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Notes

Preparation and X-ray Crystal Structure of the Polymeric Zirconium(IV) Oxalate Complex $[K_2\{Zr(C_2O_4)_3\}\cdot H_2C_2O_4\cdot H_2O]_n$

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Introduction

The aqueous solution chemistry of zirconium(IV) has proved to be quite complicated due to the hydrolytic behavior of group 4 complexes even in strong acid solutions.[1,2] The existence of zirconium(IV) complexes with carbon oxoanions has been well documented,[3] but only a few have been characterized by single-crystal X-ray studies.[4−8] Among these, the crystal structures of two oxalate complexes of zirconium (IV) containing the tetrakis(oxalato)zirconate(IV) ion, $[Zr(C_2O_4)_4]^{4-}$, have been reported.[4,5]

As part of our interest in zirconium(IV) carboxylate complexes,[8] we now report a new zirconium oxalate complex whose composition and structure constitute a significant departure from those previously known. We present here the synthesis and crystal structure of the novel polymeric zirconium oxalate compound $[K_2\{Zr(C_2O_4)_3\}\cdot H_2C_2O_4\cdot H_2O]_n$, and discuss its relationship to the known zirconium oxalates.

Experimental Section

All commercially available reagents and chemicals were of analytical or reagent-grade purity and used as received. Water was purified by a Millipore Milli-Q system yielding 18 M Ω cm water. Elemental analyses (C, H) were performed at INQUIMAE (Instituto de Quimica de Materiales, Medio Ambiente y Energia) 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. Thermogravimetric analyses were recorded on a Mettler TG-50 thermal analyzer in a dynamic atmosphere of air at a heating rate of 10 °C min^{-1}. X-ray powder diffraction (XRPD) data were collected using monochromated Cu Kα radiation on a Phillips X'Pert diffractometer.

Table 1. Crystallographic Data for **1**

formula: $C_8H_4K_2O_{17}Zr$	fw = 541.53
cryst syst: monoclinic	space group: *Cc* (No. 9)
$a = 16.465(5)$ Å	$T = 22$ °C
$b = 11.149(3)$ Å	$\lambda = 0.710\,73$ Å
$c = 8.939(3)$ Å	$\mu = 1.34$ mm^{-1}
$\beta = 107.93(1)°$	$R_{int}{}^{a} = 0.034$
$V = 1561.2(8)$ Å^3	$R1^{b}$ $[F^2 > 2\sigma(F^2)] = 0.029$
$Z = 4$	wR2^{c} $[F^2 > 2\sigma(F^2)] = 0.066$
$F(000) = 1064$	S^{d} $[F^2] = 1.114$
$d_{calcd} = 2.30$ g cm^{-3}	

^{a} $R_{int} = \sum|F_o^2 - F_o(\mathrm{mean})^2|/\sum F_o^2$. ^{b} $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. ^{c} $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$. ^{d} $S = [\sum[w(F_o^2 - F_c^2)^2]/(n - p)]^{1/2}$.

Preparation of $[K_2\{Zr(C_2O_4)_3\}\cdot H_2C_2O_4\cdot H_2O]_n$. To a solution of $ZrOCl_2\cdot 8H_2O$ (1.6 g, 0.005 mol) in water (100 mL), oxalic acid 2-hydrate (3.7 g, 0.030 mol) was added in small portions. A 0.3 g of KOH sample in 5 mL of water was added dropwise under stirring to adjust the pH to ∼2. After being stirred for 10 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 from a white slurry, washed with cold water, and dried under vacuum for 12 h. Yield: 1.20 g, 45% calculated on the basis of the zirconium used. Anal. Calcd (found) for $C_8H_4K_2O_{17}Zr$: C, 17.73 (17.65); H, 0.74 (0.75). IR (KBr disk, cm^{-1}): 3630 (m), 3445 (s), 2924 (m), 1736 (vs), 1692 (vs), 1676 (vs), 1632 (vs), 1560 (m), 1389 (vs), 1362 (s), 1314 (m), 1236 (m), 1196 (vs), 910 (m), 812 (s), 795 (m), 690 (m), 538 (m), 484 (s), 318 (s).

