Articles

Molecular and Crystal Structures of New Binuclear Thiooxalate-Bridged Complexes: (μ-Trithiooxalato-S,S′:S′,S″)bis[bis(triphenylphosphine)silver(I)], the First Verified Simultaneously End-on/Side-on Coordinated Thiooxalate, and (μ-1,1-Dithiooxalato-S,O:S′,O′)bis[bis(triphenylphosphine)metal(I)] (Metal = Copper, Silver)

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Synthesis, crystal and molecular structures of three binuclear complexes with bridging trithiooxalate (trto) or 1,1-dithiooxalate (i-dto) are reported. $[(Ph_3P)_2Ag]_2(trto)$(**1**) is triclinic, space group $P\bar{1}$ (No. 2) with $Z = 2$, $a = 11.645(2)$ Å, $b = 13.473(2)$ Å, $c = 23.304(5)$ Å, $\alpha = 82.09(3)°$, $\beta = 84.17(2)°$, $\gamma = 64.41(1)°$, and $V = 3263(2)$ Å^3. The compound represents the first authentic case of an end-on coordinating thio-oxalate. One silver atom is side-on bound, whereas the other one links two sulfur atoms end-on leaving the oxalate oxygen non-coordinated. The bridging trto ligand exhibits a torsion angle along C–C of 50(1)°. $[(Ph_3P)_2M]_2$(i-dto) (M = Cu (**2a**), Ag (**2b**)) are monoclinic, space group $P2_1/c$ (No. 14) with $Z = 4$, $a = 23.629(2)$ Å, $b = 13.723(1)$ Å, $c = 20.512(2)$ Å, $\beta = 104.06(1)°$, and $V = 6452(2)$ Å^3 for M = Cu and $a = 23.605(8)$ Å, $b = 13.737(4)$ Å, $c = 20.522(6)$ Å, $\beta = 103.92(2)°$, and $V = 6459(6)$ Å^3 for M = Ag. The bridging i-dto ligand links the metal centers side-on/side-on symmetrically, but is far from being planar showing a torsion angle along C–C of 19.3(5)°.

Introduction

Thiooxalates provide possibilities for both low-strained five-membered (side-on) or four-membered (end-on) chelate rings just for topological reasons. There are papers dealing with the coordination chemistry of monothiooxalate (mto),[1–6] tetrathiooxalate (tto),[7–9] and 1,2-dithiooxalate (dto).[10–14] The synthesis,[15] structures,[16,17] and vibration spectra[18] of alkaline salts of trithiooxalate (trto) and 1,1-dithiooxalate (i-dto) were reported already in the 1970s. In contrast little is known of their ligand properties.[19] One reason for that might be the high tendency of the ligands to form coordination polymers. Recently we reported the first complexes of trithiooxalate and 1,1-dithiooxalate.[20–23] In this paper we present the X-ray crystal structures of the binuclear compounds $[(Ph_3P)_2Ag]_2$(trto) and $(Ph_3P)_2M]_2$(i-dto) (M = Cu, Ag).

Experimental Section

Preparation of Compounds. K_2trto and K_2i-dto were prepared according to Stork and Mattes.[4] The crude products contain large amounts of KCl responsible for varying compositions K_2trto·nKCl and K_2i-dto·nKCl. They are more stable than the neat potassium thiooxalates, which are sensitive toward light, air, and moisture. Therefore, we used the crude products directly for the preparation of the complexes. Trithiooxalate can be stabilized as $(Ph_4As)_2$trto (mp 137–138 °C, from acetone/ether) or $(BzPh_3P)_2$trto (mp 116–118 °C, from dichloromethane/2-propanol) by precipitation from aqueous solutions of K_2trto with a 2-fold molar excess of the large cations.

