Crystal Structure and Absolute Configuration of Cobalt-doped α-Hexaaquazinc(II) Selenate

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The title complex is isomorphous with α-$[Ni(OH_2)_6][SO_4]$ with space group either $P4_{1}2_{1}2$ or $P4_{3}2_{1}2$, $a = 6.953(4)$, $c = 18.33(2)$ Å, and $Z = 4$. Intensity data have been collected by equi-inclination Weissenberg methods and the 433 independent reflections judged visually. The resulting structure has been solved by the heavy-atom method and refined by full-matrix least squares to a final R value of 0.107. Although doped to 38 mol % with Co^{II}, the structure shows no demonstrable difference from that expected for the pure complex. From the absolute configuration determined by the Bijvoet method, and circular-dichroism measurements made on the same crystal, it is found that space group $P4_{1}2_{1}2$ correlates with a negative rotational strength in the major ligand-field bands of $[Co(OH_2)_6]^{2+}$.

CRYSTALS belonging to any of 15 non-centric classes should all exhibit the phenomena of optical activity [*e.g.* optical rotatory dispersion (o.r.d.) and circular dichroism (c.d.)], presuming suitable chromophores are present.† In practice, however, useful measurements of single-crystal optical activity are limited to non-biaxial crystals, in which the complication of linear birefringence can be avoided. Of such crystals, perhaps the most intriguing representatives are those which, although enantiomorphous, contain no intrinsically chiral molecular units. The structures of these crystals are of particular interest since it is the packing of the atoms, ions, and/or molecules in the lattice which is the sole source of the optical activity. (When such crystals are dissolved or melted all the optical activity disappears.)

One early recognized example of a non-chiral compound, which nevertheless crystallizes in a chiral and also non-biaxial space group, is hexa-aquanickel(II) sulphate. The so-called α modification was found to conform to either $P4_{1}2_{1}2$ or $P4_{3}2_{1}2$.[1,2] The natural optical activity associated with the ligand-field transitions of the $[Ni(OH_2)_6]^{2+}$ ion in these tetragonal crystals was first quantitatively measured by Underwood *et al.*[3] Numerous subsequent studies revealed the extent of information which might be obtained from such investigations.[4-11] No other divalent transition-metal sulphate exhibits a chiral phase isomorphous with α-$[Ni(OH_2)_6][SO_4]$. However, several other salts of hexa-aquametal ions, such as $[Ni(OH_2)_6][SO_3]$,[12] $[Mg(OH_2)_6][HPO_3]$,[13] and $[Mg(OH_2)_6][SeO_3]$,[14] do have non-biaxial enantiomorphous phases. Of these, the salts of hexa-aqua-zinc and -magnesium are particularly interesting since they may be used as host crystals for the study of bivalent transition-metal ion optical activity associated with ligand-field transitions. Such use of α-$[Zn(OH_2)_6][SeO_4]$ has been reported for $[Fe(OH_2)_6]^{2+}$,[15] for $[Co(OH_2)_6]^{2+}$, $[Ni(OH_2)_6]^{2+}$, and $[Cu(OH_2)_6]^{2+}$,[15-17] and for $[Mn(OH_2)_6]^{2+}$.[18] It has long been known[19,20] that α-$[Zn(OH_2)_6][SeO_4]$ is morphologically isomorphous with α-$[Ni(OH_2)_6][SO_4]$, but the complete structure has not been reported. In order to further the understanding of the optical activity of hexa-aquametal ions in this and other related crystals the complete structure and absolute configuration of α-$[Zn(OH_2)_6][SeO_4]$ has been determined. The crystal used for this study was doped with Co^{II} for the purpose of associating the lattice chirality with the signs of rotational strength in the ligand-field bands of the various ions which have been doped in it. This association has been reported elsewhere.[21] Here we report the details of the crystallographic investigation and correct the error in the original report.‡

EXPERIMENTAL

Single crystals of α-$[(Zn,Co)(OH_2)_6][SeO_4]$ were obtained by seeding a concentrated aqueous solution of zinc selenate and cobalt selenate with a small single crystal of α-hexaaquazinc(II) selenate and slowly evaporating at 5 °C. The specimens used for *X*-ray diffraction study were fragments

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† Enantiomorphism is, strictly speaking, limited to 11 of these 15: 1, 2, 222, 4, 422, 32, 3, 6, 622, 23, and 432; the other four special cases being *m*, *mm*2, $\bar{4}$, and $\bar{4}2m$.

