

Crystal and Molecular Structure of the Tri- μ -chlorobis[(η^3 -allyl)dicarbonyl-tungstate(II)]

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The complex $(C_2H_5)_4NW_2Cl_3(\eta^3-C_3H_5)_2(CO)_4$ prepared from the anion $W(CO)_5Cl$, crystallizes in the monoclinic system, space group $P2_1/c$ with cell dimensions $a = 10.788(5)$, $b = 13.061(1)$, $c = 18.836(7)$ Å, $\beta = 112.48(7)^\circ$, $Z = 4$. The structure was determined from three circle diffractometer data and refined by full matrix least-squares to $R = 0.055$ for 2328 independent reflections with $F > 3\sigma(F)$. In the anion the two independent W atoms are each bonded to an allyl group and two carbonyl groups in a fac-arrangement. The two metal atoms are bridged by three chlorine atoms.

Introduction

Allyl chloride reacts with halogenopentacarbonyl anions of tungsten and molybdenum to give the tri- μ -chlorobis[(η^3 -allyl)dicarbonyltungstate(molybdate)] [1]. We have shown in a previous paper [2] that the first step in this reaction is the formation of the dichlorotricarbonyl(η^3 -allyl)tungstate in which the three ligands Cl, Cl and allyl group are in a fac-arrangement while M.D. Murdoch [1] proposed a mer-arrangement on a spectroscopic basis. As part of our investigation on the structural properties of halogenocarbonyl complexes of group VI metals, we report here the structure of the tetraethylammonium tri- μ -chlorobis(η^3 -allyl)dicarbonyltungstate.

Experimental

All preparations were carried out under dry nitrogen or argon using solvents free from moisture and oxygen by standard procedures. The preparation of the complex has been previously reported [1]. Single crystals were obtained by the following way: 2 g of $(C_2H_5)_4N[W(CO)_5Cl]$ are dissolved in 30 ml benzene; 5 ml acetonitrile and 5 ml allyl chloride are added and the solution is stirred 8 hours at room temperature. A yellow product is formed which is filtered off, washed with benzene, and dried under

vacuum. The powder is then stirred with hot toluene to give a yellow solution which is filtered off. By keeping the solution at $0^\circ C$, single crystals are formed after a few days.

Crystal Data

$C_{18}H_{30}NCl_3O_4W_2$, $M = 798.2$, monoclinic, $a = 10.788(5)$, $b = 13.061(1)$, $c = 18.836(7)$ Å, $\beta = 112.48(7)^\circ$, $U = 2452$ Å³, $d_m = 2.17$, $d_c = 2.16$, $Z = 4$, $\lambda = 0.71069$ Å, $\mu = 102.8$ cm⁻¹, space group $P2_1/c$ from systematic absences $h0l$, $l = 2n + 1$, $0k0$, $k = 2n + 1$.

Crystals are very sensitive to oxygen and were mounted under dry nitrogen on Lindeman glass capillaries. Symmetry and systematic absences consistent with the monoclinic space group $P2_1/c$ were determined from Laue and precession photographs. Experimental density d_m was measured using the floating technique with a tetrachloromethane–dibromoethane mixture. A crystal of dimensions approximately $0.36 \times 0.28 \times 0.04$ mm was selected for intensity measurements and was set up on a laboratory made automatic three circle diffractometer. Cell dimensions and orientation matrix were obtained by least squares analysis from the setting angles of 9 reflections chosen from various regions of reciprocal space ($0.22 < \sin \theta / \lambda < 0.29$ Å⁻¹). MoK α radiation was used with a graphite monochromator set in front of the counter. The scintillation counter was fitted with a pulse-height analyser tuned to accept 90% of the MoK α peak. The take off angle was 3° .

