Inorg. Chem. **1997,** *36,* 3198−3200

Notes

A Binuclear Zirconium(IV) Oxalate Complex with a μ-Oxalate Coordination Mode. Crystal Structure of $K_6[\{Zr(C_2O_4)_3\}_2(\mu\text{-}C_2O_4)]\cdot 4H_2O$

Ricardo Baggio,[†] Maria Teresa Garland,[‡] and Mireille Perec*,[§]

Departamento de Física, Comisión Nacional de Energía Atómica, Avda. del Libertador 8250, 1429 Buenos Aires, Argentina, Departamento de Física, Facultad de Ciencias Físicas y Matemáticas, Universidad de Chile, Avda. Blanco Encalada 2008, Casilla 487-3, Santiago, Chile, and Departamento de Química Inorgánica, Analítica y Química Física, INQUIMAE, Universidad de Buenos Aires, Ciudad Universitaria, Pabellón II, 1428, Buenos Aires, Argentina

Received November 18, 1996

Introduction

The complexity of aqueous systems containing zirconium(IV) is well-known.[1,2] In particular, the existence of zirconium oxalates isolated from aqueous solution has been extensively documented,[3] but to date only three compounds have been fully characterized by single-crystal X-ray studies. Among these, the crystal structures of the mononuclear $Na_4[Zr(C_2O_4)_4]\cdot 3H_2O$ and $K_4[Zr(C_2O_4)_4]\cdot 5H_2O$ ($Zr:C_2O_4$ ratio = 1:4) have been reported.[4,5] More recently, the polymeric $[K_2\{Zr(C_2O_4)_3\}\cdot H_2C_2O_4\cdot H_2O]_n$ ($Zr:C_2O_4$ ratio = 1:3) showing a zigzag chain of oxalate-bridged zirconium atoms along the c-axis has been described.[6] In the three complexes all of the zirconium atoms are found in 8-fold coordination.

We report herein the preparation and structure of the novel binuclear zirconium(IV) oxalate-bridged complex $K_6[\{Zr(C_2O_4)_3\}_2(\mu\text{-}C_2O_4)]\cdot 4H_2O$ (**1**) ($Zr:C_2O_4$ ratio = 1:3.5), isolated from the reaction of $ZrOCl_2\cdot 8H_2O$ with oxalic acid and potassium oxalate in water at pH ca. 1.5. The characterization of **1** is of interest in the development of zirconium(IV) carboxylate chemistry since the occurrence of binuclear zirconium(IV) carboxylates is rare.[3]

Experimental Section

All reagents employed were commercially available analytical or reagent-grade purity substances and used as received. Water was purified by a Millipore Milli-Q system yielding 18 MΩ cm water. Elemental analyses (C, H) were performed with a Carlo Erba EA 1108 analyzer. Infrared spectra were recorded as KBr disks or as mulls in Nujol with a Nicolet 510P FT-IR spectrophotometer.

Preparation of $K_6[\{Zr(C_2O_4)_3\}_2(\mu\text{-}C_2O_4)]\cdot 4H_2O$. To a solution of $ZrOCl_2\cdot 8H_2O$ (1.6 g, 0.005 mol) in water (100 mL), oxalic acid dihydrate (1.9 g, 0.015 mol), and potassium oxalate monohydrate (0.9 g, 0.005 mol) dissolved in 50 mL of water were added from a dropping funnel under stirring. The pH of the solution was adjusted to ca. 1.5 by addition of small volumes of 0.1 M aqueous KOH. After being stirred for 12 h at 80 °C, the solution was filtered and allowed to stand in a stoppered flask at ambient temperature. After 2 months colorless crystals of the product were separated by filtration, washed with cold water, and dried under vacuum for 6 h. Yield: 2.0 g, 75% based on zirconium. Anal. Calcd for $C_{14}H_8K_6O_{32}Zr_2$: C, 15.20; H, 0.72. Found: C, 15.13; H, 0.69. IR (KBr disk, cm^{-1}): 3522 (m), 2920 (w), 2479 (w), 1752 (s), 1717 (vs), 1694 (vs), 1397 (vs), 1381 (vs), 1265 (s), 1244 (m), 907 (m), 853 (w), 812 (s), 797 (s), 602 (w), 527 (s), 488 (m), 318 (vs).

