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Two scandium–biuret complexes: $[Sc(C_2H_5N_3O_2)(H_2O)_5]Cl_3{\cdot}H_2O$ and $[Sc(C_2H_5N_3O_2)_4](NO_3)_3$

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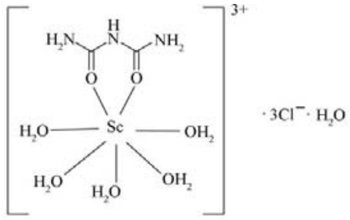
The scandium(III) cations in the structures of pentaaqua(biuret-κ^2O,O')scandium(III) trichloride monohydrate, $[Sc(C_2H_5N_3O_2)(H_2O)_5]Cl_3{\cdot}H_2O$, (I), and tetrakis(biuret-κ^2O,O')scandium(III) trinitrate, $[Sc(C_2H_5N_3O_2)_4](NO_3)_3$, (II), are found to adopt very different coordinations with the same biuret ligand. The roles of hydrogen bonding and the counter-ion in the establishment of the structures are described. In (I), the Sc^{3+} cation adopts a fairly regular pentagonal bipyramidal coordination geometry arising from one *O*,*O*′-bidentate biuret molecule and five water molecules. A dense network of N—H⋯Cl, O—H⋯O and O—H⋯Cl hydrogen bonds help to establish the packing, resulting in dimeric associations of two cations and two water molecules. In (II), the Sc^{3+} cation (site symmetry 2) adopts a slightly squashed square-antiprismatic geometry arising from four *O*,*O*′-bidentate biuret molecules. A network of N—H⋯O hydrogen bonds help to establish the packing, which features [010] chains of cations. One of the nitrate ions is disordered about an inversion centre. Both structures form three-dimensional hydrogen-bond networks.

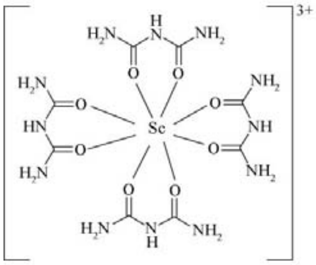
Comment

Compared with other first-row transition elements, the coordination chemistry of Sc^{3+} has not been extensively investigated, perhaps in part owing to the historically high cost of scandium compounds. Even so, it is clearly defined as a relatively weak class-a acceptor and shows a preference for O-atom donor ligands (Greenwood & Earnshaw, 1997), although coordination to N atoms and halide ions has been observed (*e.g.* Ripert *et al.*, 1999). Scandium(III) is notably flexible in its coordination preference; for example, it can adopt six- [*e.g.* $Sc(H_2O)_6{\cdot}Sc(CH_3SO_3)_6$; Lindquist-Reis *et al.*, 2006], seven- {*e.g.* $[Sc(H_2O)_7]Cl_3$; Lim *et al.*, 2000}, eight- $[Sc(H_2O)_8{\cdot}3CF_3SO_3$; Abbasi *et al.*, 2005] and nine-coordination $[Sc(H_2O)_9{\cdot}3CF_3SO_3$; Castellani *et al.*, 1995] in its mononuclear aqua complexes.

Biuret (biur), H_2N–CO–NH–CO–NH_2 (or $C_2H_5N_3O_2$), has long been recognized as a ligand in coordination chemistry (Wiedemann, 1848). In low-pH or neutral conditions, biuret exhibits *O*,*O*′-bidentate coordination to metal cations [*e.g.* with Zn (Nardelli *et al.*, 1963), Cu (Freeman & Smith, 1966) or Ni (Lawson & Harrison, 2005)]. When biuret is deprotonated under basic conditions, *N*,*N*′-bidentate coordination can arise [*e.g.* with Cu (Pajunen & Pajunen, 1982)]. In this paper, we describe the syntheses and structures of two new scandium–biuret complexes, *viz.* $[Sc(biur)(H_2O)_5]Cl_3{\cdot}H_2O$, (I), and $[Sc(biur)_4](NO_3)_3$, (II). In the former, the Sc^{3+} ion is seven-coordinate, and in the latter, eight coordinate.