The intensity of each independent reflection with $\sin \theta / \lambda < 0.55$ was measured with a $\theta/2\theta$ scan at room temperature. Scan range of $0.60^\circ + 0.345t g \theta$ was used with a scan speed in θ of 1.9 deg min⁻¹. Background was measured for 28 seconds at both ends of scan in fixed position. Reflections with counting rates greater than $7,000$ c. sec⁻¹ were corrected for counting loss. The intensities of two standard reflections (2 0 4) and (1 1 0) were monitored every 100 reflections; no significant fluctuations were observed. Corrections for Lorentz and polarization effects were

TABLE I. Fractional Atomic Coordinates with e.s.d.s in Parentheses.

Atom	x/a	y/b	z/c
W(1)	0.3487(1)	0.08183(8)	0.18150(5)
W(2)	0.2518(1)	0.19585(7)	-0.00224(6)
Cl(1)	0.3231(6)	0.2680(4)	0.1309(3)
Cl(2)	0.1399(6)	0.0749(5)	0.0632(3)
Cl(3)	0.4458(6)	0.0768(5)	0.0761(3)
C(11)	0.248(3)	0.089(2)	0.247(1)
O(11)	0.178(3)	0.090(3)	0.282(1)
C(12)	0.328(2)	-0.060(2)	0.204(1)
O(12)	0.310(3)	-0.147(2)	0.214(1)
C(21)	0.109(3)	0.294(2)	-0.046(1)
O(21)	0.031(2)	0.355(2)	-0.071(1)
C(22)	0.351(2)	0.303(2)	-0.023(1)
O(22)	0.407(2)	0.373(2)	-0.041(1)
C(13)	0.465(3)	0.159(3)	0.297(2)
C(14)	0.556(3)	0.122(2)	0.259(2)
C(15)	0.562(4)	0.011(2)	0.255(2)
C(23)	0.086(3)	0.130(2)	-0.112(1)
C(24)	0.205(3)	0.081(3)	-0.095(1)
C(25)	0.315(4)	0.146(2)	-0.103(2)
N	-0.159(2)	0.317(2)	0.085(1)
C(1)	-0.007(3)	0.339(2)	0.117(2)
C(2)	-0.194(3)	0.286(3)	0.152(2)
C(3)	-0.177(3)	0.228(2)	0.026(2)
C(4)	-0.243(3)	0.409(3)	0.048(2)
C(5)	0.041(3)	0.422(3)	0.177(2)
C(6)	-0.135(3)	0.196(3)	0.194(2)
C(7)	-0.326(3)	0.195(2)	-0.013(2)
C(8)	-0.226(3)	0.446(2)	-0.028(2)

made. An absorption correction was applied [3]. The absorption coefficient μ was 10.3 mm^{-1} ; transmission factors ranged from 0.091 to 0.690. Each structure factor was assigned a standard deviation $\sigma = (F_x \Delta I) / 2I$ where I was the integrated intensity and ΔI the error. Of the 3423 independent reflections, only 2326 with $F > 3\sigma(F)$ were used in subsequent calculations.

Structure Determination

The structure was solved by heavy-atom techniques. The tungsten atoms were found from Patterson function. The subsequent F_o syntheses indicated the Cl, C, O and N atoms. Atomic positions were refined by full-matrix least squares with isotropic temperature factors. Convergence was reached at $R = 0.16$. Structure factors were then corrected for absorption. R dropped to 0.086. The introduction of anisotropic temperature factors led to $R = 0.055$ and $R_w = 0.059$. The agreement factors were defined as $R = \Sigma(|F_o - F_c|) / \Sigma|F_o|$ and $R_w = \{\Sigma(w|F_o - F_c|)^2 / \Sigma(w|F_o|)^2\}^{1/2}$. All calculations were performed using standard programs [4]. The scattering factors were taken from International Tables for X-ray Crystallography (1974), including f' and f'' for tungsten atom. A weighting scheme based on counting statistics, $w = \Delta I / 2F$, was employed for calculating R_w . No attempts to locate hydrogen atoms were made.

