

This difference may reflect the replacement of one Cu-S bond by a weaker Cu-OH₂ bond in the latter complex if the monomer involves an S₃O donor set with a structural arrangement similar to that observed in the crystalline polymer. Alternatively, the lower K_{CuL} may largely be ascribable to increased internal ligand strain if a flattened tetrahedral complex is formed with an S₄ donor set. In fact, however, both monomeric conformations clearly result in a significantly lowered K_{CuL} value since, as noted above, the experimental value must reflect the more stable Cu(I) species. We favor the former species. Future physical measurements and molecular mechanical calculations will be aimed at differentiating between these two possibilities.

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Registry No. [Cu^I(Et₂-2,3,2-S₄)](ClO₄), 93778-95-1; [Cu^{II}(Et₂-2,3,2-S₄)(OH₂)(OCIO₃)](ClO₄), 93645-97-7; [Cu^I([14]aneS₄)](ClO₄), 93645-99-9.

Supplementary Material Available: Listings of all atomic positional parameters (including calculated hydrogen positional parameters), thermal parameters, and the final observed and calculated structure factors for all three compounds (31 pages). Ordering information is given on any current masthead page.

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Structure of Tantalum Cresoxide

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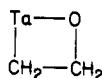
The synthesis of tantalum cresoxide (II) from TaCl₅ and NaO-*p*-C₆H₄CH₃ is reported. The crystal structure of II was determined for C₇₀H₇₀O₁₀Ta₂. Cell dimensions: $a = 12.17$ (1) Å, $b = 18.02$ (1) Å, $c = 14.71$ (1) Å, $\beta = 91.17$ (6)°. The crystals are monoclinic of space group $P2_1/n$ with $Z = 4$. The structure of II is a dimer with two bridging cresoxides. The structure is discussed in terms of multiple bonding between Ta and O. The solid-state structure of II is compared to the solution structure of II (¹³C NMR and ¹H NMR) and to the solution structure of Ta₂(OPh)₁₀ (I).

Introduction

The structure of metal alkoxides has been widely studied by a number of groups in recent years.¹ Far less work has focused on the structure of metal phenoxide complexes.²

During an investigation of tantalum phenoxide, it was found that little accurate structural information was available for this compound. In fact, since the first report³ of its synthesis very few references to the compound exist at all.⁴ The structure as derived from NMR data for tantalum methoxide has been reported,⁵ and it is a dimer with two bridging methoxides. Titanium phenoxide is the closest analogue of tantalum phenoxide for which a crystal structure determination has been made.⁶

Recently, it was reported that tantalum ethoxide "Ta₂(OEt)₁₀" catalyzed the deuteration (on the methyl group only) of ethanol with D₂.⁷ It was proposed that a four-membered ring intermediate was in part responsible for this reaction.



This would require that a monomeric tantalum ethoxide be present to some extent, and some evidence for this was given.⁷ Recently, a dimeric structure was proposed for tantalum phenoxide on the basis of infrared analysis.⁸

Bradley and co-workers measured the nuclearity of a number of tantalum alkoxides.⁹ As the steric requirement increased (from ethyl to isopropyl to *tert*-butyl), the complexes were found to be

Table I. Crystal Data and Summary of Intensity Data for II

formula	C ₇₀ H ₇₀ O ₁₀ Ta ₂
mol wt	1433.21
lattice const	$a = 12.17$ (1) Å $b = 18.02$ (1) Å $c = 14.71$ (1) Å $\beta = 91.17$ (6)°
λ	0.710 69 Å
temp	ambient
radiation	Mo K α monochromatized
space group	$P2_1/n$ (no space group ambiguities)
Z	2
μ	36.4 cm ⁻¹ (no abs cor applied)
diffractometer	Nicolet P3F automated diffractometer
geometry	ω -2 θ scan
conditions	$4 \leq 2\theta \leq 50^\circ$ $0 \leq h \leq 13$ $0 \leq k \leq 22$ $-18 \leq l \leq 18$
no. of reflns	5063 colld; 2700 unique obsd reflns with $F > 4\sigma(F)$
struct determ	direct methods; SHELXTL program package
R	0.0600
R_w	0.0558
w^{-1}	$\sigma^2(F) + 0.00032F^2$; $\Sigma w(F_o - F_c)^2$

monomeric. In the present work, the structure of tantalum phenoxide was investigated in order to firmly determine the molecularity of the molecule. In addition, NMR results (vide infra) suggested that there may be some ring carbon-metal interactions not unlike those found in a number of ortho-metallated complexes.¹⁰ Thus, it was of interest to learn what interaction (if any) existed between the phenoxide rings with each other or of the phenoxide rings with the metal.

