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Simple synthetic method and structural characteristics of (1,3-propanediaminetetraacetato)cobalt(II) complexes: uniform crystal packing in a series of metal(II) complexes with 1,3-propanediaminetetraacetate ligand

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Abstract

Starting from Ba[Ba(1,3-pdta)]$\cdot$2H$_2$O three new hexadentate cobalt(II) complexes $[M^{II}(H_2O)_6][Co^{II}(1,3\text{-pdta})]\cdot 2H_2O$ (M^{II} = Ba (**1**), Co (**2**) and Mg (**3**)) (where 1,3-pdta represents the 1,3-propanediaminetetraacetate ion) have been prepared and characterized. Presented in this paper, the crystal structures of the complexes containing Co^{II} and Mg^{II} counter cations are isomorphic, as are the other crystal structures of metal(II) complexes with 1,3-pdta ligand, so far reported in the literature. The complexes crystallize in the space group *Pnna* of the orthorhombic crystal system. The structural unit consists of discrete $[Co^{II}(1,3\text{-pdta})]^{2-}$ and $[M^{II}(H_2O)_6]^{2+}$ octahedra, and two water solvent molecules all of which lie on a twofold axis of symmetry. The complex cations and anions alternate in the crystal lattice each being octahedrally surrounded by the counter ions. Electronic absorption spectra of $[Co^{II}(1,3\text{-pdta})]^{2-}$ complexes are presented and discussed in terms of octahedral distortion in edta-type Co^{II} complexes.

Keywords: Co^{II}-edta-type complexes; Crystal packing; Electronic absorption spectra

1. Introduction

Transition metal complexes of edta (ethylenediaminetetraacetate ion) and edta-like ligands show varieties in coordination number (C.N.) and stereochemistry. Factors governing the stereochemistry of M-edta-type complexes include the d-electron configuration and the size of the central metal ion (M). These influence differences in bond lengths (M–N and M–O), ring strain, and the ligand configuration [1–6]. Besides that, the role of chelate ring size appeared to be important in determining C.N., geometry and complex stability [7].

For complexes containing edta or edta-like ligands forming five-membered diamine rings (E rings), the *gauche* character of the ethylenic backbone was found to be significant factor in determining the nature of the coordination polyhedron [3,8]. The *staggered* ethylenic backbone of edta, with an N–C–C–N torsion angle of nearly 55°, tends to cause the six donor atoms to adopt a pseudooctahedral configuration when the metal–donor atom bonds are shorter than approximately 2.05 Å [9]. Although longer bond distances favor the formation of structures twisted toward a trigonal prism, a truly trigonal-prismatic configuration is not favored in the edta complexes because this would require the ethylenediamine ring system to be planar [3,8]. However,

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eclipsed ethylenic backbone of edta, with an N–C–C–N torsion angle of 0° was found in the crystal structure of $Na_2[Fe^{II}(edta)(H_2O)]\cdot 2NaClO_4\cdot 6H_2O$ [10] having mono-capped trigonal-prismatic geometry.

Cobalt(II) ion with ligands edta and *o*-phdta (*o*-phenylenediaminetetraacetate ion) forms hexadentate complexes, $[Co^{II}(H_2O)_4Co^{II}(edta)]\cdot 2H_2O$, and $Na_2[Co^{II}(H_2O)_6][Co^{II}(o\text{-phdta})]_2\cdot 4H_2O$, for which structural and spectral characteristics are available [8]. Both complex anions are significantly distorted from an ideal octahedral structure. The coordination polyhedron of $[Co^{II}(o\text{-phdta})]^{2-}$ complex anion containing the nearly planar N–C–C–N linkage of *o*-phdta is twisted much more away from an octahedral and toward trigonal-prismatic configuration than is $[Co^{II}(edta)]^{2-}$.

