

The Crystal Structure, Thermal Behaviour and IR Spectrum of Cadmium Hydrogenselenite Nitrate

MARKKU LESKELÄ,^a JUSSI VALKONEN^b and TUULA LESKELÄ

Department of Chemistry, Helsinki University of Technology, SF-02150 Espoo 15, Finland; Present addresses: ^a Department of Chemistry, University of Oulu, SF-90570 Oulu 57, Finland and ^b Department of Chemistry, University of Jyväskylä, SF-40100 Jyväskylä 10, Finland

$\text{Cd}(\text{HSeO}_3)\text{NO}_3$ was crystallized from nitric acidic solution of cadmium selenite. The compound was characterized on the basis of thermal analysis and its IR-spectrum and the structure was determined from single crystal X-ray data. The crystals are orthorhombic with space group *Pbca* (No. 61). The unit cell parameters are $a=6.359(1)$, $b=8.945(2)$, and $c=16.648(4)$ Å, $Z=8$. The structure was refined with 1112 reflections to the *R*-value of 0.033.

The Cd atoms are eight-coordinated with five oxygen atoms from selenite groups and three oxygen atoms from nitrate groups in the coordination sphere. The NO_3^- and HSeO_3^- ions act as bridging ligands. The bicapped trigonal prismatic CdO_8 polyhedra form layers along the *xy*-plane sharing four corners and one edge with each other. The layers are bonded together by hydrogen bonds.

The cadmium(II) ion can coordinate in many different ways, possibly owing to its electron configuration which shows a filled *d*-orbital. A large number of crystal structures of cadmium compounds have been determined in the last forty years, and in these the coordination number of cadmium has been found to vary between 2 and 8. The coordination number 2 has only once been detected in solid structures, and number 3 never; but coordination number 2 exists in cadmium halides in gas phase.^{1,2} Coordination number 3 has also been found in solution in spectroscopic studies.^{3,4}

Four-coordination is very common in cadmium crystals. The coordination sphere is then formed by larger donor atoms like halogens, sulfur and

phosphorus. The CdO_4 unit is very rare but oxygen atoms are often found in combination with larger atoms in four-coordinate systems of cadmium.^{2,5} More than twenty structures are known where cadmium has coordination number five (Fig. 1). In most cases the compounds have polymeric structure, but monomeric and dimeric structures are known as well. The donor atoms in five coordination are again usually larger atoms, but some CdN_5 and CdO_5 coordination kernels have been determined.^{5,6}

Nearly 60 % of the known cadmium compounds exhibit six-coordination and the coordination polyhedron in almost all cases is octahedron (Fig. 1). The coordination sphere may be formed by just one type of donor atom (N, O, S, etc.) or by two or three types.^{5,6}

With polydentately acting ligands cadmium forms coordination polyhedra with coordination numbers 7 and 8. Seven-coordination is quite common, but eight-coordinated compounds of cadmium are few (Fig. 1 and Table 5). These higher coordination systems are formed by small donor atoms, usually by nitrogen and oxygen.

A survey of 240 crystal structures of cadmium compounds published up to the end of 1982 revealed that the calculated average coordination number of Cd(II) is 5.82.⁷ The distribution of different coordination numbers is presented in Fig. 1.

The present work on the structure of cadmium hydrogenselenite nitrate, besides giving additional structural data of divalent cadmium compounds, continues the investigations into the structural chemistry of inorganic selenites carried

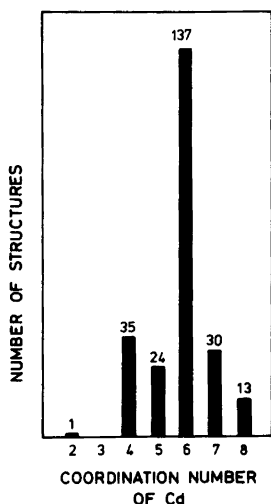


Fig. 1. Distribution of different coordination numbers in solid cadmium(II) structures as reported in the literature.

out in the Laboratory of Inorganic and Analytical Chemistry at the Helsinki University of Technology.⁸⁻¹⁰

