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GRANT N00014-89-J-3198

R&T Code b41c013dar

Technical Report No. 16

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"A Di(μ -oxo)bridged Ruthenium Dimer

by

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To be published in Acta Cryst.

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April 1992

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93-00473



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REPORT DOCUMENTATION PAGE

Form Approved
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1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE		3. REPORT TYPE AND DATES COVERED Technical	
4. TITLE AND SUBTITLE A Di(u-oxo)bridged Ruthenium Dimer.				5. FUNDING NUMBERS G N00014-89-J3198	
6. AUTHOR(S) W. P. Schaefer, J. M. Power, J. A. Labinger and J. E. Bercaw					
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Division of Chemistry California Institute of Technology Pasadena, CA. 91125				8. PERFORMING ORGANIZATION REPORT NUMBER 16	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research Chemistry Division 800 N. Quincy Street Arlington, VA. 22217-5000				10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES					
12a. DISTRIBUTION/AVAILABILITY STATEMENT This document has been approved for public release and sale: its distribution is unlimited.				12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) [LOEt(H ₂ O)Ru(μ-O) ₂ Ru(OH ₂)LOEt]Cl ₂ · 2H ₂ O · C ₆ D ₆ (LOEt = (C ₅ H ₅)Co(P(O)-(OC ₂ H ₅) ₂) ₃) has a core structure similar to that found in the triflate salt, with Ru-Ru distance 2.476(1) Å and Ru-μ-O distance 1.894(4) Å. The bound water molecules (Ru-O, 2.045(5)Å) are hydrogen bonded to an oxygen atom attached to the opposite Ru atom and to a Cl ⁻ ion; the solvent water is hydrogen bonded to a bridging O atom and to a Cl ⁻ ion.					
14. SUBJECT TERMS				15. NUMBER OF PAGES	
				16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified		18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified		19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	
				20. LIMITATION OF ABSTRACT UL	

A Di(μ -oxo) bridged Ruthenium Dimer

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(Received _____ ; Accepted _____)

DTIC QUALITY INSPECTED 6

Abstract

$[\text{LOEt}(\text{H}_2\text{O})\text{Ru}(\mu\text{-O})_2\text{Ru}(\text{OH}_2)\text{LOEt}]\text{Cl}_2 \cdot 2\text{H}_2\text{O} \cdot \text{C}_6\text{D}_6$ ($\text{LOEt} = (\text{C}_5\text{H}_5)\text{Co}(\text{P}(\text{O})(\text{OC}_2\text{H}_5)_2)_3$) has a core structure similar to that found in the triflate salt, with Ru-Ru distance 2.476(1) Å and Ru- μ -O distance 1.894(4) Å. The bound water molecules (Ru-O, 2.045(5) Å) are hydrogen bonded to an oxygen atom attached to the opposite Ru atom and to a Cl^- ion; the solvent water is hydrogen-bonded to a bridging O atom and to a Cl^- ion.

Comment

The structure of $[\text{LOEt}(\text{H}_2\text{O})\text{Ru}(\mu\text{-O})_2\text{Ru}(\text{OH}_2)\text{LOEt}][\text{CF}_3\text{SO}_3]_2$ was previously reported (Power, Evertz, Henling, Schaefer, Labinger, & Bercaw, 1990, hereafter Power *et al.*). Both the relative terminal and bridging oxygen to ruthenium distances, and the ^1H NMR spectrum, support the above formulation. However, it was not possible to eliminate conclusively the structural alternative $[\text{LOEt}(\text{HO})\text{Ru}(\mu\text{-OH})_2\text{Ru}(\text{OH})\text{LOEt}]$, owing in part to disorder in the triflate anion. Accordingly, we undertook the preparation and structural characterization of the corresponding chloride salt, in hopes that we could locate the hydrogen atoms of the coordinated water and finally resolve this issue. While this was not achieved, we have been able to infer the hydrogen atom locations from a hydrogen

* Contribution No. 8625

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bonding model; this provides convincing evidence that the terminal ligands are in fact water molecules and not hydroxide ions.