‡ In the original paper[21] the space group was reported to be $P4_{3}2_{1}2$ for negative axial c.d. peaks in the *d–d* transitions of $[Co(OH_2)_6]^{2+}$. The correction of a subsequently discovered indexing error makes the correct space group $P4_{1}2_{1}2$.

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of one of the relatively large crystals which resulted. Because of the cleavage characteristics of the crystals, ideally shaped fragments of suitable size were not readily available. The specimen used for intensity data collection was selected as approximating a square prism. It was sealed in a glass capillary with a drop of its mother liquor to prevent loss of water. The mole percentage of cobalt was determined with a Beckman model 495 integral atomic-absorption spectrometer, using another larger fragment of the same crystal. The approximate dimensions of the crystal fragment used in the structure solution were 0.17 × 0.22 × 0.35 mm with a μr value of 1.60 for Cu-K_α radiation (μ 139.2 cm^{-1} based on Co replacing 38% of the Zn). Rotating this crystal about the 0.35-mm axis, the absorption correction factor, A^*, changed from 11.8 to 5.28 over the range of θ values in the diffraction data.

Preliminary rotation and equi-inclination Weissenberg data, collected about the [110] axis (the 0.35-mm axis), indicated a tetragonal space group with $a = 6.953(4)$ Å, $c = 18.33(2)$ Å, $Z = 4$, and $D_c = 2.371$ g cm^{-3}. Systematic extinctions were consistent with either space group $P4_12_12$ (no. 92) or $P4_32_12$ (no. 96).[22]

Six levels of equi-inclination Weissenberg data were collected by rotating about the [110] axis of the crystal described above. The intensity data were recorded on multiple film packets, consisting of five Ilford G-type films separated from each other by a sheet of paper to attenuate the most intense reflections such that they could be judged at least twice. Each film packet was exposed to nickel-filtered Cu-K_α radiation for 48 h. The resulting 433 independent reflections were judged visually against a set of standard spots prepared from the 206 reflection. The data were corrected for exposure time and spot shape. Additional corrections were computed for $\alpha_1 - \alpha_2$ separation and the Lorentz-polarization factors using the program FORDAP.[23] An approximate absorption correction was made assuming a cylindrically shaped crystal with an average radius of 0.011 5 cm. (Due to the variations in the crystal dimensions along the 0.35-mm axis, an absorption correction based on a cylinder was made as the most practical approximation.) Computations were carried out on the IBM-370-135 computer of the Triangle Universities Computation Center.

Structure Solution and Refinement.—The positional parameters of the oxygen atoms in α-$[Ni(OD_2)_6][SO_4]$ were employed as a first approximation for those of the oxygen atoms in the selenate. The resulting structure-factor calculation, based on all the non-hydrogen atoms in the unit cell and the scattering factors for Zn^0, Co^0, Se^0, and O^0,[24] yielded a conventional R value of 0.20. The structure was refined by full-matrix least-squares using program UCLS.[25] During refinement the scattering factors used for the metal atom were weighted averages of the zinc and cobalt factors based on the mol % of cobalt in the crystal. The initial isotropic refinement for three cycles lowered the R value to 0.142. Inclusion of anomalous-dispersion corrections [26] for Zn, Co, and Se yielded an R value of 0.124 after two cycles. Rejudging a few intensity data, which gave poor agreement between $F_{obs.}$ and $F_{calc.}$, and refining for five more cycles yielded a final R value of 0.107 in space group $P4_12_12$. The final three-dimensional Fourier electron-density map revealed no new peaks larger than 1.05 e Å^{-3}. Since the structure is clearly isomorphous with that of α-$[Ni(OD_2)_6]$-$[SO_4]$,[2] and the determination of the absolute configuration did not require it, an anisotropic refinement was not carried out. Final observed and calculated structure factors and thermal parameters are in Supplementary Publication No. 22258 (5 pp.).*