$[(Ph_3P)_2Ag]_2$(trto) (1). A concentrated pyridine solution of 2 mmol $(Ph_3P)_3$AgCl was added drop by drop to 1 mmol $(Ph_4As)_2$trto, dissolved in 20 mL of pyridine under stirring. Cautious addition of 10 mL of

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Table 1. Crystallographic Data for **1** and **2a**

	1	**2a**
formula	$C_{74}H_{60}OP_4S_3Ag_2$	$C_{74}H_{60}O_2P_4S_2Cu_2$
fw	1401.1	1296.4
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$
a, Å	11.645(2)	23.629(2)
b, Å	13.473(2)	13.723(1)
c, Å	23.304(5)	20.512(2)
α, deg	82.09(1)	
β, deg	84.17(1)	104.06(1)
γ, deg	64.41(1)	
V, Å^3	3263(2)	6452(2)
Z	2	4
d_{calcd}, gcm^{-3}	1.426	1.335
d_{obsd}, gcm^{-3}	1.42(1)	1.33(1)
cryst size, mm	0.3 × 0.3 × 0.5	0.3 × 0.5 × 0.5
μ (MoK_α), cm^{-1}	8.253	8.645
diffractometer	Enraf-Nonius CAD4	Enraf-Nonius CAD4
radiation	Mo Kα, graphite monochromated	Mo Kα, graphite monochromated
temp, °C	20(1)	20(1)
scan method	ω-2θ	ω-2θ
data collcn range (2θ)	$\theta < 25°$	$\theta < 28°$
no. of data collcd	11392	16888
no. of unique data	8000	15440
no. of observed data	3995 (>2.5σ(*I*))	7784 (>2.5σ(*I*))
R	0.048	0.053
R_w	0.059	0.047

water precipitated the crude product which can be purified by reprecipitation from dichloromethane/2-propanol.

$[(Ph_3P)_2M]_2$(i-dto), M = Cu (2a), M = Ag (2b). A solution of 1 mmol of K_2i-dto (as K_2i-dto·4.5KCl) in 40 mL of water was extracted with a dichloromethane solution of 2 mmol of $(Ph_3P)_3$MCl (M = Cu, Ag). The deeply colored organic phase was separated, filtered, and diluted by the same amount of 2-propanol. After reduction of the volume in vacuo the dark colored crystals can be filtered off and purified as described for (**1**).

Elemental analyses verify the composition of the compounds.

X-ray Crystallography. Suitable crystals were obtained after dissolving the crude complexes in dichloromethane, covering the solution with an 2-propanol layer and storing at room temperature for some days in the dark.

Crystal data and details of data collection are given in Table 1.

Results and Discussion

Up to now all published X-ray structures with thiooxalate ligands show exclusively side-on coordination regardless whether they are acting as bridging or terminal ligands. There are three X-ray structures of complexes with 1,2-dithio- or tetrathiooxalate linking two equal metal centers.[8,13,14] In all cases the bridging thiooxalate was found as being strictly planar with an inversion center bisecting the C−C bond. Because of assignment uncertainties of the IR frequencies of binuclear trto complexes, e.g. an absorption at 1620 cm^{-1} hinting at a noncoordinated C═O entity, we have undertaken X-ray structure investigations and ab initio SCF calculations (see below). Another question was: How does the 1,1-dithiooxalate fit into the series of the other thiooxalates?

A. Structure of (1). The unit cell packing and the molecular structure are shown in Figures 1 and 2. The atomic coordinates along with the isotropic thermal parameters of the compound are given in Table 2. Selected bond distances and angles are presented in Table 3.

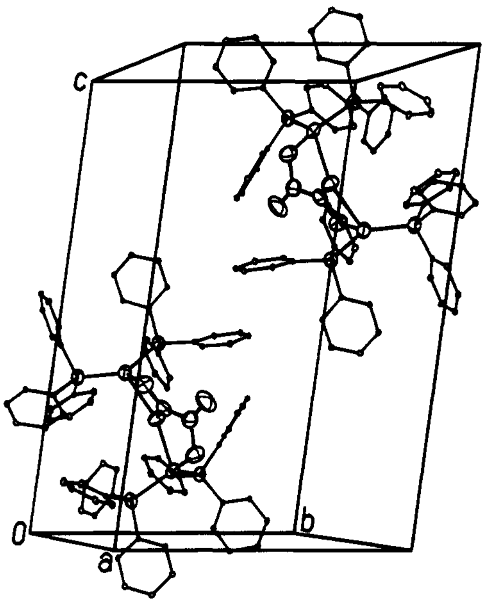

Figure 1. View of the unit cell of $[(Ph_3P)_2Ag]_2$(trto) (**1**).