Final parameters are given in Table 1, with selected distances and angles in Figure 2. The core geometry of the Ru dimer resembles closely that found earlier (our values quoted first, then those of Power *et al.*, (1990): Ru-Ru, 2.476(1), 2.505(1) Å; Ru- μ -O, 1.891(4) and 1.897(4) Å, 1.909(4) and 1.926(4) Å; Ru-OH₂, 2.045(5), 2.050(4) Å; Ru-Ru-OH₂, 91.7(1)°, 91.6(1)°. Distances and angles in the Kläui (1979) ligand are about as we have found earlier: around Co things are normal, but the ethoxy groups show large displacement parameters and thus unusual (artificial) distances and angles. A drawing of the molecule showing the numbering is in Figure 1.

The Ru cations crystallize with two Cl⁻ ions per dimer, two moles of H₂O per dimer and one deuterobenzene molecule per dimer. The benzene has no significant interactions with other atoms; its closest contact is C22...H12b, 2.81(1) Å, essentially a van der Waals distance. The Cl⁻ and H₂O do however form with the cation a hydrogen bonded group. Coordinated water O2 donates an H bond across the dimer to O4', 2.613(7) Å away, and another to Cl, 2.927(5) Å away; these two bonds subtend an angle of 105.2(2)°. The Cl⁻ ion also receives a hydrogen bond from solvent W 3.200(9) Å distant; W's other hydrogen atom forms an H bond to bridging O1, 3.151(9) Å away. O2 and W do not appear to accept H bonds—not surprising, considering the few donors available. The closest approach is H2...W, 2.57(1) Å, a van der Waals distance. The packing is shown in Figure 2.

Acknowledgement

This work was supported by the National Science Foundation (Grant No. CHE-8901593) and by the Office of Naval Research (Grant No. N00014-89-J-3198).

Lists of assigned hydrogen parameters, anisotropic displacement parameters, complete distances and angles, and observed and calculated structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP XXXXX (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, ENGLAND.

References

- Cromer, D. T. (1974). *International Tables For X-ray Crystallography*, Vol. IV, pp. 149-151. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
- Cromer, D. T. & Waber, J. T. (1974). *International Tables For X-ray Crystallography*, Vol. IV, pp. 99-101. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
- Duchamp, D. J. (1964). Am. Crystallogr. Assoc. Meet., Bozeman, Montana, Paper B14, p. 29.
- Johnson, C. K. (1976). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Oak Ridge, Tennessee, USA.
- Kläui, W. (1979). *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **34b**, 1403-
- Larson, A. C. (1967). *Acta Cryst.* **23**, 644-665.
- Power, J. M., Everts, K., Henling, L. M., Marsh, R. E., Schaefer, W. P., Labinger, J. A. & Bercaw, J. E. (1990). *Inorg. Chem.* **29**, 5058-5065.

Legends for Figures.

Figure 1. An ORTEP drawing of the molecule with 20% probability ellipsoids showing the numbering system. Unnumbered atoms are related to numbered ones by an inversion center midway between the Ru atoms. Hydrogen atoms are shown as circles of small, arbitrary size.

Figure 2. An ORTEP drawing of the outline of a unit cell, projected onto the *bc* plane. The contents of a cell, plus three additional cations and benzene molecules (20% probability ellipsoids, hydrogens omitted) are shown.