The size and flexibility of the trimethylenediamine ring (T) in $[M(1,3\text{-pdta})]^{n-}$ (M = Co^{III}, [11] Cr^{III}, [12] Rh^{III}, [12] Fe^{III}, [5,13] V^{III}, [14] Cu^{II} [15,16] and Ni^{II} [17]) complexes, with respect to the $[M(edta)]^{n-}$ (Co^{III}, [18] Fe^{III}, [19] Co^{II}, [8,20] Ni^{II} [21] and Cu^{II}, [20]), serve to relieve some of the angular strain in the equatorial plane, as evidenced from the already published crystal data [22] and from the results presented in this paper. We report here a simple method for the preparation of (1,3-propanediaminetetraacetato)cobalt(II) complexes starting from the corresponding Ba^{II} complex, $Ba[Ba(1,3\text{-pdta})]\cdot 2H_2O$ [15]. Three complexes of Co^{II}, containing different counter ions, $[M^{II}(H_2O)_6][Co^{II}(1,3\text{-pdta})]\cdot 2H_2O$ (M^{II} = Ba (**1**), Co (**2**) and Mg (**3**)) have been prepared and characterized. Crystals of the complexes **2** and **3** have been subjected to X-ray analysis. The electronic absorption spectra of cobalt(II) complexes are discussed.

2. Experimental

2.1. Compounds preparation

All commercially obtained reagent-grade chemicals were used without further purification. The preparation of barium (1,3-propanediaminetetraacetato)barium(II) dihydrate, $Ba[Ba(1,3\text{-pdta})]\cdot 2H_2O$, has been reported elsewhere [15,23].

2.1.1. Preparation of hexaaquabarium (1,3-propanediaminetetraacetato)cobalt(II) dihydrate, $[Ba(H_2O)_6][Co^{II}(1,3\text{-pdta})]\cdot 2H_2O$ (1)

2.81 g of $CoSO_4\cdot 7H_2O$ (0.0100 mol) was dissolved in 25 cm^3 of H_2O at 60 °C. To this solution, solid $Ba[Ba(1,3\text{-pdta})]\cdot 2H_2O$ (6.13 g, 0.0100 mol) was added and the reaction mixture was heated (60 °C) with stirring for 20 min. The precipitated $BaSO_4$ was removed by filtration. To the dark pink filtrate, the same volume of ethanol was added and the solution was left to stand in a refrigerator overnight. Light pink crystals of $[Ba(H_2O)_6][Co^{II}(1,3\text{-pdta})]\cdot 2H_2O$ (**1**) were collected, washed with ethanol, then ether, and air-dried. Yield: 4.50 g (70%). Recrystallization was accomplished from hot water by adding ethanol and cooling of the solution in a refrigerator. *Anal.* Calc. for $[Ba(H_2O)_6][Co^{II}(1,3\text{-pdta})]\cdot 2H_2O$ (**1**), $BaCoC_{11}H_{30}N_2O_{16}$ (FW = 642.63): C, 20.56; H, 4.71; N, 4.36. Found: C, 21.11; H, 4.24; N, 4.50%.

2.1.2. Preparation of hexaaquacobalt(II) (1,3-propanediaminetetraacetato)cobalt(II) dihydrate, $[Co^{II}(H_2O)_6][Co^{II}(1,3\text{-pdta})]\cdot 2H_2O$ (2)

To the dark pink solution obtained after removing $BaSO_4$ in Section 2.1.1 a solid $CoSO_4\cdot 7H_2O$ (2.81 g, 0.0100 mol) was added and the mixture was stirred with heating (60 °C) for 20 min. The precipitated $BaSO_4$ was removed by filtration. To the obtained filtrate 5–6 ml of ethanol was added and the solution was left in a refrigerator for several hours. The light pink crystals of $[Co^{II}(H_2O)_6][Co^{II}(1,3\text{-pdta})]\cdot 2H_2O$ (**2**) were collected, washed with ethanol, then ether and air-dried. Yield: 4.7 g (83%). Recrystallization was easily achieved from hot water by adding ethanol and cooling at room temperature. *Anal.* Calc. for $[Co^{II}(H_2O)_6][Co^{II}(1,3\text{-pdta})]\cdot 2H_2O$ (**2**), $Co_2C_{11}H_{30}N_2O_{16}$ (FW = 564.23): C, 23.42; H, 5.36; N, 4.96. Found: C, 23.49; H, 5.32; N, 5.11%.

