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X-ray structure determination of bis{(-[*N*-(2-[2-hydroxyethylamino]ethyl)salicylaldiminato]-perchlorate cadmium(II))}monohydrate ([(Cd sadol $ClO_4)_2] \cdot H_2O$) and two modifications of bis{(-[*N*-(2-[2-hydroxyethylamino]ethyl)salicylaldiminato]-perchlorate cadmium(II))} ([(Cd sadol $ClO_4)_2$])

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Abstract

Preparations and the X-ray structure determinations of the compound bis{(-[*N*-(2-[2-hydroxyethylamino]ethyl)salicylaldiminato]-perchlorate cadmium(II))} monohydrate $[\{Cd(C_{11}H_{15}N_2O_2)(ClO_4)\}_2] \cdot H_2O$ ([(Cd sadol $ClO_4)_2] \cdot H_2O$) and of two modifications of bis{(-[*N*-(2-[2-hydroxyethylamino]ethyl)salicylaldiminato]-perchlorate cadmium(II))} $[\{Cd(C_{11}H_{15}N_2O_2)(ClO_4)\}_2]$ ([(Cd sadol $ClO_4)_2$]) were carried out. (Hsadol is the abbreviation for *N*-[2-(2-hydroxyethylamino)ethyl]salicylaldimine.) In each of these compounds Cd is coordinated by three N and three O atoms in a strongly distorted octahedron. Each perchlorate anion is coordinated by one oxygen to a Cd atom. The hydrated molecule is the first known compound where Cd is coordinated by perchlorate and not coordinated by water though water is present. Water is an acceptor of a moderate hydrogen bond. Water can be drawn out from [(Cd sadol $ClO_4)_2] \cdot H_2O$ by careful heating and desiccation while the structure transforms into phase α of [(Cd sadol $ClO_4)_2$]. On the other hand phase α can absorb water at room temperature easily, transforming into the original monohydrate. Both compounds – the monohydrate and the phase α – can be considered as extreme representatives of the series which differ by degree of hydration.

Keywords: Coordination chemistry; Schiff bases; Cd compounds; X-ray structure determination; Hydrogen bonding; Reversible absorption and desorption of water

1. Introduction

The studied compounds were prepared in the course of a research program devoted to studying of metal complexes with tetradentate Schiff bases. In contrast to other metals, cadmium tends to form dimeric structures [1]. The Schiff base of the present compound is unsymmetric because its symmetry is only 1 in difference to more common Schiff bases like H_2salen (bis(salicylidene)ethylenediamine) or H_2salphen (bis(salicylidene)ethylenediamine) [2]. The present paper reports a study of Cd complexes with a slightly altered Schiff base which derived from *N*-(2-aminoethyl)aminoethanol. In addition, the investigation of the coordination properties of Cd is of interest because of the environmental aspects and biological activity of Cd.

2. Experimental

2.1. Preparation of [(Cd sadol $ClO_4)_2] \cdot H_2O$

To a hot ethanolic solution of 4.19 g (0.01 mol) $[Cd(H_2O)_6](ClO_4)_2$ and 2.08 g (0.01 mol) Hsadol was

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slowly added 0.56 g (0.01 mol) KOH in aqueous ethanol while the solution was stirred. The mixture was stirred for another hour, filtered and the filtrate was allowed to evaporate slowly for several days at room temperature. The crystals formed were washed with cold ethanol and ether and dried in air. The yield was 2.6 g (60 wt%). This compound was the first one that was prepared in the studied series of the compounds. The attempts to prepare water-free compounds were based on a structure analysis that discovered a weakly bound water molecule (see below).

2.2. Preparation of [(Cd sadol ClO_4)$_2$] – phase α

The crystals of [(Cd sadol ClO_4)$_2$] · H_2O were heated at 373 K for several hours. The dehydration was checked by weighing. The amount of absorbed water varied continuously and depended on temperature and partial pressure of water.

(The behaviour of [(Cd sadol ClO_4)$_2$] · H_2O and phase α is similar to zeolites in this respect.) During repeated dehydration and rehydration the shape and yellow colour as well as transparency of the crystals did not alter. The experiments with dehydration and absorption of water were checked by weighing, infrared spectroscopy and a single-crystal X-ray diffraction experiment that is discussed below.

2.3. Preparation of [(Cd sadol ClO_4)$_2$] – phase β

To 15 ml of a hot methanolic solution of 0.4 g of [(Cd sadol ClO_4)$_2$] · H_2O an equal volume of 1-propanol was added. The solution was allowed to evaporate at 313–323 K for 1 day. Tiny crystals were washed with ether and dried in air. The yield was about 90 wt%.

