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Sodium (Ethylenediaminetetraacetato)-gallate(III) Trihydrate

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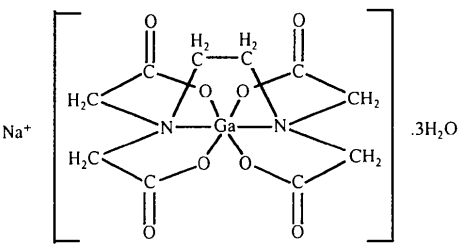
Abstract

Sodium [(1,2-ethanediyldinitrilo-κ^2N,N')tetraacetato-$\kappa^4O,O'',O''''',O'''''''$]gallate(III) trihydrate, $Na[Ga(C_{10}H_{12}N_2O_8)].3H_2O$, contains six-coordinate Ga^{III} ions, each of which is bonded to two amino N atoms and four acetate O atoms. No water molecule is bound to the Ga^{III} ion. The structure of the complex is made up of Na^+ cations, complex $[Ga(edta)]^-$ anions and three water molecules of crystallization. The Na^+ ions have a distorted octahedral O-atom environment.

Comment

The structures of trivalent metal complexes with polyaminopolycarboxylate ligands have recently attracted much attention in connection with whether or not additional water molecules are bound to the central metal ion in solution, since water coordination plays a key role in the interpretation of anomalous physicochemical and thermodynamic properties of the complexes (Nakamura, Yamaguchi, Wakita, Nomura & Choppin, 1993; Choppin, 1993). Our previous X-ray absorption fine structure study of a series of lanthanoid(III) ethylenediaminetetraacetato (edta) complexes in aqueous solution has shown that the total coordination number switches from nine to eight at Dy^{III}, where the number of additionally coordinated water molecules changes from three to two (Nakamura *et al.*, 1993; Choppin, 1993). A similar change in the coordination number for the lanthanoid(III)–edta complexes also takes place in the solid state, but at a different ion, Yb^{III} (Nassimbeni, Wright, van Niekerk & McCallum, 1979).

The polyaminopolycarboxylate complexes of the Group 13 elements (Al, Ga, In and Tl) in aqueous solution may also show a coordination-number change when the ionic radii decreases from Tl^{III} to Al^{III}. To our knowledge, only the crystal structures of an Al^{III}–edta and an In^{III}–edta complex have been determined so far, namely those of $K[Al(edta)].2H_2O$ (Polynova, Bel'skaya, Banus, Porai-Koshits & Martynenko, 1970) and $Na_3[In(edta)(SO_3)].4H_2O$ (Agre, Kozlova, Trunov & Ershova, 1981). The Al^{III} ion in the former is coordinated by six atoms: two amino N atoms and four carboxylate O atoms (it should be noted, however, that the atomic coordinates reported in the literature for this compound do not give a correct structure, and the structure should be redetermined). The In^{III} ion in $Na_3[In(edta)(SO_3)].4H_2O$ is, on the other hand, coordinated by seven atoms: two amino N atoms, four carboxylate O atoms and one additional O atom from a sulfite ion. The structure of a Ga^{III}–edta complex is, therefore, of interest, since the ionic radii of the ions increase in the order $Al^{III} < Ga^{III} < In^{III}$. In this paper, we report the structure of the sodium salt of a Ga^{III}–edta complex, (I).



(I)

An *ORTEP*II (Johnson, 1976) plot of the complex anion in (I) is shown in Fig. 1. The Ga^{III} ions have typical sixfold coordination, by two amino N atoms and four acetate O atoms. The environment of the Na^+ cation is best described in terms of its position at the centre of a highly distorted octahedron of O atoms.

The coordination number of Ga^{III} in the title compound is thus lower than that of In^{III} in $Na_3[In(edta)(SO_3)].4H_2O$ (Agre, Kozlova, Trunov & Ershova, 1981), which is probably a consequence of the difference in the ionic radii of Ga^{III} and In^{III} (Shannon,

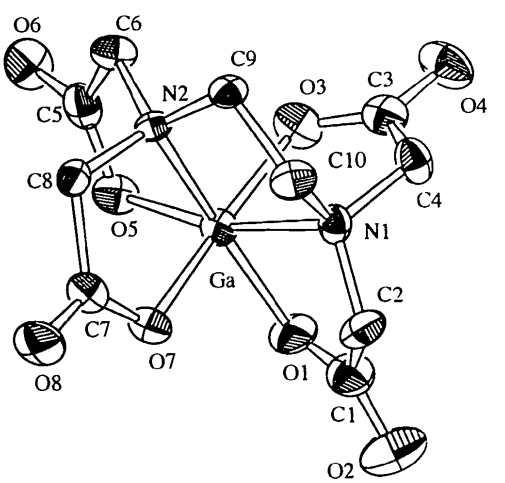


Fig. 1. *ORTEP*II (Johnson, 1976) plot of $Na[Ga(C_{10}H_{12}N_2O_8)].3H_2O$. Displacement ellipsoids are drawn at the 50% probability level.

