Volume 33
Number 12
June 8, 1994

Inorganic Chemistry

Communications

A Linear Symmetric Chain with the -Cl-Zr-Cl-Zr- Unit. Crystal Structure and Convenient Syntheses of Chlorotrineopentylzirconium

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Received February 3, 1994

Polymeric chains with linear symmetric -X–M–X–M- (M = metals; X = halogens) repeating units are rarely seen.[1] $Tl_2Mn^{III}F_5{\cdot}H_2O$ is reported to have a symmetric linear chain with a $-F-Mn^{III}F_4-F-Mn^{III}F_4-$ repeating unit and hydrogen bonds between the H_2O and fluorine atoms.[1a] A two-dimensional network is observed with linear symmetric $-Cl-CdCl_4-Cl-CdCl_4-$ chains in $CdCl_5(denH_3)$ (den = diethylenetriamine).[1b] In our recent studies of the reaction between Np_3Zr-Cl (Np = $Me_3CCH_2^-$) (**1**) and $Li(THF)_3Si(SiMe_3)_3$ to make an alkyl silyl complex $Np_3Zr-Si(SiMe_3)_3$,[2] we were surprised to find that Np_3Zr-Cl (**1**) crystallizes in polymeric chains with a strictly linear symmetric $-Cl-ZrNp_3-Cl-ZrNp_3-$ repeating unit. To our knowledge, this is the first example of linear symmetric -X–M–X–M- chains in which M has a d^0 configuration. We report here three convenient syntheses of Np_3Zr-Cl and its crystal structure.

Complex **1** has been synthesized through the reaction between Np_2Mg and $Np_2ZrCl_2(Et_2O)_2$, which was prepared *in situ* (25% yield).[3a] We have explored some general approaches to **1**. The new syntheses of **1** are summarized in eqs 1–3.[4]

$$\mathrm{ZrCl_4 + 3NpLi \rightarrow Np_3ZrCl + 3LiCl} \qquad (1)^{4a}$$

$$\mathrm{ZrCl_4 + 3Np_4Zr \rightarrow 4Np_3ZrCl} \qquad (2)^{4b}$$

$$\mathrm{Np_4Zr + HCl \rightarrow Np_3ZrCl + Np{-}H} \qquad (3)^{4c}$$

Equations 1 and 2 are based on the metathetic reactions of $ZrCl_4$ with 3 equiv of NpLi and 3 equiv of Np_4Zr,[3b] respectively. The reaction of Np_4Zr with 1 equiv of HCl/Et_2O solution offers another approach to **1**. Complex **1** obtained by the method in eq 1 was purified by sublimation. Compound **1** from syntheses in eqs 2 and 3 was separated by crystallization or used *in situ* without further purification to make $Np_3ZrSi(SiMe_3)_3$.[2]

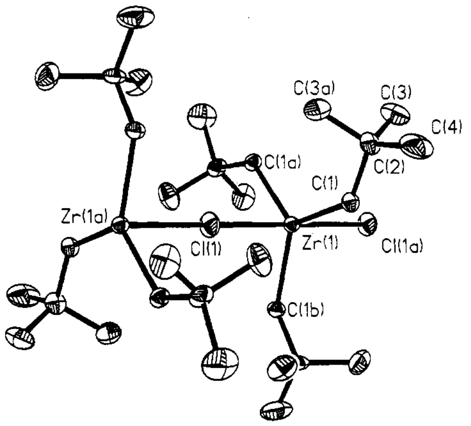
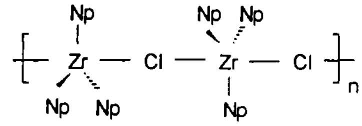


Figure 1. ORTEP view of two units of Np_3ZrCl (**1**) with thermal ellipsoids drawn at the 50% probability level. Selective bond lengths (Å) and angles (deg): Zr(1)–Cl(1) = 2.547 (1), Zr(1)–C(1) = 2.200 (4); Cl(1)–Zr(1)–Cl(1a) = 180.0, Zr(1)–Cl(1)–Zr(1a) = 180.0, Cl(1)–Zr(1)–C(1) = 90.0, C(1)–Zr(1)–C(1a) = 120.0, Zr(1)–C(1)–C(2) = 130.5 (2).

