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A Novel Structure of Spontaneously Resolved Germanium(IV) Complex with Ethylenediaminetriacetatemonoacetic Acid (Hedta)

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Abstract

The crystal and molecular structures of the complex formed when $GeCl_4$ was mixed with the disodium salt of ethylenediaminetetraacetic acid (Na_2H_2edta) in hot water, have been determined by single crystal X-ray diffraction techniques. The crystal is monoclinic with the space group $P2_1$, $a = 10.905(2)$, $b = 9.691(2)$, $c = 6.533(1)$ Å, $\beta = 99.60(1)°$ and $Z = 2$, and it is found to be spontaneously resolved. The complex has a novel composition of $[Ge(OH)(Hedta)]\cdot H_2O$ in which edta serves as a pentadentate ligand with one acetate group protonated and freed from coordination, and with the sixth coordination site occupied by an OH^- ion, forming a six-coordinate and electrically neutral complex.

Introduction

Various types of coordination have been found in the metal complexes with ethylenediaminetetraacetate (edta) [1, 2], and it has been accepted [2–5] that the higher the charge on the metal ion and the larger its radius, the greater the coordination number (*CN*) that its edta complex takes, provided that the metal ion has an electronic configuration of d^0, d^5 (high spin), or d^{10}. For example, three tetravalent metal ions, $Ti^{4+}(d^0)$ [4], $Zr^{4+}(d^0)$ [6], and $Sn^{4+}(d^{10})$ [7] take a *CN* greater than 6, when complexed with edta, additional coordination site(s) being occupied by water molecule(s). This suggests that these metal ions are all too big in size for a tetravalent ion to be surrounded octahedrally by edta alone. Ge^{4+} ion with a d^{10} configuration like Sn^{4+} ion, however, has a smaller radius (0.670 Å) [8] than Ti^{4+} ion (0.745 Å) [8] smallest in size among the above three metal ions. Thus, Ge^{4+} ion might be expected to form a six-coordinate octahedral complex with edta. With this expectation in mind, X-ray crystallographic analysis was made for the Ge(IV)–edta complex.

Experimental

Preparation of Ge(IV)–edta Complex

$[Ge(OH)(Hedta)]\cdot H_2O$ was prepared according to Langer's method [9], starting with $GeCl_4$ and Na_2H_2edta. The IR spectrum recorded on a Shimadzu FTIR 4000, agreed completely with that recorded by Langer. Elemental analysis data were consistent with the above composition.

X-ray Measurements

The crystal used for the data collection had dimensions of 0.25 × 0.30 × 0.42 mm. Determination of cell constants and collection of intensity data of reflection were carried out on a Rigaku AFC-5 diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Unit cell constants were determined by least-squares refinement of 25 reflections. Intensity data of reflection were collected by an ω–2θ scan mode up to $2\theta = 55°$. No absorption correction was made (μ(Mo Kα) = 22.8 cm^{-1}). The number of reflections included in the structure analysis ($F_o > 3\sigma(F_o)$) was 1683. All the crystallographic data are given in Table 1.

TABLE 1. Crystallographic data for $[Ge(OH)(Hedta)]\cdot H_2O$

Crystal system	monoclinic
Space group	$P2_1$
Z	2
Cell dimensions	
a (Å)	10.905(2)
b (Å)	9.691(2)
c (Å)	6.533(1)
β (°)	99.60(1)
V (Å^3)	680.7(2)
Density (obs.) (g/cm^3)	1.92
Density (calc.) (g/cm^3)	1.94
No. unique reflections	1777
No. reflections with $\|F_o\| > 3\sigma(F_o)$	1683
Final R (%)	3.6
Absolute configuration	$\Delta(R,R)\Lambda(G,R)$

Determination and Refinement of Structure

$P2_1$ was chosen as the space group on the basis of the systematic absence of reflection for $0k0$

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($k = 2n + 1$) and Z of 2 estimated from the measured density of the complex. The subsequent success of the structure determination confirmed the validity of our choice.