(I)



(II)

Compound (I) is a hydrated molecular salt containing a new $[Sc(biur)(H_2O)_5]^{3+}$ complex ion, three charge-balancing chloride ions and one uncoordinated water molecule. The Sc^{3+} ion in (I) is coordinated to seven O atoms (Fig. 1 and Table 1) in a slightly distorted pentagonal bipyramidal arrangement. The *O*,*O*′-bidentate biuret molecule occupies two of the equatorial positions, and a six-membered chelate ring results. The mean equatorial O—Sc—O bond angle is 73.0° and the

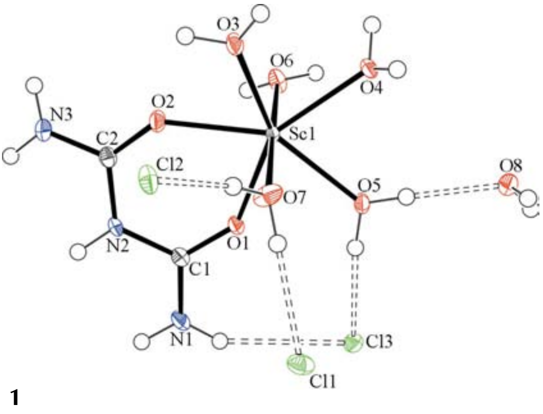


Figure 1
A view of the molecular structure of (I), showing 50% probability displacement ellipsoids (arbitrary spheres for the H atoms). Hydrogen bonds are indicated by double-dashed lines.

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axial O6—Sc1—O7 bond angle is 177.98 (4)°. The axial Sc—O bond lengths are slightly shorter than their equatorial equivalents. In $[Sc(H_2O)_7]X_3$ (X = Cl and Br; Lim *et al.*, 2000), a very similar scandium geometry arises, although the complete complex cation is generated by twofold symmetry in these cases.

It has been noted previously (Carugo *et al.*, 1992) that the biuret molecule can be regarded as two planar amide fragments linked by an NH bridge. Here, the dihedral angle between the N1/C1/O1/N2 and N2/C2/O2/N3 units is 13.21 (9)°. The Sc^{3+} cation deviates from the N1/C1/O1/N2 and N2/C2/O2/N3 mean planes by −0.501 (3) and 0.157 (3) Å, respectively.

On progressing along the chain formed by atoms N1, C1, N2, C2 and N3 (Fig. 1), the C—N bond lengths in (I) exhibit a short–long–long–short (slls) pattern, although all of them are intermediate between typical C—N single (1.47 Å) and C═N double (1.30 Å) bond lengths, consistent with a significant degree of electronic delocalization over the entire biuret molecule (Carugo *et al.*, 1992). This slls bond-length alternation pattern is the most common one seen in biurets, although others are also possible (Harrison, 2007).

The component species in (I) are linked by a dense network of N—H···Cl, O—H···Cl and O—H···O hydrogen bonds (Table 2). Perhaps the most interesting of these are the O—H···O links, which result in $[Sc(biur)(H_2O)_5{\cdot}H_2O]_2$ inversion dimers (Fig. 2) in which the graph-set motif (Bernstein *et al.*, 1995) is $R_4^2(12)$. Of the other hydrogen bonds, atoms Cl1, Cl2 and Cl3 accept four, six and five, respectively.

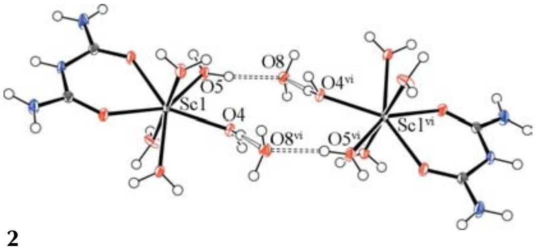

Figure 2
A view of the centrosymmetric $[Sc(biur)(H_2O)_5{\cdot}H_2O]_2$ dimer in (I), with the hydrogen bonds indicated by double-dashed lines. [Symmetry code: (vi) $-x + 1, -y + 1, -z + 2$.]