EXPERIMENTAL

Preparation of the crystals. Selenous acid precipitated cadmium ions from cadmium acetate solution in the form of a light, microcrystalline powder. According to chemical analysis and X-ray powder diffraction pattern the chemical composition was CdSeO₃. For crystal preparation 0.2 g of this anhydrous selenite was dissolved in 20 cm³ of 5 M nitric acid and the solution was evaporated over a period of several weeks in a covered vessel at room temperature. Large needle-like, colourless, transparent crystals were obtained. The chemical composition Cd(HSeO₃)NO₃ calculated for the crystals has not previously been reported in the literature. This was the second time we obtained a compound containing selenite and nitrate anions. The first compound was yttrium diselenite nitrate.^{10,18}

Thermal methods of analysis. The thermo-analytical investigations were carried out with a MOM Q-Derivatograph apparatus, recording simultaneously the TG, DTG and DTA curves. The heating rate varied between 1.5 and 10 °C min⁻¹ and the sample size was 100 mg. The heating atmosphere was static air. Aluminium oxide crucibles were used as sample holders and

alumina was the reference material in DTA measurements.

IR-spectra. The infrared spectra were recorded on a Perkin-Elmer 521 instrument using KBr pellet technique.

Data collection. Conditions for unit cell determination and data collection are listed in Table 2. Semi-empirical absorption corrections were made on the basis of a ϕ -scan with five different 2θ -values. The largest measured relative reduction in intensity was from 1.00 to 0.39. The crystal data are given in Table 2.

The space group was determined from systematic absences in the original reflections. The positions of Cd and Se atoms were determined with direct methods of the program package MULTAN 80.¹¹ The positions of the O and N atoms were determined from the electron density difference map after refinement of the sites of Cd and Se atoms. The refinement was calculated with the program XRAY 76¹² and unit weights were employed. The scattering factors were those of Cromer and Mann for neutral atoms.¹³ The pictures were drawn with the program ORTEP which was a part of the program XRAY 76. Lists of structure factors as well as anisotropic thermal

Table 1. IR absorption frequencies for Cd(HSeO₃)NO₃ in the range 4000–300 cm⁻¹.

Frequency (cm ⁻¹)		Assignment
3600–3300	w	$\nu(\text{OH})$
2490	w	$\nu(\text{OH})$
2390	w	
1620	w	
1455	m	$\delta(\text{OH})$
1350, 1380	vs	
1275	m	$\nu_3(\text{NO}_3)$
1035	m	$\delta(\text{OH})$
845	m	$\nu_1(\text{NO}_3)$
830	m	
805	w	
780	m	$\nu_2(\text{NO}_3)$
740	s	$\nu_4(\text{NO}_3)$
715	sh	
675	w	
635	w	
605	w	$\nu_3(\text{SeO}_3)$
495	m	
465	m	
425	m	$\nu_2(\text{SeO}_3)$
380	w	
360	wv	
320	w	
		$\nu_4(\text{SeO}_3)$

Table 2. Crystal data and conditions for data collection for Cd(HSeO₃)NO₃.

Formula	Cd(HSeO ₃)NO ₃
Formula weight	302.38
Crystal system	orthorhombic
Diffractometer	Syntex P2 ₁
Radiation	MoK α
Monochromator	graphite crystal
Crystal size	0.2×0.2×0.5 mm ³
Space group	Pbca (No. 61)
<i>a</i>	6.359(1) Å
<i>b</i>	8.945(2) Å
<i>c</i>	16.648(4) Å
<i>V</i>	949.1(4) Å ³
<i>Z</i>	8
<i>D</i> _x	4.23 g/cm ³
<i>D</i> _m	4.2 g/cm ³
μ (MoK α)	121.3 cm ⁻¹
Unit cell determination	
Number of reflections	25
2 θ range	29.8–31.7°
Data collection	
Collection method	2 θ : θ
Scan speed	1.5–3.0°/min
2 θ range	5–65°
Max. <i>hkl</i>	9,13,24
Number of independent reflections collected	2020
Number of independent reflections refined	1112 (<i>I</i> >3 σ (<i>I</i>))
<i>R</i> (isotropic)	0.040
<i>R</i> (anisotropic)	0.033

parameters are available from the authors upon request.

