Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Double complexes $[Co(NH_3)_5(H_2O)]_2[Zr_3F_{18}]\cdot 6H_2O$ and $[Co(NH_3)_6]_2[Zr_3F_{18}]\cdot 6H_2O$

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Received 18 April 2007
Accepted 20 August 2007
Online 22 September 2007

The structures of orthorhombic bis[pentaammineaquacobalt(III)] tetra-μ_2-fluorido-tetradecafluoridotrizirconium(IV) hexahydrate (space group *Ibam*), $[Co(NH_3)_5(H_2O)]_2[Zr_3F_{18}]\cdot 6H_2O$, (I), and bis[hexaamminecobalt(III)] tetra-μ_2-fluorido-tetradecafluoridotrizirconium(IV) hexahydrate (space group *Pnna*), $[Co(NH_3)_6]_2[Zr_3F_{18}]\cdot 6H_2O$, (II), consist of complex $[Co(NH_3)_x(H_2O)_y]^{3+}$ cations with either m [in (I)] or $\overline{1}$ and 2 [in (II)] symmetry, $[Zr_3F_{18}]^{6-}$ anionic chains located on sites with 222 [in (I)] or 2 [in (II)] symmetry, and water molecules.

Comment

Double salts built from both cationic and anionic metal complexes represent an intensively studied field of modern chemistry (Du *et al.*, 2005; Gubanov *et al.*, 2003; Korenev *et al.*, 1996; Korolkov *et al.*, 2005). Special attention has been paid to the unique products of their thermal decomposition which, in many cases, yields nanoparticles of metal solid solutions. The latter can be used in many areas of applied chemistry, such as powder metallurgy and catalysis. The decomposition of double complexes in an oxygen atmosphere may afford complex ceramics with unusual properties. The title double complexes, $[Co(NH_3)_5H_2O]_2[Zr_3F_{18}]\cdot 6H_2O$, (I), and $[Co(NH_3)_6]_2[Zr_3F_{18}]\cdot 6H_2O$, (II), are expected to yield nanosized ceramic powders.

The two title compounds have isotypic structures. The octahedral coordination of the Co^{III} cation is similar in both cases, the only difference being the presence of a water molecule instead of ammonia in (I) (Figs. 1 and 2). Both structures include an analogous $[Zr_3F_{18}]^{6-}$ anion with a trimeric chain structure. The terminal Zr atoms are seven-coordinated with a distorted pentagonal–bipyramidal geometry. The central Zr atoms are coordinated by eight F atoms forming a distorted square antiprism. The average Zr—F distance of 2.08 (9) Å is the same in both compounds.

The chain defined by the Zr atoms of the trimeric anion is parallel to the crystallographic *a* axis in both cases (Figs. 3 and 4). In spite of similar unit-cell dimensions, the two compounds have different local symmetries. In (I), the anion has point symmetry 222 and the Co atom is located on a mirror plane. In (II), the anion occupies a position of symmetry 2 and the

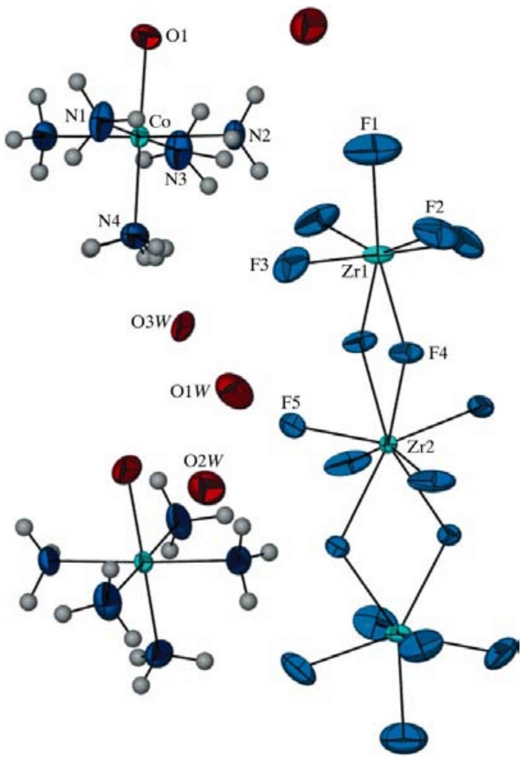

Figure 1
The structure of compound (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