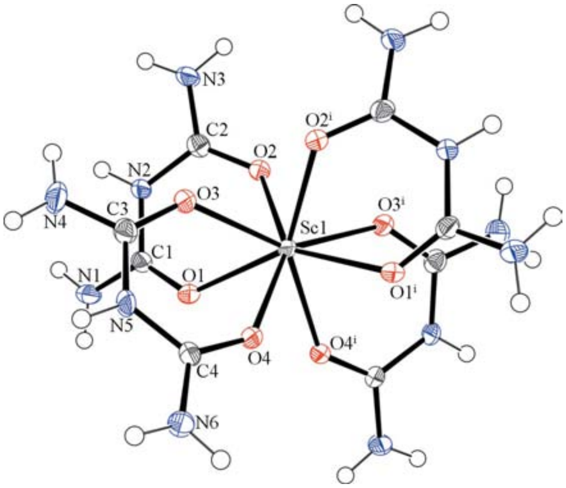

Figure 3
A view of the $[Sc(biur)_4]^{3+}$ complex ion in (II), showing 50% probability displacement ellipsoids (arbitrary spheres for the H atoms). [Symmetry code: (i) $-x + 1, y, -z + \frac{1}{2}$.]

The asymmetric unit of (II) contains one Sc^{3+} ion (site symmetry 2), two biuret molecules and two nitrate ions, one of which is disordered about an inversion centre. Crystal symmetry generates an $[Sc(biur)_4]^{3+}$ complex ion (Fig. 3), in which the Sc^{III} ion adopts a squashed square-antiprismatic geometry (Table 3 and Fig. 4). The r.m.s. deviation from the mean plane of the four O atoms forming one square face [O1, O2, O3^{i} and O4^{i}; symmetry code: (i) $-x + 1, y, -z + \frac{1}{2}$] is 0.004 Å, and atom Sc1 is displaced from this plane by 1.190 (1) Å. Owing to crystal symmetry, the same values apply to the other four O atoms (O1^{i}, O2^{i}, O3 and O4). The dihedral angle between the two sets of O atoms is 1.20 (9)°.

Both biuret molecules in (II) exhibit the slls C—N bond-length pattern. The dihedral angle between the N1/C1/O1/N2 and N2/C2/O2/N3 fragments is 20.35 (9)°, indicating an unusually high degree of twisting, and that between N4/C3/O3/N5 and N5/C4/O4/N6 is 11.76 (18)°. The deviations of the Sc^{3+} ion from the mean planes of the biuret fragments are −0.139 (4) Å for N1/C1/O1/N2, −1.323 (4) Å for N2/C2/O2/N3, 0.848 (5) Å for N4/C3/O3/N5 and −0.171 (5) Å for N5/C4/O4/N6.

The structure of (II) is completed by two nitrate ions, one of which is disordered about an inversion centre. A network of

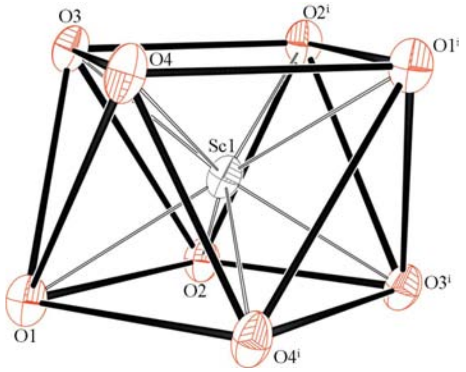

Figure 4
A detail of (II), showing the squashed square-antiprismatic geometry of the scandium(III) ion. [Symmetry code: (i) $-x + 1, y, -z + \frac{1}{2}$.]

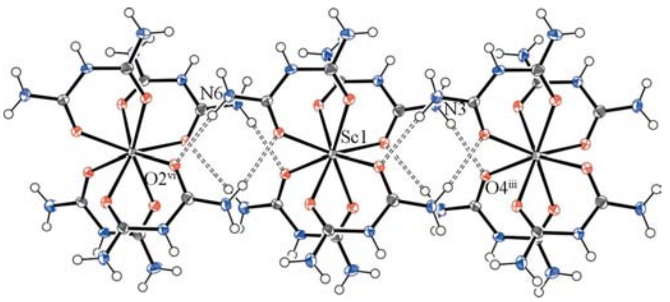

Figure 5
Part of a hydrogen-bonded [010] chain of $[Sc(biur)]^{3+}$ cations in (II), with the N—H···O hydrogen bonds indicated by double-dashed lines. [Symmetry codes: (iii) $-x + 1, y + 1, -z + \frac{1}{2}$; (vi) $-x + 1, y - 1, -z + \frac{1}{2}$.]