2.1.3. Preparation of hexaaquamagnesium (1,3-propanediaminetetraacetato)cobalt(II) dihydrate, $[Mg(H_2O)_6][Co^{II}(1,3\text{-pdta})]\cdot 2H_2O$ (3)

$[Mg(H_2O)_6][Co^{II}(1,3\text{-pdta})]\cdot 2H_2O$ (**3**) was prepared by the similar procedure as for complex **2**. Solid $MgSO_4\cdot 7H_2O$ (2.47 g, 0.0100 mol) was added to the dark pink filtrate obtained after removing $BaSO_4$ in Section 2.1.1 The mixture was stirred with heating for 20 min at 60 °C. The precipitated $BaSO_4$ was removed and complex **3** was crystallized by adding 5–6 ml of ethanol and cooling in a refrigerator for several hours. The orange–red crystals of $[Mg(H_2O)_6][Co^{II}(1,3\text{-pdta})]\cdot 2H_2O$ (**3**) were filtered, washed with ethanol, then ether, and air-dried. Yield: 4.16 g (78%). Recrystallization of the orange–red compound was easily achieved from hot water by adding ethanol and cooling at room temperature. *Anal.* Calc. for $[Mg(H_2O)_6][Co^{II}(1,3\text{-pdta})]\cdot 2H_2O$ (**3**), $MgCoC_{11}H_{30}N_2O_{16}$ (FW = 529.61): C, 24.95; H, 5.71; N, 5.29. Found: C, 24.64; H, 5.66; N, 5.49%.

2.2. Physical measurements

The electronic absorption spectra were recorded on a Perkin–Elmer spectrophotometer and for these measurements about 5×10^{-2} M aqua solutions were used. Elemental microanalyses for carbon, hydrogen, and nitrogen were done by the Department of Chemistry, University of Edinburgh, UK.

2.3. Crystallographic data collection and refinement of the structures

The crystal data for $[Co^{II}(H_2O)_6][Co^{II}(1,3\text{-pdta})]\cdot 2H_2O$ (**2**) and $[Mg(H_2O)_6][Co^{II}(1,3\text{-pdta})]\cdot 2H_2O$ (**3**) and the parameters of data collection are summarized in Table 1. The intensity data were measured with a KM4CCD kappa-geometry diffractometer [24] using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 120(2) K. The structures were solved by direct methods using SHELXS-97 [25] and refined by least-squares techniques with SHELXL-97 [26]. The intensity data were corrected for Lp effects as well as for absorption. Anisotropic thermal parameters were employed for the non-hydrogen atoms. All hydrogen atoms were found in the Fourier map and refined isotropically. A Siemens Stereochemical Workstation was used to prepare drawings [27].

Table 1
Crystal data summary for $[Co^{II}(H_2O)_6][Co^{II}(1,3\text{-pdta})]\cdot 2H_2O$ (**2**) and $[Mg(H_2O)_6][Co^{II}(1,3\text{-pdta})]\cdot 2H_2O$ (**3**)

