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Ammonium diaqua(ethylenediaminetetraacetato)scandium(III) trihydrate

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Abstract

The title complex, $(NH_4)[Sc(C_{10}H_{12}N_2O_8)(H_2O)_2]\cdot 3H_2O$, was synthesized in aqueous solution as a precursor compound for scandia–zirconia solid composite oxide electrolytes. The structural determination shows that the Sc^{3+} ion is coordinated by four O and two N atoms of the ethylenediaminetetraacetate (edta) ligand, and by two water molecules. All of the four carboxylate groups are monodentate. A distorted square antiprism is formed around the Sc^{3+} ion by the eight ligating atoms.

Comment

The coordination chemistry of scandium with poly-aminopolycarboxylic acids such as ethylenediaminetetraacetic acid (EDTA) has been studied in detail for analytical purposes, but no crystal structures of scandium complexes of EDTA have been reported. In our present study, we have exploited the advantages of the thermal decomposition of coordination compounds, *viz.* formation of pure crystalline phases and small homogeneous particles (van Doorn *et al.*, 1998), to synthesize scandia–zirconia composite oxide electrolytes. The title complex, (I), was synthesized as a precursor compound and its crystal structure has been determined.

(I)
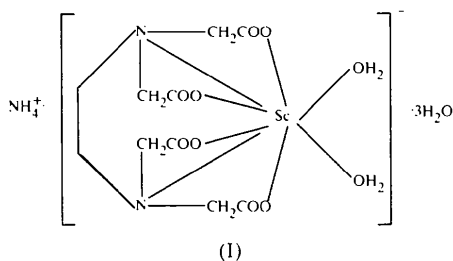
Certainly, the following discussions are helpful and meaningful in the understanding of the relationship between the precursor structure and the thermal decomposition reaction in synthesizing the target scandia–zirconia composite oxide. Crystallographic determination has revealed the structural features of the title complex.

Complex (I) has a discrete structure composed of $[Sc(edta)(H_2O)_2]^-$ anions, NH_4^+ cations and two solvent water molecules. The Sc^{3+} ion has coordination number 8, which includes four O and two N atoms of the ethylenediaminetetraacetate (edta) ligand, and two O atoms of coordinated water. These eight atoms form a distorted square antiprism around the Sc^{3+} ion, in which the two parallel planes contain atoms N1/O1/O3/O9 and N2/O5/O7/O10. Such a high coordination number is common for Sc^{3+} (Willey *et al.*, 1992); it was also observed in a polyaminopolycarboxylic scandium(III) heteronuclear complex with manganese, [MnSc(dtpa)(H_2O)_2]·2H_2O (dtpa is diethylenetriaminepentaacetic acid; Zhang *et al.*, 1995), in which the Sc^{3+} ion is coordinated by five O and three N atoms of dtpa. In (I), the mean Sc—O distance is 2.189 (2) Å, which is about 0.27 Å shorter than the mean Sc—N distance [2.458 (2) Å]. The mean Sc—O and Sc—N distances in the title complex are both longer than those in [MnSc(dtpa)(H_2O)_2]·2H_2O [2.158 (3) and 2.435 (3) Å, respectively]. On the other hand, in comparison with six-coordinated scandium(III) complexes, the mean Sc—O bond length in (I) is much longer than those in $\{[Sc_2(Gly)_6](ClO_4)_6\}_n$ (Gly is glycine; Yan *et al.*, 1996) and $[Sc(ClCH_2CO_2)_3]_n$ (Sugita *et al.*, 1987) [2.066 (7) and 2.075 (6) Å, respectively]. This phenomenon arises from the enlargement of the coordination sphere round the Sc^{3+} ions from six-coordinated to eight-coordinated. There are two types of hydrogen bond, namely O—H···O between water of solvation and the carboxylate groups, and N—H···O between NH_4^+ and the carboxylate groups, with mean D···A distances of 2.800 (3) and 2.995 (3) Å, respectively. The four carboxylate groups of the edta ligand in (I) are all monodentate, as found in the lanthanum(III)–edta complex Na[La(edta)(H_2O)_4]·3H_2O with coordination number 10 (Lind *et al.*, 1965). However, the coordination number of the Sc^{3+} ion in (I)

is lower than that of the lanthanum complex because the ionic radius of Sc^{3+} is much smaller than that of La^{3+}.