Experimental Section

All operations were carried out in a Vacuum Atmospheres drybox filled with Argon. TaCl₅ was sublimed before use. ¹H NMR were recorded on a Varian EM 390 NMR spectrometer. ¹³C{¹H} NMR were recorded on a Varian FT 80 NMR spectrometer (20 MHz).

(10) Lewis, L. N., unpublished results.

- (1) Bradley, D. C.; Mehrottra, R. C.; Gaur, D. P. "Metal Alkoxides"; Academic Press: London, 1978.
- (2) Malhotra, K. C.; Martin, R. L. *J. Organomet. Chem.* **1982**, *159*.
- (3) Funk, H.; Niederlander, K. *Chem. Ber.* **1929**, *62*, 1688.
- (4) Mehrottra, R. C.; Rai, A. K.; Kapoor, P. N.; Bohra, R. *Inorg. Chim. Acta* **1976**, *16*, 237.
- (5) Bradley, D. C. *Adv. Inorg. Chem. Radiochem.* **1972**, *15*, 259.
- (6) Svetich, G. W.; Voge, A. A. *Acta Crystallogr.* **1972**, *B28*, 1760.
- (7) Nugent, W. A.; Ovenall, D. W.; Holmes, S. J. *Organometallics* **1983**, *2*, 161.
- (8) Malhotra, K. C.; Banerjee, U. K.; Chaudhry, S. C. *J. Ind. Chem.* **1980**, *57*, 868.
- (9) Bradley, D. C.; Chakravarti, B. N.; Chatterjee, A. K.; Wardlaw, W.; Whitley, A. *J. Chem. Soc.* **1958**, 99.

Table II. Atom Coordinates ($\times 10^4$) and Temperature Factors (10^3 \AA^2)

atom	x	y	z	U_{equiv}^a
Ta	4489 (1)	762 (1)	4391 (1)	53 (1)*
O(1)	4260 (7)	66 (4)	5503 (6)	55 (3)*
O(2)	5114 (7)	1148 (5)	3369 (7)	66 (4)*
O(3)	5388 (7)	1393 (5)	5155 (6)	61 (3)*
O(4)	3583 (8)	109 (5)	3695 (7)	79 (4)*
O(5)	3226 (8)	1376 (5)	4605 (7)	71 (4)*
C(1)	3441 (10)	140 (7)	6170 (9)	51 (5)*
C(2)	3576 (13)	633 (9)	6864 (11)	91 (7)*
C(3)	2832 (17)	663 (12)	7535 (13)	111 (10)*
C(4)	1945 (18)	238 (12)	7532 (12)	101 (9)*
C(5)	1759 (13)	-216 (10)	6843 (11)	96 (8)*
C(6)	2527 (11)	-272 (8)	6138 (11)	69 (6)*
C(7)	1094 (17)	205 (14)	8289 (13)	189 (15)*
C(8)	5400 (11)	1168 (7)	2488 (11)	59 (6)*
C(9)	4794 (15)	840 (9)	1803 (11)	90 (7)*
C(10)	5147 (18)	849 (10)	940 (14)	118 (10)*
C(11)	6091 (18)	1202 (10)	677 (11)	120 (9)*
C(12)	6680 (14)	1517 (10)	1368 (12)	112 (9)*
C(13)	6351 (12)	1514 (8)	2248 (10)	75 (6)*
C(14)	6524 (19)	1199 (11)	-277 (12)	175 (14)*
C(15)	5693 (13)	2110 (7)	5309 (9)	57 (6)*
C(16)	6786 (13)	2281 (8)	5508 (10)	76 (7)*
C(17)	7111 (14)	2982 (8)	5689 (12)	94 (8)*
C(18)	6375 (14)	3554 (8)	5652 (11)	88 (7)*
C(19)	5296 (15)	3399 (9)	5477 (13)	112 (9)*
C(20)	4930 (15)	2672 (9)	5298 (12)	94 (8)*
C(21)	6687 (16)	4358 (8)	5881 (13)	117 (9)*
C(22)	2794 (12)	-356 (7)	3390 (9)	58 (5)*
C(23)	2988 (13)	-888 (8)	2742 (10)	67 (6)*
C(24)	2196 (12)	-1369 (8)	2459 (11)	79 (7)*
C(25)	1151 (12)	-1347 (7)	2795 (11)	76 (6)*
C(26)	952 (11)	-829 (8)	3453 (11)	76 (6)*
C(27)	1727 (11)	-334 (8)	3736 (10)	71 (6)*
C(28)	331 (14)	-1906 (10)	2497 (14)	127 (10)*
C(29)	2232 (11)	1591 (7)	4337 (9)	50 (5)*
C(30)	2024 (11)	1699 (8)	3429 (10)	69 (6)*
C(31)	991 (12)	1949 (8)	3151 (10)	73 (6)*
C(32)	164 (13)	2052 (9)	3726 (12)	91 (8)*
C(33)	389 (14)	1906 (8)	4631 (12)	91 (8)*
C(34)	1403 (12)	1668 (8)	4946 (11)	73 (6)*
C(35)	-965 (13)	2367 (11)	3445 (14)	134 (11)*