Table 1. Crystallographic Data for **1**

$C_{14}H_8K_6O_{32}Zr_2$	space group: $P2_1/n$ (No.14)
$a = 9.037(1)$ Å	$T = 22$ °C
$b = 13.332(2)$ Å	$\lambda = 0.710\,73$ Å
$c = 13.081(3)$ Å	$\rho_{obsd} = 2.31(2)$ g cm^{-3};
$\beta = 93.38(1)°$	$\rho_{calcd} = 2.33$ g cm^{-3}
$V = 1573.3(5)$ Å^3	$\mu = 1.58$ mm^{-1}
$Z = 2$	R1^a $[F^2 > 2\sigma(F^2)] = 0.027$
fw = 1105.24	wR2^b $[F^2 > 2\sigma(F^2)] = 0.071$

^{a} R1: $\sum||F_o| - |F_c||/\sum|F_o|$. ^{b} wR2: $[\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

X-ray Crystallography. Crystallographic data are summarized in Table 1. A colorless crystal of good diffracting power was mounted in a glass fiber on a Siemens R3m diffractometer equipped with a graphite-monochromator and Mo Kα ($\lambda = 0.710\,73$ Å) radiation. The unit cell parameters were determined by least-squares refinement of 25 reflections. Intensity data were collected in the range $4.36 \le 2\theta \le 50.10°$ by the $\omega-2\theta$ scan technique. Within index ranges ($0 \le h \le 9$, $0 \le k \le 15$, $-15 \le l \le 15$), 2622 unique reflections were collected. Intensities were corrected for Lorentz and polarization effects, and a semi-empirical absorption correction (ψ-scan) was also applied. Two standard reflections were monitored every 98 and showed no systematic changes. The structure was solved by a combination of direct methods and difference Fourier syntheses. Refinement of the structure was done by full-matrix least-squares based on F^2, with anisotropic thermal parameters for the non-hydrogen atoms. The water hydrogen atoms, however, could not be located and therefore were not included in the structure factor calculations. Computer programs used in this study were SHELXLTL/PC,[7a] SHELXL 93,[7b] and CSD.[8] Selected interatomic distances and angles are listed in Table 2.

Results and Discussion

The reaction involving $ZrOCl_2\cdot 8H_2O$, oxalic acid, and potassium oxalate in 1:3:1 ratio in aqueous solution kept at pH ca. 1.5 by addition of KOH afforded the novel binuclear compound $K_6[\{Zr(C_2O_4)_3\}_2(\mu\text{-}C_2O_4)]\cdot 4H_2O$ (**1**) in good yield. The complex is a stable crystalline solid and can be kept in a dry atmosphere for extended periods of time. The FT-IR spectrum shows several strong bands in the range 1752−1694 cm^{-1} and at 1397 and 1381 cm^{-1}, respectively. The former are characteristic of carbonyl groups and of asymmetric RCO_2^{2-} modes whereas the latter are characteristic of RCO_2^{2-} symmetric modes. The Δ values $[\Delta = \nu(CO_2^-)_{asym} - \nu(CO_2^-)_{sym}]$ above 297 cm^{-1} point to the unidentate and/or bridging bidentate

---

[†] Comisión Nacional de Energía Atómica.

[‡] Universidad de Chile.

[§] Universidad de Buenos Aires.

(1) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley-Interscience: New York, 1988.

(2) Intorre, B. I.; Martell, A. E. *J. Am. Chem. Soc.* **1960**, *82*, 358.

(3) Fay, R. C. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: Oxford, England, 1987; Vol. 3, p 411.

(4) Glen, G. L.; Silverton, J. V.; Hoard, J. L. *Inorg Chem*. **1963**, *2*, 250.

(5) Kojic-Prodic, B.; Ruzic-Toros, Z.; Sljukic, M. *Acta Crystallogr., Sect. B* **1978**, *34*, 2001.

(6) Baggio, R.; Garland, M. T.; Perec, M. *Inorg. Chem*. **1997**, *36*, 737.

(7) (a) Sheldrick, G. M. SHELXTL-PC. Version 4.2. Siemens Analytical X-Ray Instruments Inc., Madison, WI, 1991. (b) Sheldrick, G. M. SHELXL-93, Program for Crystal Structure Refinement. University of Gottingen, Germany, 1993.

(8) CSD: Cambridge Structural Database. Allen, F. H.; Kennard, O.; Taylor, R. *Acc. Chem. Res.* **1983,** *16*, 146.