Formula	$CoCoC_{11}H_{30}N_2O_{16}$	$MgCoC_{11}H_{30}N_2O_{16}$
Formula weight	564.23	529.61
Temperature (K)	120 (2)	
Wavelength Mo Kα (Å)	0.71073	
Crystal system	orthorhombic	
Space group	*Pnna*	
a (Å)	13.216(3)	13.214(3)
b (Å)	11.693(2)	11.648(2)
c (Å)	13.743(3)	13.803(3)
V (Å^3)	2123.8(8)	2124.5(8)
Z	4	
D_{calc} (g cm^{-3})	1.765	1.656
μ (mm^{-1})	1.643	0.919
$F(0\,0\,0)$	1168	1108
Crystal size (mm)	0.45 × 0.40 × 0.30	0.60 × 0.20 × 0.10
θ Range (°)	4.09–25.02	4.10–25.02
Index ranges	$-15 \le h \le 13$ $-13 \le k \le 11$ $-16 \le l \le 15$	$-14 \le h \le 15$ $-10 \le k \le 13$ $-16 \le l \le 16$
T_{min}, T_{max}	0.525, 0.638	0.707, 1.000
N_{total}	10 212	15 373
$N_{ind.}$	1870	1872
$N_{obs.}$	1812 $[I > 2\sigma(I)]$	1799 $[I > 2\sigma(I)]$
Refinement method	full-matrix least-squares F^2	
$S(F^2)$	1.066	1.202
R	0.0216 $[I > 2\sigma(I)]$	0.0320 $[I > 2\sigma(I)]$
wR	0.0589	0.0678
Weighting scheme	$w = 1/[s^2(F_o)^2 + (0.0334P)^2 + 1.5881P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[s^2(F_o)^2 + (0.0287P)^2 + 1.5343P]$ where $P = (F_o^2 + 2F_c^2)/3$
ρ_{max} ρ_{min} (e Å^{-3})	0.332, −0.409	0.309, −0.375

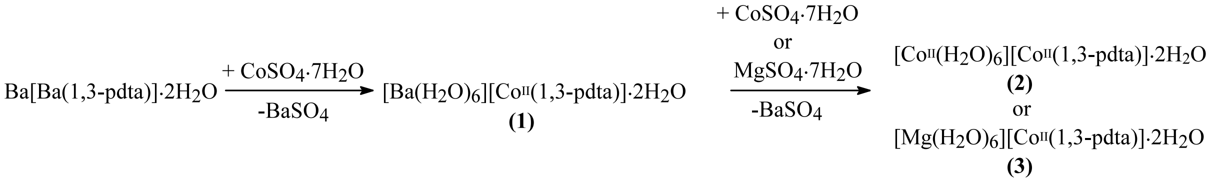
3. Results and discussion

The $[M^{II}(H_2O)_6][Co^{II}(1,3\text{-pdta})]\cdot 2H_2O$ (M^{II} = Ba (**1**), Co (**2**) and Mg (**3**); 1,3-pdta is 1,3-propanediaminetetraacetate), $[Mg(H_2O)_6][Cu^{II}(1,3\text{-pdta})]\cdot 2H_2O$, [15] and $[Mg(H_2O)_6]$ $[Ni^{II}(1,3\text{-pdta})]\cdot 2H_2O$ [17] complexes were prepared applying the same method starting from the corresponding Ba^{II} complex, $Ba[Ba(1,3\text{-pdta})]\cdot 2H_2O$. The course of the reaction for preparation of the cobalt(II) complexes is shown in Scheme 1. All three cobalt(II) compounds were obtained in a very good yield.

3.1. The crystal structures of $[Co^{II}(H_2O)_6][Co^{II}(1,3\text{-pdta})]\cdot 2H_2O$ (2) and $[Mg(H_2O)_6][Co^{II}(1,3\text{-pdta})]\cdot 2H_2O$ (3)

The crystals of the studied complexes $[M^{II}(H_2O)_6][Co^{II}(1,3\text{-pdta})]\cdot 2H_2O$ (M^{II} = Co (**2**) and Mg (**3**) appear to be isomorphic with all other (1,3-propanediaminetetraacetato) metal(II) complexes ($[M^{II}(H_2O)_6][Cu^{II}(1,3\text{-pdta})]\cdot 2H_2O$ (M^{II} = Mg [15] or Mn [16], and $[Mg(H_2O)_6][Ni^{II}(1,3\text{-pdta})]\cdot 2H_2O$ [17]). An ORTEP drawing of the $[Mg(H_2O)_6][Co^{II}(1,3\text{-pdta})]\cdot 2H_2O$ (**3**), is depicted in Fig. 1, where the numbering scheme adopted for the respective atoms is also given. Metal–ligand bond lengths and angles, averaged for the two structures, are listed in Table 2.