^a Asterisks denote equivalent isotropic U values defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Tantalum Phenoxide (I). TaCl_5 (2.0 g, 5.6 mmol) and NaOPh (3.3 g, 0.028 mol) were combined in 40 mL of toluene and stirred for 2 h. A white precipitate was filtered from a yellow filtrate. The toluene was removed in vacuo to give a yellow-orange powder in quantitative yield. The solid was recrystallized from toluene and hexane to give cream-colored crystals. The material was extremely moisture sensitive, precluding elemental analysis. $^1\text{H NMR}$ (CDCl_3): δ 7.5–6.5 (very complicated mult), 6.04 (d, 7 Hz). $^{13}\text{C NMR}$ (CDCl_3): δ 161.13 (i), 159.88 (j), 129.69 (m), 128.70 (m), 124.05 (p), 122.06 (o), 121.72 (p), 120.07 (o), 119.51 (p), 119.27 (o).

Tantalum Cresoxide (II). TaCl_5 (1 g, 2.8 mmol) and $\text{Na-}p\text{-OC}_6\text{H}_4\text{CH}_3$ were combined in 30 mL of toluene and stirred for 12 h. A solid was filtered and washed with CH_2Cl_2 . The combined toluene and methylene chloride filtrates were taken to dryness in vacuo. The yellow solid obtained was recrystallized from diethyl ether and hexane to yield cream-colored crystals in quantitative yield; mp 186 °C. Anal. Calcd for $\text{C}_{35}\text{H}_{35}\text{O}_5\text{Ta}$ (performed by the Analytical Laboratory): C, 58.66; H, 4.89; Ta, 25.28. Found: C, 58.05; H, 4.79; Ta, 29.05. FDMS: m/e 1432. $^1\text{H NMR}$ (CDCl_3): δ 7.17 (AB quart, $J = 8.4$ Hz, 1.3), 6.8 (complex mult, 5.2), 5.97 (d, $J = 8.4$ Hz, 1.3), 2.32 (s, 1.0), 2.22 (s, 2.2), 2.17 (s, 2.2). $^{13}\text{C NMR}$ (CDCl_3): δ 159.34 (i), 157.81 (i), 129.69 (m), 128.81 (m), 121.76 (o), 119.87 (o), 119.04 (o); para not observed due to decreased NOE, δ 20.59 (CH₃).

Structure Determination. Single cream-colored crystals (prisms) of $\text{C}_{70}\text{H}_{70}\text{O}_{10}\text{Ta}_2$ were obtained by crystallization from diethyl ether and hexane. A suitable crystal (0.2 \times 0.2 \times 0.2 mm) was sealed in a glass capillary in the glovebox. Crystal data are summarized in Table I. Compound II was centrosymmetric. All non-hydrogen atoms were refined anisotropically. Fractional atomic coordinates and temperature factors are given in Table II. Bond distances and angles are summarized in Tables III and IV.