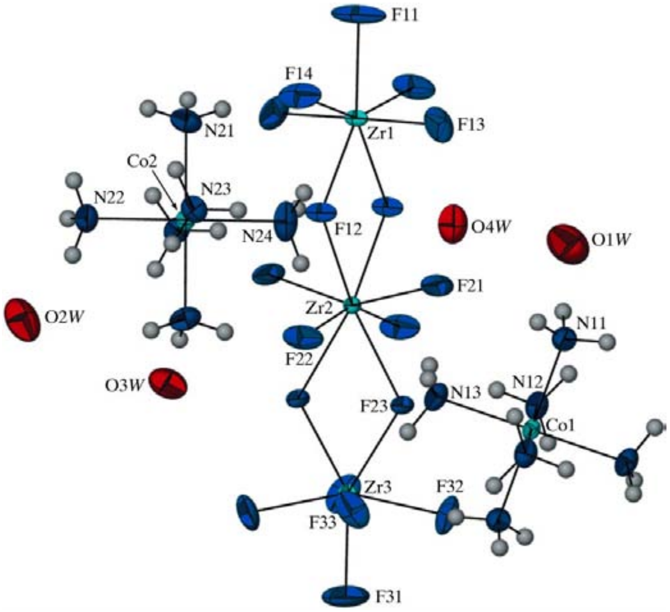

Figure 2
The structure of compound (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

DOI: 10.1107/S010827010704108X

unique Co1 and Co2 atoms are located on an inversion centre and a twofold axis, respectively.

Both compounds contain several solvent water molecules that form a hydrogen-bond network with the NH_3 ligands and the F atoms of the anions, with an average distance of 2.67 Å for (I) and 2.79 Å for (II). Differential thermal analysis and thermogravimetric analysis data (Derivatograf NETZCH STA 409) show that (II) loses about 5.5 water molecules over the 333–373 K range, whereas (I) loses water in three stages, at 333–393 (two H_2O), 393–443 (four H_2O) and 443–513 K (two H_2O). These data confirm the presence of three types of water molecules in (I): the first stage of weight loss corresponds to water molecules with contacts to hydrogen-bond acceptor atoms of more than 3 Å, the second stage corresponds to the loss of all hydrogen-bonded water molecules with an average distance of 2.66 Å, and the last stage represents the loss of coordinated water molecules.

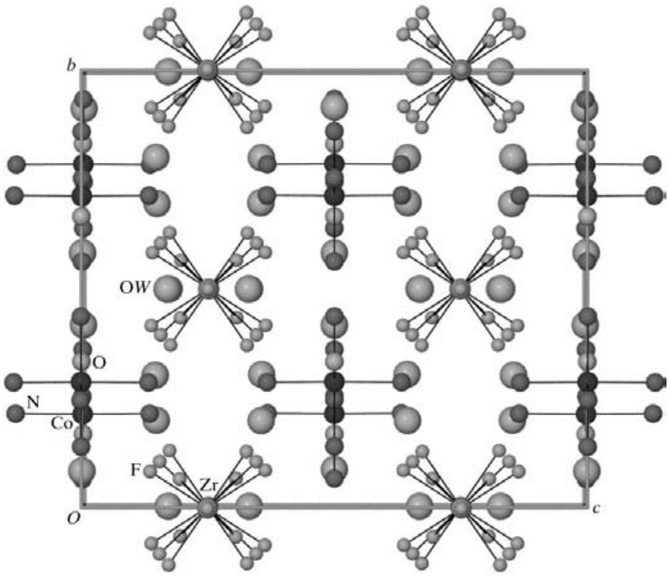

Figure 3
A packing diagram for (I), viewed along the *a* axis. The $[Zr_3F_{18}]^{6-}$ anions have a chain structure aligned long the *a* axis. Atom labels only indicate the chemical types.

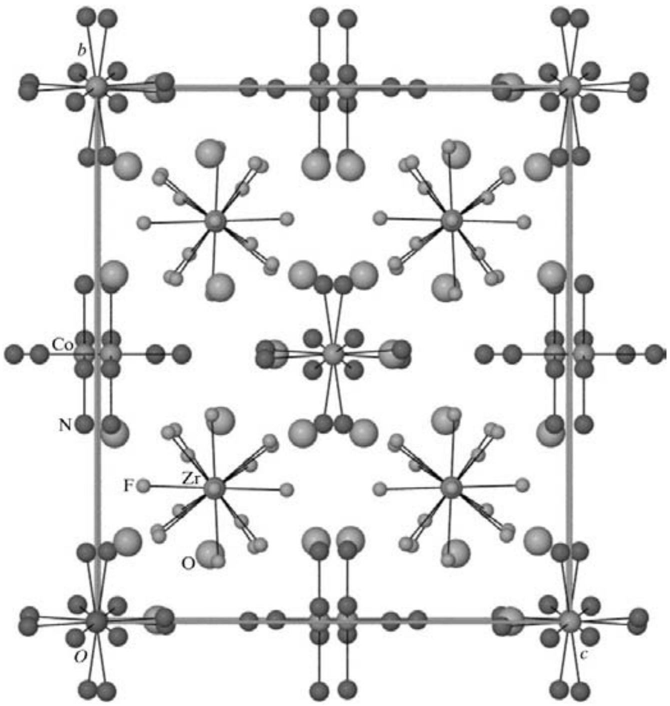

Figure 4
A packing diagram for (II), viewed along the *a* axis. The structure of the $[Zr_3F_{18}]^{6-}$ anion differs from that in (I). Atom labels only indicate the chemical types.