2.4. Proof of the reversibility of water exchange between [(Cd sadol ClO_4)$_2$] · H_2O and [(Cd sadol ClO_4)$_2$] – phase α by a single crystal X-ray diffraction experiment

In order to prove reversibility of water exchange a single desiccated crystal of [(Cd sadol ClO_4)$_2$] – phase α was chosen. This sample was left exposed in air at room temperature for one month in order to get water to be absorbed. Then a single-crystal diffraction experiment was taken on a diffractometer with a CCD-camera at room temperature. The structure determination of this sample proved reversibility of water exchange. The refinement resulted in $R_{obs} = 0.0311$, $R_{all} = 0.0345$, $wR_{obs} = 0.0877$, $wR_{all} = 0.0948$, the twinning fraction resulted in 0.348(1) for 6653 reflections from which 6291 ones were considered as observed, otherwise the conditions, except the weighting scheme of the refinement, were the same as for the reported structure of [(Cd sadol ClO_4)$_2$] · H_2O. Since the quality of this sample is below the reported one its refined parameters are not published. Experimental details regarding the X-ray experiments and the pertinent structure refinements are given in Tables 1–3 for each of the title structures.

3. Discussion

The metric of the lattice of [(Cd sadol ClO_4)$_2$] · H_2O is very close to orthorhombic. Therefore it was assumed that the structure may be twinned though no domains were observed in the crystals when viewed in the microscope under the polarized light. During the diffractometer experiment no splitting of the collected diffractions was observed. The assumed twinning can be expressed by the following Eq. (1) or (2):

$$(a_2 \quad b_2 \quad c_2) = (a_1 \quad b_1 \quad c_1)\begin{pmatrix} -1 & 0 & \frac{2c}{a}\cos\beta \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \tag{1}$$

$$(a_2 \quad b_2 \quad c_2) = (a_1 \quad b_1 \quad c_1)\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ \frac{2a}{c}\cos\beta & 0 & 1 \end{pmatrix}. \tag{2}$$

Into the respective non-diagonal matrix elements (1,3) or (3,1) enter the values of the unit cell parameters. The values of these non-diagonal matrix elements (1,3) or (3,1) are close to zero (~0.005). For practical reasons these matrix elements were replaced by 0 during the calculation.

If no twinning was assumed the R factors converged to the values: $R_{obs} = 0.0314$, $wR_{obs} = 0.0809$, $R_{all} = 0.0327$, $wR_{all} = 0.0814$, 467 parameters, otherwise the conditions for the refinement except the weighting scheme were the same as in Table 1. Thus the twinning in the title structure that is published in this article is significant whenever the minor-domain fraction is small (Table 1). The above mentioned experiment with absorption of water into the dehydrated phase α shows that the observed twinning is physically substantiated.

The structure of [(Cd sadol ClO_4)$_2$] · H_2O is close to the hypothetical structure which would crystallize in *Pbca*. The average intensity of the reflections which otherwise would be absent in *Pbca* is considerably weaker ($I/\sigma(I) = 75$, 280 diffractions, 39 absent) compared with the rest of the reflections ($I/\sigma(I) = 407$, 5400 diffractions, 195 absent).

Indeed, the most interesting point of the present structure determination is that [(Cd sadol ClO_4)$_2$] · H_2O can release water while transforming into phase α of [(Cd sadol ClO_4)$_2$] and that the latter structure can absorb water in reverse, transforming thus into the former

Table 1
Crystal data and structure refinement for $[(\mathrm{Cd\ sadol\ ClO_4})_2]\cdot H_2O$

Formula	$[\{(C_{11}H_{15}Cd\ N_2O_2)ClO_4)\}\cdot(H_2O)]$
Formula weight	856.22
Temperature (K)	151
Wavelength (Å)	Mo (Kα) 0.71073
Instrument	κ-geometry diffractometer Enraf-Nonius CAD4-MACHIII-PC, graphite monochromator
Crystal system	monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a (Å)	10.6236(9)
b (Å)	19.058(3)
c (Å)	14.3230(10)
α (°)	90
β (°)	90.058(10)
γ (°)	90
Volume (Å^3)	2899.9(6)
Number of reflections for the determination of the unit cell	25
Θ range of reflections for the determination of the unit cell (°)	14–15
Z	4
Density (calculated) (Mg/m^3)	1.961
Absorption coefficient (mm^{-1})	1.723
$F(000)$	1704
Crystal size (mm)	$0.57\times0.51\times0.49$
Crystal shape and colour	prism; yellow
Θ range for data collection (°)	1.78 to 25.98
Index ranges	$h=0\rightarrow13$; $k=0\rightarrow23$; $l=-17\rightarrow17$
Reflections collected	6026
Standard reflections	3; frequency 60 min; intensity decay 4%
Scan	$\omega/2\theta$
Absorption correction	ψ-scans of 10 reflections – Platon for Windows [11] $T_{\min}=0.825$, $T_{\max}=0.9898$
Scattering factors	International Tables, Vol. C, 4.2.6.8 and 6.1.1.4
Number of independent reflections	5680 [$R_{\mathrm{int}}=0.0378$]
Number of independent reflections ($I\geqslant2\sigma(I)$)	5481
Completeness to theta = 25.98° (%)	100.0
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	5680/30/468
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0305P)^2+3.985P]$, where $P=(F_o^2+2F_c^2)/3$
Goodness-of-fit on F^2	1.123
Final R indices ($I\geqslant2\sigma(I)$)	$R_{\mathrm{obs}}=0.0219$, $wR_{\mathrm{obs}}=0.0583$
R indices (all data)	$R_{\mathrm{all}}=0.0233$, $wR_{\mathrm{all}}=0.0591$
Extinction method	SHELXL 97 (Sheldrick, 1997 [12])
Extinction coefficient	0.00668(17)
Largest differential peak and hole (e Å^{-3})	0.996 and −0.737
Minor domain fraction	0.0284(4)
Used software	
Data collection	Enraf-Nonius Software [13]
Cell refinement	Enraf-Nonius Software [13]
Data reduction	JANA2000 [14]
Molecular graphics	Platon for Windows, Spek, 2002 [11]
Structure solution	SHELXS 86, Sheldrick, 1986 [15]
Structure refinement	SHELXL 97, Sheldrick, 1997 [12]