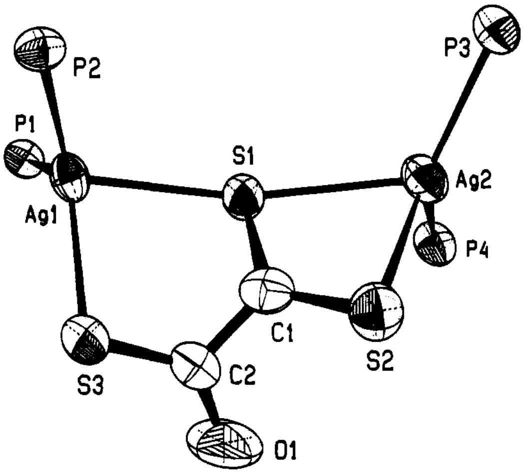

Figure 2. ORTEP drawing of the central unit of the complex (**1**). Ellipsoids are drawn with 50% probability boundaries, and phenyl rings have been omitted for the sake of clarity.

Table 2. Selected Atomic Coordinates and Equivalent Isotropic Temperature Factors, U_{eq} (Å^2), in $[(Ph_3P)_2Ag]_2$(trto) (**1**)

atom	*x*	*y*	*z*	U_{eq}[a]
Ag(1)	0.4025(1)	0.3674(1)	0.0445(1)	0.0531(4)
Ag(2)	0.3715(1)	0.1564(1)	0.3525(1)	0.0682(4)
P(1)	0.2037(2)	0.5391(2)	0.1328(1)	0.048(1)[b]
P2	0.4499(2)	0.2178(2)	0.0827(1)	0.051(1)[b]
P(3)	0.3216(2)	0.0075(2)	0.3432(1)	0.062(1)[b]
P(4)	0.2471(2)	0.3057(2)	0.4177(1)	0.062(1)[b]
S(1)	0.3757(2)	0.2934(2)	0.2555(1)	0.073(1)
S(2)	0.5975(2)	0.1579(2)	0.3272(1)	0.078(2)
C(1)	0.5210(9)	0.2654(7)	0.2773(4)	0.066(5)
C(2)	0.5846(9)	0.3419(8)	0.2542(4)	0.080(6)
S(3)	0.5985(3)	0.3710(2)	0.1817(1)	0.092(2)
O(1)	0.6246(11)	0.3743(9)	0.2923(4)	0.175(8)

[a] Equivalent isotropic *U* defined as one-third of trace of the orthogonalized U_{ij} tensor. [b] Carbon atoms of phenyl rings omitted. See the supplementary material.

Remarkable results can be seen in Figure 2. Both metal centers are bound to the bridging ligand in different ways, forming either a five-membered chelate ring (side-on coordination) as well as four-membered chelate ring (end-on coordination) simultaneously. It is thus the first authentic example for an end-on coordinated thiooxalate ligand. Each silver atom is coordinated to two sulfur and two phosphorus atoms forming a distorted tetrahedron. The oxalate oxygen is not involved in any coordination (see Figure 2). Therefore, the C−O bond length does not differ notably from those found in alkaline salts of thiooxalates (Cs_2i-dto·CsCl·H_2O, 1.26(1) Å;[16] K_2dto, 1.227

Table 3. Selected Bond Distances (Å) and Angles (deg) for $[(Ph_3P)_2Ag]_2(trto)$ (**1**)

Bond Distances			
Ag(1)−P(1)	2.472(2)	Ag(1)−S(1)	2.680(2)
Ag(1)−P(2)	2.473(2)	Ag(1)−S(3)	2.545(3)
Ag(2)−P(2)	2.447(3)	Ag(2)−S(1)	2.725(2)
Ag(2)−P(4)	2.516(2)	Ag(2)−S(2)	2.645(3)
C(1)−S(1)	1.68(1)	C(1)−C(2)	1.52(2)
C(1)−S(2)	1.696(8)	C(2)−O(1)	1.25(2)
C(2)−S(3)	1.69(1)		
P(1)−C(11)	1.817(9)	P(3)−C(71)	1.838(8)
P(1)−C(21)	1.828(8)	P(3)−C(81)	1.83(1)
P(1)−C(31)	1.82(1)	P(3)−C(91)	1.81(1)
P(2)−C(41)	1.834(7)	P(4)−C(101)	1.82(1)
P(2)−C(51)	1.835(8)	P(4)−C(111)	1.82(1)
P(2)−C(61)	1.81(1)	P(4)−C(121)	1.831(8)
Bond Angles			
P(1)−Ag(1)−P(2)	119.86(8)	S(1)−C(1)−S(2)	122.3(7)
P(3)−Ag(2)−P(4)	124.12(9)	O(1)−C(2)−S(3)	126(1)
S(1)−Ag(1)−S(3)	81.82(9)		
S(1)−Ag(2)−S(2)	66.87(8)		
Ag(1)−S(1)−Ag(2)	161.4(1)	S(1)−C(1)−C(2)−O(1)	50(1)