The structure was solved by a standard heavy-atom method, and the parameters for all the non-hydrogen atoms were refined anisotropically. Several cycles of the block-diagonal least-squares refinement reduced the R value ($R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$) to 0.042. Since this complex was found to be spontaneously resolved, its absolute configuration was determined at this stage by using anomalous dispersion coefficients of Cromer and Liberman [10]. The R value of 0.046 was derived when the wrong absolute configuration was assumed. In the subsequent refinement the positions of hydrogen atoms were included assuming a bond distance of 1.09 Å for each C–H bond and tetrahedral angles around each carbon atom. The final refinement including these H atoms with isotropic temperature factors caused the R value to converge to 0.036.

In the refinement the quantity minimized was $\Sigma w(|F_o| - k|F_c|)^2$. The weighting scheme used was $w = (\sigma cs^2)^{-1}$, where σcs is the standard deviation obtained from the counting statistics for each reflection. All the atomic scattering factors were taken from Cromer and Waber [11]. The final atomic coordinates for non-hydrogen atoms with the thermal parameters are given in Table 2 (according to the numbering schemes adopted in Fig. 2). All computations were carried out on a HITAC computer at the Hiroshima University Information Processing Center. The computer programs used were UNICS-III [12] and ORTEP [13].

Results and Discussion

General Background

In the course of our structural studies on the transition metal complexes with edta-type ligands, we have discussed in detail the essential factors which determine the structures of these complexes [5]. Of particular importance is the ligand field stabilization energy (LFSE) which usually favors an octahedral structure for those complexes with partially-filled d orbitals. However, when the central metal has a d^0, d^5 (high spin) or d^{10} electronic configuration, the contribution of LFSE is diminished greatly, and the effect of size and charge of the metal becomes relatively dominant [2–5]. In Fig. 1 some metal–edta complexes with such configurations are classified, as a function of their coordination number (*CN*) and the size of the central metal ions. Since two structural types (*CN* = 6 and 7) are known for the Fe(III) complex [14, 15], Fe^{3+} ion may well have a 'critical' radius between *CN* = 6 and 7 for a tervalent ion [5]. For a divalent ion, the 'critical' radius between *CN* = 6 and 7 is found around the Zn^{2+} or Mg^{2+} ion, and a *CN* changes from 7 to 8 between Cd^{2+} and Ca^{2+} ions. For a

TABLE 2. Positional and thermal parameters for $[Ge(OH)(Hedta)]\cdot H_2O$[a]

Atom	x	y	z	B_{eq} (Å^2)[b]
Ge	0.30604(5)	0.64795(14)	0.94139(8)	1.3
O1	0.28178(37)	0.49152(44)	0.76853(63)	1.6
O2	0.45829(37)	0.58825(46)	1.09246(62)	1.6
O3	0.33410(39)	0.81856(46)	1.08217(62)	1.8
O4	0.35002(47)	0.37384(51)	0.52010(76)	2.6
O5	0.65620(35)	0.64604(80)	1.17599(62)	2.6
O6	0.24192(52)	1.01004(54)	1.15768(80)	3.0
O7	−0.15112(40)	0.67618(52)	0.51915(75)	3.0
O8	−0.04476(46)	0.86675(66)	0.49688(125)	5.1
O9	0.20789(40)	0.58826(50)	1.11231(65)	2.0
OW1	0.13602(53)	0.29892(61)	1.00636(91)	3.8
N1	0.42194(42)	0.71116(54)	0.73636(68)	1.4
N2	0.16809(42)	0.75905(52)	0.74427(73)	1.5
C1	0.44158(59)	0.59172(68)	0.60630(95)	1.9
C2	0.53978(54)	0.74931(68)	0.87222(97)	1.9
C3	0.14266(57)	0.88390(67)	0.86656(106)	2.0
C4	0.35217(52)	0.47537(63)	0.63076(82)	1.4
C5	0.55718(44)	0.65569(103)	1.06179(76)	1.7
C6	0.24309(58)	0.90960(64)	1.04767(90)	1.8
C7	0.05418(50)	0.67451(62)	0.68880(94)	1.9
C8	−0.05032(56)	0.75198(76)	0.55907(106)	2.4
C9	0.36011(55)	0.82866(66)	0.61042(95)	1.8
C10	0.22314(56)	0.79403(72)	0.55415(88)	1.9