compound. It is remarkable that absorption of water takes place in the vicinity of every second Schiff base, resulting thus in an ordered structure (Figs. 1 and 2). This means that only a half of the docking sites of water is preferred and that water is absorbed in an ordered way. The observed twinning on both crystals that were used for data collection indicates the existence of sufficiently large domains with ordered hydrated and not hydrated molecules of $[(\mathrm{Cd\ sadol\ ClO_4})_2]$. Figs. 1–3 illustrate structural features of phase α as well because the water-free molecules in $[(\mathrm{Cd\ sadol\ ClO_4})_2]\cdot H_2O$ and those in phase α of $[(\mathrm{Cd\ sadol\ ClO_4})_2]$ are similar. Moreover, the molecules in both structures are packed in the same way.

Inspecting $[(\mathrm{Cd\ sadol\ ClO_4})_2]\cdot H_2O$ and phase α of $[(\mathrm{Cd\ sadol\ ClO_4})_2]$ we found channels parallel to the

Table 2
Crystal data and structure refinement for [(Cd sadol $ClO_4)_2$] – phase α

Formula	[{($C_{11}H_{15}Cd\ N_2O_2$)(Cl O_4)}]
Formula weight	838.21
Temperature (K)	291(2)
Wavelength (Å)	Mo (Kα) 0.71073
Instrument	4-circle diffractometer Nonius Kappa CCD, graphite monochromator
Crystal system	orthorhombic
Space group	*Pbca*
Unit cell dimensions	
a (Å)	10.6739(2)
b (Å)	18.9316(4)
c (Å)	14.3531(3)
α (°)	90
β (°)	90
γ (°)	90
Volume (Å^3)	2900.39(10)
Number of reflections for the determination of the unit cell	60 525
Θ range of reflections for the determination of the unit cell (°)	1.0–27.48
Z	4
Density (calculated) (Mg/m^3)	1.920
Absorption coefficient (mm^{-1})	1.718
$F(000)$	1664
Crystal size (mm)	0.5 × 0.3 × 0.15
Crystal shape and colour	prism; yellow
Θ range for data collection (°)	3.42–27.50
Index ranges	$h = -13 \rightarrow 13$; $k = -24 \rightarrow 24$; $l = 0 \rightarrow 18$
Reflections collected	39 326
Standard reflections	3; frequency 60 min; intensity decay 4%
Scan	ω
Absorption correction	empirical SORTAV (Blessing, 1997 [16]) $T_{\min} = 0.447$, $T_{\max} = 0.721$
Scattering factors	International Tables, Vol. C, 4.2.6.8 and 6.1.1.4
Number of independent reflections	3331 [$R_{\text{int}} = 0.0631$]
Number of independent reflections ($I \geqslant 2\sigma(I)$)	2674
Completeness to theta = 25.98 (%)	99.8
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	3331/0/206
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0588P)^2 + 3.8941P]$, where $P = (F_o^2 + 2F_c^2)/3$
Goodness-of-fit on F^2	1.052
Final R indices ($I \geqslant 2\sigma(I)$)	$R_{\text{obs}} = 0.0402$, $wR_{\text{obs}} = 0.1018$
R indices (all data)	$R_{\text{all}} = 0.0532$, $wR_{\text{all}} = 0.1071$
Extinction method	SHELXL 97 (Sheldrick, 1997 [12])
Extinction coefficient	0.0025(3)
Largest differential peak and hole (e Å^{-3})	0.688 and −1.174
Used software	
Data collection	COLLECT Nonius BV, 1997–2000 [17]
Cell refinement	HKL Denzo and Scalepack Otwinowski & Minor, 1997 [18]
Data reduction	HKL Denzo and Scalepack Otwinowski & Minor, 1997 [18]
Molecular graphics	Platon for Windows Spek, 2002 [11]
Structure solution	SHELXS 86, Sheldrick, 1986 [15]
Structure refinement	SHELXL 97, Sheldrick, 1997 [12]

b-axis through which water molecules might escape (cf. Figs. 6 and 7). Indeed, releasing and incorporating of water molecules into the structure must be accompanied by appropriate inclination of the perchlorate molecule – cf. the pertinent angles Cd–O–Cl in [(Cd sadol $ClO_4)_2] \cdot H_2O$ and phase α (Table 4).