N—H···O hydrogen bonds (Table 4) link the component species into a three-dimensional array. The most notable are the N3—H3*A*···O4^{iii} and N6—H6*A*···O2^{vi} links [symmetry codes: (iii) $-x + 1, y + 1, -z + \frac{1}{2}$; (vi) $-x + 1, y - 1, -z + \frac{1}{2}$], which lead to [010] chains of cations containing $R_2^2(8)$ loops (Fig. 5).

The Sm^{3+} equivalent to the complex ion seen in (II) has been described by Haddad (1987) in $[Sm(biur)_3](NO_3)_3$, and indeed the overall structures of (II) and $[Sm(biur)_3](NO_3)_3$ are isostructural but not isomorphous.

A short nitro-O6···C1 contact of 2.904 (3) Å occurs in the crystal structure of (II), which could be another example of a short through-space O···C electrostatic interaction (O'Leary & Wallis, 2007).

Experimental

To prepare (I), 0.1 *M* aqueous solutions of $ScCl_3$ (10 ml) and biuret (10 ml) were mixed and a small quantity of dilute hydrochloric acid was added, resulting in a colourless solution. Colourless blocks of (I) grew over several days as the water evaporated. Compound (II) was prepared in the same way, with 0.1 *M* $Sc(NO_3)_3$ replacing the scandium chloride solution. Large colourless slabs of (II) grew as the water evaporated.

Compound (I)

Crystal data

$[Sc(C_2H_5N_3O_2)(H_2O)_5]Cl_3 \cdot H_2O$
$M_r = 362.50$
Monoclinic, $P2_1/c$
$a = 15.2430$ (7) Å
$b = 7.5653$ (5) Å
$c = 14.1276$ (9) Å
$\beta = 117.247$ (4)°
$V = 1448.39$ (15) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 1.09$ mm^{-1}
$T = 120$ (2) K
0.40 × 0.20 × 0.15 mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2003)
$T_{min} = 0.670$, $T_{max} = 0.854$
17376 measured reflections
3308 independent reflections
2988 reflections with $I > 2\sigma(I)$
$R_{int} = 0.025$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.023$
$wR(F^2) = 0.060$
$S = 1.06$
3308 reflections
155 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.41$ e Å^{-3}
$\Delta\rho_{min} = -0.50$ e Å^{-3}

Compound (II)

Crystal data

$[Sc(C_2H_5N_3O_2)_4](NO_3)_3$
$M_r = 643.36$
Monoclinic, $C2/c$
$a = 19.2409$ (13) Å
$b = 7.0167$ (4) Å
$c = 17.4653$ (13) Å
$\beta = 107.344$ (4)°
$V = 2250.7$ (3) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.45$ mm^{-1}
$T = 120$ (2) K
0.18 × 0.12 × 0.10 mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2003)
$T_{min} = 0.924$, $T_{max} = 0.957$
12063 measured reflections
2581 independent reflections
1704 reflections with $I > 2\sigma(I)$
$R_{int} = 0.070$

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

Sc1—O7	2.1109 (11)	Sc1—O5	2.1572 (10)
Sc1—O6	2.1242 (11)	Sc1—O2	2.1595 (10)
Sc1—O1	2.1377 (10)	Sc1—O3	2.1629 (10)
Sc1—O4	2.1541 (10)		