RESULTS AND DISCUSSION

Thermal analysis. The thermal decomposition of cadmium hydrogenselenite nitrate begins at about 200 °C depending slightly on the heating rate (Fig. 2). At first the liberation of nitrogen oxides is rapid, but becomes slower above 250 °C. The decomposition reaction has two DTG and DTA maxima but no clear intermediate plateau can be observed. The pure CdSeO₃ phase is formed only at about 500 °C. The decomposition of cadmium selenite shows only one reaction stage between 750 and 900 °C. This endothermic reaction is the liberation of sele-

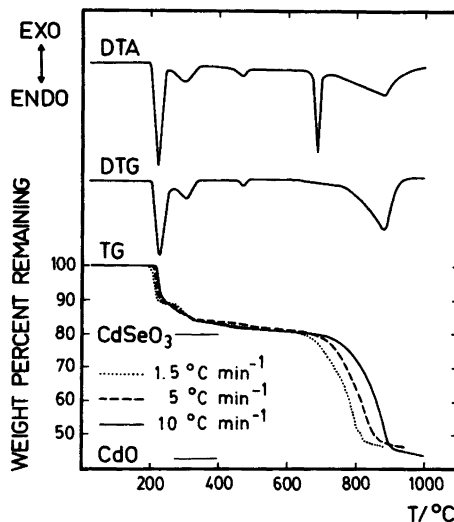


Fig. 2. The TG, DTG and DTA curves of Cd(HSeO₃)NO₃ in air atmosphere (heating rate 10 °C min⁻¹) and the effect of heating rate on the TG curve.

nium dioxide with the formation of cadmium oxide. In the DTA curve, however, there is a sharp endothermic peak at 690 °C, obviously due to the melting of cadmium selenite.

The effect of heating rate on the decomposition of Cd(HSeO₃)NO₃ is presented also in Fig. 2. The shape of the curves is similar but the decomposition temperatures are higher with higher heating rate. The heating rate has a particularly marked effect on the decomposition of anhydrous cadmium selenite.

IR-spectra. The absorption frequencies observed in the IR-spectrum of Cd(HSeO₃)NO₃ are presented in Table 1. The assignment of the bands has been carried out according to the literature.^{14–18}

The deformation vibrations of the selenite ion are located in the region 300–500 cm⁻¹ and the corresponding stretching frequencies are in the regions 600–750 cm⁻¹ and 830–850 cm⁻¹. The strongest absorption bands in the spectrum are caused by the nitrate ion. Its deformation vibrations are at 780 and 805 cm⁻¹ and stretching vibrations at 1035 and 1350–1410 cm⁻¹. The very strong peak at 1330–1390 cm⁻¹ is a doublet.

The IR-spectrum also shows many peaks of the OH-group, both stretching and deformation vibrations. These peaks originate from the hydro-

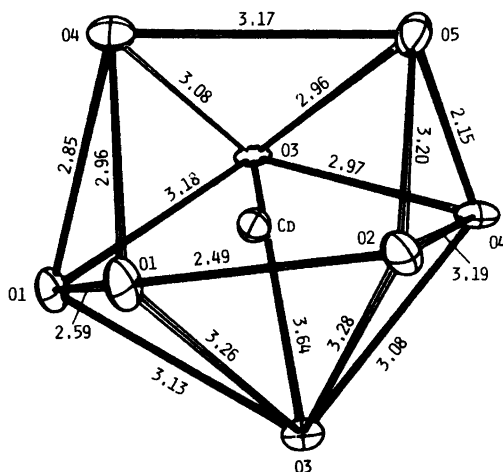


Fig. 3. The coordination polyhedron around the Cd atom. Edge lengths are in Ångströms and estimated standard deviations are less than 0.011 Å.

genselenite ion, which contains an O–H bond. The peaks at 2390 and 2490 cm^{-1} indicate that the structure contains hydrogen bonds.

The IR-frequencies of selenite and hydrogenselenite ions are so close together that it is difficult to distinguish them on the basis of the selenite vibrations.^{17–18} The presence of OH-vibrations in the hydrogenselenite makes the differentiation easier.

Crystal structure. The eight-coordination of cadmium makes the present structure very com-

Table 3. Fractional positional parameters and isotropic thermal parameters for $\text{Cd}(\text{HSeO}_3)\text{NO}_3$.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$100 \cdot U_{\text{iso}}^a$
Cd	0.6450(1)	0.3399(1)	0.0561(1)	1.31(1)
Se	0.1550(2)	0.4135(1)	0.1054(1)	1.02(2)
N	0.3289(17)	0.1254(11)	0.3233(6)	1.54(18)
O1	0.3447(14)	0.4860(9)	0.0494(5)	1.59(15)
O2	0.6825(14)	0.7645(10)	0.3610(5)	1.91(18)
O3	0.4961(12)	0.8189(9)	0.0383(4)	1.08(14)
O4	0.7425(14)	0.0807(11)	0.1127(5)	1.77(16)
O5	0.7013(14)	0.7619(12)	0.1950(6)	2.14(18)
O6	0.4384(17)	0.0409(11)	0.2818(6)	2.51(20)
H ^b	0.175	0.763	0.200	–

^a From the isotropic refinement. ^b Not refined.