Determination of the absolute configuration, discussed in the next section, confirmed that the space group of the crystal studied was $P4_12_12$ rather than $P4_32_12$. The final positional parameters with their standard deviations for α-$[(Zn,Co)(OH_2)_6][SeO_4]$ in the $P4_12_12$ space group are given in Table 1. After the last refinement cycle the maximum change in any oxygen-atom co-ordinate and isotropic temperature factor was 1.72×10^{-5} [x co-ordinate of O(5)] and 9.01×10^{-4} Å^2 [O(2)], respectively. The final zinc and selenium atomic co-ordinates changed by 2.9×10^{-6} and 1.8×10^{-6}, respectively, while the isotropic temperature factors changed by 3.7×10^{-4} Å^2 and 2.0×10^{-4} Å^2, respectively, in the last refinement cycle.

TABLE 1

Final atomic co-ordinates (× 10^4) in $P4_12_12$ symmetry with standard deviations in parentheses

	x	y	z
Zn	2 159(10)	2 159	0
Se	7 146(8)	7 146	0
O(1)	1 734(30)	9 549(28)	0 537(9)
O(2)	4 763(26)	2 572(27)	0 569(8)
O(3)	3 625(26)	0 691(26)	9 120(8)
O(4)	6 177(30)	6 180(30)	0 730(9)
O(5)	9 547(29)	6 725(31)	0 070(10)

Absolute Configuration.—In the tetragonal space groups $P4_12_12$ and $P4_32_12$, for $h = 0$, $h = k$, $k = 0$, and $l = 0$, $|F_{hkl}| = |F_{\bar{h}\bar{k}\bar{l}}| = |F_{\bar{h}kl}| = |F_{h\bar{k}l}| = |F_{hk\bar{l}}|$, even in the presence of anomalous scatterers. However, for other reflections these equalities do not hold and the magnitudes of the differences will be directly related to the size of the anomalous-dispersion factors. Since the anomalous-dispersion corrections for the heavy atoms in the structure reported here are relatively large ($\Delta f' = -2.027$ and $\Delta f'' = 2.002$ for the weighted contribution from Co and Zn; $\Delta f' = -1.060$ and $\Delta f'' = -1.310$ for Se), the intensity differences should be clearly observable.[27]

The absolute configuration was determined by comparing $(F_c)_{hkl}/(F_c)_{hk\bar{l}}$ to $(I^{\frac{1}{2}})_{hkl}/(I^{\frac{1}{2}})_{hk\bar{l}}$, where $I^{\frac{1}{2}}$ is the square root of the observed intensity. [The quotient $(I^{\frac{1}{2}})_{hkl}//(I^{\frac{1}{2}})_{hk\bar{l}}$ should approximate $(F_o)_{hkl}/(F_o)_{hk\bar{l}}$ since all the scaling factors and corrections will be the same for hkl and $hk\bar{l}$.] Assuming $P4_12_12$ symmetry (positional parameters from Table 1), 189 ratios of $(F_c)_{hkl}/(F_c)_{hk\bar{l}}$ were found from the 433 observable independent reflections, which do not obey Friedel's law ($h \neq k$, $h \neq 0$, $k \neq 0$, $l \neq 0$). Of these 189 reflections, 13 values of $(I)_{hk\bar{l}}$ were not observable in the photographic data. Comparison of $(F_c)_{hkl}/(F_c)_{hk\bar{l}}$ with $(I^{\frac{1}{2}})_{hkl}/(I^{\frac{1}{2}})_{hk\bar{l}}$ for the remaining 176 quotients revealed 15

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

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quotients having values greater than 1.00 for the F_c quotient while the $I^{\frac{1}{2}}$ quotient was less than 1.00, or *vice versa*, and five values of $(I^{\frac{1}{2}})_{hkl}/(I^{\frac{1}{2}})_{hk\bar{l}}$ which were judged to be exactly equal to 1.00. The discrepancy in the 15 pairs which show disagreement is presently unexplained, although 13 of the 15 are intense to very intense reflections, and as such particularly vulnerable to absorption errors. The five where the $I^{\frac{1}{2}}$ quotient is 1.00 involve weak to very weak reflections. If (in deference to the uncertainty of the absorption problem) only the values $0.9 \leqslant (I^{\frac{1}{2}})_{hkl}/(I^{\frac{1}{2}})_{hk\bar{l}} \leqslant 1.1$ are considered, only six out of 93 show disagreement and all those which disagree involve intense reflections. From these considerations it seems certain that the absolute configuration of the α-[(Zn,Co)$(OH_2)_6$][SeO_4] crystal used was, therefore, $P4_12_12$.