Experimental

Crystals of (I) were grown from an aqueous solution prepared at room temperature by the reaction of 0.001 *M* solutions of $[Co(NH_3)_5Cl]Cl_2$ (100 ml) and $K_2[ZrF_6]$ (150 ml). After one week, deep-purple crystals were collected by filtration and dried in air. Crystals of (II) were grown from the reaction of aqueous 0.001 *M* solutions of $[Co(NH_3)_6]Cl_3$ (100 ml) and $K_2[ZrF_6]$ (150 ml). After 4 d, fine yellow crystals were collected and dried in air. The crystal size was 2–3 mm for both (I) and (II).

Compound (I)

Crystal data

$[Co(NH_3)_5(H_2O)]_2[Zr_3F_{18}]\cdot 6H_2O$
M_r = 1047.99
Orthorhombic, *Ibam*
a = 16.1440 (4) Å
b = 12.7191 (3) Å
c = 14.6859 (3) Å
V = 3015.56 (12) Å^3
Z = 4
Mo *K*α radiation
μ = 2.23 mm^{-1}
T = 293 (2) K
0.17 × 0.12 × 0.12 mm

Data collection

Bruker Nonius X8 APEX CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2004)
T_{min} = 0.703, T_{max} = 0.775
10490 measured reflections
1614 independent reflections
1460 reflections with $I > 2\sigma(I)$
R_{int} = 0.033

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.109
S = 1.11
1614 reflections
113 parameters
6 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 1.52 e Å^{-3}
$\Delta\rho_{min}$ = −2.37 e Å^{-3}

Table 1
Selected bond lengths (Å) for (I).

Co1—O1	1.947 (6)	Zr1—F2	2.045 (4)
Co1—N1	1.949 (7)	Zr1—F3	1.995 (4)
Co1—N2	1.956 (5)	Zr1—F4	2.137 (3)
Co1—N3	1.969 (7)	Zr2—F4	2.205 (3)
Co1—N4	1.911 (7)	Zr2—F5	2.015 (3)
Zr1—F1	2.032 (7)		

Compound (II)

Crystal data

$[Co(NH_3)_6]_2[Zr_3F_{18}]\cdot 6H_2O$
M_r = 1046.02
Orthorhombic, *Pnna*
a = 16.0370 (3) Å
b = 14.6920 (2) Å
c = 12.9942 (2) Å
V = 3061.64 (9) Å^3
Z = 4
Mo *K*α radiation
μ = 2.20 mm^{-1}
T = 293 (2) K
0.26 × 0.20 × 0.16 mm

Data collection

Bruker Nonius X8 APEX CCD area-detector diffractometer	20871 measured reflections
Absorption correction: multi-scan (*SADABS*; Bruker, 2004)	3136 independent reflections
$T_{\min} = 0.599$, $T_{\max} = 0.720$	2608 reflections with $I > 2\sigma(I)$
	$R_{\rm int} = 0.031$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.041$	211 parameters
$wR(F^2) = 0.110$	H-atom parameters constrained
$S = 1.19$	$\Delta\rho_{\max} = 1.24$ e Å^{-3}
3136 reflections	$\Delta\rho_{\min} = -2.23$ e Å^{-3}

Table 2
Selected bond lengths (Å) for (II).

Co1—N11	1.953 (4)	Zr1—F14	2.051 (3)
Co1—N12	1.957 (4)	Zr2—F12	2.211 (3)
Co1—N13	1.967 (4)	Zr2—F21	2.013 (3)
Co2—N21	1.953 (4)	Zr2—F22	2.008 (3)
Co2—N22	1.944 (6)	Zr2—F23	2.230 (3)
Co2—N23	1.959 (4)	Zr3—F23	2.132 (3)
Co2—N24	1.960 (6)	Zr3—F31	2.061 (6)
Zr1—F11	2.067 (5)	Zr3—F32	2.013 (4)
Zr1—F12	2.143 (3)	Zr3—F33	2.021 (3)
Zr1—F13	1.993 (3)		

The H atoms of the water molecules were not located for either compound. The H atoms of the NH_3 ligands were determined by geometry (N—H = 0.89 Å) and some of these ligands were disordered over two orientations [N1, N3 and N4 in (I), and N22 and N24 in (II)]. Atoms F11 and F31 in (II) were displaced from special positions and disordered over two general sites with 50% occupancy.

For both compounds, data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2004); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Bruker, 2004); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BC3047). Services for accessing these data are described at the back of the journal.

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