S0020-1669(96)01382-1 CCC: $14.00

Table 2. Bond Lengths (Å) and Selected Interatomic Angles (deg) for **1**[a]

Zr1−O41	2.136(2)	Zr1−O21	2.156(2)
Zr1−O51	2.170(2)	Zr1−O61	2.179(2)
Zr1−O11	2.198(2)	Zr1−O31	2.205(2)
Zr1−O71	2.265(2)	Zr1−O72^a	2.323(2)
K1−O42^b	2.563(3)	K1−O12^c	2.566(2)
K1−O71	2.650(2)	K1−O52^d	2.872(2)
K1−O61	2.895(2)	K1−O1W^d	2.896(3)
K1−O31	2.957(2)		
K2−O52^e	2.772(2)	K2−O62^e	2.799(2)
K2−O51	2.811(2)	K2−O32^f	2.830(3)
K2−O1W	2.831(3)	K2−O22^g	2.847(3)
K2−O11	2.852(2)	K2−O72^a	2.917(2)
K3−O41	2.884(3)		
K3−O31^h	2.888(2)	K3−O11	2.907(2)
K3−O21^h	2.909(2)	K3−O1W^e	3.074(3)
K3−O52^e	3.074(2)	K3−O72^a	3.093(2)
K3−O2W^a	3.154(4)	K3−O61^h	3.174(2)
O41−Zr1−O21	99.07(9)	O41−Zr1−O51	145.81(9)
O21−Zr1−O51	91.79(8)	O41−Zr1−O61	141.64(9)
O21−Zr1−O61	83.12(8)	O51−Zr1−O61	71.60(7)
O41−Zr1−O11	75.38(8)	O21−Zr1−O11	71.81(8)
O51−Zr1−O11	77.50(8)	O61−Zr1−O11	139.25(8)
O41−Zr1−O31	71.97(9)	O21−Zr1−O31	75.26(8)
O51−Zr1−O31	142.20(8)	O61−Zr1−O31	71.67(8)
O11−Zr1−O31	128.46(8)	O41−Zr1−O71	84.28(8)
O21−Zr1−O71	148.42(8)	O51−Zr1−O71	102.98(8)
O61−Zr1−O71	75.56(7)	O11−Zr1−O71	138.31(7)
O31−Zr1−O71	76.05(8)	O41−Zr1−O72^a	75.77(9)
O21−Zr1−O72^a	141.79(8)	O51−Zr1−O72^a	75.74(8)
O61−Zr1−O72^a	124.47(8)	O11−Zr1−O72^a	70.27(7)
O31−Zr1−O72^a	134.55(8)	O71−Zr1−O72^a	69.61(7)
O12−C1−O11	125.4(3)	O12−C1−C2	121.5 (3)
O11−C1−C2	113.1(2)	O22−C2−O21	125.2 (3)
O22−C2−C1	121.6(3)	O21−C2−C1	113.2 (3)
O32−C3−O31	126.0(4)	O32−C3−C4	121.3 (4)
O31−C3−C4	112.7(3)	O42−C4−O41	124.4 (4)
O42−C4−C3	122.4(4)	O41−C4−C3	113.2 (3)
O52−C5−O51	125.5(3)	O52−C5−C6	122.0 (3)
O51−C5−C6	112.5(2)	O62−C6−O61	125.8 (3)
O62−C6−C5	121.3(3)	O61−C6−C5	112.9 (2)
O72−C7−O71	127.6(3)	O72−C7−C7^a	116.9 (3)
O71−C7−C7^a	115.5(3)		

[a] Symmetry codes: (a) $-x, -y + 1, -z + 2$; (b) $-x + 1, -y + 1, -z + 2$; (c) $-x + {}^1/_2, y + {}^1/_2, -z + {}^3/_2$; (d) $x + {}^1/_2, -y + {}^3/_2, z + {}^1/_2$; (e) $-x - {}^1/_2, y - {}^1/_2, -z + {}^3/_2$; (f) $x - 1, y, z$; (g) $-x, -y + 1, -z + 1$; (h) $-x + {}^1/_2, y - {}^1/_2, -z + {}^3/_2$.

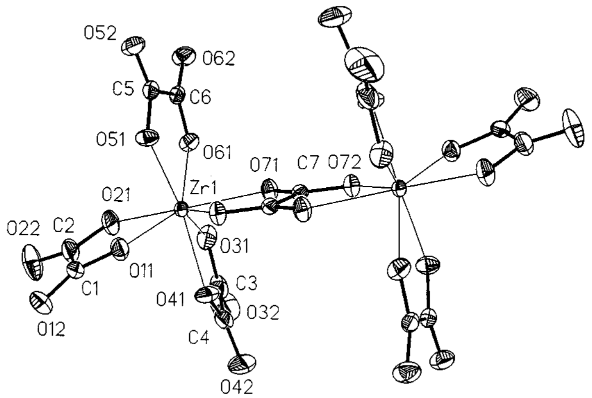

Figure 1. Diagram showing the structure of anionic $[\{Zr(C_2O_4)_3\}_2(\mu\text{-}C_2O_4)]^{6-}$ with atom labels (50% thermal ellipsoids).