Table III. Bond Lengths (\AA)

Ta–O(1)	2.084 (8)	Ta–O(2)	1.836 (10)
Ta–O(3)	1.924 (9)	Ta–O(4)	1.898 (10)
Ta–O(5)	1.925 (9)	Ta–O(1')	2.134 (8)
O(1)–C(1)	1.418 (15)	O(1)–Ta'	2.134 (8)
O(2)–C(8)	1.348 (19)	O(3)–C(15)	1.360 (16)
O(4)–C(22)	1.345 (17)	O(5)–C(29)	1.324 (16)
C(1)–C(2)	1.360 (21)	C(1)–C(6)	1.338 (18)
C(2)–C(3)	1.354 (26)	C(3)–C(4)	1.323 (30)
C(4)–C(5)	1.318 (25)	C(4)–C(7)	1.539 (28)
C(5)–C(6)	1.413 (22)	C(8)–C(9)	1.370 (22)
C(8)–C(13)	1.367 (20)	C(9)–C(10)	1.348 (27)
C(10)–C(11)	1.375 (29)	C(11)–C(12)	1.356 (25)
C(11)–C(14)	1.509 (26)	C(12)–C(13)	1.362 (23)
C(15)–C(16)	1.391 (22)	C(15)–C(20)	1.374 (22)
C(16)–C(17)	1.348 (21)	C(17)–C(18)	1.365 (22)
C(18)–C(19)	1.362 (25)	C(18)–C(21)	1.534 (21)
C(19)–C(20)	1.407 (23)	C(22)–C(23)	1.376 (19)
C(22)–C(27)	1.405 (20)	C(23)–C(24)	1.354 (21)
C(24)–C(25)	1.375 (22)	C(25)–C(26)	1.369 (21)
C(25)–C(28)	1.478 (22)	C(26)–C(27)	1.357 (20)
C(29)–C(30)	1.368 (20)	C(29)–C(34)	1.370 (20)
C(30)–C(31)	1.389 (20)	C(31)–C(32)	1.340 (22)
C(32)–C(33)	1.378 (26)	C(32)–C(35)	1.536 (23)
C(33)–C(34)	1.377 (22)		

Table IV. Bond Angles (deg)

O(1)–Ta–O(2)	159.2 (4)	O(1)–Ta–O(3)	88.9 (4)
O(2)–Ta–O(3)	90.8 (4)	O(1)–Ta–O(4)	88.0 (4)
O(2)–Ta–O(4)	92.2 (4)	O(3)–Ta–O(4)	176.9 (4)
O(1)–Ta–O(5)	95.6 (4)	O(2)–Ta–O(5)	105.2 (4)
O(3)–Ta–O(5)	90.6 (4)	O(4)–Ta–O(5)	89.3 (4)
O(1)–Ta–O(1')	68.2 (4)	O(2)–Ta–O(1')	91.0 (4)
O(3)–Ta–O(1')	88.6 (3)	O(4)–Ta–O(1')	90.7 (4)
O(5)–Ta–O(1')	163.8 (4)	Ta–O(1)–C(1)	126.3 (7)
Ta–O(1)–Ta'	111.8 (4)	C(1)–O(1)–Ta'	121.7 (7)
Ta–O(2)–C(8)	156.4 (9)	Ta–O(3)–C(15)	143.9 (8)
Ta–O(4)–C(22)	165.8 (9)	Ta–O(5)–C(29)	148.0 (9)
O(1)–C(1)–C(2)	120.3 (12)	O(1)–C(1)–C(6)	121.3 (12)
C(2)–C(1)–C(6)	118.4 (13)	C(1)–C(2)–C(3)	120.1 (15)
C(2)–C(3)–C(4)	122.1 (18)	C(3)–C(4)–C(5)	119.3 (18)
C(3)–C(4)–C(7)	125.5 (18)	C(5)–C(4)–C(7)	115.1 (18)
C(4)–C(5)–C(6)	120.1 (16)	C(1)–C(6)–C(5)	119.8 (14)
O(2)–C(8)–C(9)	123.3 (13)	O(2)–C(8)–C(13)	119.8 (13)
C(9)–C(8)–C(13)	116.8 (15)	C(8)–C(9)–C(10)	120.7 (17)
C(9)–C(10)–C(11)	123.6 (18)	C(10)–C(11)–C(12)	114.5 (17)
C(10)–C(11)–C(14)	124.7 (17)	C(12)–C(11)–C(14)	120.6 (18)
C(11)–C(12)–C(13)	123.3 (16)	C(8)–C(13)–C(12)	121.0 (14)
O(3)–C(15)–C(16)	120.2 (12)	O(3)–C(15)–C(20)	121.0 (14)
C(16)–C(15)–C(20)	118.8 (13)	C(15)–C(16)–C(17)	121.7 (14)
C(16)–C(17)–C(18)	120.6 (16)	C(17)–C(18)–C(19)	118.8 (14)
C(17)–C(18)–C(21)	123.0 (15)	C(19)–C(18)–C(21)	117.9 (14)
C(18)–C(19)–C(20)	121.8 (15)	C(15)–C(20)–C(19)	118.2 (16)
O(4)–C(22)–C(23)	122.3 (13)	O(4)–C(22)–C(27)	121.4 (12)
C(23)–C(22)–C(27)	116.3 (13)	C(22)–C(23)–C(24)	121.8 (14)
C(23)–C(24)–C(25)	121.9 (15)	C(24)–C(25)–C(26)	116.9 (14)
C(24)–C(25)–C(28)	119.9 (14)	C(26)–C(25)–C(28)	123.1 (14)
C(25)–C(26)–C(27)	122.2 (14)	C(22)–C(27)–C(26)	120.8 (13)
O(5)–C(29)–C(30)	118.9 (12)	O(5)–C(29)–C(34)	121.0 (12)
C(30)–C(29)–C(34)	120.1 (13)	C(29)–C(30)–C(31)	118.7 (13)
C(30)–C(31)–C(32)	123.1 (15)	C(31)–C(32)–C(33)	116.5 (15)
C(31)–C(32)–C(35)	124.0 (16)	C(33)–C(32)–C(35)	119.3 (16)
C(32)–C(33)–C(34)	122.9 (16)	C(29)–C(34)–C(33)	118.5 (15)