Phase β of [(Cd sadol $ClO_4)_2$] (Figs. 4 and 5) paradoxically does not absorb water, though the density of phase β is considerably lower than that of phase α (Tables 2 and 3). The cavities between the molecules in phase β are distributed more isotropically than in phase α as it can be deduced from the distances between the inversion centres on which the dimeric molecules of the Schiff bases reside. The distances are: 4 × 8.9435, 2 × 10.6739, 4 × 10.8667, 2 × 14.3531 Å for phase α while 2 × 9.5059, 2 × 9.8408, 4 × 10.0782, 4 × 11.2482, 4 × 13.6822 Å for phase α. Therefore it can also be deduced that the cavities between the dimeric molecules in phase β are more isotropic than those in phase α. The fact that only every second molecule in phase α can be hydrated while phase β is resistant to hydration indicates that the dimensions of the cavities in phase α are

Table 3
Crystal data and structure refinement for [(Cd sadol ClO_4)$_2$] – phase β

Formula	[{($C_{11}H_{15}CdN_2O_2$)(ClO_4)}]
Formula weight	838.21
Temperature (K)	291(2)
Wavelength (Å)	Mo (Kα) 0.71073
Instrument	4-circle diffractometer Nonius Kappa CCD,
Graphite monochromator	
Crystal system	monoclinic
Space group	$P2_1/n$
Unit cell dimensions	
a (Å)	9.5059(5)
b (Å)	9.8408(5)
c (Å)	16.4006(11)
α (°)	90
β (°)	99.210(10)
γ (°)	90
Volume (Å^3)	1514.43(15)
Number of reflections for the determination of the unit cell	5694
Θ range of reflections for the determination of the unit cell (°)	1.02–25.03
Z	2
Density (calculated) (Mg/m^3)	1.838
Absorption coefficient (mm^{-1})	1.645
$F(000)$	832
Crystal size (mm)	$0.20 \times 0.165 \times 0.15$
Crystal shape and colour	prism; yellow
Θ range for data collection (°)	3.69–25.15
Index ranges	$h = -11 \rightarrow 11$; $k = -11 \rightarrow 11$; $l = -19 \rightarrow 19$
Reflections collected	9824
Standard reflections	3; frequency 60 min; intensity decay 4%
Scan	ϕ
Absorption correction	none
Scattering factors	International Tables, Vol. C, 4.2.6.8 and 6.1.1.4
Number of independent reflections	3331 [$R_{\text{int}} = 0.0631$]
Number of independent reflections ($I \geqslant 2\sigma(I)$)	2039
Completeness to theta = 25.98 (%)	98.2
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	2661/0/206
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0432P)^2 + 1.6542P]$, where $P = (F_o^2 + 2F_c^2)/3$
Goodness-of-fit on F^2	1.043
Final R indices ($I \geqslant 2\sigma(I)$)	$R_{\text{obs}} = 0.0402$, $wR_{\text{obs}} = 0.0897$
R indices (all data)	$R_{\text{all}} = 0.0647$, $wR_{\text{all}} = 0.1038$
Extinction method	SHELXL 97 (Sheldrick, 1997 [12])
Extinction coefficient	0.0046(9)
Largest differential peak and hole (e Å^{-3})	0.554 and −0.441
Used software	
Data collection	COLLECT Nonius BV, 1997–2000 [17]
Cell refinement	HKL Denzo and Scalepack Otwinowski & Minor, 1997 [18]
Data reduction	HKL Denzo and Scalepack Otwinowski & Minor, 1997 [18]
Molecular graphics	Platon for Windows Spek, 2002 [11]
Structure solution	SHELXS 86, Sheldrick, 1986 [15]
Structure refinement	SHELXL 97, Sheldrick, 1997 [12]

about the critical size that enables water molecules to be incorporated into the structure.

Another interesting point is that water in [(Cd sadol ClO_4)$_2$]·H_2O is not coordinated to Cd atoms directly. A search in the Cambridge Crystallographic Database System [3,4] showed that the present structure is the first example of a compound where Cd is coordinated by perchlorate but not by water while both perchlorate and water molecules are present in the structure.

In contrast to the hydrated molecule, the perchlorates bonded to the water-free molecules of the Schiff bases are not disordered. The reason consists in the presence of the intramolecular hydrogen bonds in these water-free molecules. The hydrogen-bond donors in these molecules are the atoms O22 in [(Cd sadol ClO_4)$_2$]·H_2O and O2 in the phases α and β of [(Cd sadol ClO_4)$_2$], respectively, while the pertinent perchlorate oxygen is a hydrogen-bond acceptor in

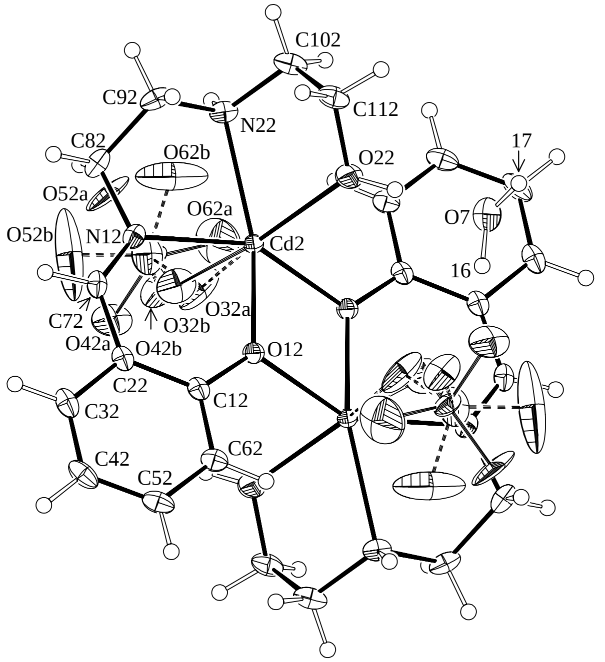

Fig. 1. View of the hydrated molecule in [(Cd sadol $ClO_4)_2] \cdot H_2O$ with 40% probability displacement ellipsoids.