[a]e.s.d.s given in parentheses. [b]$B_{eq} = \frac{8}{3}\pi^2(U_{11} + U_{22} + U_{33})$.

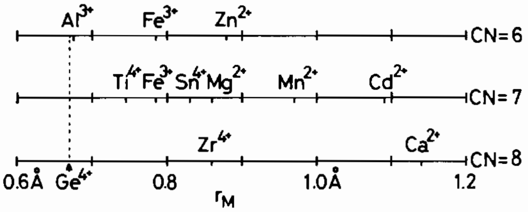

Fig. 1. Classification of edta complexes of some metal ions with d^0, d^5 or d^{10} configuration as a function of size of the metal ions and coordination number (CN).

tetravalent ion, a change in *CN* is found between Sn^{4+} and Zr^{4+} ions. In addition, when the d^{10} and d^0 metal ions with similar size and the same charge are compared, the former are apt to take a smaller *CN*; Zn^{2+} (d^{10}, $r_M = 0.880$ Å, $CN = 6$) versus Mg^{2+} (d^0, $r_M = 0.860$ Å, $CN = 7$), Sn^{4+} (d^{10}, $r_M = 0.83$ Å, $CN = 7$) versus Zr^{4+} (d^0, $r_M = 0.86$ Å, $CN = 8$) and Cd^{2+} (d^{10}, $r_M = 1.09$ Å, $CN = 7$) versus Ca^{2+} (d^0, $r_M = 1.14$ Å, $CN = 8$). Then, it is expected that a tetravalent metal ion which is smaller in size than Ti^{4+} ion and has a d^{10} configuration if possible, for example the Ge^{4+} ion similar in size to the Al^{3+} ion, may form an octahedral complex with edta, i.e. [Ge(edta)]·$2H_2O$ which satisfies the elemental analysis data.

Another expectation emerges from the following. In 1964 Langer [9] successfully prepared edta complexes of some tetravalent metal ions including Ge^{4+} by simply mixing metal(IV) tetrachloride with Na_2H_2edta in hot water. He tentatively proposed a binuclear structure for the Ge(IV)–edta complex in which two halves of edta were coordinated to the separate Ge^{4+} ions, on the basis of the IR spectrum, thermal analysis, and the small size of the Ge^{4+} ion. Of the edta complexes he prepared, the Ti(IV), Zr(IV) and Sn(IV) complexes were later subjected to X-ray analysis; [Ti(H_2O)(edta)] [4] and [Sn(H_2O)(edta)] [7] are seven-coordinate and [Zr(H_2O)$_2$(edta)]·$2H_2O$ [6] is eight-coordinate, with water molecule(s) occupying additional coordination site(s). Since all of these complexes are prepared under similar acidic conditions and the Ge^{4+} ion is smaller in size than the Ti^{4+} ion only by 0.075 Å, the Ge(IV) complex may adopt a seven-coordinate structure similar to that of the Ti(IV) complex, viz. [Ge(H_2O)(edta)]·H_2O, the composition of which is also consistent with the elemental analysis data.

