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N,N-Dimethylformamide Complex of Aluminium(III) Perchlorate

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Abstract

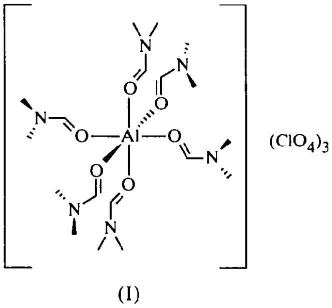
Hexakis(*N,N*-dimethylformamide-*O*)aluminium(III) triperchlorate, $[Al\{(CH_3)_2NCHO\}_6](ClO_4)_3$, has an octahedral coordination structure with the center of symmetry at the Al^{3+} ion. One of the anions is disordered and the other centers on the twofold axis. Each *N,N*-dimethylformamide (DMF) ligand coordinates *via* its O atom in the sp^2 lone-pair direction. Although the vicinity of the Al atom is crowded with six planar ligands, no serious steric hindrance is found in the coordination structure. The intramolecular bond lengths of the coordinated DMF show clear variations from those of non-coordinated DMF and are in accord with the sequence of metal–DMF interactions: $Sb^V > Si^{IV} > Al^{III} > Ca^{II}$.

Comment

Interaction of Al ions with peptides is of crucial importance in understanding the cause and process of Alzheimer's disease (AD), and the possible role played by aluminium (Fasman, 1996; Savory *et al.*, 1996). Al, Fe and Zn ions bind to β-amyloid peptide, which is the main component of AD plaques, and enhance aggregation (Mantyh *et al.*, 1993). Although the precise site of interaction is not known, carboxyl and hydroxyl residues in the peptide are primary candidates for metal coordination (Fasman, 1996). It is also possible that interaction with the backbone amide carbonyl O atoms promotes the β-sheet conformation of an amyloid fragment (Laczkó *et al.*, 1996).

Binding of metal ions to amides is of special relevance to conformation transitions of polypeptides and proteins. *N*-Methylacetamide has been used for model investigations (Chakrabarti *et al.*, 1981), but it was subject to the limitation that the secondary amide could be affected by anions strongly hydrogen bonded to the N—H site. Therefore, a tertiary amide, *N,N*-dimethylformamide (DMF), was proposed as the simplest model ligand to investigate the metal–peptide backbone interactions, and the systematic variation in structures of coordinated DMF molecules to alkali and alkaline earth metal ions was reported (Rao *et al.*, 1984).

Detailed structural knowledge of an aluminium–DMF complex would help to clarify the strength of the interaction of the Al^{3+} ion with the peptide backbone and possible steric hindrance in the metal environment. In view of this, we have isolated a single crystal of the title compound, (I), and performed an X-ray diffraction analysis.



(I)

The Al^{3+} ion is located at an inversion center and is surrounded by the DMF molecules in a regular octahedral arrangement (Fig. 1). One of the anions is at a general position and its O atoms (O131–O142) are disordered; the other anion (Cl2–O22) centers on a twofold axis, with four O atoms (two crystallographically independent ones and their equivalents) forming a tetrahedron.

The Al—O bond distances [1.875 (2)–1.882 (2) Å] fall within the range expected for octahedral aluminium complexes with neutral O-atom donors (Taylor, 1987). The DMF molecules are essentially planar. The Al—O—C angles [126.5 (2)–130.2 (2)°] and the Al—O—C—N torsion angles [magnitude 160.9 (2)–177.6 (2)°] show that the metal is approximately coplanar with each amide plane and in the lone-pair direction of each carbonyl group (*trans* to the N atom). A slight deviation of these angles from the idealized values (120 and 180°)

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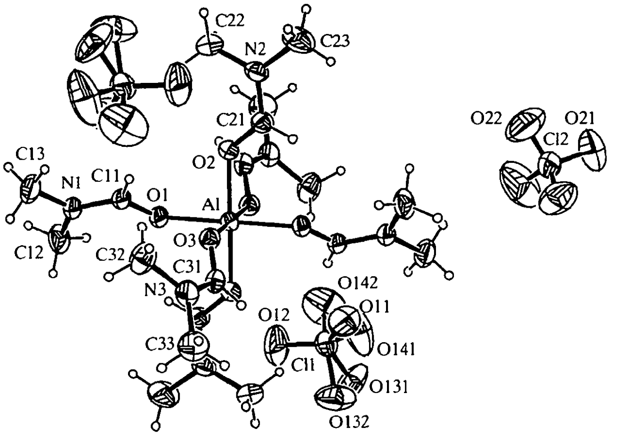