1976): Ga^{III} has an ionic radius 0.18 Å smaller than that of In^{III}, and hence there is not enough room in the primary coordination shell of the Ga^{III} ion to accommodate a seventh atom.

Experimental

Crystals of the title compound was prepared by refluxing 5 mmol of gallium oxide and 10 mmol of H_4edta in 250 ml of water and periodically adding small sodium hydroxide pellets until the oxide dissolved. The pH of the solution was adjusted to 4.5 by adding aqueous NaOH. After slow evaporation of the solvent at room temperature, colourless crystals appeared. The density D_m was measured by flotation in $CHCl_3/CH_2BrCH_2Br$.

Crystal data

$Na[Ga(C_{10}H_{12}N_2O_8)].3H_2O$	Mo $K\alpha$ radiation
M_r = 434.97	λ = 0.7107 Å
Orthorhombic	Cell parameters from 22 reflections
$P2_12_12_1$	θ = 10.09–15.57°
a = 10.186 (4) Å	μ = 1.798 mm^{-1}
b = 23.842 (4) Å	T = 298 K
c = 6.620 (3) Å	Prismatic
V = 1607.7 (8) $Å^3$	0.3 × 0.3 × 0.2 mm
Z = 4	Colourless
D_x = 1.797 Mg m^{-3}	
D_m = 1.806 Mg m^{-3}	

Data collection

Rigaku AFC-5*R* diffractometer	1641 observed reflections [$I > 3\sigma(I)$]
$\omega/2\theta$ scans	θ_{max} = 27.52°
Absorption correction: ψ scan (North, Phillips & Mathews, 1968)	$h = 0 \rightarrow 13$
	$k = 0 \rightarrow 31$
	$l = 0 \rightarrow 9$
T_{min} = 0.870, T_{max} = 0.999	3 standard reflections monitored every 150 reflections
2170 measured reflections	intensity decay: 1.4%
2170 independent reflections	

Refinement

Refinement on F	$(\Delta/\sigma)_{max}$ = 0.002
R = 0.055	$\Delta\rho_{max}$ = 0.518 e $Å^{-3}$
wR = 0.063	$\Delta\rho_{min}$ = −0.570 e $Å^{-3}$
S = 2.780	Extinction correction: none
1641 reflections	Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Table 4.2.6.8)
226 parameters	
H atoms not located	
$w = 1/\sigma^2(F)$	

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters ($Å^2$)*

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
Ga	0.15530 (9)	0.16820 (4)	0.0038 (2)	0.0250 (2)
Na	0.2932 (4)	0.3928 (2)	−0.2926 (8)	0.046 (1)
O(1)	0.0978 (7)	0.1057 (3)	−0.160 (1)	0.042 (2)
O(2)	0.0591 (9)	0.0152 (4)	−0.139 (2)	0.072 (3)
O(3)	0.3218 (7)	0.1761 (3)	−0.1515 (10)	0.039 (2)
O(4)	0.5071 (7)	0.1325 (4)	−0.233 (1)	0.052 (3)
O(5)	0.0974 (7)	0.2368 (3)	−0.118 (1)	0.033 (2)
O(6)	0.1610 (7)	0.3260 (3)	−0.141 (1)	0.045 (2)
O(7)	0.0011 (6)	0.1558 (3)	0.1785 (10)	0.031 (2)
O(8)	−0.0979 (7)	0.1846 (3)	0.456 (1)	0.047 (2)
O(*W*1)	0.1186 (8)	0.4307 (3)	−0.471 (2)	0.072 (3)
O(*W*2)	0.2376 (9)	0.4378 (4)	0.034 (2)	0.083 (4)
O(*W*3)	0.4251 (9)	0.4608 (4)	−0.476 (2)	0.092 (4)
N(1)	0.2631 (7)	0.1048 (3)	0.154 (1)	0.026 (2)
N(2)	0.2162 (7)	0.2206 (3)	0.236 (1)	0.022 (2)
C(1)	0.108 (1)	0.0583 (6)	−0.069 (2)	0.044 (4)
C(2)	0.175 (1)	0.0555 (4)	0.135 (2)	0.039 (3)
C(3)	0.407 (1)	0.1369 (5)	−0.127 (2)	0.035 (3)
C(4)	0.3909 (9)	0.0961 (5)	0.047 (2)	0.034 (3)
C(5)	0.165 (1)	0.2799 (4)	−0.055 (2)	0.037 (3)
C(6)	0.2580 (9)	0.2730 (4)	0.127 (1)	0.030 (3)
C(7)	−0.0092 (9)	0.1873 (4)	0.336 (2)	0.030 (3)
C(8)	0.1014 (9)	0.2321 (4)	0.368 (2)	0.028 (3)
C(9)	0.3221 (9)	0.1902 (4)	0.349 (2)	0.027 (3)
C(10)	0.284 (1)	0.1270 (4)	0.366 (2)	0.034 (3)