Table 2
Hydrogen-bond geometry (Å, °) for (I).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···Cl3	0.88	2.62	3.4148 (14)	152
N1—H2···Cl2^{i}	0.88	2.53	3.2883 (14)	145
N2—H3···Cl2^{ii}	0.88	2.45	3.1609 (12)	138
N3—H4···Cl2^{iii}	0.88	2.74	3.4239 (14)	136
N3—H5···Cl2^{ii}	0.88	2.75	3.4882 (14)	142
O3—H6···Cl1^{iv}	0.83	2.27	3.0662 (11)	163
O3—H7···Cl2^{v}	0.90	2.24	3.1245 (11)	167
O4—H8···Cl3^{iv}	0.88	2.18	3.0519 (11)	173
O4—H9···O8^{vi}	0.85	1.84	2.6929 (15)	176
O5—H10···Cl3	0.89	2.30	3.1671 (11)	164
O5—H11···O8	0.85	1.89	2.7274 (14)	174
O6—H12···Cl1^{iii}	0.85	2.21	3.0477 (11)	169
O6—H13···Cl3^{vii}	0.86	2.21	3.0691 (11)	175
O7—H14···Cl1	0.86	2.14	3.0014 (11)	179
O7—H15···Cl2	0.93	2.10	3.0229 (11)	173
O8—H16···Cl3^{viii}	0.91	2.27	3.1512 (11)	165
O8—H17···O1^{viii}	0.89	2.51	3.2003 (15)	135
O8—H17···Cl1^{vii}	0.89	2.62	3.3161 (11)	135

Symmetry codes: (i) $x, -y + \frac{1}{2}, z - \frac{1}{2}$; (ii) $-x, -y + 1, -z + 1$; (iii) $x, y + 1, z$; (iv) $x, -y + \frac{1}{2}, z + \frac{1}{2}$; (v) $-x, y + \frac{1}{2}, -z + \frac{3}{2}$; (vi) $-x + 1, -y + 1, -z + 2$; (vii) $-x + 1, y + \frac{1}{2}, -z + \frac{3}{2}$; (viii) $-x + 1, y - \frac{1}{2}, -z + \frac{3}{2}$.

Table 3
Selected bond lengths (Å) for (II).

Sc1—O2	2.1600 (18)	Sc1—O3	2.1945 (17)
Sc1—O4	2.1830 (18)	Sc1—O1	2.2905 (18)

Table 4
Hydrogen-bond geometry (Å, °) for (II).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···O6^{vii}	0.88	2.09	2.966 (3)	171
N1—H1*B*···O7^{ii}	0.88	2.37	3.163 (3)	150
N2—H2···O6^{ii}	0.88	2.24	2.971 (3)	140
N2—H2···O7^{ii}	0.88	2.31	3.139 (3)	156
N3—H3*A*···O4^{iii}	0.88	2.18	3.040 (3)	167
N3—H3*B*···O6^{ii}	0.88	2.23	2.923 (3)	135
N3—H3*B*···O10^{iv}	0.88	2.35	2.887 (5)	119
N3—H3*B*···O8	0.88	2.48	3.206 (5)	141
N4—H4*A*···O9	0.88	2.02	2.779 (5)	144
N4—H4*A*···O10^{iv}	0.88	2.20	3.054 (5)	165
N4—H4*B*···O7^{v}	0.88	2.35	3.094 (3)	142
N5—H5···O7^{v}	0.88	2.07	2.904 (3)	158
N6—H6*A*···O2^{vi}	0.88	2.34	3.193 (3)	162
N6—H6*B*···O5^{v}	0.88	2.14	2.997 (3)	164

Symmetry codes: (ii) $-x + 1, -y + 1, -z$; (iii) $-x + 1, y + 1, -z + \frac{1}{2}$; (iv) $-x + \frac{1}{2}, -y + \frac{3}{2}, -z$; (v) $x - \frac{1}{2}, y - \frac{1}{2}, z$; (vi) $-x + 1, y - 1, -z + \frac{1}{2}$; (vii) $-x + 1, -y, -z$.

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.051$
$wR(F^2) = 0.122$
$S = 1.05$
2581 reflections
204 parameters
3 restraints
H-atom parameters constrained
$\Delta\rho_{max} = 0.60$ e Å^{-3}
$\Delta\rho_{min} = -0.39$ e Å^{-3}

N-bound H atoms were positioned geometrically (N—H = 0.88 Å) and refined as riding [$U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(N)]. Water H atoms were located in difference maps and refined as riding in their as-found relative positions [$U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(O)].

For both compounds, data collection: *COLLECT* (Nonius, 1998); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997), and *SORTAV* (Blessing, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3214). Services for accessing these data are described at the back of the journal.

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