Table 4. Bond distances (Å) in $\text{Cd}(\text{HSeO}_3)\text{NO}_3$ and angles (°) around Se, N and H atoms.

Cd–O1	2.321(8)	O1–Se–O2	92.8(4)
–O1	2.351(8)	O1–Se–O3	103.6(3)
–O2	2.589(8)	O2–Se–O3	99.3(4)
–O3	2.304(7)		
–O3	2.310(7)		
–O4	2.578(8)	O4–N–O5	116.1(9)
–O4	2.462(8)	O4–N–O6	121.5(9)
–O5	2.609(8)	O5–N–O6	122.3(9)
Se–O1	1.656(8)	O2–H–O5	171.7
–O2	1.778(8)		
–O3	1.699(7)		
N–O4	1.261(12)		
–O5	1.276(12)		
–O6	1.241(13)		
H–O2	1.02		
–O5	1.76		

plex. The coordination polyhedron around cadmium consists of five oxygen atoms belonging to the selenite groups and three to the nitrate groups.

The three common polyhedra for eight-coordination are dodecahedron, bicapped trigonal prism and square antiprism. Porai-Koshits and Aslanov³⁰ have developed a testing system for choosing the polyhedron for eight-coordination (see also Refs. 31 and 32). The test consists of two types of angles designated δ and ϕ , which are listed in Table 6 for theoretical polyhedra and for the CdO_8 polyhedron in $\text{Cd}(\text{HSeO}_3)\text{NO}_3$. On the basis of these values the CdO_8 polyhedron is best described as an irregular bicapped trigonal prism distorted towards a dodecahedron.

The Cd–O distances (Table 4) are in good agreement with the values for eight-coordinated cadmium compounds reported in the literature (Table 5). The capping atoms O3 are nearest to cadmium and the nitrate oxygen O5 has the longest Cd–O distance. Every bicapped trigonal prism polyhedron is connected to five other polyhedra, one through a common edge (O1–O1) (Fig. 5), and four through a common corner (O3, O3, O4, O4). Together they form the layer structure shown in Fig. 6.

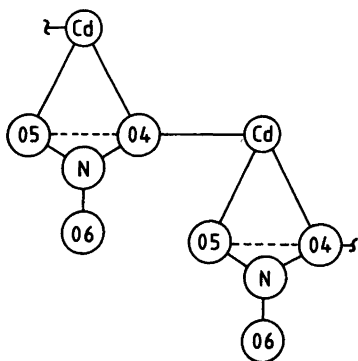
The edge lengths in the bicapped trigonal prism vary from 2.15 to 3.64 Å (Fig. 3). The O4–O5 distance 2.15 Å is abnormally short, but it is between the coordinating atoms of the

Table 5. Eight-coordinated cadmium compounds.

Compound	Coordination core	Cd-X, bond length (Å)	Ref.
CdF ₂	CdF ₈	1.97	19
CdMoO ₄	CdO ₈	2.28–2.51	20
Cd(NO ₃) ₂ ·4H ₂ O	CdO ₈	2.26–2.59	21
CaCd(OAc) ₄ ·6H ₂ O	CdO ₈	2.29–2.68	22
Cd(H ₃ IO ₆) ₃ ·3H ₂ O	CdO ₈	2.23–2.79	23
Cd(maleate)·2H ₂ O	CdO ₈	2.20–2.84	24
α-CdUO ₄	CdO ₈	2.42–2.61	25
Cd ₃ TeO ₆	CdO ₈	2.24–3.01	26
CdY ₄ Mo ₃ O ₁₆	CdO ₈	2.22–2.52	33
Cd(1,8-naphthylpyridine) ₄ (ClO ₄) ₂	CdN ₈	2.39–2.74	27
Cd(1,4,10,13-tetraoxa-7,16-diazacyclo-octadecane)I ₂	CdO ₄ N ₂ I ₂	Cd-O	2.48–2.81
		Cd-N	2.48
		Cd-I	2.83
Cd(<i>N</i> -annulene)(CH ₃ OH)(ClO ₄) ₂ (H ₂ O)	CdO ₆ N ₂	Cd-O	2.24–2.33
		Cd-N	2.50–2.79
Cd(HSeO ₃)NO ₃	CdO ₈	2.31–2.61	Present work