Table 2. *Selected geometric parameters (Å, °)*

Ga—O(1)	1.933 (7)	Na—O(6)	2.313 (8)
Ga—O(3)	1.992 (7)	Na—O(7')	2.529 (8)
Ga—O(5)	1.917 (7)	Na—O(8')	2.409 (8)
Ga—O(7)	1.973 (6)	Na—O(*W*1)	2.317 (9)
Ga—N(1)	2.115 (8)	Na—O(*W*2)	2.48 (1)
Ga—N(2)	2.077 (7)	Na—O(*W*3)	2.43 (1)
O(1)—Ga—O(3)	92.4 (3)	O(6)—Na—O(7')	92.5 (3)
O(1)—Ga—O(5)	109.2 (3)	O(6)—Na—O(8')	86.3 (3)
O(1)—Ga—O(7)	88.4 (3)	O(6)—Na—O(*W*1)	92.4 (3)
O(1)—Ga—N(1)	82.5 (3)	O(6)—Na—O(*W*2)	77.7 (3)
O(1)—Ga—N(2)	165.8 (3)	O(6)—Na—O(*W*3)	175.7 (4)
O(3)—Ga—O(5)	87.9 (3)	O(7')—Na—O(8')	53.0 (2)
O(3)—Ga—O(7)	174.0 (3)	O(7')—Na—O(*W*1)	166.7 (4)
O(3)—Ga—N(1)	82.4 (3)	O(7')—Na—O(*W*2)	97.4 (3)
O(3)—Ga—N(2)	94.1 (3)	O(7')—Na—O(*W*3)	89.5 (3)
O(5)—Ga—O(7)	97.5 (3)	O(8')—Na—O(*W*1)	115.1 (4)
O(5)—Ga—N(1)	165.2 (3)	O(8')—Na—O(*W*2)	145.9 (3)
O(5)—Ga—N(2)	83.7 (3)	O(8')—Na—O(*W*3)	91.9 (3)
O(7)—Ga—N(1)	91.8 (3)	O(*W*1)—Na—O(*W*2)	95.7 (4)
O(7)—Ga—N(2)	83.9 (3)	O(*W*1)—Na—O(*W*3)	84.8 (4)
N(1)—Ga—N(2)	85.8 (3)	O(*W*2)—Na—O(*W*3)	105.8 (4)

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

Data collection and cell refinement were performed using *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). *TEXSAN* (Molecular Structure Corporation, 1993) was used for data reduction. The structures was solved by Patterson (*PATTY*; Beurskens *et al.*, 1992) and Fourier techniques (*DIRDIF*92; Beurskens *et al.*, 1992). All non-H atoms were refined anisotropically using *TEXSAN LS*. Molecular graphics were prepared using *ORTEP*II (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: OH1086). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Double and Triple Interpenetrations of the Three-Dimensional Frameworks [Cd(mea)(daptn){Ni(CN)$_4$}] and [Cd(mea)(dahxn){Ni(CN)$_4$}].H$_2$O (mea = 2-Aminoethanol, daptn = 1,5-Diaminopentane, dahxn = 1,6-Diaminohexane)

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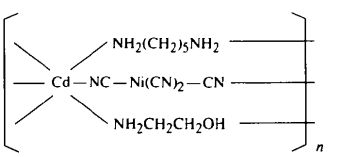
Abstract