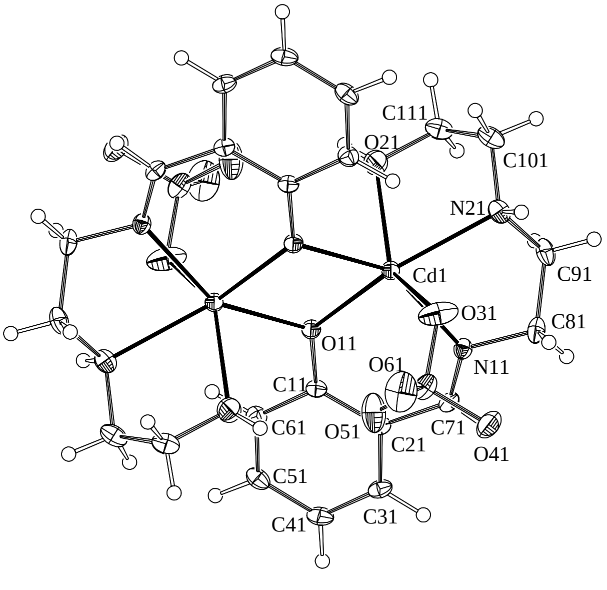

Fig. 2. View of the water-free molecule in [(Cd sadol $ClO_4)_2] \cdot H_2O$ with 40% probability displacement ellipsoids.

water-free molecules (Table 5). The O–H$\cdots$O hydrogen bonds anchor the perchlorates in the water-free molecules and prevent the perchlorates from being disordered. In the hydrated molecule the position of the perchlorate cannot be stabilized because the hydrogen-bond acceptor is the water oxygen. The displacement ellipsoids of the oxygens that belong to the disordered perchlorate are affected by smeared electron density due to disorder. This is the reason why the displacement

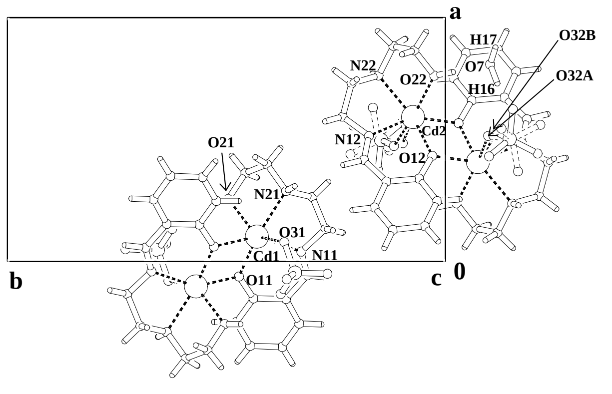

Fig. 3. Localization of the independent molecules of [(Cd sadol $ClO_4)_2] \cdot H_2O$ in the unit cell.

ellipsoids of the perchlorate oxygens are elongated (Fig. 1). The distances between water oxygens and perchlorate oxygens are similar to those as in $[Cd(H_2O)_6](ClO_4)_2$ (3.0 Å) [5]. The water molecule itself is involved in weak hydrogen bonds to perchlorate oxygens as a hydrogen-bond donor (Table 5). Several distances which indicate presence of the C–H$\cdots$O perchlorate hydrogen bonds [6] were found in [(Cd sadol $ClO_4)_2] \cdot H_2O$ and in phase β (Table 5).

The bond-lengths between Cd and O in the Cd–O–Cl perchlorate moiety in 13 hits ($R_{\mathrm{val}} < 0.10$) which were found in [3,4] span the range from 2.204 (Aqua-(tris(1-isopropyl-4-t-butyl-2-imidazolyl)phosphine)-perchlorato- cadmium perchlorate (RABHUX – a reference code of [4] as are other six-character chains composed of capital letters that are given below) [7]) to 2.653 Å (aqua-(1,4,7,10,13-pentathiacyclopentadecane)-(perchlorato-O)-cadmium(II) perchlorate (PAFHOT) [8]). The angle Cd–O–Cl perchlorate in the so far determined structures falls into the interval 117.53 ((*N*-bis(2-(methylthio)ethyl)-*N*-(6-pivaloylamido-2-pyridylmethyl) amine)-(perchlorato)-cadmium(ii) perchlorate methanol solvate (XALXUD) [9]) – 154.42° (catena(bis(μ_2-*N*,*N*-(2-pyridyl)-(4-pyridylmethyl)amine)-bis(perchlorato)cadmium) (GOHCIP) [10]).