Atomic coordinates and anisotropic components of temperature factors are shown in Tables I and II. Bond lengths and angles, with estimated standard

TABLE II. Anisotropic Temperature Factors with e.s.d.s in Parentheses. The parameters enter the expression for the structure factor in the form: $\exp[-0.25(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

Atom	B(11)	B(22)	B(33)	B(12)	B(13)	B(23)
W(1)	3.51(4)	3.33(4)	2.83(4)	0.13(4)	1.09(3)	0.30(4)
W(2)	3.62(4)	2.75(3)	2.74(4)	0.12(4)	1.09(3)	0.07(4)
Cl(1)	4.2(3)	3.2(2)	3.2(2)	0.0(2)	1.7(2)	-0.4(2)
Cl(2)	3.5(2)	3.9(3)	4.5(3)	-0.7(2)	0.0(2)	0.7(2)
Cl(3)	4.6(3)	3.8(2)	3.2(2)	0.8(2)	1.9(2)	0.1(2)
C(11)	4.4(11)	6.3(13)	1.4(8)	0.5(11)	-0.1(8)	1.8(9)
O(11)	8.1(14)	13.4(20)	7.0(12)	-0.4(14)	5.7(12)	1.4(14)
C(12)	2.8(9)	7.0(17)	1.9(8)	-0.2(9)	1.5(7)	-1.3(9)
O(12)	12.8(19)	3.6(9)	7.0(13)	-0.7(10)	0.2(13)	1.5(9)
C(21)	3.5(11)	5.5(13)	3.3(10)	0.0(11)	-0.1(8)	1.2(10)
O(21)	5.8(11)	5.6(10)	6.2(11)	2.0(9)	1.0(9)	1.6(9)
C(22)	4.3(11)	4.5(11)	1.3(7)	0.9(10)	0.5(7)	-0.9(8)
O(22)	6.2(10)	5.4(9)	5.5(9)	0.2(8)	3.6(8)	1.6(7)
C(13)	6.8(16)	8.3(19)	4.3(13)	0.7(14)	4.2(13)	-1.5(12)
C(14)	3.6(13)	6.3(16)	5.8(16)	-1.1(11)	-3.3(12)	0.0(13)
C(15)	7.7(19)	4.8(14)	4.6(14)	0.4(13)	0.8(13)	0.3(11)
C(23)	8.2(19)	4.9(13)	1.9(10)	-1.7(13)	-0.3(11)	-1.0(9)
C(24)	4.1(12)	6.7(14)	2.3(9)	2.1(12)	-2.0(8)	-0.5(11)
C(25)	8.6(20)	5.4(14)	5.1(14)	-2.1(14)	4.7(14)	-2.4(12)

(continued on facing page)

TABLE II. (continued)

Atom	B(11)	B(22)	B(33)	B(12)	B(13)	B(23)
N	5.9(11)	3.5(8)	3.3(8)	0.9(8)	2.3(8)	0.6(7)
C(1)	3.4(11)	4.8(13)	5.8(14)	0.0(9)	0.5(10)	-0.0(11)
C(2)	6.0(17)	6.6(17)	5.7(15)	1.3(14)	2.7(13)	0.5(13)
C(3)	3.6(12)	4.1(12)	5.7(14)	0.3(9)	-1.1(11)	-0.0(10)
C(4)	3.4(12)	5.7(15)	7.8(17)	0.8(12)	2.2(12)	-1.3(15)
C(5)	5.6(14)	6.0(15)	6.5(15)	0.0(13)	2.9(12)	0.8(14)
C(6)	7.4(18)	6.4(16)	4.0(14)	1.1(16)	2.9(13)	0.9(14)
C(7)	8.3(18)	2.8(10)	5.0(15)	-0.7(12)	1.1(14)	-0.5(11)
C(8)	7.2(17)	6.0(17)	6.8(16)	-0.0(13)	5.3(15)	0.8(12)

TABLE III. Interatomic Distances (Å) and Bond Angles (°).