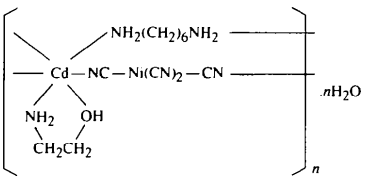
catena-Poly[cadmium-[μ-(2-aminoethanol-*N*:*O*)-μ-[μ-cyano-1κ*N*:2κ*C*-[*trans*-bis(cyano-*C*)nickel(II)]-μ-cyano-1κ*N*:2κ*C*]-μ-(1,5-diaminopentane-*N*:*N*′)]], [Cd{Ni(CN)$_4$}(C$_2$H$_7$NO)(C$_5$H$_{14}$N$_2$)], (1), has a three-dimensional structural unit composed of a distorted Cd-cornered rectangular box edged by *catena*-μ-1,5-diaminopentane, *catena*-μ-2-aminoethanol and *catena*-μ-*trans*-NC—Ni(CN)$_2$—CN- bridges. The void space in one of the frameworks is filled with another framework to give a doubly interpenetrating framework structure. *catena*-Poly[[(2-aminoethanol-*N*,*O*)cadmium]-[μ-[μ-cyano-1κ*N*:2κ*C*-[*trans*-bis(cyano-*C*)nickel(II)]-μ-cyano-1κ*N*:2κ*C*]-μ-(1,6-diaminohexane-*N*:*N*′)] monohydrate], [Cd{Ni(CN)$_4$}(C$_2$H$_7$NO)(C$_6$H$_{16}$N$_2$)].H$_2$O, (2), contains 2-aminoethanol ligands chelated to Cd, which decreases the number of *catena*-μ-bridges about the Cd^{2+} ion to four, two each of *catena*-μ-1,6-diaminohexane and *catena*-μ-*trans*-NC—Ni(CN)$_2$—CN-, giving a distorted adamantoid unit. The void space is occupied by two other frameworks and a water molecule to give a triply interpenetrating framework.

Comment

The three-dimensional (3D) host frameworks of the Hofmann-diam type clathrates [Cd(diam)Ni(CN)$_4$].*x*G [diam = NH$_2$(CH$_2$)$_n$NH$_2$, *n* = 2–9, *x* = 0.5–2, *G* = aromatic guest species; Iwamoto, 1984, 1991] have topologies identical to the two-dimensional (2D) networks of [Cd(CN—Ni$_{1/4}$)$_4$]$_n$ spanned by one-dimensional (1D) [-Cd—diam-]$_n$ linkages. Without enclathration of any aromatic guests, topologically variegated series of the complexes CdNi(CN)$_4$.2diam.*x*H$_2$O (*n* = 2–7 and 9, *x* = 0, 1 or 2; Yuge, Mamada, Asai, Nishikiori & Iwamoto, 1995) have been obtained from aqueous solutions containing CdCl$_2$, K$_2$[Ni(CN)$_4$], NH$_2$(CH$_2$)$_2$OH (mea) and the relevant diamine. Their various structures have been shown to comprise single 1D chains (*n* = 2), triple 1D chains (*n* = 5), double 1D chains (*n* = 6), 2D networks (*n* = 3, 4), 3D frameworks (*n* = 9) and fourfold interpenetrating 3D frameworks (*n* = 7). Among them, [Cd(daptn)$_2$Ni(CN)$_4$].H$_2$O [(1′), daptn = 1,5-diaminopentane] has a 1D chain structure of Cd atoms triply spanned by two *catena*-μ-daptn ligands and a *catena*-μ-*cis*-NC—Ni(CN)$_2$—CN- entity. [Cd(H$_2$O)$_2$(dahxn)$_2$][Ni(CN)$_4$] [(2′), dahxn = 1,6-diaminohexane)] consists of discrete [Ni(CN)$_4$]$^{2-}$ anions and cationic 1D chains with a double span of *catena*-μ-dahxn ligands between the *trans*-[Cd(H$_2$O)$_2$]$^{2+}$ units. Under preparation conditions similar to those for (1′) and (2′), the mea complexes [Cd(mea)(daptn){Ni(CN)$_4$}], (1), and [Cd(mea)(dahxn){Ni(CN)$_4$}].H$_2$O, (2), have been obtained.



(1)



(2)

Compounds (1) and (2) both crystallize in the space group *C*2/*c*. The mea moiety acts as a bridging ligand in (1), but as a chelating ligand in (2). The N and O atoms