and 1.239 Å;[24] $K_2trto{\cdot}KCl$, 1.24(3) Å[17]). However, it should be noted that this C−O distance agrees with the C−O bond length in the corresponding side-on/side-on coordinated 1,2-dithiooxalate (1.213(9) Å)[14] or 1,1-dithiooxalate (1.28(2) and 1.27(2) Å). The C−C bond distance (1.52(2) Å) corresponds to a single bond, found also for other thiooxalates regardless if coordinated or not. The trto bridging ligand is not planar exhibiting a torsion angle (along the C−C axis) of 50(1)°, the largest one ever found for a coordinated thiooxalate ligand.

As expected, the Ag−S bond toward that sulfur coordinated simultaneously to both Ag atoms are longer than the other two Ag−S bonds and also significantly longer than those found in the silver binuclear complexes with dto and i-dto. This is due to the fact that the average Ag−S bond to the end-on coordinated silver is somewhat weaker than to the side-on.

Thus, the situation corresponds to these of the four Au−S and Cu−S bond lengths in $MoS_3O[Au(PPh_3)_2](AuPPh_3)$[25] or $MoS_3O[Cu(PPh_3)_2](CuPPh_3)$[26] with a central MoS_3O unit of three coordinated sulfurs and one noncoordinated oxygen consisting of an identical donor atom set as in the trithiooxalate bridging ligand. However, in these two examples the comparable differences in bond lengths should be caused more by the differences in the coordination number of the d^{10}-metal centers (one or two PPh_3 coligands) than by the topology of the bridging ligand (MoS_3O) where the chelate rings are almost equal.

The compound $[(Ph_3P)_2Ag]_2(mnt)$ (mnt = maleonitriledithiolate) contains also one sulfur atom bound simultaneously to two $(Ph_3P)_2Ag$ units; however, the bonding situation is quite different.[27]

B. Structure of $[(Ph_3P)_2M]_2(i\text{-}dto)$ (M = Cu, Ag). Figures 3 and 4 show the unit cell packing and the molecular structure of $[(Ph_3P)_2Cu]_2(i\text{-}dto)$(**2a**). The structural parameters and selected bond distances and angles are given in Tables 4 and 5. The silver complex **2b** is isomorphous to **2a**.

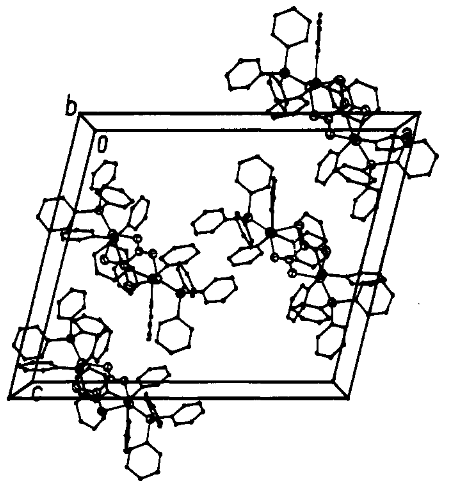

Figure 3. View of the unit cell of $[(Ph_3P)_2Cu]_2(i\text{-}dto)$ (**2a**).

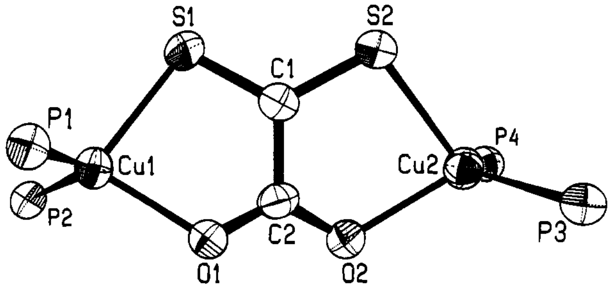

Figure 4. ORTEP drawing of the central unit of the complex (**2a**). Ellipsoids are drawn with 50% probability boundaries, and phenyl rings have been omitted for the sake of clarity.