	W(1)-W(2)	3.539(3)	
W(1)-Cl(1)	2.588(6)	W(2)-Cl(1)	2.508(6)
W(1)-Cl(2)	2.492(7)	W(2)-Cl(2)	2.570(6)
W(1)-Cl(3)	2.576(6)	W(2)-Cl(3)	2.572(6)
W(1)-C(11)	1.93(3)	W(2)-C(21)	1.93(3)
W(1)-C(12)	1.93(3)	W(2)-C(22)	1.90(3)
W(1)-C(13)	2.28(3)	W(2)-C(23)	2.31(2)
W(1)-C(14)	2.22(2)	W(2)-C(24)	2.21(3)
W(1)-C(15)	2.37(3)	W(2)-C(25)	2.34(3)
C(11)-O(11)	1.17(3)	C(21)-O(21)	1.12(3)
C(12)-O(12)	1.18(3)	C(22)-O(22)	1.20(3)
C(13)-C(14)	1.49(5)	C(23)-C(24)	1.35(4)
C(14)-C(15)	1.46(4)	C(24)-C(25)	1.51(4)
Cl(1)-W(1)-Cl(2)	76.8(2)	Cl(1)-W(2)-Cl(2)	76.9(2)
Cl(1)-W(1)-Cl(3)	76.0(2)	Cl(1)-W(2)-Cl(3)	77.4(2)
Cl(1)-W(1)-C(11)	100.6(9)	Cl(1)-W(2)-C(21)	93.7(8)
Cl(1)-W(1)-C(12)	167.4(6)	Cl(1)-W(2)-C(22)	87.1(6)
Cl(2)-W(1)-Cl(3)	78.7(2)	Cl(2)-W(2)-Cl(3)	77.4(2)
Cl(2)-W(1)-C(11)	92.1(7)	Cl(2)-W(2)-C(21)	99.7(8)
Cl(2)-W(1)-C(12)	90.9(6)	Cl(2)-W(2)-C(22)	164.0(6)
Cl(3)-W(1)-C(11)	170.6(6)	Cl(3)-W(2)-C(21)	171.1(8)
Cl(3)-W(1)-C(12)	104.9(6)	Cl(3)-W(2)-C(22)	99.6(7)
C(11)-W(1)-C(12)	77(1)	C(21)-W(2)-C(22)	81(1)
W(1)-C(11)-O(11)	175(2)	W(2)-C(21)-O(21)	177(2)
W(1)-C(12)-O(12)	177(2)	W(2)-C(22)-O(22)	176(2)
C(13)-C(14)-C(15)	114(3)	C(23)-C(24)-C(25)	115(3)
	W(1)-Cl(1)-W(2)	87.9(2)	
	W(1)-Cl(2)-W(2)	88.7(2)	
	W(1)-Cl(3)-W(2)	86.9(2)	

deviations calculated from the full variance-covariance matrix, are given in Tables III and IV. The observed and computed structure factors are available from the Editor.

Description of the Structure and Discussion

The unit cell contains four dimeric anions $[W_2Cl_3(CO)_4(C_3H_5)_2]^-$ and four tetraethylammonium

cations. A stereo view of the packing is presented on Fig. 1. The anion, formally a complex of W(II), is shown on Fig. 2. From a structural point of view both the tungsten atoms can be seen at the center of an octahedron, the apices of which are occupied by the allyl group, two carbonyl groups and three chlorine atoms. The three chlorine atoms are in a *fac*-arrangement, bridging both tungsten atoms. Each part of this dimeric system has a similar geometry