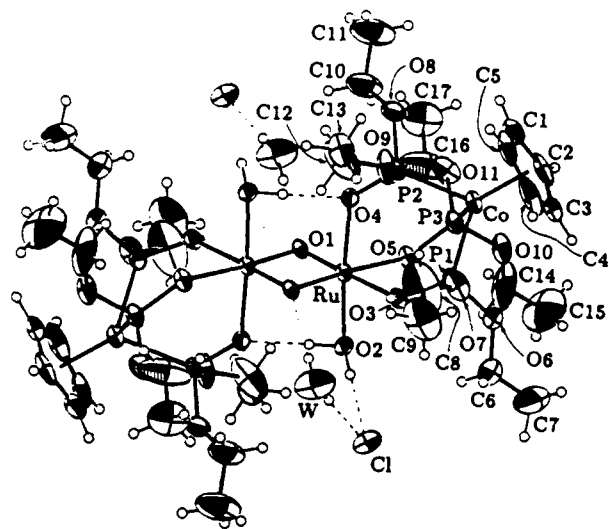


Figure 1.

Schaefer, Power, Sabinger & Percaw

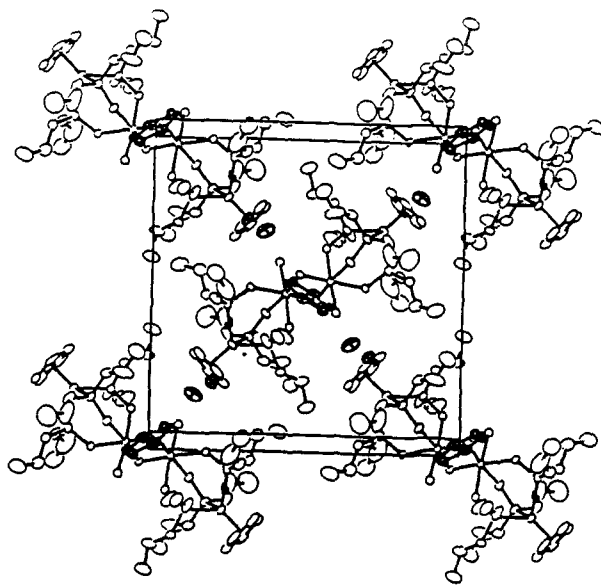


Figure 2.

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APPENDIX 2

Experimental form to be completed for each structure (hard-copy submission)

EXPERIMENTAL DETAILS	
E.s.d.'s should be given where appropriate. Please complete separate form for each compound studied	
Compound [e.g. (1), (2) etc.] 1	
CRYSTAL DATA	
Chemical formula $Ru_2O_2Cl_2[(C_5H_5)_2Co(P(O)(OC_2H_5)_2)_3]_2 \cdot C_6D_6 \cdot 2H_2O$	Crystal system MONOCLINIC
M_r 1495.85	Space group $P2_1/n$
a (Å) 12.074(3)	α (°) 90
b (Å) 16.304(4)	β (°) 94.34(2)
c (Å) 16.369(5)	γ (°) 90
Z 2	D_m (Mg m ⁻³)
V (Å ³) 3213.1(15)	D_c (Mg m ⁻³) 1.55
Radiation $MoK\alpha$	No. of reflections for lattice parameters 25
Wavelength (Å) 0.71073	θ range for lattice parameters (°) 15-17
Absorption coefficient (mm ⁻¹) 1.28	Temperature (K) 293
Crystal source SYNTHESIZED BY JMP	
Crystal colour BROWN	Crystal description TRUNCATED TETRAGONAL BIPYRAMID
Crystal size (mm) 0.11 x 0.20 x 0.22	
DATA COLLECTION	
Diffractometer type ENRAF-NONIUS CAD-4	Collection method OMEGA SCANS
Absorption correction type (circle appropriate description) analytical integration empirical re/delf sphere cylinder none	Absorption correction (T_{min} , T_{max}) -
No. of reflections measured 7079	R_{int} 0.021
No. of independent reflections 2999	θ_{max} (°) 17.5
No. of observed reflections 2999	No. of standard reflections (and interval) THREE, EVERY 10,000 SECONDS
Criterion for observed ALL REFLECTIONS USED	Variation of standards 1.8% TOTAL DECAY
h_{min} -10	h_{max} 10
k_{min} -14	k_{max} 14
l_{min} 0	l_{max} 14

EXPERIMENTAL DETAILS (continued)

