Inorganica
Chimica Acta
Preliminary Communication

A tris-(μ_2-I) face-sharing dizirconium(III) complex, $[1,4\text{-}Zr_2I_7(PEt_3)_2]^-$; the first such dizirconium species

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(Received September 30, 1993)

Abstract

We report here the first example of a $[1,4\text{-}Zr_2X_7L_2]^-$ species, in the compound $[NBu_4][Zr_2I_7(PEt_s)_2]$. It was prepared by reduction of ZrI by $HSn(n\text{-}Bu)_3$ followed by addition of $[NBu_4]I$ and PEt_3, all reagents being used in the correct stoichiometric ratio. The yield was *c.* 17%. X-ray crystallography showed that the anion is a face-sharing bioctahedron with a Zr–Zr distance of 3.171(3) Å and it is concluded that there is a Zr–Zr sigma bond. The compound forms monoclinic crystals in space group $P2_1/m$ (No. 11) with $a=11.577(1)$, $b=12.808(1)$, $c=16.860(1)$ Å, $\beta=98.78(1)°$, $V=2470.6(6)$ Å^3 and $Z=2$. With 167 parameters refined on 1603 reflections having $F^2>3\sigma(F^2)$ the final R factors were $R=6.14\%$ and $R_w=7.37\%$.

Key words: Crystal structures; Zirconium complexes, Dinuclear complexes

Relatively few Zr–Zr bonded binuclear complexes have been structurally characterized [1–4] and they are nearly all of the edge-sharing type [1–3], although face-sharing bioctahedra are, in general, very common [5]. We report here the first example of a simple $[Zr_2X_7L_2]^-$ species, which is relatively easy to prepare and which has been fully characterized by X-ray crystallography. The compound is $[NBu_4][1,4\text{-}Zr_2I_7(PEt_3)_2]$, where the numerical descriptors are used according to a recently proposed scheme [6].

The only previously reported Zr–Zr bonded dinuclear compounds with μ-I ligands were edge-sharing $Zr_2I_6(PR_3)_4$ molecules [3] in which the Zr–Zr distances were 3.39–3.44 Å. Even though these Zr–Zr distances may seem relatively long there is strong support from molecular orbital calculations [3, 7] for the assignment of direct sigma bonding between the metal atoms.

In the preparation, manipulations were carried out under an argon atmosphere by using standard vacuum-line and Schlenk techniques. The solvents were freshly distilled under nitrogen from the appropriate drying reagents. ZrI_4 and PEt_3 were purchased from Strem Chemicals (ZrI_4 obtained from this supplier was free of I_2) and used as received. The tetrabutylammonium iodide (Aldrich Co.) was recrystallized from benzene and then dried at 80 °C on a vacuum line for 12 h.

ZrI_4 (0.599 g, 1.0 mmol) was stirred in 25 ml of benzene and $HSn(n\text{-}Bu)_3$ (0.28 ml, 1.04 mmol) was added dropwise. The addition of $HSn(n\text{-}Bu)_3$ caused a rapid effervescence, presumably H_2, and the formation of a red–brown precipitate on the bottom of the reaction vessel. After 24 h of stirring, the precipitate was isolated by decantation and washed with two 10 ml portions of fresh benzene solvent. In a separate flask, $[NBu_4]I$ (0.369 g, 1.0 mmol) and PEt_3 (0.15 ml, 1.0 mmol) were added to 20 ml of benzene. This solution was then transferred by cannula to the flask containing the reduced zirconium iodide precipitate. The mixture was stirred for 24 h. The resulting light brown solution was filtered into a Schlenk tube and layered with 25 ml of hexanes. Upon standing for one week, the solution afforded brown crystalline plates. The crystalline yield was 110 mg (16.7%).

The structure determination was carried out in a routine fashion by employing methods standard in our laboratory. All intensity data were corrected for Lorentz and polarization effects and isotropic decay. An empirical absorption correction based on the DIFABS method [8] was also applied. The calculations were conducted on a microvax II computer with the SDP software package. Direct methods [9] revealed the positions of the zirconium and iodine atoms. The remaining non-hydrogen atoms were found from alternating series of least-squares refinements and difference Fourier maps. The $[NBu_4]^+$ and $[1,4\text{-}Zr_2I_7(PEt_3)_2]^-$ ions reside on crystallographic mirror planes. In the cation, one butyl group extended in two directions at the methyl carbon atom (C(23a) and C(23b)). The two sites, C(23a) and C(23b), are related to each other by a mirror plane and were refined at 0.5 occupancy. Additional crystallographic data are compiled in Table 1. Positional parameters are listed in Table 2 and important bond distances and angles are listed in Table 3.