Table 4. Selected Atomic Coordinates and Equivalent Isotropic Temperature Factors, U_{eq} (Å^2), in $[(Ph_3P)_2Cu]_2(i\text{-}dto)$ (**2a**)

atom	x	y	z	U_{eq}[a]
Cu(1)	0.34347(2)	0.52510(3)	0.58983(2)	0.0383(2)
Cu(2)	0.15732(2)	0.31454(4)	0.41658(2)	0.0414(2)
P(1)	0.33057(4)	0.68828(8)	0.58611(5)	0.0379(3)[b]
P(2)	0.42472(5)	0.44623(7)	0.64231(5)	0.0363(3)[b]
P(3)	0.09853(4)	0.38504(8)	0.32562(5)	0.0369(3)[b]
P(4)	0.16061(5)	0.15067(8)	0.43256(5)	0.0395(4)[b]
S(1)	0.25759(5)	0.47122(9)	0.61382(5)	0.0505(4)
S(2)	0.15572(5)	0.3939(1)	0.51628(6)	0.0515(4)
C(1)	0.2255(2)	0.4295(3)	0.5373(2)	0.036(1)
C(2)	0.2614(2)	0.4227(3)	0.4847(2)	0.038(1)
O(1)	0.3076(1)	0.4723(2)	0.4938(1)	0.043(1)
O(2)	0.2436(1)	0.3679(2)	0.4349(1)	0.046(1)

[a] Equivalent isotropic U defined as one-third of trace of the orthogonalized $\mathbf{U}_{ij}$ tensor. [b] Carbon atoms of phenyl rings omitted. See supplementary material.

Considering the thiophilic behavior of the "$M(PPh_3)_2$" units and the bonding situation in $[(Ph_3P)_2Ag]_2(trto)$ described above, the side-on/side-on coordination is rather surprising. In contrast to other binuclear symmetrically bridged thiooxalate complexes[8,13,14] the bridging 1,1-dithiooxalate is far from being planar, with a torsion angle (along the C−C bond) of 19.3(5)° (see Figure 4).

The C−S bond distances in $[(Ph_3P)_2Cu]_2(i\text{-}dto)$ are somewhat longer and the C−O bond distances are significantly shorter than those in the compound of the isomeric ligand, 1,2-dithiooxalate (dto), $[(Ph_3P)_2Ag]_2(dto)$, obviously a consequence of differences in π electron delocalization.

C. MO Calculations. Why is the oxygen of trithiooxalate not involved in any coordination? The unusual side-on/end-on coordination mode should be caused by the electronic structure of the bridging group. For possible answer we carried out ab initio SCF calculations for trithiooxalate and the related ligands 1,1-dithiooxalate and tetrathiooxalate. Keeping planar molecular structures the geometries of the systems were fully optimized using the minimal STO-3G basis set.

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Table 5. Selected Bond Distances (Å) and Angles (deg) for $[(Ph_3P)_2Cu]_2$(i-dto) (**2a**)

	Bond Distances		
Cu(1)−P(1)	2.259(1)	Cu(1)−S(1)	2.322(1)
Cu(1)−P(2)	2.239(1)	Cu(1)−O(1)	2.076(3)
Cu(2)−P(3)	2.256(1)	Cu(2)−S(2)	2.319(1)
Cu(2)−P(4)	2.271(1)	Cu(2)−O(2)	2.112(3)
C(1)−S(1)	1.670(4)	C(1)−C(2)	1.529(6)
C(1)−S(2)	1.676(4)	C(2)−O(2)	1.256(5)
C(2)−O(1)	1.261(5)		
P(1)−C(11)	1.824(4)	P(3)−C(71)	1.825(4)
P(1)−C(21)	1.828(4)	P(3)−C(81)	1.840(5)
P(1)−C(31)	1.837(4)	P(3)−C(91)	1.839(4)
P(2)−C(41)	1.837(4)	P(4)−C(101)	1.831(5)
P(2)−C(51)	1.832(4)	P(4)−C(111)	1.833(4)
P(2)−C(61)	1.824(4)	P(4)−C(121)	1.836(4)
	Bond Angles		
P(2)−Cu(1)−P(1)	126.05(4)	S(1)−C(1)−S(2)	122.6(3)
P(3)−Cu(2)−P(4)	122.46(4)	O(1)−C(2)−O(2)	123.4(4)
S(1)−Cu(1)−O(1)	85.02(9)		
S(2)−Cu(2)−O(2)	84.51(9)	S(1)−C(1)−C(2)−O(1)	−19.3(5)