Results and Discussion

As shown in Figure 1, tantalum cresoxide (II) is a dimer with two bridging cresoxide groups. The Ta–Ta distance is 3.493 (1) \AA , which is larger by 0.5 \AA than a single Ta–Ta bond reported. Thus, the Ta–Ta distance in II is considered a nonbonding distance.¹¹

The bridging cresoxide oxygen–tantalum bond distances, 2.109 (0.022) \AA , are somewhat longer than the equivalent distance in $[\text{Ti}(\text{OPh})_3(\text{HOPh})]_2(\mu\text{-OPh})_2$, 2.04 (0.02) \AA .⁵ The bridging oxygen to tantalum distances are longer (0.21 \AA) than the terminal

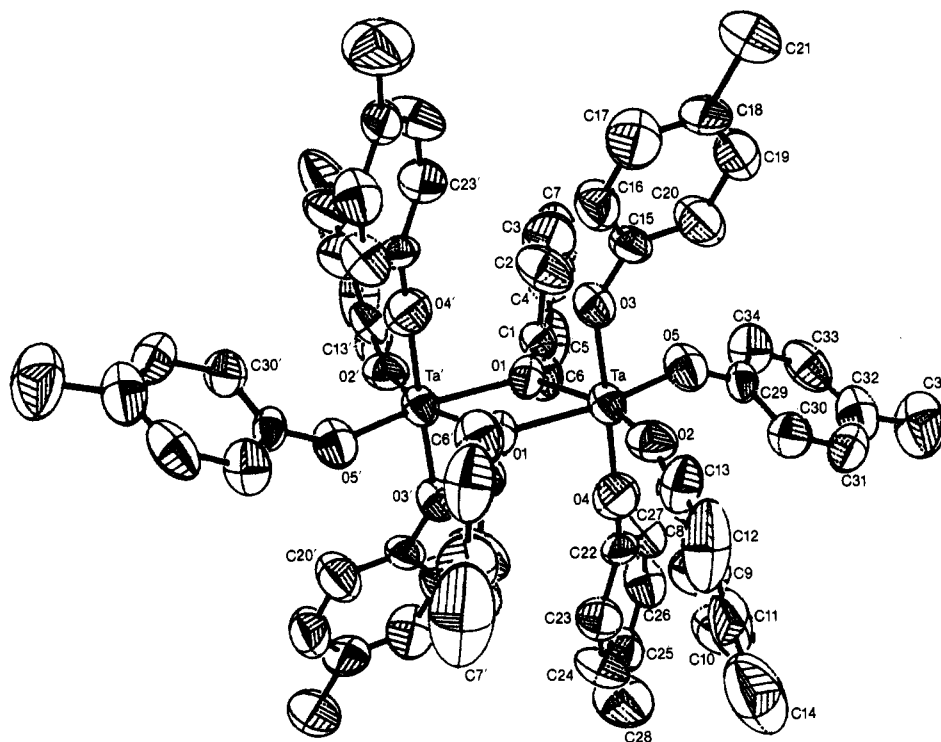
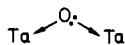


Figure 1. View of $[\text{Ta}(p\text{-OC}_6\text{H}_4\text{CH}_3)_2]_2$ (II).

oxygen-tantalum distances. Such lengthening is commonly observed when comparing bridging and terminal ligands in the same molecule.