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Elsevier Sequoia
SSDI 0020-1693(93)03750-5

TABLE 1 Crystal data for $[NBu_4][Zr_2I_7(PEt_3)_2]$

Formula	$Zr_2I_7P_2NC_{28}H_{66}$
Formula weight	1549.6
Space group	$P2_1/m$ (No. 11)
Systematic absences	$0k0$ $(k=2n+1)$
a (Å)	11.577(1)
b (Å)	12.808(1)
c (Å)	16.860(1)
α (°)	90
β (°)	98.78(1)
γ (°)	90
V (Å^3)	2470.6(6)
Z	2
D_{calc} (g/cm^3)	2.083
Crystal size (mm)	0.15×0.10×0.20
μ(Kα) (cm^{-1})	390.37 (Cu)
Data collection instrument	Rigaku AFC5R
Radiation monochromated (Å)	Cu Kα, 1.54184
Orientation reflections: no., range	25, $42 \leqslant 2\theta \leqslant 48$
Temperature (°C)	21 (±2)
Scan method	ω–2θ
Data collection range, θ (°)	$4 \leqslant 2\theta \leqslant 115$
No. unique data, total with $F_o^2 > 3\sigma(F_o^2)$	3364, 1603
No. parameters refined	167
Transmission factors max., min.	1.000, 0.1052
R^a	0.06140
R_w^b	0.07373
Quality-of-fit indicator^c	1.407
Largest shift/e.s.d., final cycle	0.13
Largest peak (e/Å^3)	1.467

$^aR = \Sigma||F_o|-|F_c||/\Sigma|F_o|$ $^bR_w = [\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$, $w = 1/\sigma^2(|F_o|)$. ^{c}Quality-of-fit $= [\Sigma w(|F_o|-|F_c|)^2/(N_{obs}-N_{param})]^{1/2}$.

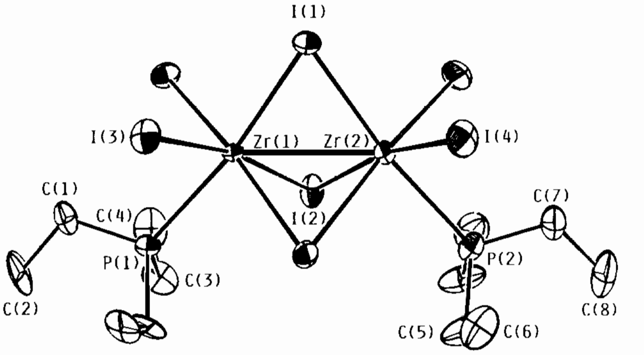

Fig. 1. An ORTEP drawing of the $[1,4\text{-}Zr_2I_7(PEt_3)_2]^-$ ion. The thermal ellipsoids are at the 50% level.

The structure of the $[1,4\text{-}Zr_2I_7(PEt_3)_2]^-$ ion is shown in Fig. 1. It can be seen that of the two possible isomers with one PEt_3 on each metal atom, the one formed, the 1,4-isomer, is the more symmetrical one. The anion has strict crystallographic mirror symmetry, with the mirror plane containing P(1), P(2), Zr(1), Zr(2) and I(1), but the virtual symmetry is C_{2v}. The various metal to ligand distances are in the correct ranges. It is interesting that the Zr–I_b distances *trans* to Zr–P bonds are shorter than those *trans* to Zr–I_t bonds. Thus the *trans* influence of the PEt_3 ligands is less than that of the I_t ligands. This unusual situation is attributable to the lack of any Zr–P π-bonding and the long Zr–P distances.

TABLE 2 Positional and equivalent isotropic displacement parameters and e.s.d.s. for $[NBu_4][Zr_2I_7(PEt_3)_2]$

Atom	x	y	z	B_{eq}^{a} (Å^2)
Zr(1)	0.4771(2)	0.250	0.2945(1)	2.24(6)
Zr(2)	0.2517(2)	0.250	0.1615(2)	3.03(7)
I(1)	0.2445(2)	0.250	0.3301(1)	5.37(7)
I(2)	0.4436(1)	0.1001(2)	0.1623(1)	4.58(4)
I(3)	0.5360(2)	0.4137(2)	0.4057(1)	4.77(4)
I(4)	0.0905(2)	0.4186(2)	0.1406(1)	6.16(5)
P(1)	0.7157(8)	0.250	0.2826(5)	3.3(2)
P(2)	0.2294(9)	0.250	−0.0050(6)	4.5(3)
N	0.349(2)	0.750	0.305(2)	8(1)
C(1)	0.806(3)	0.250	0.381(2)	6(1)
C(2)	0.945(3)	0.250	0.371(3)	10(2)
C(3)	0.774(2)	0.143(2)	0.224(2)	5.7(8)
C(4)	0.767(2)	0.033(2)	0.263(2)	7.1(9)
C(5)	0.305(3)	0.361(3)	−0.054(2)	8(1)
C(6)	0.257(3)	0.462(3)	−0.038(2)	8(1)
C(7)	0.079(3)	0.250	−0.054(2)	7(1)
C(8)	0.060(4)	0.250	−0.148(3)	10(2)
C(10)	0.265(4)	0.656(4)	0.314(3)	16(2)*
C(11)	0.237(3)	0.614(4)	0.373(2)	12(1)*
C(12)	0.152(3)	0.549(4)	0.391(3)	13(1)*
C(13)	0.064(5)	0.514(6)	0.411(4)	23(3)*
C(20)	0.473(7)	0.750	0.347(6)	23(4)*
C(21)	0.565(5)	0.750	0.333(4)	15(2)*
C(22)	0.676(6)	0.750	0.386(5)	17(3)*
C(23a)	0.72(1)	0.750	0.46(1)	22(7)*
C(23b)	0.762(9)	0.750	0.372(7)	12(4)*
C(30)	0.334(5)	0.750	0.209(4)	13(2)*
C(31)	0.368(7)	0.750	0.157(5)	20(3)*
C(32)	0.342(6)	0.750	0.062(4)	15(2)*
C(33)	0.244(6)	0.750	0.023(5)	17(3)*