X-ray Crystallography. Crystallographic data are summarized in Table 1. A colorless crystal of good diffracting power having the dimensions 0.33 × 0.24 × 0.16 mm 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 $3° \leq 2\theta \leq 58.5°$ by the $\omega-2\theta$ scan technique. Within index ranges ($-22 \leq h \leq 20$, $-1 \leq k \leq 14$, $0 \leq l \leq 11$), 2043 unique reflections were collected. Intensities were corrected for Lorentz and polarization effects, and a semiempirical 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 methods based on F^2, with anisotropic thermal parameters for the non-hydrogen atoms.

The oxalic acid hydrogen atoms were located in difference Fourier maps, and their positions refined in the final stages with a restrained geometry ($d(\mathrm{O-H}) = 0.85(3)$ Å) and a common isotropic displacement parameter. 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[9] and SHELXL 93.[10] Selected interatomic distances are listed in Table 2.

Results and Discussion

The new polymer $[K_2\{Zr(C_2O_4)_3\}\cdot H_2C_2O_4\cdot H_2O]_n$ (**1**) was isolated from an aqueous mixture of $ZrOCl_2\cdot 8H_2O$ and $H_2C_2O_4$ adjusted to pH ∼ 2 by addition of KOH. Since the product retains 81% of the added K$^+$, the role of KOH as a source of

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Table 2. Selected Bond Lengths (Å) for **1**^{a}

Zr1−O32	2.112(7)	Zr1−O42	2.133(6)
Zr1−O71	2.170(6)	Zr1−O81	2.195(6)
Zr1−O51^{a}	2.241(6)	Zr1−O62	2.255(6)
Zr1−O61^{a}	2.292(6)	Zr1−O52	2.319(5)
K1−O41	2.702(7)	K1−O41^{b}	2.753(7)
K1−O11	2.799(9)	K1−O62^{c}	2.845(7)
K1−O81^{c}	2.886(6)	K1−O21^{b}	2.903(7)
K1−O31	2.928(9)	K1−O61^{d}	2.993(6)
K1−O21	3.078(7)	K2−O82^{e}	2.748(7)
K2−O82	2.724(7)	K2−O1W^{g}	2.851(10)
K2−O52^{f}	2.827(6)	K2−O51^{h}	2.918(6)
K2−O42^{f}	2.915(7)	K2−O72	3.044(8)
K2−O22^{i}	3.009(7)	C1−O11	1.298(9)
C1−C2	1.523(8)	C2−O21	1.201(9)
C1−O12	1.200(7)	C3−C4	1.521(9)
C2−O22	1.319(8)	C3−O32	1.312(11)
C3−O31	1.227(11)	C4−O42	1.325(10)
C4−O41	1.237(11)	C5−O51	1.243(9)
C5−C6	1.532(6)	C6−O61	1.261(10)
C5−O52	1.235(9)	C7−C8	1.542(10)
C6−O62	1.270(11)	C7−O72	1.201(11)
C7−O71	1.302(12)	C8−O82	1.203(10)
C8−O81	1.258(10)		

^{a} Symmetry transformations used to generate equivalent atoms: (a) $x, -y+1, z-{}^{1}/_{2}$; (b) $x, -y+2, z-{}^{1}/_{2}$; (c) $x+{}^{1}/_{2}, y+{}^{1}/_{2}, z$; (d) $x+{}^{1}/_{2}, -y+{}^{3}/_{2}, z-{}^{1}/_{2}$; (e) $x, -y+2, z+{}^{1}/_{2}$; (f) $x-{}^{1}/_{2}, y+{}^{1}/_{2}, z$; (g) $x-{}^{1}/_{2}, -y+{}^{5}/_{2}, z-{}^{1}/_{2}$; (h) $x-{}^{1}/_{2}, -y+{}^{3}/_{2}, z-{}^{1}/_{2}$; (i) $x-{}^{1}/_{2}, y-{}^{1}/_{2}, z$.

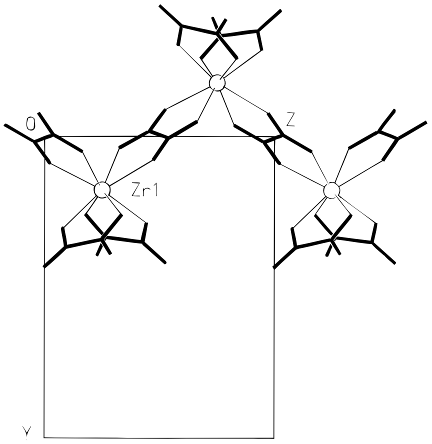

Figure 1. Schematic diagram showing the polymeric zigzag chain in **1** running along the *c*-axis direction.