The bond-distances and angles in the moiety $\mathrm{Cd} < \overset{\mathrm{O}}{\underset{\mathrm{O}}{\;}} > \mathrm{Cd}$ are sensitive to the overall bonding of Cd, i.e., they depend on the coordination number of the Cd atoms and also on the bonding of the bridging oxygens. The values regarding the molecules in our study are comparable to those in bis((2-*N*-(2-(2-aminoethylamino)ethyl)-salicylideneaminato-*O*,*O*,*N*,*N*′,*N*″)-ethanol-cadmium(II)) diperchlorate (VEGLAU) [3,4] which was determined by [1]. In this compound the appropriate distances equal to 2.250 and 2.284 Å.

The dimer molecules in all the studied compounds are similar. Table 6 lists the root-mean-square fits [11] of these molecules. The molecule of phase β differs most from the rest of the molecules. It is also of interest that the distance Cd(2)–O(22) significantly differs

Table 4
Selected bond lengths [Å] and angles [°] for $[(\mathrm{Cd\ sadol\ ClO_4})_2]\cdot\mathrm{H_2O}$, $[(\mathrm{Cd\ sadol\ ClO_4})_2]$ – phase α, $[(\mathrm{Cd\ sadol\ ClO_4})_2]$ – phase β

$[(\mathrm{Cd\ sadol\ ClO_4})_2]\cdot\mathrm{H_2O}$				$[(\mathrm{Cd\ sadol\ ClO_4})_2]$ – phase α		$[(\mathrm{Cd\ sadol\ ClO_4})_2]$ – phase β	
1st molecule (non-hydrated)		2nd molecule (hydrated)					
Bond lengths							
Cd(1)–O(11)	2.2674(16)	Cd(2)–O(12)	2.2633(16)	Cd–O(1)	2.270(2)	Cd–O(1)	2.248(3)
Cd(1)–O(11)$^{\mathrm{i}}$	2.1885(16)	Cd(2)–O(12)$^{\mathrm{ii}}$	2.1958(16)	Cd–O(1)$^{\mathrm{ii}}$	2.193(3)	Cd–O(1)$^{\mathrm{iii}}$	2.174(4)
Cd(1)–N(11)	2.2409(19)	Cd(2)–N(12)	2.246(2)	Cd–N(1)	2.239(3)	Cd–N(1)	2.244(5)
Cd(1)–N(21)	2.358(2)	Cd(2)–N(22)	2.357(2)	Cd–N(2)	2.351(3)	Cd–N(2)	2.308(5)
Cd(1)–O(21)	2.3576(19)	Cd(2)–O(22)	2.3040(17)	Cd–O(2)	2.361(3)	Cd–O(2)	2.364(5)
Cd(1)–O(31)	2.567(2)	Cd(2)–O(32A)	2.523(10)	Cd–O(3)	2.540(5)	Cd–O(3)	2.501(5)
		Cd(2)–O(32B)	2.511(18)				
O(11)–C(11)	1.329(3)	O(12)–C(12)	1.324(3)	O(1)–C(1)	1.322(4)	O(1)–C(1)	1.322(6)
N(21)–C(101)	1.477(3)	N(22)–C(102)	1.478(3)	N(2)–C(10)	1.470(7)	N(2)–C(10)	1.472(9)
C(101)–C(111)	1.511(4)	C(102)–C(112)	1.515(4)	C(10)–C(11)	1.514(7)	C(10)–C(11)	1.494(10)
O(21)–C(111)	1.429(3)	O(22)–C(112)	1.426(3)	O(2)–C(11)	1.422(6)	O(2)–C(11)	1.416(9)
Cl(1)–O(31)	1.448(2)	Cl(2A)–O(32A)	1.446(7)	Cl–O(3)	1.392(4)	Cl–O(3)	1.416(5)
		Cl(2B)–O(32B)	1.432(11)				
Cl(1)–O(41)	1.4188(19)	Cl(2A)–O(42A)	1.449(5)	Cl–O(4)	1.383(4)	Cl–O(4)	1.403(5)
		Cl(2B)–O(42B)	1.411(10)				
Cl(1)–O(51)	1.437(2)	Cl(2A)–O(52A)	1.375(4)	Cl–O(5)	1.403(5)	Cl–O(5)	1.419(6)
		Cl(2B)–O(52B)	1.396(11)				
Cl(1)–O(61)	1.433(2)	Cl(2A)–O(62A)	1.431(7)	Cl–O(6)	1.424(5)	Cl–O(6)	1.416(4)
		Cl(2B)–O(62B)	1.439(11)				
N(21)–H(141)	0.9495	N(22)–H(142)	0.8643	N(2)–H(14)	0.8344	N(2)–H(14)	0.8997
O(21)–H(151)	0.8423	O(22)–H(152)	0.8903	O(2)–H(15)	0.8583	O(2)–H(15)	0.8422
		O(7)–H(16)	0.9898				
		O(7)–H(17)	0.8794				
Bond angles							
O(21)–Cd(1)–O(31)	137.73(7)	O(22)–Cd(2)–O(32A)	154.8(3)	O(2)–Cd–O(3)	138. 15(14)	O(2)–Cd–O(3)	154.8(2)
		O(22)–Cd(2)–O(32B	147.3(5)				
Cd(1)–O(31)–Cl(1)	115.64(13)	Cd(2)–O(32a)–Cl(2a)	139.5(7)	Cd–O(3)–Cl	119. 5(3)	Cd–O(3)–Cl	100.4(1)
		Cd(2)–O(32b)–Cl(2b)	132.5(12)				
Cd(1)–O(11)–Cd(1)$^{\mathrm{i}}$	100.75(6)	Cd(2)–O(12)–Cd(2)$^{\mathrm{ii}}$	101.55(6)	Cd–O(1)–Cd$^{\mathrm{ii}}$	100.4(1)	Cd–O(1)–Cd$^{\mathrm{iii}}$	100.4(1)