^{a}Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $(4/3)[a^2\beta_{11}+b^2\beta_{22}+c^2\beta_{33}+ab(\cos\gamma)\beta_{12}+ac(\cos\beta)\beta_{13}+bc(\cos\alpha)\beta_{23}]$

The most interesting structural feature is the Zr–Zr distance of 3.171(3) Å, some 0.25 Å shorter than those in the $Zr(\mu\text{-}I)_2Zr$ cases [3]. The Zr–I_b–Zr angles, averaging 66.3°, indicate a bonding attraction between the metal atoms [5] and together with the short Zr–Zr distance leaves little doubt that a Zr–Zr single bond is present.

Supplementary material

Full listing of bond distances, bond angles, isotropic equivalent displacement parameters, and tables of observed and calculated structure factors for $[NBu_4][1,4\text{-}Zr_2I_7(PEt_3)_2]$ are available on request from author F.A.C.

TABLE 3. Selected listing of bond distances (Å) and angles (°) for $[NBu_4][Zr_2I_7(PEt_3)_2]$

Bond distances (Å)					
Zr(1)–Zr(2)	3.171(3)	Zr(2)–I(2)	2.934(3)	P(2)–C(7)	1.81(4)
Zr(1)–I(1)	2.847(4)	Zr(2)–I(4)	2.840(3)	N–C(10)	1.57(5)
Zr(1)–I(2)	2.922(3)	Zr(2)–P(2)	2 78(1)	N–C(20)	1.50(9)
Zr(1)–I(3)	2.825(2)	P(1)–C(1)	1 83(4)	N–C(30)	1 60(8)
Zr(1)–P(1)	2.800(9)	P(1)–C(3)	1 87(3)		
Zr(2)–I(1)	2.856(4)	P(2)–C(5)	1 92(3)		
Bond angles (°)					
Zr(2)–Zr(1)–I(3)	123.94(7)	Zr(1)–Zr(2)–I(4)	122.81(7)	Zr(1)–I(1)–Zr(2)	67.56(9)
Zr(2)–Zr(1)–P(1)	131.6(2)	Zr(1)–Zr(2)–P(2)	130.8(2)	Zr(1)–I(2)–Zr(2)	65.57(8)
I(1)–Zr(1)–I(2)	98.09(8)	I(1)–Zr(2)–I(2)	97 59(8)	Zr(1)–P(1)–C(1)	112(1)
I(1)–Zr(1)–I(3)	90.04(8)	I(1)–Zr(2)–I(4)	90.30(9)	Zr(1)–P(1)–C(3)	118.6(8)
I(1)–Zr(1)–P(1)	172.1(2)	I(1)–Zr(2)–P(2)	173 1(2)	Zr(2)–P(2)–C(5)	117.1(9)
I(2)–Zr(1)–I(2)′	82.14(8)	I(2)–Zr(2)–I(2)′	81.71(9)	Zr(2)–P(2)–C(7)	113(1)
I(2)–Zr(1)–I(3)	169.7(1)	I(2)–Zr(2)–I(4)	168.6(1)	C(10)–N–C(10)′	100(3)
I(2)–Zr(1)–I(3)′	90.50(5)	I(2)–Zr(2)–I(4)′	89.19(6)	C(10)–N–C(20)	121(3)
I(2)′–Zr(1)–P(1)	87.9(2)	I(2)–Zr(2)–P(2)	87 6(2)	C(10)–N–C(30)	97(3)
I(3)–Zr(1)–I(3)′	95.83(9)	I(4)–Zr(2)–I(4)′	99 0(1)	C(20)–N–C(30)	115(5)
I(3)–Zr(1)–P(1)	84 7(1)	I(4)–Zr(2)–P(2)	85 2(2)		

Numbers in parentheses are e.s d.s in the least significant digits.

Acknowledgement

We thank the Robert A. Welch foundation for support under Grant A494.

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