K^+ to stabilize the solid state structure of **1** is clearly apparent. The complex is a stable crystalline solid and can be stored in a dry atmosphere for extended periods of time. TGA measurements show that the compound is thermally stable up to 175 °C, at which temperature loss of water and oxalic acid commences.

Crystal Structure. The most interesting feature in the crystal structure of **1** is the occurrence of the novel polymeric zigzag chain of ZrO_8 dodecahedral units running parallel to the *c* axis in the crystal, Figure 1. The zirconium atoms in the chains are linked by oxalate ligands bonded in the bridging bisbidentate mode, leading to a zirconium−zirconium separation within the chains of 5.98(1) Å.

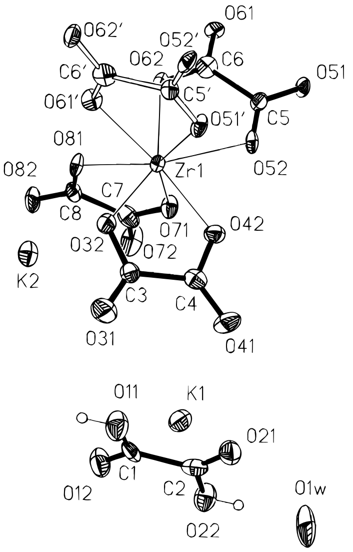

Figure 2. Coordination sphere of the zirconium atoms in **1** and atomic labeling scheme. Thermal ellipsoids drawn at the 50% probability level.

The zirconium sites exhibit distorted dodecahedral geometry with the coordination about each Zr center defined by four oxygens of two bidentate oxalate ligands (O32, O42, O71, O81) and four oxygens of two bridging bisbidentate oxalate ligands (O52, O62, O51′, O61′), Figure 2. The ZrO_8 coordination sphere is defined by two interpenetrating trapezoids (O52, O42, O32, O62 and O71, O81, O61′,O51′) including the Zr atom which exhibit slight departures from planarity (maximum departure 0.12 Å for O52 and 0.14 Å for O61′, respectively) and are nearly perpendicular (87.8(1)°). Analysis of the ZrO_8 polyhedron by the procedure described by Kepert[11] indicates that the geometry at the zirconium atom is best described as a distorted D_{2d} dodecahedron with $\Phi_A = 35°$, $\Phi_B = 106.1°$ and $\theta_A - \theta_B = 8.5°$ (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°).

Two sets of Zr−O distances are observed for the two modes of coordination of the oxalate anions to the metal center in **1**. One set consists of Zr−O bond lengths of the carboxylate oxygens O32, O42, O71, and O81 of the two bidentate ligands. These distances have a range and average value of 2.112(7)−2.195(6) and 2.152(19) Å, respectively. The second set includes the Zr−O bonds of the carboxylate oxygens O51′, O52, O61′, O62 of the two bridging bisbidentate ligands. The Zr−O distances have a range and average value of 2.241(6)−2.319(5) and 2.277(18) Å, respectively. As expected, the Zr−O bond lengths within the polymeric chain are significantly longer than those of the terminal bidentate oxalates.

The average (all bonds) Zr−O distance of 2.215(26) Å is, however, comparable to the values observed in other related complexes containing the ZrO_8 coordination polyhedron.[4,12] The O−Zr−O bite angles of the bidentate and bridging bisbidentate oxalate ligands with the metal center are acute, averaging 72.3(11) and 70.2(1)°, respectively.

The carboxylate C−O distances in the bidentate ligands are asymmetric. There are two long (average 1.299(16) Å) and two short C−O (average 1.217(9) 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 ligands the four C−O distances (average 1.252(8) Å) are comparable, and their values intermediate between those above. Other bond lengths and angles within the ligands are consistent with the values reported for a number of other transition metal oxalate compounds.[4,13]

The crystal packing diagram of **1** is presented in Figure 3. The potassium counterions play a predominant role in the

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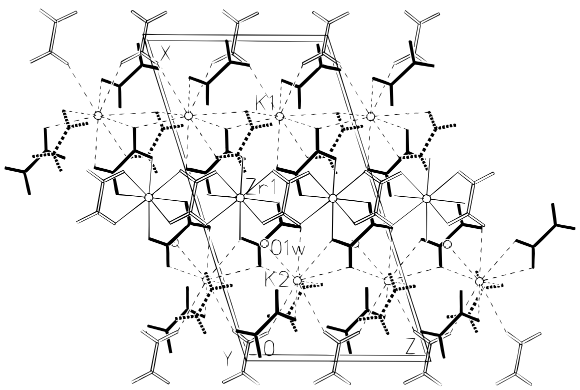