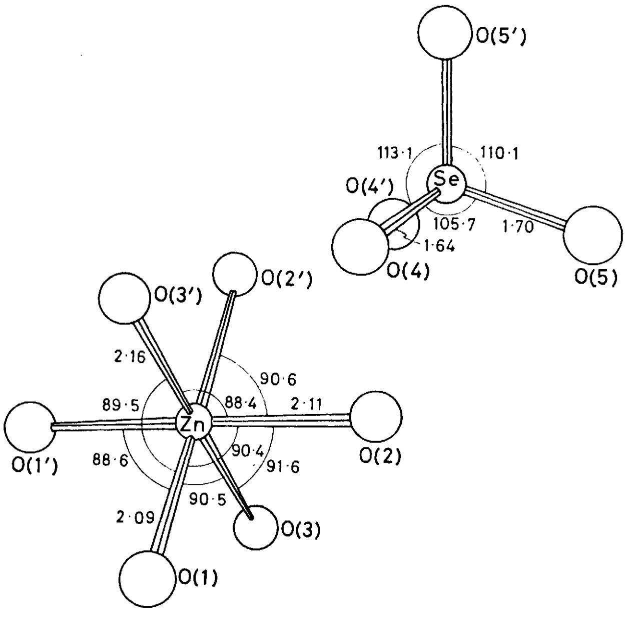

FIGURE [Zn$(OH_2)_6$][SeO_4] with bond distances and angles

Structure.—The molecular structure, plotted by program ORTEP,[28] is given in the Figure. The zinc (cobalt) and selenium atoms sit on a crystallographic two-fold axis, bisecting the O(1)–M–O(1′) and O(2)–M–O(2′) angles in the octahedron and the O(4′)–Se–O(4) and O(5′)–Se–O(5) angles in the tetrahedron (Figure). Bonded distances and angles with standard deviations calculated by program ORFFE [29] are given in Table 2. The mean M–O bond distance (2.12 Å) is in good agreement with previously reported Zn–O bond distances.[22] The O–M–O *cis* bond angles are all 90° within experimental error, except for O(1)–M–O(1′), O(2)–M–O(3), and O(2)–M–O(3′). Selenium–oxygen bond distances also are in good agreement with previous results.[29] Two bond angles O(4)–Se–O(5) and O(4)–Se–O(5′) deviate substantially from the tetrahedral angle. The shortest interionic distance between two oxygen atoms is 2.63(3) Å.

DISCUSSION

From the closeness of the average Zn–O and Co–O bond distances to those found in the literature [22] and the ease of doping cobalt into the crystal, the structure described here may clearly be considered to be that of the host, α-[Zn$(OH_2)_6$][SeO_4]. The average M–O distances are, in fact, so close (2.10 and 2.13 Å for ZnO and CoO, respectively) that it is unlikely that any significant difference in M–O bond lengths would be observed between this solution and that from comparable data for pure α-[Zn$(OH_2)_6$][SeO_4]. This conclusion is even more specifically supported by comparing the structures of the Tutton salts.[30,31] Here also the metal is surrounded by six water oxygens with a site symmetry of 2. The Zn–O distances of the Tutton salt are 2.129, 2.117, and 2.075 Å and the Co–O distances are 2.107, 2.106, and 2.070 Å, compared to 2.09, 2.11, and 2.16 Å in the cobalt-doped zinc selenate. Furthermore, compared to the structure of the isomorphous α-[Ni$(OD_2)_6$][SO_4],[2] the selenate M–O distances fail to show any variation (range 0.08 Å in both cases) which might be ascribed to the presence of a static Jahn–Teller distortion in the $^4T_{1g}$ ground state of octahedral Co^{II}. (The ground state of octahedral Ni^{II} is $^3A_{2g}$ and thus not susceptible to Jahn–Teller distortion.[2]). Thus, despite the failure of pure hydrated cobalt(II) selenate to adopt an enantiomorphous phase isomorphous to α-[Zn$(OH_2)_6$][SeO_4], α-[Ni$(OH_2)_6$]-[SeO_4], and α-[Ni$(OH_2)_6$][SO_4] (all $P4_{1,3}2_12$), cobalt ions easily adapt themselves to the zinc selenate structure and in concentrations up to *ca.* 40 mol % cause no demonstrable distortion of the host lattice (within the limits of this determination).