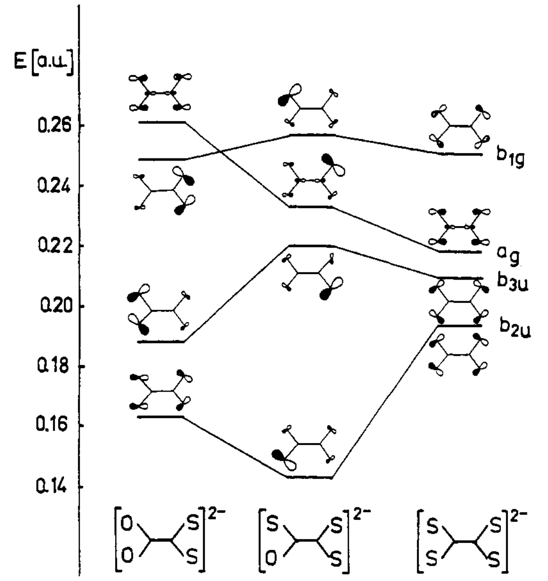

Figure 5. Molecular orbital scheme for the highest σ lone pair orbitals of i-dto, trto, and tto.

Figure 5 shows the highest occupied molecular orbitals of the systems under study. Only the in-plane σ donor orbitals are represented, π orbitals have been omitted. For tto we get the four donor orbitals b_{1g}, a_g, b_{3u}, and b_{2u}, which is in agreement with the detailed EHT MO anlaysis of Alvarez et al.[28] Merely, a modified order of the orbitals results due to the ab initio SCF procedure. But this does not influence the argument of these authors namely that because of the more effective overlap between the ligand and the metal orbitals the side-on (or dithiolene-like) coordination mode is preferred in comparison to the end-on (or dithiocarboxylate-like). For i-dto the molecular orbital picture is only slightly modified, thus indicating a similar coordination behavior confirmed by the X-ray structures of $[(Ph_3P)_2M]_2$(i-dto) (M = Cu, Ag), reported in this paper. For trto, however, the situation changes. Now a group of three donor orbitals mainly localized at the sulfur atoms is significantly separated from one low-lying orbital localized at the oxygen. From this follows that the upper three orbitals should act as donor orbitals in the usual manner, whereas the oxygen in-plane lone pair should have a much weaker donor ability responsible for the non-coordinated oxygen and, therefore, for the simultaneous side-on/end-on coordination in $[(Ph_3P)_2Ag]_2$(trto). A second remarkable structural feature is the large torsion angle along the C−C axis. Usually, the trithiooxalate bridges are planar moieties. Regardless of any steric repulsion there is an electronic reason for this torsion. There would be only three electron pairs for four Ag−S bonds in a planar trto bridge. Due to the torsion with a relatively large angle a former π lone pair orbital of trto now overlaps with the acceptor orbitals of the $[Ag(PR_3)_2]^+$ group in the side-on position. Thus, two of the lone pairs of the sulfur atom S(1) become involved in the coordination leading to a total of four electron pairs for the four Ag−S bonds. From the shared donation arising from the sulfur atom S(1), it can be concluded that the two bonds between S(1) and the silver atoms are weaker then the remaining two coordinative bonds. This should be at least one reason for the experimental fact that the bond distances Ag(1)−S(1) and Ag(2)−S(1) are longer than Ag(1)−S(3) and Ag(2)−S(2).

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Supplementary Material Available: Listings of final atomic coordinates (Tables IIs and IVs), anisotropic thermal parameters (Tables VIs and VIIs) and hydrogen atom coordinates (Tables VIIIs and IXs) (18 pages). Ordering information is given on any current masthead page. Structure factor tables are available from L.G. upon request.

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