The terminal tantalum-oxygen distances range from 1.836 (10) to 1.925 (9) Å; the average Ta-terminal oxygen distance is 1.896 (7) Å. The equatorial plane is defined as containing the bridging cresoxide oxygens O(1) and O(1') and O(2) and O(5). There is no apparent difference between the Ta-O(ax) vs. Ta-O(eq) distances within experimental error.

The Ta-O distances are shorter than one would expect for a Ta-O single bond (a $\text{Mo}^{\text{VI}}\text{-O}$ single bond has been estimated at 2.00–2.05 Å).¹² A W-O single bond is found to be 2.041 (6) Å.¹³ The short bond distance is ascribed to multiple bonding between Ta and phenoxide ($d\pi\text{-}p\pi$).^{12,14} Some π bonding between cresoxide and Ta is reasonable if the EAN rule is in force in this molecule. If the bridging cresoxides are counted as three-electron donors



and the terminal ligands are counted as one-electron donors, then each Ta atom has 12 valence electrons. By invoking metal-oxygen multiple bonding, i.e.



(three-electron donor), then the Ta atoms can achieve a closed-shell configuration.

The concept of phenoxide O-metal multiple bonding can be correlated to the M-O distance for a number of metal phenoxides (Table V). To begin with, one needs to count electrons by considering all ligands neutral and counting terminal phenoxide as a one-electron donor. In Table I, this is N . Then, one subtracts N from 18 to see how many electrons are needed to obtain a closed-shell configuration. Another way to view $18 - N$ is that the greater the value for $18 - N$, the more multiple-bond character should be expected for the terminal phenoxides in the complex. As shown in the table, as $18 - N$ increases, $d_{\text{M-O}}$ decreases (these

Table V. M-O Distance vs. Electron Donation for Some Metal Phenoxide Structures

complex	N	$18 - N$	av $d_{\text{M-O}}$ (terminal)
$\text{Re}(\text{Oph})_4(\text{PMe}_3)_2$ ¹⁵	15	3	2.03 (2)
II	12	6	1.896 (20)
$\text{WCl}_2(\text{Oph})_4$ ¹⁴	12	6	1.86 (7)
$[\text{Ti}(\text{Oph})_4(\text{HOph})]_2$ ^{a,b}	12	6	1.86 (2)
$[\text{TiCl}_2(\text{Oph})_2]_2$ ¹⁶	10	8	1.76 (2)

^a Distances in Å. Distances normalized to Ta ionic radius of 1.34 Å. $d_{\text{M-O}}(\text{terminal}) = d_{\text{M-O}} - |r_{\text{Ta}} - r_{\text{M}}|$, where $d_{\text{M-O}}$ is the reported metal-oxygen distance, r_{Ta} is the tantalum ionic radius, and r_{M} is the metal ionic radius. ^b Terminal HO-Ph ligand is a two-electron donor.

distances have been normalized to the Ta covalent radius).

The Ta-O-C(terminal) angles range from 143.9 (8) to 165.8 (9), 153.5 (2)° average. The Ta-O-C angles are also consistent with the notion of multiple bonding between Ta and OAr. It was recently shown that the M-OC angle of an isopropoxide ligand is 25–30° smaller than that of a phenoxide ligand in the same molecule. This is consistent with metal-phenoxide multiple bonding; a more linear M-OC arrangement permits a greater degree of $d\pi\text{-}p\pi$ overlap.¹² In II, the shorter Ta-O distances (Ta-O(2) and Ta-O(4)) correspond to the more obtuse angles, consistent with greater π donation for these phenoxides.

