)–C(7)	116.6 (3)	O(3)–N(1)–O(4)	116.3 (3)
O(3)–C(1)–O(1)	125.4 (3)	O(3)–N(1)–O(5)	121.5 (3)
C(2)–C(1)–O(1)	117.9 (3)	O(4)–N(1)–O(5)	122.2 (3)
C(7)–C(1)–O(1)	119.6 (3)	C(1)–O(1)–Zn	124.5 (2)
C(1)–C(2)–C(3)	124.3 (3)	C(3)–O(2)–C(6)	120.6 (2)
C(2)–C(3)–C(4)	122.6 (3)	N(1)–O(3)–Zn	107.6 (2)
C(2)–C(3)–O(2)	113.0 (3)		

O(1') and O(3') are twofold-axis-related to O(1) and O(3) respectively.

Table 3. Zn tetrahedral coordination

	$d(\text{Å})$	Reference
Bis(2,6-dimethyl-4-pyrone)-dinitratozinc	1.979 (2) 2.037 (2)	This work
Bis(thiourea)zinc acetate	1.973 (6) 1.954 (8)	Cavalca, Gasparri, Andreotti & Domiano (1967)
Tris(thiourea)zinc sulphate	1.975 (9)	Andreotti, Cavalca & Musatti (1968)
Dichlorobis(1,2-dihydro-1,5-dimethyl-2-phenyl-3H-pyrazol-3-one)zinc	1.997 (4) 2.019 (6)	Cingi, Guastini, Musatti & Nardelli (1972)
Dinitratobis(pyridine)zinc	2.044 (12) 2.047 (13)	Cameron, Taylor & Nuttall (1971)

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***cis*-1,1,2,2,3,4,4,5,5,6-Decamethyl-1,2,4,5-tetrastannacyclohexane, C<sub>12</sub>H<sub>32</sub>Sn<sub>4</sub>**

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**Abstract.**  $M_r = 651.1$ , monoclinic,  $P2_1/n$ ,  $a = 10.650(6)$ ,  $b = 12.313(6)$ ,  $c = 16.409(6)$  Å,  $\beta = 95.27(5)^\circ$ ,  $U = 2125(3)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 2.04$  Mg m<sup>-3</sup>, Mo K $\alpha$ ,  $\lambda = 0.71069$  Å,  $\mu = 4.7$  mm<sup>-1</sup>,  $F(000) = 1216$ ,  $T = 294(1)$  K, final  $R = 0.030$  for 2057 unique diffractometer data ( $F_o > 3\sigma$ ) and 148 refined parameters. The molecule is in the boat conformation. The Sn–Sn bond lengths are 2.775(2) and 2.766(2) Å.

**Introduction.** Although the structures of cyclohexane and its derivatives are well documented, relatively little is known about the structures of metallacyclohexanes. We have recently prepared a series of tetrastannacyclohexanes with methyl groups attached to tin (Mitchell & Fabisch, 1983), while Jurkschat & Gielen (1982) have described the preparation of a tetrastannacyclohexane with phenyl groups bonded to tin.

NMR spectroscopic studies indicate a possible change in ring geometry on replacing methylene protons on the ring carbons by methyl groups. In order to get more information regarding possible changes of ring conformation on the introduction of different substituents we decided to determine the crystal structure of 1,1,2,2,3,4,4,5,5,6-decamethyl-1,2,4,5-tetrastannacyclohexane; this is a particularly interesting molecule since it can in principle exist as the *cis* or *trans* isomer. However, its preparation leads to the formation of only one molecular species; <sup>13</sup>C NMR shows that the methyl groups on tin are non-equivalent, in contrast to the situation for the corresponding octa- and dodecamethyltetrastannacyclohexanes, which show only one methyltin resonance.

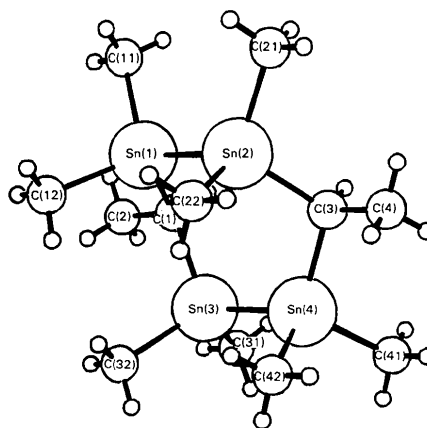


Fig. 1. General view of the molecule.

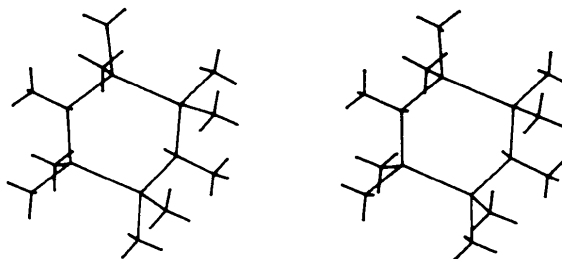


Fig. 2. Stereoscopic view of the molecule.