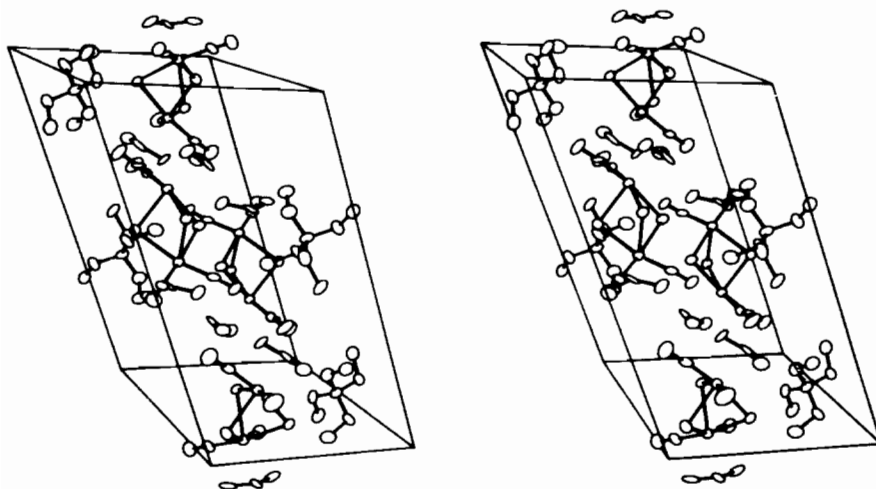


Fig. 1. Stereoscopic view of the unit cell.

TABLE IV. Interatomic Distances (Å) and Bond Angles (°) in the Tetraethylammonium Cation.

N-C(1)	1.54(3)	C(1)-N-C(2)	107(2)
N-C(2)	1.52(4)	C(1)-N-C(3)	104(2)
N-C(3)	1.56(3)	C(1)-N-C(4)	113(2)
N-C(4)	1.51(4)	C(2)-N-C(3)	113(2)
C(1)-C(5)	1.52(4)	C(2)-N-C(4)	107(2)
C(2)-C(6)	1.42(4)	C(3)-N-C(4)	112(2)
C(3)-C(7)	1.55(4)	N(1)-C(1)-C(5)	116(2)
C(4)-C(8)	1.58(4)	N(1)-C(2)-C(6)	119(3)
		N(1)-C(3)-C(7)	112(2)
		N(1)-C(4)-C(8)	114(2)

to that of $[\text{WCl}_2(\eta\text{-allyl})(\text{CO})_2\text{P}(\text{C}_6\text{H}_5)_3]$ [2], with one of the bridging chlorines replacing the P atom. It can be noticed that both the allyl groups in the dinuclear unit are *trans* to two different chlorine atoms. This is inconsistent with the structure proposed by H. D. Murdoch on the basis of spectroscopic data [1]. A similar dinuclear anion with three bridging chlorine atoms has been recently described with molybdenum instead of tungsten [5], and a comparison on bond lengths and bond angles can be made.

On the basis of covalent radii arguments W-Cl and Mo-Cl should be of the same order which is observed within experimental error: 2.55 and 2.57 Å (mean value) respectively. Two of the W-Cl bonds, *viz.* W(1)-Cl(2) 2.492(7) and W(2)-Cl(1) 2.508(6) Å are much shorter than the other four [2.570(6)-2.588(6) Å]. These two shorter bonds are *trans* to the allyl group while the other four are all *trans* to a carbonyl ligand. These last four values may be compared to 2.571(4) and 2.542(3) Å observed in $[\text{WCl}_2(\eta\text{-allyl})(\text{CO})_2\text{P}(\text{C}_6\text{H}_5)_3]^-$ [2], where it was

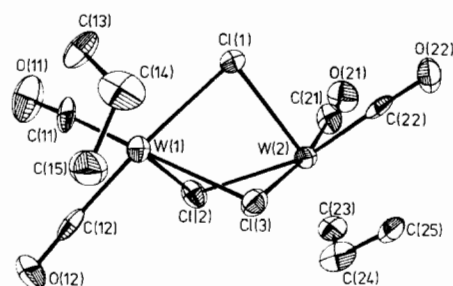


Fig. 2. ORTEP drawing of the anion. The ellipsoids represent 30% electron probability.

suggested that W-Cl bonds were weakened by the *trans* influence of carbonyl groups. The shortest W-Cl bonds *trans* to the allyl groups may be related to a lower π -acceptor ability of the allyl group with regard to the CO group.