Figure 1 displays the geometry around two Np_3Zr-Cl units in the solid state.[5] The crystal packing diagrams showing the -Zr–Cl–Zr–Cl- chain structure are given in Figures 2 and 3. The chain is strictly linear and symmetric as imposed by the symmetry of a $P6_3/m$ space group (structure **I**). There is a 6_3 screw axis with center of symmetry ($6_3/m$) through each polymeric chain. Each Zr atom adopts a trigonal bipyramidal geometry as defined by the crystallographic symmetry. The angles between the neopentyl and the chloride ligands (C–Zr–Cl) are 90.0°, indicating the Zr–Cl bonds are perpendicular to the plane formed by the zirconium and three α-carbon atoms. The two adjacent Np_3Zr moieties are arranged in a staggered conformation presumably to reduce the steric strain. The bond lengths Zr(1a)–Cl(1) and Zr(1)–Cl(1) are 2.547(1) Å. In comparison, two bridging Zr–Cl lengths [2.498(2) and 2.655(2) Å] are observed in the crystal structure of $ZrCl_4$, which adopts a $-ZrCl_2-(\mu-Cl)_2-ZrCl_2-(\mu-$



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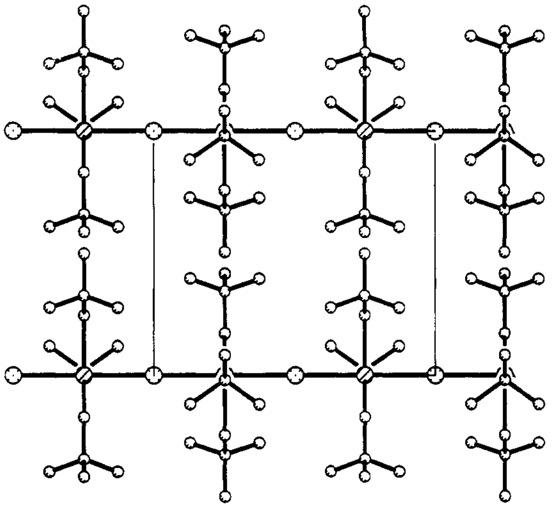

Figure 2. Projection packing diagram of the crystal down the *a* axis.

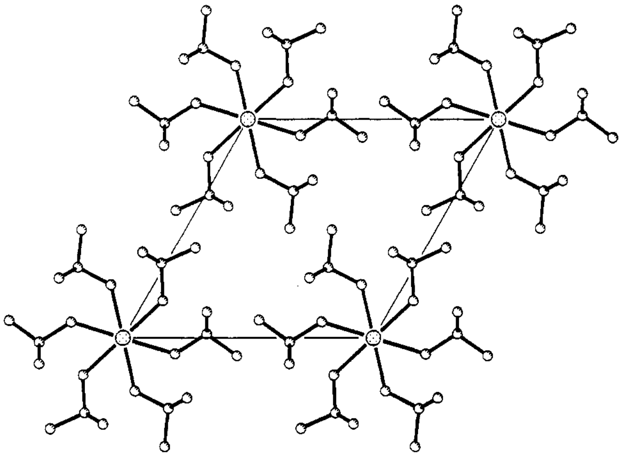

Figure 3. Projection packing diagram of the crystal down the *c* axis.

Cl)$_2$– chain structure.[6] The Zr–Cl bond in **1** is longer than the terminal Zr–Cl bond length 2.307(2) Å in $ZrCl_4$.[6] Crystal packing diagrams (Figures 2 and 3) display the arrangement of the linear symmetric chains with respect to the crystal lattices. There are four polymeric chains occupying four edges of a unit cell in a direction parallel to the *c* axis.

Bridging chloride ligands between two metal atoms normally have M–Cl–M angles around 109° such that the four electron pairs around each chlorine atom are in a tetrahedral orientation. However linear chloride-bridged compounds have been previously reported for late transition metals with d^n configurations.[1] Symmetric or nonsymmetric chains with linear dinuclear –M–M–X–M–M–X repeating units have been observed in $Ru_2(O_2CCH_3)_4Cl\cdot 2H_2O$,[7a] $Ru_2(O_2CCH_2CH_3)_4Cl$,[7a] $M'_4[Pt_2(P_2O_5H_2)_4X]\cdot nH_2O$ (M′ = K, NH_4; X = Cl, Br),[7b–e] and $M_2(CH_3CS_2)_4I$ (M = Ni,[7f] Pt[7g]). Studies are underway to examine the properties of Np_3ZrCl (**1**) and the features of its one-dimensional chains with the linear symmetric –Zr–Cl–Zr–Cl– unit.