REFINEMENT

Treatment of hydrogen atoms (circle appropriate entry, or describe in box below) refall refxyz refU (noref)	$F(F)$ or 1
$R(ONF)$ 0.040 FOR 2265 REFLECTIONS WITH $F_o^2 > 3\sigma(F_o^2)$	No. of parameters refined 343
$wR(ON F^2)$ 0.008	No. of reflections used in refinement 2999
S 1.75	Weighting scheme $w = 1/\sigma^2(F_o^2)$
$(\Delta/\sigma)_{max}$ 0.09	$(\Delta\rho)_{min}$ ($e \text{ \AA}^{-3}$) REF - 0.55
Extinction correction method (if applied) N.A.	$(\Delta\rho)_{max}$ ($e \text{ \AA}^{-3}$) +1.41, NEAR RU +0.57 ELSEWHERE
Primary- and secondary-extinction values -	Source of atomic scattering factors CROMER & WABER, 1974

Please enter below, in grammatically correct text, details of any novel or unusual features of the experimental procedure; method used to measure density, discussion of absolute structure and justification of unusually high R values or shift-to-e.s.d. values >1.0 should be included (attach extra sheet if necessary)

A chemical structural diagram should be attached to this form.

The remainder of the manuscript should consist of (i) double-spaced typed text and tables set out under the standard subheadings of §3 of the full Notes, (ii) figures and figure legends, (iii) supplementary data for deposition (see §4), (iv) signed Transfer of Copyright Agreement form, and (v) letter of submission.

The data were corrected for absorption by an empirical method based on psi scans, but the resulting goodness of fit for merging - 1.6 - was so much worse than without the correction - 0.977 - that we used the uncorrected data. Hydrogen atoms were placed at calculated positions except for those on O2 and W, where they were put on the line to the acceptor atom, O-H \sim 0.88 Å; hydrogen atoms were repositioned near the end of the refinement. The weights were taken as $1/\sigma^2(F_o^2)$; variances ($\sigma^2(F_o^2)$) were derived from counting statistics plus an additional term, $(0.014I)^2$; variances of the merged data were obtained by propagation of error plus another additional term, $(0.014\bar{I})^2$. Atomic scattering factors and values for $\Delta f'$ were taken from Cromer and Waber (1974) and Cromer (1974); the programs used were those of the CRYM Crystallographic Computing System (Duchamp, 1964) and ORTEP (Johnson, 1976). The secondary extinction correction was that of Larson (1967).

Table 1. Final Non-Hydrogen Coordinates and Displacement Parameters for



x, y, z and $U_{eq}^a \times 10^4$				
Atom	x	y	z	U_{eq}
Ru	5184.4(5)	5715.1(4)	4794.7(4)	361(2)
Co	4659.8(8)	7397.6(6)	3098.9(7)	456(3)
P1	4359(2)	7573(1)	4370(1)	485(6)
P2	3889(2)	6211(1)	3054(1)	442(6)
P3	6258(2)	6863(1)	3449(1)	489(6)
O1	5985(4)	4733(3)	4641(3)	377(12)
O2	6143(4)	5928(3)	5858(3)	487(14)
O3	4479(4)	6840(3)	4933(3)	478(14)
O4	4308(4)	5565(3)	3687(3)	451(13)
O5	6378(4)	6333(3)	4213(3)	464(15)
O6	5157(6)	8268(3)	4717(4)	792(20)
O7	3191(5)	7961(4)	4479(4)	805(20)
O8	3908(6)	5801(4)	2206(4)	899(25)
O9	2602(5)	6303(4)	3108(5)	874(25)
O10	7159(5)	7552(4)	3567(4)	832(22)
O11	6635(5)	6352(4)	2701(4)	746(19)
C1	4557(15)	7620(7)	1861(6)	864(37)
C2	5364(8)	8111(9)	2237(9)	848(37)
C3	4901(17)	8602(7)	2796(8)	990(47)
C4	3775(16)	8431(10)	2744(11)	1133(50)