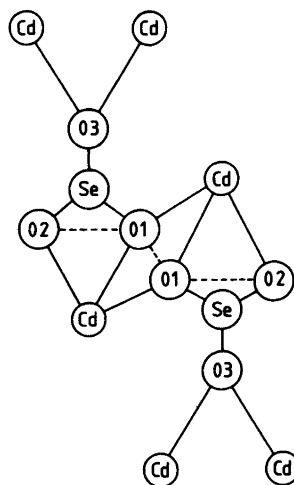
Table 6. Values of δ and ϕ for theoretical dodecahedron, square antiprism and bicapped trigonal prism,^{30–32} and experimental values for the CdO₈ polyhedron in Cd(HSeO₃)NO₃.

Polyhedron	δ (°)				ϕ (°)
Dodecahedron	29.5	29.5	29.5	29.5	0.0
Square antiprism	0.0	0.0	52.5	52.5	24.5
Bicapped trigonal prism	0.0	21.7	48.2	48.2	16.1
Cd(HSeO ₃)NO ₃	18.0	35.4	50.9	51.4	12.4

Fig. 4. A schematic illustration of the coordination of the nitrate ion. The broken line indicates the edge of the CdO₈ polyhedron.

bidentate nitrate group (Fig. 4). The edge O3–O3 is considerably longer than the other edges as the O3 atoms form a common corner with two other polyhedra.

The nitrate group is regular and planar. It acts as a bidentate ligand as shown in Fig. 4, with O4 and O5 connected to the same cadmium and O6 free. The oxygen atom O4 is also connected to

Fig. 5. A schematic presentation of the coordination of the selenite ion. The broken line indicates the edge of the CdO₈ polyhedron.

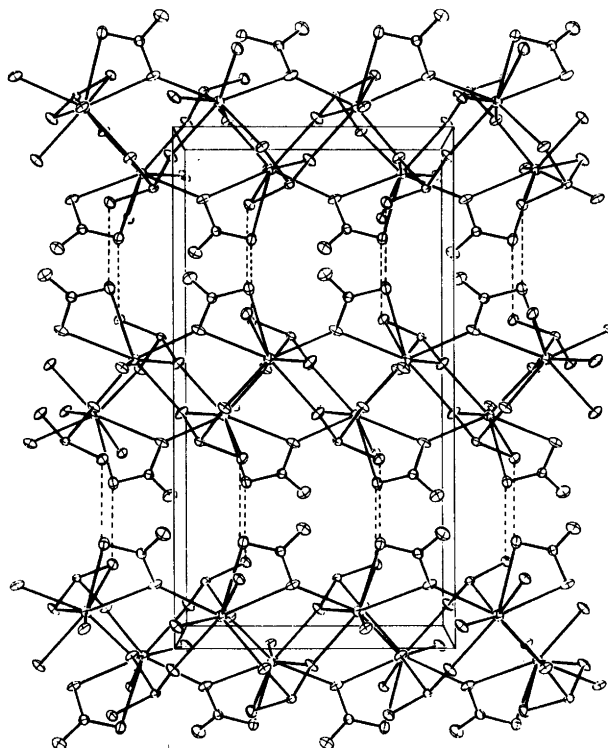


Fig. 6. The layer structure of $\text{Cd}(\text{HSeO}_3)\text{NO}_3$ along the a -axis. The broken lines indicate hydrogen bonds.

another cadmium atom and forms a common corner between two bicapped trigonal prisms around cadmium. The N–O6 distance is shortest, because the other N–O distances have been stretched out through coordination to cadmium.

Distances between Se and O atoms are normal compared with literature values.⁸ Because the group is hydrogenselenite, one Se–O distance is longer than the other two through the stretching influence of the hydrogen atom. All three oxygen atoms of the hydrogenselenite group are connected to cadmium, as shown in Fig. 5. Oxygen atoms O1 and O2 are connected to the same cadmium and form one edge of the bicapped trigonal prism. The third oxygen atom O3 is connected to two cadmium atoms and forms a common corner for two polyhedra around cadmium.

The structure is layered as shown in Fig. 6. Infinite layers are parallel to xy -plane and connected together by hydrogen atoms of hydrogen-

selenite groups. The hydrogen atoms lie between layers, connected to atoms O2 and O5 with distances 1.02 and 1.76 Å and with angle 171.7°.

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