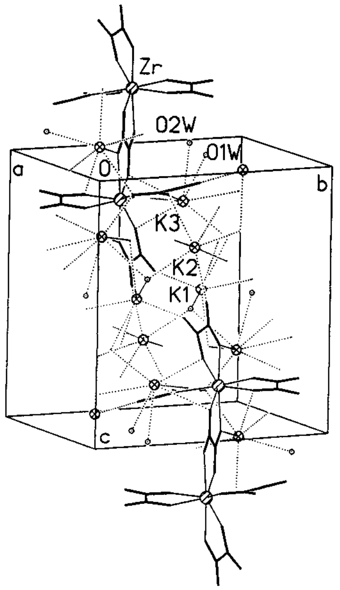

Figure 2. Schematic packing diagram of $K_6[\{Zr(C_2O_4)_3\}_2(\mu\text{-}C_2O_4)]\cdot 4H_2O$. K···O interactions are shown by dotted points, and water molecules, by small open circles.

behavior of the carboxylate groups of the ligands,[9] as confirmed by the X-ray study below.

Crystal Structure. The structure of **1** consists of binuclear $[\{Zr(C_2O_4)_3\}_2(\mu\text{-}C_2O_4)]^{6-}$ anions, K^+ cations, and solvent water molecules. A view of the anion is shown in Figure 1. Principal bond distances and angles are listed in Table 2. A packing diagram showing the contents of the unit cell is given in Figure 2. The most interesting feature is the occurrence of a centrosymmetric binuclear μ-oxalate anion with a crystallographic inversion center located at the midpoint of the C7−C7′ bond relating the two terminal $[Zr(C_2O_4)_3]^{2-}$ units. The bridging oxalate anion is perfectly planar within experimental error (0.1°), and the two Zr atoms lie 0.1223(3) Å out of this plane. As a result, the geometries at the two Zr(IV) centers are identical, with ligation provided by six oxygen atoms of the bidentate oxalates (O31, O41, O11, O21, O51, O61) and two oxygen atoms of the bridging bisbidentate oxalate (O71, O72′). The two ZrO_8 dodecahedral units formed show a Zr···Zr separation of 6.01 Å within the dimer. A closely related centrosymmetrical binuclear anion, $[Zr_2(CO_3)_6(\mu\text{-}OH)_2]^{6-}$, has been previously determined by X-ray crystallography in $M_6[Zr_2(CO_3)_6(\mu\text{-}OH)_2]$ (M = K, NH_4).[10,11] Each zirconium atom is 8-fold, the coordination being provided by six carbonate and two μ-OH oxygens with a Zr···Zr distance of 3.49 Å.

The ZrO_8 coordination sphere in **1** is defined by two interpenetrating trapezoids (O31, O41, O51, O61 and O11, O21, O71, O72′) including the Zr atom which exhibit slight departures from planarity (maximum departure 0.177(2) Å for O41 and 0.176(2) Å for O71, respectively) and are nearly orthogonal (91.67(5)°). Analysis of the ZrO_8 polyhedron by the procedure described by Kepert[12] indicates that the geometry at the zirconium atom is best described as a distorted D_{2d} dodecahedron with $\Phi_A = 35.5°$, $\Phi_B = 107.1°$, and $\Theta - \Theta_B = 9.4°$ (the corresponding values for a regular triangular dodecahedron are 37.3, 108.6, and 0° and for a regular square antiprism 38.9, 108.8, and 24.4°).

The Zr−O bonds are unequal, the bonds to the six carboxylate oxygens O31, O41, O11, O21, O51, and O61 of the bidentate ligands have a range and average value of 2.136(2)−2.205(2) and 2.174(10) Å, respectively. The two Zr−O bonds to the oxygens O71 and O72′ of the bridging bisbidentate oxalate are

---

(9) Deacon, G. B.; Phillips, R. J. *Coord. Chem. Rev.* **1980**, *33*, 227.

(10) Gorbunova, Yu. E.; Kuznetsov, V. G.; Kovaleva, E. S. *J. Struct. Chem. (Engl. Transl.)* **1968**, *9*, 815.

(11) Clearfield, A. *Inorg. Chim. Acta* **1970**, *4*, 166.

(12) Kepert, D. L. *Prog. Inorg. Chem.* **1978**, *24*, 179.