Description of Molecular Structure

In Fig. 2 the molecular structure of the Ge(IV)–edta complex is drawn, where the numbering schemes

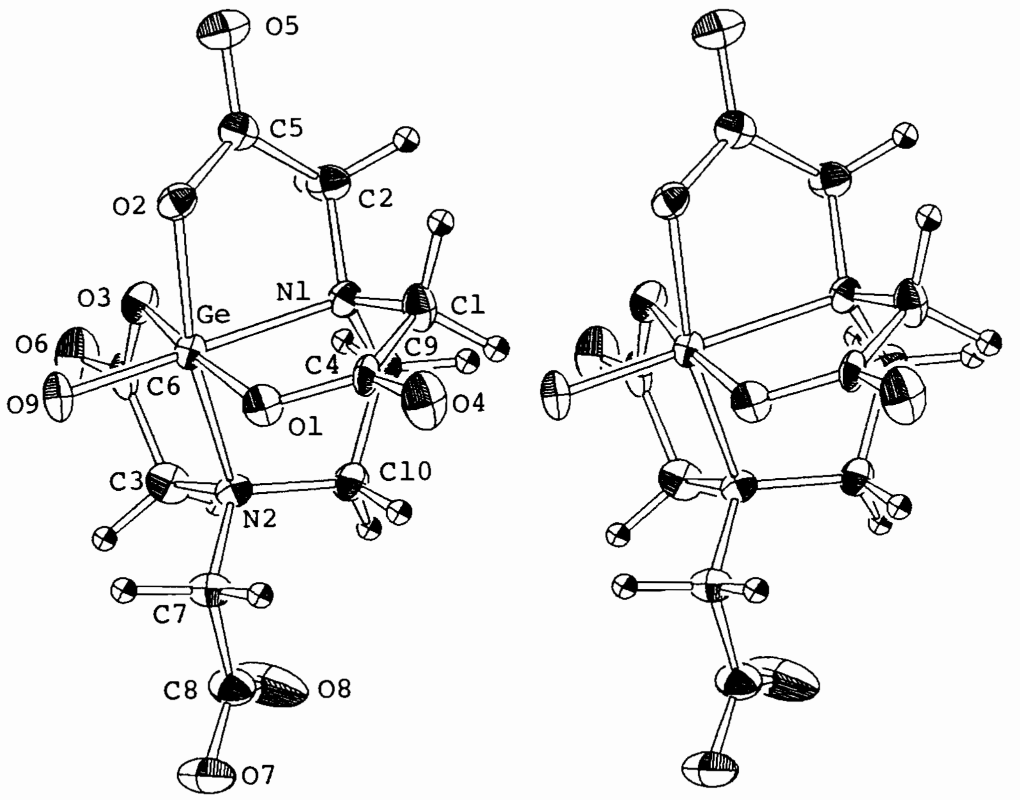

Fig. 2. A stereoview of the Δ(*R,R*)Λ(*G,R*)-[Ge(OH)(Hedta)] complex.

are given for the respective atoms. The bond distances and angles within the complex are listed in Tables 3 and 4, respectively.

The molecular structure in Fig. 2 is at variance not only with our expectations mentioned above, but also with Langer's proposal; edta serves as a pentadentate ligand with one of its acetate groups protonated and thus freed from coordination, and with the sixth site occupied by an OH^- ion, forming an octahedral and electrically neutral complex [Ge(OH)(Hedta)]. In this respect, the Ge(IV) complex bears a structural resemblance to the [M(III)(H_2O)(Hedta)]-type complexes (M = Cr(III) [16], Fe(III) [17], Co(III) [18], Ga(III) [17], and Rh(III) [19]) obtained from acidic solutions, except that the sixth site is occupied by an OH^- ion but not by H_2O. In all of these 'acidic' edta complexes, the protonated acetate group is always the one which otherwise forms a *G* ring strained more than an *R* ring [20], and it assumes a common conformation [18]. In addition, a comparison of the bond distances between the O7–C8 and O8–C8 bonds (Table 3) confirms that the proton is attached to the O7 atom *trans* to the N2 atom, which is also common to all of the above 'acidic' complexes [18].