Symmetry code: (i) $-x, -y+1, -z+1$; (ii) $-x+1, -y, -z+1$; (iii) $-x+2-y+1, -z+1$.

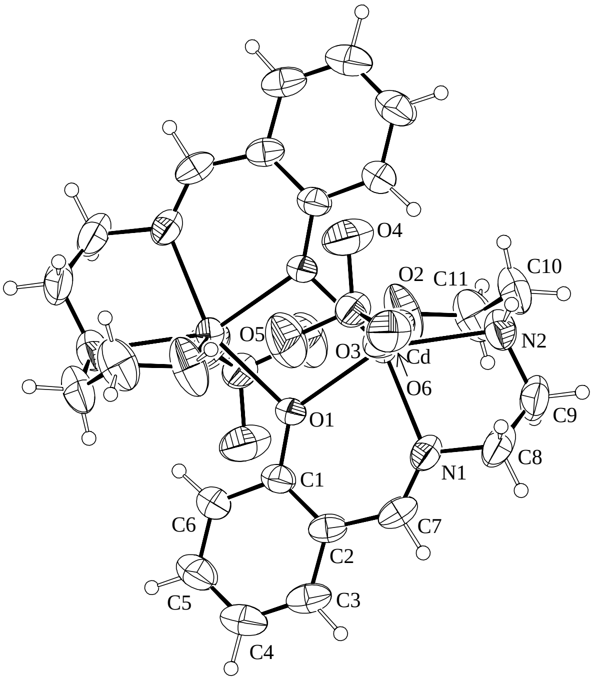

Fig. 4. A molecule of $[(\mathrm{Cd\ sadol\ ClO_4})_2]$ – phase β with 40% probability displacement ellipsoids.

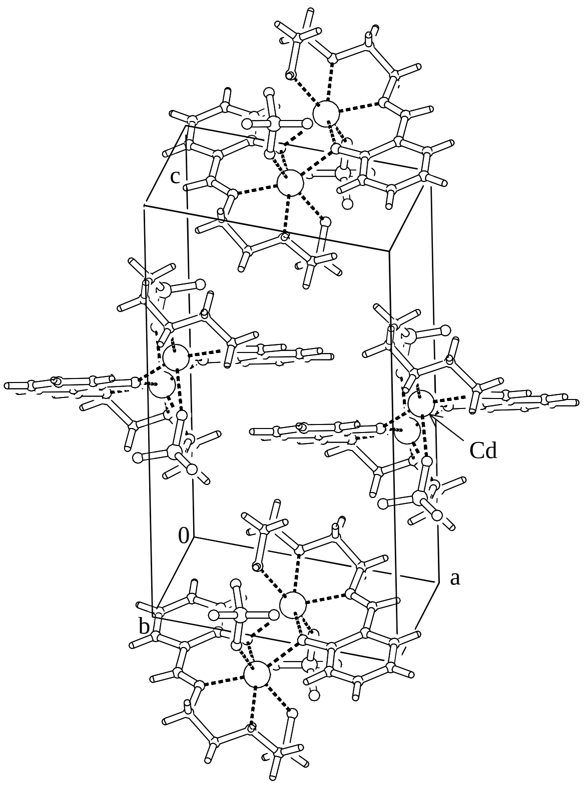

Fig. 5. View of the unit cell of $[(\mathrm{Cd\ sadol\ ClO_4})_2]$ – phase β.

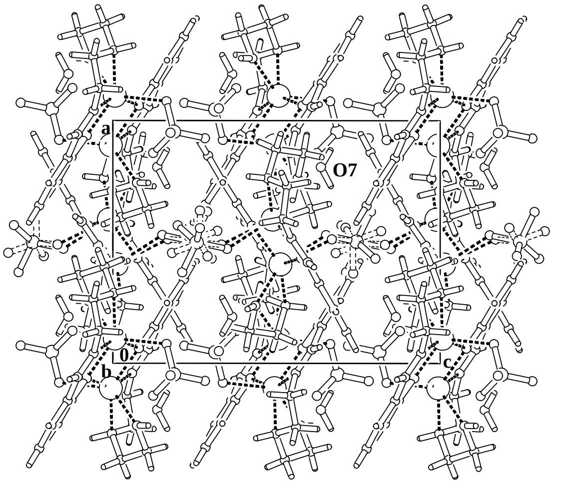

Fig. 6. View of the unit cell of [(Cd sadol $ClO_4)_2$]$\cdot H_2O$ along the *b*-axis. The water oxygen O7 is labelled. Cf. Fig. 7.