Table 1. (Cont.)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
C5	3574(11)	7837(10)	2169(10)	1005(47)
C6	5363(16)	8483(9)	5523(9)	1756(69)
C7	6005(18)	9139(12)	5701(10)	2268(85)
C8	2319(14)	7640(12)	4742(14)	2240(84)
C9	1623(14)	7969(11)	5212(11)	1875(68)
C10	4344(12)	5121(9)	1953(8)	1327(55)
C11	4239(16)	4954(10)	1120(9)	1987(77)
C12	1848(10)	5761(10)	3248(8)	1530(62)
C13	708(8)	5944(7)	3146(7)	994(39)
C14	8031(15)	7619(10)	4087(13)	2210(83)
C15	8637(15)	8238(13)	4210(14)	2422(92)
C16	7500(14)	5826(12)	2716(9)	1995(77)
C17	7744(12)	5437(10)	2046(10)	1561(56)
Cl	5501(2)	6983(2)	7189(2)	873(8)
W	3015(6)	6402(6)	6677(5)	1417(32)
C20	4578(12)	9323(6)	340(6)	770(33)
C21	5677(11)	9499(7)	482(6)	718(32)
C22	3901(7)	9818(8)	-136(7)	692(33)

$$^a U_{eq} = \frac{1}{3} \sum_i \sum_j [U_{ij}(a_i^* a_j^*)(\vec{a}_i \cdot \vec{a}_j)]$$

**Table 2. Selected Distances and Angles for
 $[\text{LOEt}(\text{H}_2\text{O})\text{Ru}(\mu\text{-O})_2\text{Ru}(\text{OH}_2)\text{LOEt}]^{2+} \cdot 2\text{Cl}^- \cdot 2\text{H}_2\text{O}$.**

	Distance(Å)		Angle(°)
Ru -O1	1.897(4)	O2 -Ru -O1	89.7(2)
Ru -O2	2.045(5)	O3 -Ru -O1	173.7(2)
Ru -O3	2.042(5)	O4 -Ru -O1	90.9(2)
Ru -O4	2.043(5)	O5 -Ru -O1	88.3(2)
Ru -O5	2.050(5)	O1 -Ru -O1'	98.3(2)
Ru -O1'	1.891(4)	O3 -Ru -O2	88.1(2)
Co -P1	2.157(2)	O4 -Ru -O2	175.4(2)
Co -P2	2.146(2)	O5 -Ru -O2	86.5(2)
Co -P3	2.154(2)	O1 -Ru -O2	92.6(2)
P1 -O3	1.509(5)	O4 -Ru -O3	90.8(2)
P1 -O6	1.567(7)	O5 -Ru -O3	85.6(2)
P1 -O7	1.568(7)	O1 -Ru -O3	87.7(2)
P2 -O4	1.536(5)	O5 -Ru -O4	89.0(2)
P2 -O8	1.543(7)	O1 -Ru -O4	91.8(2)
P2 -O9	1.570(7)	O1 -Ru -O5	173.3(2)
P3 -O5	1.519(5)	P2 -Co -P1	92.8(1)
P3 -O10	1.566(7)	P3 -Co -P1	90.6(1)
P3 -O11	1.577(6)	P3 -Co -P2	91.3(1)
		O3 -P1 -Co	117.9(2)
		O6 -P1 -Co	107.6(3)

Table 2. (Cont.)

	Angle(°)
O7 -P1 -Co	112.4(3)
O4 -P2 -Co	118.4(2)
O8 -P2 -Co	112.6(3)
O9 -P2 -Co	109.9(3)
O5 -P3 -Co	118.5(2)
O10 -P3 -Co	110.1(3)
O11 -P3 -Co	108.3(2)
Ru -O1 -Ru'	81.7(2)
P1 -O3 -Ru	131.7(3)
P2 -O4 -Ru	129.6(3)
P3 -O5 -Ru	129.5(3)