If electrical neutrality is taken into account for the Ge(IV) complex, the sixth ligand must be an OH^- ion but not H_2O. However, the position of proton is not determined with certainty by X-ray analysis. The Ge–OH bond in [Ge(OH)(Hedta)] is compared in length with the M–OH_2 bonds in [M(III)(H_2O)(Hedta)] and [M(IV)$(H_2O)_n$(edta)] (n = 1 or 2) in Table 5. It is evident that the M–O bond length as well as the *D* value, the M–O bond length minus the ionic radius of M, is much smaller in the [Ge(OH)(Hedta)] complex, consistent with the coordination of the OH^- ion to Ge(IV). However, when we remember that this complex is prepared under acidic conditions like [M(III)(H_2O)(Hedta)] and [M(IV)$(H_2O)_n$(edta)] complexes and that one acetate group is similarly protonated, it is surprising

TABLE 3. Intramolecular bond distances (Å) for [Ge(OH)(Hedta)]·H_2O[a]

Bond		Bond		Bond	
Ge–O1	1.882(4)	O4–C4	1.219(8)	N2–C3	1.501(9)
Ge–O2	1.876(5)	O5–C5	1.209(13)	N2–C7	1.482(8)
Ge–O3	1.892(5)	O6–C6	1.211(9)	N2–C10	1.506(9)
Ge–O9	1.768(5)	O7–C8	1.312(9)	C1–C4	1.516(9)
Ge–N1	2.081(5)	O8–C8	1.189(11)	C2–C5	1.521(12)
Ge–N2	2.106(5)	N1–C1	1.473(8)	C3–C6	1.493(9)
O1–C4	1.286(7)	N1–C2	1.482(8)	C7–C8	1.503(10)
O2–C5	1.305(11)	N1–C9	1.498(8)	C9–C10	1.515(9)
O3–C6	1.319(8)				

[a] e.s.d.s given in parentheses.

TABLE 4. Intramolecular bond angles (°) for [Ge(OH)(Hedta)]·H_2O[a]

Angle		Angle		Angle	
O1–Ge–O2	95.21(20)	Ge–O2–C5	116.51(52)	N2–C3–C6	112.34(54)
O1–Ge–O3	172.11(21)	Ge–O3–C6	116.45(40)	O1–C4–O4	123.96(58)
O1–Ge–O9	94.36(21)	Ge–N1–C1	107.60(38)	O1–C4–C1	116.90(53)
O1–Ge–N1	83.72(20)	Ge–N1–C2	104.30(38)	O4–C4–C1	119.13(56)
O1–Ge–N2	91.73(20)	Ge–N1–C9	108.14(38)	O2–C5–O5	122.84(90)
O2–Ge–O3	87.51(20)	C1–N1–C2	110.28(49)	O2–C5–C2	115.45(76)
O2–Ge–O9	98.21(22)	C1–N1–C9	112.10(49)	O5–C5–C2	121.71(87)
O2–Ge–N1	81.39(20)	C2–N1–C9	113.92(49)	O3–C6–O6	121.21(60)
O2–Ge–N2	163.49(21)	Ge–N2–C3	105.26(37)	O3–C6–C3	117.09(55)
O3–Ge–O9	92.57(22)	Ge–N2–C7	110.56(36)	O6–C6–C3	121.69(61)
O3–Ge–N1	89.39(21)	Ge–N2–C10	106.09(38)	N2–C7–C8	112.81(52)
O3–Ge–N2	83.77(20)	C3–N2–C7	110.74(48)	O7–C8–O8	123.00(75)
O9–Ge–N1	177.99(23)	C3–N2–C10	113.09(49)	O7–C8–C7	111.34(59)
O9–Ge–N2	96.17(22)	C7–N2–C10	110.86(48)	O8–C8–C7	125.66(73)
N1–Ge–N2	84.52(21)	N1–C1–C4	111.45(52)	N1–C9–C10	107.47(51)
Ge–O1–C4	118.51(39)	N1–C2–C5	108.47(59)	N2–C10–C9	111.24(53)

[a] e.s.d.s given in parentheses.