Acknowledgment is made to the University of Tennessee for financial support. The X-ray diffractometer was purchased with a grant from the U.S. Department of Energy (DE-FG05-87ER75378).

Supplementary Material Available: Listings of complete crystallographic data for **1** (5 pages). Ordering information is given on any current masthead page.

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(4) The solvents used here were dried by refluxing in K–benzophenone ketyl and distilled before use. All operations were conducted in an atmosphere of Ar. The Schlenk flasks used in the syntheses had been flame-dried under vacuum. (a) The synthesis as shown in eq 1: NpLi (2.00 g, 25.6 mmol) dissolved at 0 °C in a mixture of 10 mL of Et_2O, and 10 mL of hexanes was added in 15 min to sublimed $ZrCl_4$ (2.40 g, 10.3 mmol, 20% excess) suspended in 10 mL of stirring Et_2O at 0 °C. The mixture was warmed with stirring to 23 °C overnight. The cloudy brown solution was filtered, and volatiles were removed under vacuum. Sublimation of the brown solid at 60 °C gave 1.15 g (3.38 mmol, 40% yield based on NpLi) of yellow Np_3ZrCl (**1**) containing a small amount of $ZrNp_4$. Decomposition was observed during the sublimation. (b) The synthesis as shown in eq 2: Np_4Zr (0.500 g, 1.33 mmol) dissolved in 20 mL of Et_2O at 0 °C was added to a suspension of sublimed $ZrCl_4$ (0.103 g, 0.442 mmol) in 15 mL of Et_2O at 0 °C. The mixture was stirred at −2 °C for 18 h. The solvent was removed by vacuum to give a yellow solid of Np_3ZrCl (**1**, yield 93%) containing a small amount (6 mol %) of Np_4Zr. (c) The synthesis as shown in eq 3: Np_4Zr (0.192 g, 0.511 mmol) dissolved in 2 mL of Et_2O was cooled to −78 °C. A 5.11-mL volume of 0.10 M HCl/Et_2O (0.511 mmol) solution made from 1.0 M HCl/Et_2O (Aldrich) was added dropwise to the stirring Np_4Zr solution over 15 min. The solution was warmed to 23 °C in 5 h with stirring. Volatiles were removed by vacuum to give a yellow solid **1** (167 mg, yield 96%) with a small amount of Np_4Zr. (d) Data for **1**: ^1H NMR (benzene-d_6, 250 MHz, 23 °C) δ 1.54 (CH_2), 1.09 (CMe_3);[3a] $^{13}C\{^1H\}$ NMR (benzene-d_6, 62.9 MHz, 23 °C) δ 103.5 (CH_2), 35.5 (CMe_3), 34.3 (CMe_3); IR (KBr pellet, 23 °C, cm^{-1}) 2950 (vs), 2858 (vs), 2802 (vs), 2704 (m), 1468 (vs), 1357 (s), 1219 (vs), 1082 (m), 928 (m), 911 (m), 740 (s), 523 (vs).

(5) Crystal data for **1**: hexagonal, $P6_3/m$ (No. 176), a = 10.125(1) Å, c = 10.189(3) Å, V = 904.5(4) Å^3, Z = 2 (Np_3ZrCl formulas), R (R_w) = 3.18% (5.93%) with 364 unique reflections with $F > 4.0\sigma(F)$, GOF = 1.08, numbers of parameters refined = 32, data-to-parameter ratio = 11.4:1. The Zr atom was located by the Patterson method, and all remaining non-hydrogen atoms were located and refined anisotropically. The hydrogen atoms on the methyl groups were located from a Fourier map. The two hydrogen atoms on the CH_2 group were fixed in calculated, idealized positions [d(C–H) = 0.96 Å]. These hydrogen atoms were not refined.

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