2.265(2) and 2.323(2) Å, respectively, with an average value of 2.294(29) Å being approximately 0.12 Å longer than the former, as recently observed for the zirconium oxalate polymer.[6] The average (all bonds) Zr−O distance of 2.215(27) Å is comparable to the corresponding value of 2.202(34) Å observed in 10 other related complexes containing the ZrO_8 coordination polyhedron.[13] The O−Zr−O bite angles of the bidentate and bridging bisbidentate oxalate ligands with the metal center are acute, 71.79(11)° (average) and 69.61(7)°, respectively.

The carboxylate C−O distances in the bidentate ligands are asymmetric. There are two long (average 1.294(1) Å) and two short C−O (average 1.219(1) Å) bonds, with the oxygen atoms bonded to the metal center having the longer C−O bonds. This suggests that the negative charges of the oxalate ligands are preferentially localized onto the oxygen atoms bound to Zr(IV). In the bridging bisbidentate ligand the C−O distances 1.254(3) and 1.249(3) Å (average 1.252(8) Å) are comparable, and their values intermediate between those above. The C−C bonds of the bidentate oxalates, average 1.539(4) Å with torsional angles of 5.8(1), 10.6(1), and 2.4(1)° around C1−C2, C3−C4, and C5−C6, respectively, which may be attributed to the packing forces in the crystal. The C−C bond of the planar bridging oxalate of 1.513(5) Å is slightly shorter than the latter and also than the corresponding value in $[K_2\{Zr(C_2O_4)_3\}\cdot H_2C_2O_4\cdot H_2O]_n$ (1.532(6) Å) and in a number of other dimeric species.[14]

The potassium cations play an important role in the stabilization of the three-dimensional network of **1**, Figure 2. The principal interactions are to the negatively charged oxygen atoms of the oxalate ligands and to the oxygen atoms of the water molecules. There are seven K1···O, eight K2···O, and nine K3···O contacts in non-equivalent environments of less than 3.1 Å, usually considered the upper limit of any significant K···O interaction.[15] Similar types of complicated interactions have been found to stabilize the crystalline frameworks of $M_4[Zr(C_2O_4)_4]\cdot nH_2O$ (M = K, Na) and of polymeric $[K_2\{Zr(C_2O_4)_3\}\cdot H_2C_2O_4\cdot H_2O]_n$. It is noteworthy that hydrogen bonding does not play any significant role in the packing of **1**, whereas such interactions are very important in the above structures.

In summary, oxalate strongly complexes zirconium(IV) and displaces the μ-hydroxyl groups in the tetranuclear species $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$ present in the Zr(IV) acidic aqueous solution,[16] likely producing a large number of species. The isolation and full characterization of the simple binuclear complex **1** is of interest since it may represent an important first stage in the polymerization process in the complex aqueous zirconium(IV)−oxalate system.

Acknowledgment. This work was supported by the Universidad de Buenos Aires, by the Consejo Nacional de Investigaciones Cientificas y Tecnicas (CONICET), and Proyecto FONDECYT No. 1940515. The purchase of the single-crystal diffractometer by Fundacion Andes is gratefully acknowledged. M.P. is a member of CONICET.

Supporting Information Available: One X-ray crystallographic file, in CIF format, is available. Access information is given on any current masthead page.

IC9613826

---

(13) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1−S83.

(14) (a) Darensbourg, D. J.; Chojnacki, J. A.; Reibenspies, J. H. *Inorg. Chem.* **1992**, *31*, 3428. (b) Felthouse, T. R.; Laskowsky, E. J.; Hendrickson, D. N. *Inorg. Chem.* **1977**, *16*, 1077. (c) Bottomley, F.; Lin, E. J. B.; White, P. S. *J. Organomet. Chem.* **1981**, *212*, 341. (d) Glerup, J.; Goodson, P. A.; Hodgson, D. J.; Michelsen, K. *Inorg. Chem.* **1995**, *34*, 6255.

(15) (a) Evans, W. J.; Anwander, R.; Ansari, A. M.; Ziller, J. W. *Inorg. Chem.* **1995**, *34*, 5. (b) Clark, D. L.; Gordon, J. C.; Huffman, J. C.; Vincent-Hollis, R. L.; Watkin, J. G.; Zwick, B. D. *Inorg. Chem.* **1994**, *33*, 5903. (c) Tranqui, D.; Boyer, P.; Laugier, J.; Vulliet, P. *Acta Crystallogr.* **1977**, *B33*, 3126.

(16) Toth, L. M.; Lin, J. S.; Felker, L. K. *J. Phys. Chem.* **1991**, *95*, 3106.