Similarly it can be noticed that the W-(CO) bonds are somewhat strengthened because they are *trans* to W-Cl bonds where Cl atom is a π -donor. The W-C (carbonyl), 1.93(3) Å (mean value) is rather shorter than the value 2.02(1) Å found in $\text{W}(\text{CO})_6$ [6], and it is in good agreement with values observed either in molybdenum complex, 1.93(4) Å, [5] or in $[\text{WCl}_2(\eta\text{-allyl})(\text{CO})_2\text{P}(\text{C}_6\text{H}_5)_3]^-$ [2], 1.91(1) and 1.97(1) Å.

In the allyl groups, there is no particular feature with respect to the data obtained from other structure determinations. The distances from the tungsten atoms to the center of mass G(1) and G(2) of both allyl groups, 2.02(3) and 2.03(3) Å respectively, are consistent with values found for a d^4 electron configuration [7], as are the angles between the vectors W(1)-G(1) or W(2)-G(2) and G(1)-C(14)

TABLE V. Selected Infrared Data on Allyl Complexes.

Complex	$\nu(\text{CO}) \text{ cm}^{-1}$
I $\text{N}(\text{C}_2\text{H}_5)_4[\text{W}_2\text{Cl}_3(\text{CO})_4(\eta\text{-C}_3\text{H}_5)_2]$	1825
	1835
	1925
	1940
II $\text{As}(\text{C}_6\text{H}_5)_4[\text{Mo}_2\text{Cl}_3(\text{CO})_4(\eta\text{-C}_3\text{H}_5)_2]$	1802
	1830
	1910
	1928
III $\text{N}(\text{C}_2\text{H}_5)_4[\text{WCl}_2(\text{CO})_2(\eta\text{-C}_3\text{H}_5)\text{P}(\text{C}_6\text{H}_5)_3]$	1830
	1915

or G(2)–C(24), *i.e.* 104(4)° and 104(5)° respectively. For both allyl groups, the distances from the tungsten atoms to the apical C atoms (C(14) and C(24)) are shorter than those involving terminal carbons (Table III).

In the bridges, Cl–W–Cl angles range from 76.0 to 78.7° with no systematic variations; they are in good agreement with the values observed for $[\text{Mo}_2\text{Cl}_3(\text{CO})_4(\eta\text{-allyl})_2]^-$ [5], 77.3 to 80°. The three planes defined by the W atoms and the three Cl atoms respectively, make dihedral angles of 120, 118.3 and 121.8°.

Spectroscopic Data

The solid state infrared spectrum presents four main bands in the region 1700–2000 cm^{-1} (Table V), which may be assigned to the carbonyl stretching frequencies. These values are almost the same as those of the molybdenum homologue [5], *vide supra*, showing only a slight influence of the nature of the metal, as was observed in the compounds $\text{M}(\text{CO})_2(\text{diarsine})_2$ (M = Cr, Mo and W) [8].

Each part of the dimer, and the anion $[\text{WCl}_2(\text{CO})_2(\eta\text{-allyl})\text{P}(\text{C}_6\text{H}_5)_3]^-$ present the same arrangement of the four ligands CO and Cl around the tungsten atom, *i.e.* in the equatorial plane each CO *trans* to Cl; in the phosphine complex the Cl atoms are terminal and in the dimer the Cl atoms bridge two tungsten atoms. Although chlorine atoms play different chemical roles in the two compounds, the

infrared frequencies in the CO region are of the same order, as for the C–O distances, showing that the *trans* influence of chlorine atoms on CO group is not really affected by the occurrence of the bridge.

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