Figure 3. View of the unit cell of **1**. Zr−O bonds are drawn in single lines, K···O interactions in dashed lines, bidentate oxalates in heavy full lines, oxalic acid in heavy dashed lines, and bridging bisbidentate oxalates in open lines.

stabilization of the three-dimensional network of **1**. The principal interactions made by the potassium cations are to the negatively charged oxygen atoms of the oxalate ligands and to the oxygen atoms of the water and the oxalic acid donor molecules. There are nine K1···O and eight K2···O contacts in nonequivalent environments of less than 3.1 Å, usually considered the upper limit of any significant K···O interaction.[14]

The three-dimensional network is completed by hydrogen bonds acting between water and oxalic acid molecules with oxygen atoms of the oxalate ligands. Strong hydrogen bonding exists between O11 and O22 of the oxalic acid molecule with oxalate O71 and with water O1w respectively, $\mathrm{H11\cdots O71^{b}} = 1.86$ Å, $\mathrm{O11{-}H11\cdots O71^{b}} = 170.2°$ and $\mathrm{H22\cdots O1w^{g}} = 1.82$ Å, $\mathrm{O22{-}H22\cdots O1w^{g}} = 162.5°$. These interactions may be responsible for the twisting of the oxalic acid molecule around the C−C bond (6.7(1)°) as compared to the mean value for the oxalate ligands (1.7(4)°). Finally, the short O···O contacts $\mathrm{O1w\cdots O32^{e}} = 2.927$ Å and $\mathrm{O1w\cdots O72^{b}} = 3.04$ Å and the favorable angle $\mathrm{O32'\cdots O1w\cdots O72'} = 109.5°$ indicate the possibility for an interaction between the water molecules and the corresponding oxalate oxygen atoms (symmetry transformations are as in Table 2). Similar types of complicated interactions have been found to stabilize the crystalline frameworks of the sodium and potassium salts of the tetrakisbisbidentate anion $[\mathrm{Zr(C_2O_4)_4}]^{4-}$.

The infrared spectrum of **1** exhibits a number of very strong and well defined bands in the range 1750−1600 $\mathrm{cm^{-1}}$ and at ca. 1400 $\mathrm{cm^{-1}}$. The former are characteristic of acid carbonyl groups and of asymmetric vibrations of the $\mathrm{RCO_2^-}$ groups and overlap with the lattice water deformation modes[15] usually assigned at 1625 $\mathrm{cm^{-1}}$. In particular, the very strong and unshifted band at 1692 $\mathrm{cm^{-1}}$ indicates the presence of oxalic acid in the lattice. The bands at ca. 1400 $\mathrm{cm^{-1}}$ may correspond to the symmetric vibrations of the $\mathrm{RCO_2^-}$ groups. The Δ values [$\Delta = \nu(\mathrm{CO_2^-})_{\mathrm{asym}} - \nu(\mathrm{CO_2^-})_{\mathrm{sym}}$] above 200 $\mathrm{cm^{-1}}$ point to a monodentate carboxylate coordination[16] as confirmed by the X-ray analysis above.

Thermal decomposition of **1** was followed by TGA under an atmosphere of air. The first step in the thermogram is the weight loss of about 21% in the range 175−225 °C which corresponds to the distinct loss of the water and oxalic acid molecules. The final weight loss (about 56%) is consistent with a conversion of **1** to a residue of composition $\mathrm{K_2O_2{\cdot}ZrO_2}$. No attempt was made, however, to study the details of the pyrolysis process. The XRPD pattern of the final pyrolyzate revealed the presence of a crystalline ZrO2 phase.[17]

In summary, compound **1** represents the first crystallographically characterized structure of a zirconium(IV) carboxylate polymer. An interesting aspect in this structure is the simultaneous presence of two different coordination modes of the oxalate ligands to the zirconium metal center: bidentate and bridging bisbidentate. The latter determine zigzag polymeric chains along the *c* axis. The crystallization of **1** from a solution likely to contain a large number of species depends, we believe, upon the stabilizing effect of the potassium cations through strong dative K···O bond interactions.

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Supporting Information Available: An X-ray crystallographic file in CIF format for the title compound is available on the Internet only. Access information is given on any current masthead page.

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