TABLE 5. Comparison of M–OH_2 and M–OH bond lengths (Å) in some edta complexes

	d^n	$r(M–OH_2)$	$r(M)^a$	D^b	Reference
$[V(III)(H_2O)(edta)]^-$	d^2	2.071	0.78	1.29	21
$[Cr(III)(H_2O)(Hedta)]$	d^3	2.002	0.755	1.247	16
$[Fe(III)(H_2O)(Hedta)]$	d^5	1.990	0.785	1.205	17
$[Fe(III)(H_2O)(edta)]^-$	d^5	2.122	0.785	1.337	15
$[Co(III)(H_2O)(Hedta)]$	d^6	1.928	0.685	1.243	18
$[Ga(III)(H_2O)(Hedta)]$	d^{10}	1.952	0.760	1.192	17
$[Rh(III)(H_2O)(Hedta)]$	d^6	2.096	0.805	1.291	19
$[Ti(IV)(H_2O)(edta)]$	d^0	2.084	0.745	1.339	4
$[Zr(IV)(H_2O)_2(edta)]$	d^0	2.272	0.86	1.41	6
$[Sn(IV)(H_2O)(edta)]$	d^{10}	2.124	0.830	1.294	7
$[Os(IV)(H_2O)(edta)]$	d^4	2.049	0.770	1.279	22
$[Ge(IV)(OH)(Hedta)]$	d^{10}	1.768^c	0.670	1.098^d	this work

[a]Ionic radius of M for *CN* = 6; ref. 8. [b]$D = r(M–OH_2) - r(M)$. [c]$r(M–OH)$. [d]$r(M–OH) - r(M)$.

that the OH^- ion but not H_2O is coordinated to Ge(IV). In fact, this novel structure is unprecedented for metal–edta complexes, but it is rationalized in terms of a strong polarizing effect of the Ge(IV) brought about by its high charge-to-radius ratio; an imaginary complex $[Ge(H_2O)(Hedta)]^+$ would be an extremely strong acid or the protonation to the [Ge(OH)(Hedta)] might take place at another acetate group but not at the OH^- ligand, forming $[Ge(OH)(H_2edta)]^+$. Acid–base properties of this complex will be reported elsewhere together with those of other 'acidic' edta complexes.

Structural Comparison with Other edta Complexes

The 'acidic' edta complexes of the type $[M(H_2O)(Hedta)]$ are often isolated for tervalent metal ions, because the net charge is neutralized to null. Since the present Ge(IV) complex [Ge(OH)(Hedta)] is found to have a similar molecular structure to these 'acidic' complexes, geometries around the central metal ions are compared here. In Table 6 the bond angles of O9–M–L (L = O1, O2, O3, N1, or N2) relevant to the monodentate ligand, $H_2O(9)$ or $O(9)H^-$ ion, which is relatively indifferent to the steric demand of other ligating groups, are listed. It is seen in Table 6 that the Ge(IV) complex has a comparatively good octahedral structure despite its d^{10} configuration, but it is distorted from a regular octahedron much more than the Co(III) (low-spin d^6) and Rh(III) (low-spin d^6) complexes to which the contribution of LFSE is the greatest.

Finally, it has been shown [2–5] that the edta complex of a metal ion tends to adopt a *CN* greater than 6, when the metal ion has a high charge and/or a big ion size, and has an electronic configuration of d^0, d^5 or d^{10} (Fig. 1), and that the resulting complex has a large difference, Δ, between the averaged M–N and M–O bond lengths. The corresponding data for the edta complexes of ter- and tetravalent metal ions with such configurations are collected in Table 7, where the data for the two complexes, $[V(III)(H_2O)(edta)]^-$ (d^2) [21] and $[Os(IV)(H_2O)(edta)]$ (d^4) [22], are also given. The two complexes take exceptionally a *CN* greater than 6, though they have partially-filled d orbitals and thus more or less resist abandoning an octahedral structure.