The solid-state structure of II is preserved in solution as seen by the ¹³C NMR. Comparison of the ¹³C NMR spectra of $\text{Ta}_2(\text{OC}_6\text{H}_5)_{10}$ and $\text{Ta}_2(p\text{-OC}_6\text{H}_4\text{CH}_3)_{10}$ permits assignment of all the peaks in these spectra. One can conclude that there is no scrambling of ligands at room temperature on the NMR time scale. By using the comparison above and the integrated intensities of the carbon resonances, the resonances of the bridging phenoxides can be distinguished from those of the terminal phenoxides. Due to a lack of NOE at the para carbon in II, the para resonance was not observed. This permits assignment of the three ortho resonances at δ 121.76 and 119.87/119.04 as bridging and terminal (axial/equatorial), respectively. The two meta resonances have an integrated ratio of intensity of 3:2, consistent with an equivalent chemical shift for two terminal cresoxides and the bridging cresoxide meta resonances. The ipso carbon resonances δ 159.34 and 157.81 have an integrated ratio of intensity of 4:1 and are assigned

(12) Coffindaffer, T. W.; Rothwell, I. P.; Haftman, J. C. *Inorg. Chem.* **1983**, *22*, 2906.

(13) Chisholm, M. H.; Extine, M. J. *Am. Chem. Soc.* **1974**, *96*, 6214.

(14) Handy, L. B.; Fair, C. K. *Inorg. Nucl. Chem. Lett.* **1975**, *11*, 497.

Table VI. Average Ring Bond Distances for Phenoxides in II (Å)

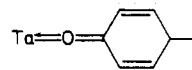
	C-O	C-C (o)	C-C (m)	C-C (p)
terminal	1.344 (20)	1.378 (22)	1.368 (21)	1.365 (23)
bridging	1.418 (15)	1.349 (20)	1.384 (23)	1.321 (27)

to the terminal and bridge cresoxides, respectively. There was only one methyl resonance in the ^{13}C NMR of II.

The ^1H NMR of II had three methyl resonances with relative areas of 1:2:2, further consistent with a static solution structure. An unusual feature of the ^1H NMR of both I and II was the appearance of an upfield doublet peak at ca. δ 6.00. This feature has been observed in the ^1H NMR spectra of complexes in which an ortho-metalated group is present. For instance, $\text{HCo}(\text{P}(\text{OPh})_3)_4$ has a single multiplet resonance at ca. δ 6.9 whereas $(\text{PhO})_2\text{POC}_6\text{H}_4\text{Co}(\text{P}(\text{OPh})_3)_3$ has multiplets at δ 7.20, 6.46, 6.79, and 6.38. This effect has been seen in several other systems.¹⁰

Examination of the nonbonded distances in II shows that the closest ortho carbon-Ta distance is 3.697 Å¹⁵ (Ta-C(30)). Thus, no ortho metalation exists in II. (See Figure 2 in supplementary material, stereoview of II.) The upfield chemical shift is consistent with the notion that the cresoxide ligands are engaged in multiple

bonding to tantalum. Removing electron density from the ring would be consistent with the observed upfield shift in the NMR, i.e., the cresoxide ligand is becoming quinone-like:



The distances about the cresoxide rings further support the notion of multiple M-O bonding. The expectation, if M-O multiple bonding occurs, is that there should be shortening of the C-O and C-C bonds with a lengthening of the ortho and para C-C bonds relative to an unperturbed phenoxide. One can use the bridging ligand as an internal reference for atom distances as a cresoxide not engaged in M-O multiple bonding. In Table VI, the average C-O and C-C (ortho, meta, and para) distances are shown for bridging vs. terminal cresoxides in II. There is large scatter in the data used to generate Table VI. The trends are that the predicted shortening of the C-O and C-C (meta) bonds was observed for the terminal vs. bridging ligands. Likewise, the expected C-C (ortho and para) lengthening of terminal vs. bridging is seen.

Registry No. I, 75888-51-6; II, 94234-92-1.

Supplementary Material Available: A stereoview of II (Figure 2) and listings of observed and calculated structure factors (Table VII), anisotropic temperature factors (Table VIII), and hydrogen coordinates (Table IX) (21 pages). Ordering information is given on any current masthead page.

(15) Edwards, P. G.; Wilkinson, G.; Hursthouse, M. B.; Malik, K. M. A. *J. Chem. Soc., Dalton Trans.* 1980, 2467.

(16) Watenpugh, K.; Caughlan, C. N. *Inorg. Chem.* 1966, 5, 1782.