The structural features of (I) are very similar to those of the zirconia–edta precursor complex [Zr(edta)-$(H_2O)_2]\cdot2H_2O$ (Pozhidaev *et al.*, 1973). This complex has the same coordination numbers, coordinating atoms and coordination pattern as (I), and the mean Zr—O and Zr—N distances are 2.12 and 2.41 Å, respectively, which are very close to those of (I). It is because of this structural similarity that nearly equal decomposition temperatures for the two precursor complexes can be anticipated, and are observed at about 853 K. As soon as the decomposition reaction is complete, the crystallizing reaction can go on almost simultaneously and, accordingly, good conditions have been created for obtaining the required small homogeneous particles of the phase-pure composite oxide.
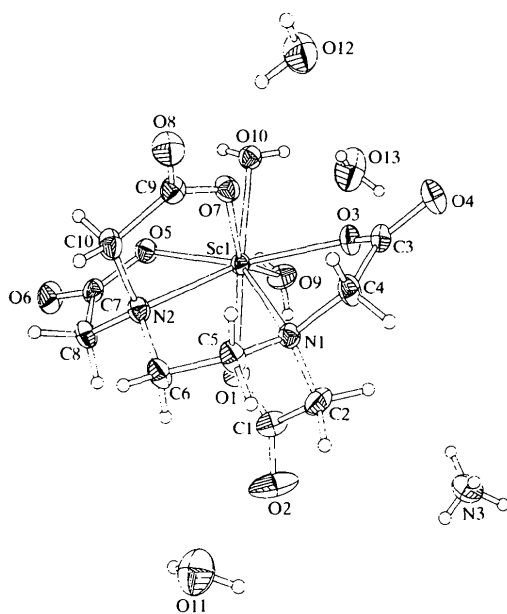

Fig. 1. A diagram of the title complex (*SHELXTL/PC*; Sheldrick, 1990) with the numbering scheme and 50% probability displacement ellipsoids.

Experimental

The title complex was prepared by the reaction between scandium hydroxide (1 mmol) and EDTA (1 mmol) in deionized water (10 ml) under mild heating. When the solution became transparent, it was adjusted to pH 7 by adding dilute ammonia solution dropwise. The solution was then filtered and allowed to evaporate slowly in air at room temperature. After several days, colourless crystals were produced (yield 34%). Analysis found: C 27.0, H 5.3, N 9.0%; calculated for $C_{10}H_{26}N_3O_{13}Sc$: C 27.2, H 5.9, N 9.5%. IR (KBr pellet, cm^{-1}): 3246–3423 [*s, br,* ν(OH)], 1623 [*vs,* ν_{as}(COO$^-$)], 1401 [*s,* ν_s(COO$^-$)], 1113 [*ms,* ν(CN)].

Crystal data

(NH$_4$)[Sc(C$_{10}$H$_{12}$N$_2$O$_8$)-
  (H$_2$O)$_2$)]·3H$_2$O
$M_r = 441.30$
Monoclinic
$P2_1/c$
$a = 12.6512\,(10)$ Å
$b = 8.7080\,(6)$ Å
$c = 17.0124\,(12)$ Å
$\beta = 106.314\,(6)°$
$V = 1798.7\,(2)$ Å^3
$Z = 4$
$D_x = 1.630$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25
  reflections
$\theta = 11.48–13.41°$
$\mu = 0.483$ mm^{-1}
$T = 293\,(2)$ K
Plate
$0.40 \times 0.40 \times 0.10$ mm
Colourless

Data collection

Enraf–Nonius CAD-4
  MACH3 diffractometer
$\theta/2\theta$ scans
Absorption correction:
  ψ scan (North *et al.*,
  1968)
  $T_{min} = 0.936$, $T_{max} = 1.000$
4981 measured reflections
4782 independent reflections