TABLE 2

Bond distances and angles of α-[(Zn,Co)$(OH_2)_6$][SeO_4] with standard deviations in parentheses

Distances (Å)

Zn–O(1)	2.09(2)	Se–O(4)	1.64(2)
Zn–O(2)	2.11(2)	Se–O(5)	1.70(2)
Zn–O(3)	2.16(2)		

Angles (°)

O(1)–Zn–O(1′)	88.6(11)	O(2)–Zn–O(3′)	88.4(7)
O(1)–Zn–O(2)	90.4(7)	O(3)–Zn–O(3′)	180.0(30)
O(1)–Zn–O(2′)	178.5(7)	O(4)–Se–O(4′)	109.2(13)
O(1)–Zn–O(3)	90.5(7)	O(4)–Se–O(5)	105.7(10)
O(1)–Zn–O(3′)	89.5(7)	O(4)–Se–O(5′)	113.1(10)
O(2)–Zn–O(2′)	90.6(10)	O(5)–Se–O(5′)	110.1(15)
O(2)–Zn–O(3)	91.6(7)		

The determination of the absolute configuration of the α-[Zn$(OH_2)_6$][SeO_4] lattice relative to the sign of Δε for [Co$(OH_2)_6$]$^{2+}$ makes possible the corresponding association of the signs of Δε in the axial c.d. of the ligand-field bands of [Ni$(OH_2)_6$]$^{2+}$, [Cu$(OH_2)_6$]$^{2+}$, [Fe$(OH_2)_6$]$^{2+}$, and [Mn$(OH_2)_6$]$^{2+}$ by means of multiple-doping experiments.[15,16] The signs of all the major ligand-field bands in these systems are the same in a given crystal;

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that is, the $P4_12_12$ structure gives rise to negative ligand-field axial c.d. peaks in all the guest ions.*

For nickel-doped α-$[Zn(OH_2)_6][SeO_4]$ Katō *et al.*[16] showed that Δε is linearly dependent on the concentration of Ni^{2+}. This indicates clearly that the lattice-induced chirality of the chromophores is essentially a localized effect and not co-operative, for example, between metal centres along the four-fold screw axis. This conclusion is supported by the theoretical calculations of Strickland and Richardson [10] on α-$[Ni(OH_2)_6]$-$[SeO_4]$. These calculations and the analysis of the c.d. spectra of nickel-, cobalt-, and copper-doped α-$[Zn(OH_2)_6][SeO_4]$ by Katō [17] give reasonable agreement with experiment for the relative magnitudes of the rotational strength of the various bands but do not predict the sign relative to the absolute configuration.

Recently Richardson and Hilmes [32] calculated the rotational strength of α-$[(Zn,Cu)(OH_2)_6][SeO]_4$ using a crystal-field model including pseudo-Jahn–Teller effects. The perturber sites providing the chiral crystal field in this model are the hydrogens of the six ligating water molecules and the four nearest-neighbour selenate anions. The calculated magnitude and temperature dependence of the rotational strength *R* are in qualitative agreement with experiment.[15] However, the calculated sign of *R* relative to the absolute configuration is opposite to that observed as determined in this work and through the multiple-doping experiments referred to above. It may be significant that the atomic positions used in the calculation [32] were actually those of the α-$[Ni(OH_2)_6][SO_4]$ structure.[2] Small differences in oxygen positions in $Na[ClO_3]$ and $Na[BrO_3]$ have been cited as the reason for the opposite signs of *R* observed for crystals of these compounds having the same absolute configuration.[33] Additional work in this area is in progress in our laboratories.

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* Exceptions to this generality are a minor component in the visible band of α-$[(Zn,Co)(OH_2)_6][SeO_4]$ at room temperature [15,16] and a narrow component of the i.r. band of α-$[Ni(OH_2)_6][SeO_4]$ observed at very low temperature and assigned to a low-symmetry field-splitting effect.[11]

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