Fig. 1. Molecular diagram of $[Al\{(CH_3)_2NCHO\}_6](ClO_4)_3$ showing the labeling of the non-H atoms. Displacement ellipsoids are shown at 30% probability levels and H atoms are drawn as small circles of arbitrary radii.

may be an indication of small steric effects due to the crowded coordination structure, as the corresponding angles in tetrahedral DMF complexes are even closer to the ideal angles (Suzuki *et al.*, 1991).

The O—C bonds [1.246 (3)–1.258 (3) Å] are longer and the carbonyl C—N bonds [1.284 (3)–1.296 (3) Å] shorter than those in non-coordinating DMF [O—C 1.221 (7) and C—N 1.315 (7) Å (Hunt *et al.*, 1976)]; the N—C(methyl) bonds [1.453 (5)–1.465 (4) Å] are again longer than in the non-coordinating case [1.425 (8)–1.441 (8) Å]. These trends are in accordance with the bond-length-variation rules of Gutmann (1978), and agree with the trends found in alkali and alkaline earth metal DMF complexes (Rao *et al.*, 1984), a silicon(IV)–DMF complex (Deppisch *et al.*, 1984) and an antimony(V)–complex (Brun & Brändén, 1966). The variation of the O—C bond lengths obeys the following sequence: $[SbCl_5(DMF)]$ [O—C 1.300 (10) Å] > $[Si(DMF)_6]I_4$ [1.261 (9)–1.289 (10) Å] > $LiCl.DMF.0.5H_2O$ (polymeric chain) [1.259 (13)–1.261 (13) Å] > $[Al(DMF)_6](ClO_4)_3$ [1.246 (3)–1.258 (3) Å] > $[CaCl_2(DMF)_2(H_2O)_2]$ [1.234 (6) Å] > $NaClO_4.2DMF$ (polymeric chain) [1.210 (10)–1.227 (10) Å] $\simeq$ non-coordinating DMF [1.221 (7) Å]. This sequence may roughly reflect the charge density of the central metal ion, with the exception of the Li complex, where DMF bridges two Li^+ ions and thus conforms to the essentially electrostatic (hard) nature of the metal–DMF interactions.

The O atom of each DMF ligand is in close contact with the carbonyl C atoms of the adjacent DMF ligands. The shortest intermolecular O···C distance [O1···C21^i and O3···C11; symmetry code: (i) $\frac{1}{2}-x$, $\frac{1}{2}-y$, $-z$] is 2.877 (3) Å, which is considerably shorter than the sum of van der Waals radii (3.2 Å; Bondi, 1964). Except for that, no unusual structural distortion or deviation from the sp^2 coordination mode of DMF is found. This is in sharp contrast to the octahedral complex of *N*,*N*-dimethylacetamide (DMA), $[Ni(CH_3CN)_2(DMA)_4](BF_4)_2$, where significant distortions are caused by the acetyl methyl groups (Suzuki & Ishiguro, 1997).

Experimental

$Al(ClO_4)_3$ DMF solvate was prepared by dissolving the hydrate in DMF and removing the excess solvent in a rotary evaporator (Takahashi *et al.*, 1996). An appropriate single crystal was obtained by recrystallization from a mixture of DMF and ethyl orthoformate, the latter acting both as the cosolvent and as a dehydrating reagent.