It is seen that the Ge(IV) complex has a relatively small Δ value for a tetravalent ion, probably due to the small size of the Ge(IV) ion, which may partly explain why the Ge(IV) complex does not adopt a seven-coordinate structure similar to that of the Ti(IV) or Sn(IV) complex; the Ge(IV) ion is so small in size and is so highly charged that it does not have a space big enough to be encircled octahedrally by edta, edta thus being forced to serve as a pentadentate ligand, and that the water molecule occupying the sixth site is polarized

TABLE 6. Comparison of O9–M–L bond angles (°) in $[M(III)(H_2O)(Hedta)]$

	d^n	O9–M–O1	O9–M–O2	O9–M–O3	O9–M–N2	O9–M–N1	Reference
$[Cr(III)(H_2O)(Hedta)]$	d^3	89.43	96.01	89.51	99.31	172.84	16
$[Fe(III)(H_2O)(Hedta)]$	d^5	89.23	98.01	90.84	104.30	169.43	17
$[Co(III)(H_2O)(Hedta)]$	d^6	87.73	93.52	91.84	93.04	175.31	18
$[Ga(III)(H_2O)(Hedta)]$	d^{10}	86.97	94.14	89.42	101.16	171.41	17
$[Rh(III)(H_2O)(Hedta)]$	d^6	91.52	94.66	87.14	96.33	175.61	19
$[Ge(IV)(OH)(Hedta)]$	d^{10}	94.36	98.21	92.57	96.17	177.99	this work

TABLE 7. Comparison of bond lengths in some edta complexes of ter- and tetravalent metal ions

	d^n	r(M) (Å)[a]	*CN*	$r(M-N)_{av}$ (Å)	$r(M-O)_{av}$ (Å)	Δ (Å)[b]	Reference
$[Al(III)(edta)]^-$	d^0	0.675	6	2.05	1.87	0.18	23
$[Ga(III)(H_2O)(Hedta)]$	d^{10}	0.76	6	2.14	1.96	0.18	17
$[V(III)(H_2O)(edta)]^-$	d^2	0.78	7	2.22	2.05	0.17	21
$[Fe(III)(edta)]^-$	d^5	0.785	6	2.18	1.97	0.21	14
$[Fe(III)(H_2O)(Hedta)]$	d^5	0.785	6	2.19	1.96	0.23	17
$[Fe(III)(H_2O)(edta)]^-$	d^5	0.785	7	2.32	2.04	0.28	15
$[Ge(IV)(OH)(Hedta)]$	d^{10}	0.67	6	2.09	1.88	0.21	this work
$[Ti(IV)(H_2O)(edta)]$	d^0	0.745	7	2.30	1.95	0.35	4
$[Os(IV)(H_2O)(edta)]$	d^4	0.77	7	2.16	2.05	0.11	22
$[Sn(IV)(H_2O)(edta)]$	d^{10}	0.83	7	2.31	2.08	0.23	7
$[Zr(IV)(H_2O)_2(edta)]$	d^0	0.86	8	2.43	2.13	0.30	6

[a] Ionic radius of M for *CN* = 6; ref. 8. [b] $\Delta = r(M-N)_{av} - r(M-O)_{av}$.

substantially by the strong field of the Ge(IV) ion to release a proton, [Ge(OH)(Hedta)] with a novel structure being thereby formed even under acidic conditions. The two complexes $[V(III)(H_2O)(edta)]^-$ and $[Os(IV)(H_2O)(edta)]$ are again exceptional in that they have a small Δ value, though they adopt a *CN* of 7.