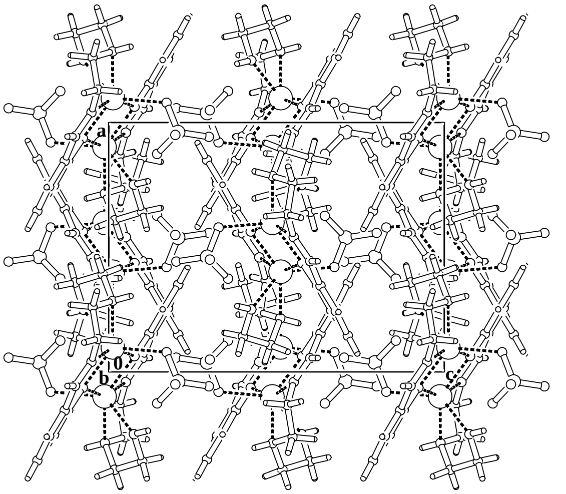

Fig. 7. View of the unit cell of [(Cd sadol $ClO_4)_2$] – phase α along the *b*-axis. Cf. Fig. 6.

from the analogous distances in the studied compound (Table 4).

4. Supplementary data

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC20 5645, CCDC205646, CCDC205647 for [(Cd sadol $ClO_4)_2$]$\cdot H_2O$, [(Cd sadol $ClO_4)_2$] – phase α and [(Cd sadol $ClO_4)_2$] – phase β, respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: (44) 1223 336-033; e-mail: deposit@ccdc.cam.ac.uk).

Table 5
Distances (Å) and angles (°) of the hydrogen-bond networks in [Cd sadol $ClO_4]_2 \cdot H_2O$ (1st and 2nd molecules) and in both modifications of [(Cd sadol $ClO_4)_2$]

D–H...A	D–H	H...A	D...A	∠) D–H...A
[Cd sadol $ClO_4]_2 \cdot H_2O$ 1st molecule – non-hydrated				
O21–H151...O51^{i}	0.84	2.20	2.859(3)	134.5
O21–H151...O62A^{x}	0.84	2.61	3.250(5)	134.2
N21–H141...O42A^{ii}	0.95	2.26	3.150(4)	155.5
N21–H141...O42B^{ii}	0.95	2.36	3.095(6)	134.4
C31–H11...O52A^{ix}	0.97	2.46	3.153(4)	127.9
C111–H121...O62A^{x}	0.97	2.43	3.128(5)	129.0
[Cd sadol $ClO_4]_2 \cdot H_2O$ 2nd molecule – hydrated				
O22–H152...O7	0.89	1.78	2.675(3)	179.0
N22–H142...O61^{iii}	0.86	2.61	3.265(3)	133.6
N22–H142...O62B	0.86	2.61	3.288(10)	136.2
O7–H16...O32A^{iv}	0.99	2.17	3.018(12)	142.7
O7–H16...O42A^{iv}	0.99	2.18	3.092(5)	152.0
O7–H16...O32B^{iv}	0.99	2.32	3.15(2)	140.1
O7–H17...O31^{v}	0.88	2.52	3.163(3)	130.9
O7–H17...O61^{v}	0.88	2.25	3.123(4)	169.9
C72–H52...O42A^{ii}	0.97	2.58	3.511(5)	162.3
C1O2–H112...O61^{iii}	0.97	2.52	3.165(3)	123.8
[(Cd sadol $ClO_4)_2$] – phase α				
O2–H15...O6^{iv}	0.86	2.12	2.839(6)	141.8
N2–H14...O4^{vi}	0.83	2.50	3.215(5)	144.7
[(Cd sadol $ClO_4)_2$] – phase β				
O2–H15...O5^{vii}	0.84	1.97	2.764(7)	156.8
N2–H14...O4^{viii}	0.90	2.43	3.205(7)	145.1
N2–H14...O6^{viii}	0.90	2.51	3.232(7)	137.2
C1O–H11...O6^{viii}	0.97	2.72	3.260(9)	115.6

i: $-x, -y+1, -z+1$; ii: $x, -y+1/2, z+1/2$; iii: $x+1, -y+1/2, z-1/2$; iv: $-x+1, -y, -z+1$; v: $-x+1, y-1/2, -z+3/2$; vi: $x+1/2, y, -z+1/2$; vii: $-x+2, -y+1, -z+1$; viii: $-x+2, -y, -z+1$; ix: $-1+x, y, z$; x: $-x+1, y+1/2, -z+1/2$.

Table 6
Unit-weight root-mean-square fit (Å) calculated by PLATON (Spek, 2002) for the pairs of the Schiff bases without H-atoms and including Cd atoms

	[(Cd sadol $ClO_4)_2$]$\cdot H_2O$ – unhydrated molecule	[(Cd sadol $ClO_4)_2$] – phase α	[(Cd sadol $ClO_4)_2$] – phase β
[(Cd sadol $ClO_4)_2$]$\cdot H_2O$ – hydrated molecule	0.081	0.066	0.177
[(Cd sadol $ClO_4)_2$]$\cdot H_2O$ – unhydrated molecule		0.037	0.133
[(Cd sadol $ClO_4)_2$] – phase α			0.130

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