Crystal data

$[Al(C_3H_7NO)_6](ClO_4)_3$
$M_r = 763.91$
Monoclinic
$C2/c$
$a = 20.252\,(2)$ Å
$b = 13.638\,(1)$ Å
$c = 13.132\,(1)$ Å
$\beta = 100.401\,(8)°$
$V = 3567.4\,(5)$ Å^3
$Z = 4$
$D_x = 1.422$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.54184$ Å
Cell parameters from 25 reflections
$\theta = 23–25°$
$\mu = 3.262$ mm^{-1}
$T = 298\,(2)$ K
Prism
0.40 × 0.40 × 0.40 mm
Colorless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.249$, $T_{max} = 0.271$
3530 measured reflections
3369 independent reflections

3023 reflections with $I > 2\sigma(I)$
$R_{int} = 0.018$
$\theta_{max} = 69.92°$
$h = -24 \rightarrow 24$
$k = 0 \rightarrow 16$
$l = 0 \rightarrow 15$
3 standard reflections
frequency: 60 min
intensity decay: 2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.056$
$wR(F^2) = 0.170$
$S = 1.089$
3369 reflections
235 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0932P)^2 + 3.6066P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.493$ e Å^{-3}
$\Delta\rho_{min} = -0.367$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0038 (3)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Al—O1	1.880 (2)	N1—C13	1.459 (4)
Al—O2	1.882 (2)	N2—C21	1.296 (3)
Al—O3	1.875 (2)	N2—C22	1.453 (5)
O1—C11	1.258 (3)	N2—C23	1.465 (4)
O2—C21	1.246 (3)	N3—C31	1.284 (3)
O3—C31	1.256 (3)	N3—C32	1.465 (4)
N1—C11	1.291 (3)	N3—C33	1.459 (4)
N1—C12	1.453 (4)		

O1—Al—O2	89.23 (7)	O2—Al—O3^i	91.32 (8)
O1—Al—O2^i	90.77 (7)	Al—O1—C11	126.5 (2)
O1—Al—O3	89.25 (7)	Al—O2—C21	130.2 (2)
O1—Al—O3^i	90.75 (7)	Al—O3—C31	129.6 (2)
O2—Al—O3	88.68 (8)		
Al—O1—C11—N1	−163.4 (2)	Al—O3—C31—N3	−160.9 (2)
Al—O2—C21—N2	177.6 (2)		

Symmetry code: (i) $\frac{1}{2} - x, \frac{1}{2} - y, -z$.

Data were corrected for Lorentz, polarization and absorption effects. Laue class and systematic absences indicated space group *Cc* or *C2/c*. The latter was chosen because the comparison of Bijvoet pairs did not suggest a non-centrosymmetric structure; an alternative analysis based on *Cc* gave practically the same structure (two ClO_4^- ions out of three are disordered) as in *C2/c*, with a slightly better fit ($R = 0.046$, $wR = 0.142$) probably due to the doubled number of parameters. The structure was solved by direct methods and subsequent difference Fourier syntheses. Full-matrix least-squares refinement was performed. A small empirical extinction parameter (x) was introduced and refined by least squares, where F_c was multiplied by $[1 + 0.001xF_c^2\lambda^3/\sin(2\theta)]^{-1/4}$. All non-H atoms were refined anisotropically. Methyl H atoms were placed at idealized positions with fixed C—H distances and H—C—H angles, and refined using a rotating model, with displacement parameters set as 1.5 times the equivalent isotropic displacement parameter of the methyl C atom. Formyl H atoms were placed at idealized positions and refined using a riding model. Disorder of the two O atoms O13 and O14 was suggested by their highly anisotropic displacement parameters, so that two positions for each atom were calculated by moving along the direction of the largest eigenvalue of the displacement tensor, with a fixed site-occupation factor of 0.5. After the refinement, the displacement parameters for O13 were still somewhat anisotropic and the Cl—O distances showed variation, but further attempts with more disordered positions did not converge. The maximum residual peak in the final difference Fourier map was near O12 (1.20 Å apart).

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *CAD*-4 *Software*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*III (Burnett & Johnson, 1996). Software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS1003). Services for accessing these data are described at the back of the journal.

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1-Phenyl-3,3-bis(triethylphosphine)-1,2-dicarba-3-platina-*closo*-dodecaborane 0.5-Dichloromethane Solvate

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Abstract

The title compound, $[Pt(C_8H_{15}B_9)(C_6H_{15}P)_2].0.5CH_2Cl_2$, crystallizes with two carbaplatinaborane molecules and one solvent molecule in the asymmetric unit. The conformation of the $\{Pt(PEt_3)_2\}$ fragment relative to

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