Spontaneous Resolution

Since the present Ge(IV)–edta complex $[Ge(OH)(Hedta)]\cdot H_2O$ is found to be spontaneously resolved, the absolute configuration of the enantiomer in the single crystal picked up by us, is determined by the anomalous dispersion technique to be Δ(*R*,*R*)Λ(*G*,*R*), *R* and *G* referring to the *R* and *G* rings, respectively. It is noteworthy that $[Co(III)(H_2O)(Hedta)]\cdot 3H_2O$ similar in molecular structure to the present Ge(IV)–edta complex, as pointed out above, is also spontaneously resolved [18]. The crystal structure of the Ge(IV) complex is depicted in Fig. 3. As seen clearly in Fig. 3, the crystal is composed of layers and significant hydrogen-bonding

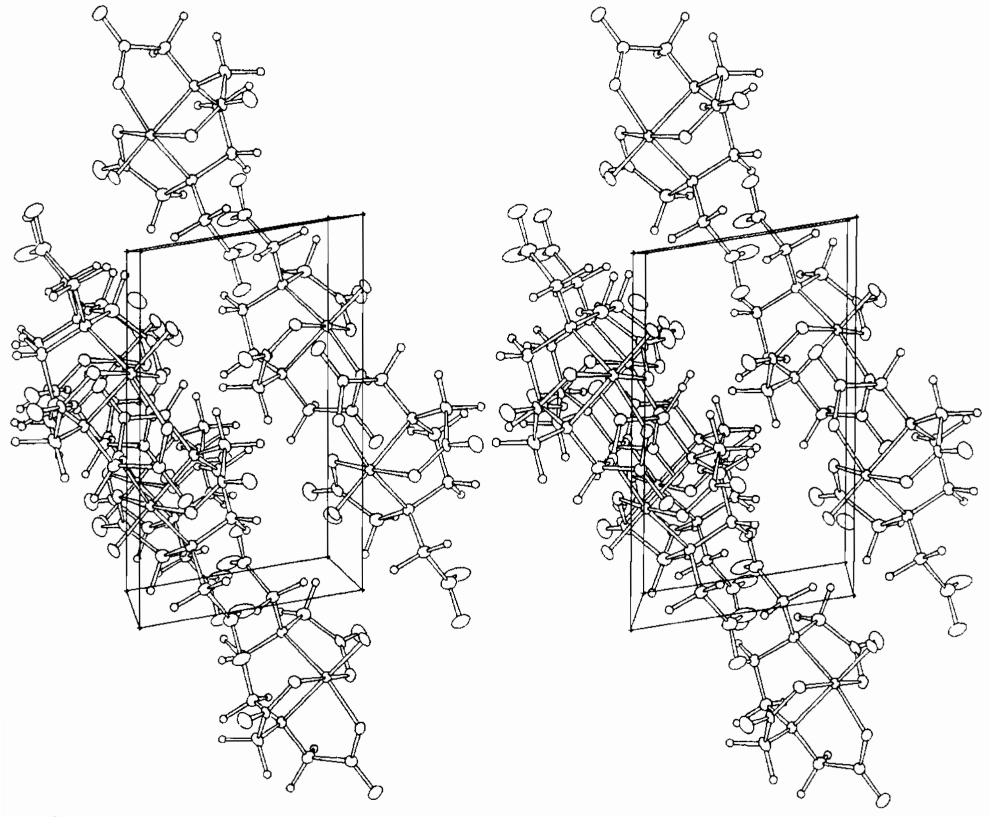

Fig. 3. A stereoview of the crystal structure along the *b* axis for Δ(*R*,*R*)Λ(*G*,*R*)-$[Ge(OH)(Hedta)]\cdot H_2O$.

interactions are found only within each of the layers. As a result, the present Ge(IV) complex [Ge(OH)(Hedta)]·H_2O bears no apparent resemblance in crystal structure to the spontaneously resolved [Co(H_2O)(Hedta)]·$3H_2O$ in which three-dimensional hydrogen-bonding networks prevail [18].

The chiroptical properties of the present Ge(IV) complex are not recorded at present, since its solubility is very low and it seems to racemize instantaneously upon dissolution in water.

Supplementary Material

Observed and calculated structure factors and anisotropic thermal parameters are available from the authors on request.

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