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Gold Dithiocarboxylates

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The first dithiocarboxylato derivatives of gold have been obtained. The compounds have stoichiometries $\text{Au}(\text{CH}_3\text{CS}_2)$, $\text{Au}(\text{PhCS}_2)$, and $\text{Au}(\text{PhCS}_2)(\text{Ph}_2\text{CCS}_2)$. The X-ray structures of the dithioacetic acid derivative and the mixed-ligand compound have been determined. $\text{Au}(\text{CH}_3\text{CS}_2)$ crystallizes in the triclinic space group $P\bar{1}$ ($Z = 2$). Lattice constants: $a = 12.087$ (4), $b = 9.698$ (3), $c = 8.862$ (3) Å; $\alpha = 95.50$ (2), $\beta = 110.57$ (2), $\gamma = 92.65$ (2)°. Least-squares refinement of 1949 observed reflections has led to a final R factor of 0.045. The structure consists of discrete tetranuclear units, $\text{Au}_4(\text{CH}_3\text{CS}_2)_4$. In the tetrameric molecule the four gold atoms are at the vertices of a rhomb. All the four ligands are bridging and are alternately above and below the plane of the metal cluster. The four equivalent Au-Au distances average 3.013 Å. The mean Au-S bond length is 2.296 Å. If one considers only the S ligands, the geometry of the gold coordination is approximately linear, the mean SAuS angle being 167.7°. $\text{Au}(\text{PhCS}_2)(\text{Ph}_2\text{CCS}_2)$ crystallizes in the triclinic space group $P\bar{1}$ ($Z = 2$). Lattice constants: $a = 18.094$ (4), $b = 11.371$ (4), $c = 4.912$ (3) Å; $\alpha = 87.40$ (2), $\beta = 98.93$ (2), $\gamma = 96.33$ (2)°. The final R value was 0.037, for 2326 observations and 120 parameters. The structure is built by monomeric molecules. The gold atom is surrounded by four sulfur atoms, in an approximately planar arrangement. The mean Au-S bond length involving the sulfur atoms of $\text{Ph}_2\text{CCS}_2^{2-}$, 2.296 (3) Å, is significantly shorter than the corresponding value of 2.369 (3) Å for the PhCS_2^- sulfur atoms. The phenyl ring of the dithiobenzoato ligand is substantially coplanar with the inner chelate rings of the molecule. Vibrational and electronic spectral information for all the compounds is reported and discussed. The Mössbauer spectrum of $\text{Au}_4(\text{CH}_3\text{CS}_2)_4$ is also reported. The isomer shift (relative to the source ^{197}Au in platinum) is 1.40 ± 0.01 mm/s; quadrupole splitting is 6.13 ± 0.02 mm/s. The presence (or absence) of direct Au-Au interactions in $\text{Au}_4(\text{CH}_3\text{CS}_2)_4$ is critically discussed on the basis of the structural and Mössbauer results.

Introduction

Multinuclear d^{10} systems with relatively short intermetallic separations have been the subject of much recent interest.¹ A basic question under study is the presence of attractive interactions between the metal centers (with formally closed shells).²⁻⁴ So far, attention has been mainly focused on Cu(I) cluster compounds. The problem of bonding in these molecules has been studied by means of extended Hückel² and SCCC³ molecular orbital calculations. An interesting structural view of the stability of such clusters has also been presented.⁵ The conclusions of these studies do not agree completely.

Unlike copper(I) (which forms clusters with two to eight metal atoms),² gold(I) appears to form relatively few multinuclear compounds.^{1b,6} Among those that are best documented, and have intermetallic distances short enough to suggest direct Au-Au interaction, there are the 1,1-dithiolato derivatives.⁷⁻⁹ All reported

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- (1) For reviews see: (a) Fackler, J. P., Jr. *Prog. Inorg. Chem.* 1976, 81, 55. (b) Puddephatt, R. J. "Topics in Inorganic and General Chemistry"; Elsevier: Amsterdam, 1978; Vol. 16.
- (2) Mehrotra, P. K.; Hoffmann, R. *Inorg. Chem.* 1978, 17, 2187 and references therein.
- (3) Avdeef, A.; Fackler, J. P., Jr. *Inorg. Chem.* 1978, 17, 2182.
- (4) Dedieu, A.; Hoffmann, R. *J. Am. Chem. Soc.* 1978, 100, 2074.
- (5) Hollander, F. J.; Coucouvanis, D. *J. Am. Chem. Soc.* 1977, 99, 6268.
- (6) Schmidbaur, H. *Angew. Chem.* 1976, 88, 830; *Angew. Chem., Int. Ed. Engl.* 1976, 15, 728.