4089 reflections with
  $I > 2\sigma(I)$
$R_{int} = 0.072$
$\theta_{max} = 29.06°$
$h = 0 \rightarrow 17$
$k = -11 \rightarrow 0$
$l = -23 \rightarrow 22$
3 standard reflections
  frequency: 60 min
  intensity decay: -0.2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.152$
$S = 1.085$
4782 reflections
301 parameters
H-atom parameters
  constrained
$w = 1/[\sigma^2(F_o^2) + (0.0998P)^2 + 0.9968P]$
  where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.004$
$\Delta\rho_{max} = 0.894$ e Å^{-3}
$\Delta\rho_{min} = -0.950$ e Å^{-3}
Extinction correction:
  SHELXL97 (Sheldrick,
  1997*a*)
Extinction coefficient:
  0.0068 (16)
Scattering factors from
  *International Tables for
  Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Sc1—O1	2.1434 (15)	Sc1—O10	2.2514 (14)
Sc1—O7	2.1440 (15)	Sc1·O9	2.2848 (15)
Sc1—O6	2.1464 (14)	Sc1—N2	2.4568 (16)
Sc1—O3	2.1665 (14)	Sc1—N1	2.4582 (16)
O1—Sc1—O7	140.44 (6)	O10—Sc1—O9	71.72 (6)
O1—Sc1—O6	89.00 (6)	O1—Sc1—N2	76.68 (5)
O7—Sc1—O6	101.33 (6)	O7—Sc1—N2	71.88 (5)
O1—Sc1—O3	104.97 (6)	O6—Sc1—N2	69.07 (6)
O7—Sc1—O3	83.24 (6)	O3—Sc1—N2	136.97 (5)
O6—Sc1—O3	152.23 (6)	O10—Sc1—N2	126.44 (6)
O1—Sc1—O10	142.81 (5)	O9—Sc1—N2	139.25 (6)
O7—Sc1—O10	76.54 (6)	O1—Sc1—N1	70.91 (5)
O6—Sc1—O10	76.33 (5)	O7—Sc1—N1	76.66 (6)
O3—Sc1—O10	78.22 (6)	O6—Sc1—N1	138.78 (5)
O1—Sc1—O9	72.86 (6)	O3—Sc1—N1	68.99 (5)
O7—Sc1—O9	145.64 (6)	O10—Sc1—N1	139.53 (6)
O6—Sc1—O9	83.84 (6)	O9—Sc1—N1	121.15 (6)
O3—Sc1—O9	77.78 (6)	N2—Sc1—N1	71.38 (5)

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···A	D—H	H···A	D···A	D—H···A
O9—H13···O6^i	0.92	1.92	2.830 (2)	173
O9—H14···O2^{ii}	0.95	1.75	2.689 (3)	171
O10—H15···O4^{iii}	0.94	1.75	2.667 (2)	164

O10—H16···O1ⁱⁱ	0.94	1.82	2.749 (2)	166
O13—H22···O12ⁱⁱⁱ	0.94	1.91	2.844 (3)	173
O13—H21···O4ⁱⁱⁱ	0.93	2.00	2.877 (3)	156
O12—H20···O8	0.95	1.86	2.801 (3)	175
O12—H19···O11ⁱᵛ	0.94	1.91	2.847 (3)	177
O11—H18···O13ⁱ	0.94	1.88	2.815 (3)	175
O11—H17···O8ᵛ	0.94	1.95	2.870 (3)	165
N3—H23···O5ⁱ	0.85	2.13	2.958 (3)	165
N3—H24···O7ᵛ	0.87	2.18	3.018 (2)	161
N3—H24···O10ᵛ	0.87	2.37	2.924 (2)	122
N3—H26···O3ᵛⁱ	0.87	2.24	2.990 (3)	145
N3—H25···O12ᵛ	0.87	2.35	3.083 (3)	144

Symmetry codes: (i) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$; (ii) $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$; (iii) $1 - x, -y, -z$; (iv) $-x, -y, -z$; (v) $x, 1 + y, z$; (vi) $1 - x, 1 - y, -z$.

All H atoms were located by difference Fourier synthesis and were refined as riding atoms.

Data collection: *CAD-4 ARGUS Software* (Nonius, 1996). Cell refinement: *CAD-4 ARGUS Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*b*). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*a*). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1990). Software used to prepare material for publication: *SHELXL97*.

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catena-Poly[[diaqua(3-cyanobenzoato-O,O')erbium]-bis-μ-(3-cyanobenzoato-O:O')]

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Abstract

The title compound, $[Er(C_8H_4NO_2)_3(H_2O)_2]_n$, has a one-dimensional chain structure bridged by carboxylate groups. The Er^{III} atom and one 3-cyanobenzoate ligand lie on a twofold axis and this ligand has its cyano group disordered over two sites. Each Er^{III} atom is surrounded by two O atoms from one chelating carboxylate group, four O atoms from four different bridging carboxylate groups and two water molecules, leading to a square-antiprism coordination polyhedron.

Comment

Carboxylate complexes of lanthanides play a significant role in the separation, analysis and even luminescence of rare earth elements. Structural information for these complexes will help in the estimation of the chelating ability of different carboxylic acids and may facilitate the design and/or synthesis of new extraction or luminescent systems. A number of carboxylates of lanthanides have been studied extensively and structurally characterized (Ma & Ni, 1996). In this paper, we report the structure of a novel complex, catena-poly[[diaqua(3-cyanobenzoato-O,O')erbium]-bis-μ-(3-cyanobenzoato-O:O')], (I), which is, to our knowledge, the first lanthanide complex of m-cyanobenzoic acid.

(I)