The structural units in the crystal structures of **2** and **3** consist of $[Co^{II}(1,3\text{-pdta})]^{2-}$ octahedra and, respectively, $[Co(H_2O)_6]^{2+}$ or $[Mg(H_2O)_6]^{2+}$ octahedra, as well as two water solvent molecules all of which lie on a special position in the unit cell. The highest symmetry (C_2) axis of the complex anion passes through the Co and C2 atoms and bisects the N(1)–Co(1)–N(1)^a bond angle (^{a} stands for the symmetry operation x, $0.5-y$, $0.5-z$) making the two glycinate (R) rings (as well as the G rings) identical. The format for describing the various chelate rings formed in these kinds of chelates was credited to Weakliem and Hoard [18]. According to the authors, G rings are those whose mean planes are more nearly parallel to the N–M–N plane and R rings are those rings whose mean planes are more nearly perpendicular to the N–M–N plane. In both structures, the six-membered (T) ring adopts a flexible *twist-boat* conformation with the average torsion angle moduli of 43.8°. The quantity that might be comparable with the value of N–C–C–N torsion angle describing the ethylenic backbone of edta ligand (approximately 55° for staggered conformation, vide supra) is the interplanar angle between the planes defined by N(1), C(1), C(1)^a and N(1)^a, C(1)^a, C(1). This angle adopts the values of 67.1° and 66.8° in the crystal structures of **2** and **3**, indicating that the stereochemistry of the N–C–C–C–N linkage should favor octahedral rather than trigonal prismatic coordination. The R rings are almost



$$\mathrm{Ba[Ba(1,3\text{-}pdta)]\cdot 2H_2O} \xrightarrow[\mathrm{-BaSO_4}]{\mathrm{+\,CoSO_4\cdot 7H_2O}} \underset{\mathbf{(1)}}{\mathrm{[Ba(H_2O)_6][Co^{II}(1,3\text{-}pdta)]\cdot 2H_2O}} \xrightarrow[\mathrm{-BaSO_4}]{\mathrm{+\,CoSO_4\cdot 7H_2O\ or\ MgSO_4\cdot 7H_2O}} \underset{\mathbf{(2)}}{\mathrm{[Co^{II}(H_2O)_6][Co^{II}(1,3\text{-}pdta)]\cdot 2H_2O}}\ \text{or}\ \underset{\mathbf{(3)}}{\mathrm{[Mg(H_2O)_6][Co^{II}(1,3\text{-}pdta)]\cdot 2H_2O}}$$

Scheme 1.

flat, while the G-rings are much more puckered and are halfway between an *envelope* and *twist* conformations. As can be seen from Table 2 the Co–O bond distances are greater in the R rings than in the G rings, the difference being 0.056 Å, and the Co–N bonds are by 0.060 Å longer than the average Co–O bond. Examination of the bond angles shows that the reported $\mathrm{Co^{II}}$-1,3-pdta complexes are less distorted from octahedral geometry than the $\mathrm{Co^{II}}$-edta complex [8] (for detailed discussion see Section 3.2).

In the presented structures, as in all other crystal structures of metal(II) with 1,3-pdta ligand so far reported [15–17], the discrete $[\mathrm{Co^{II}(1,3\text{-}pdta)}]^{2-}$ and $[\mathrm{M^{II}(H_2O)_6}]^{2+}$ octahedra alternate in the crystal in such a way that each complex anion is surrounded by six complex cations situated at the corners of a distorted octahedron and vice versa. As a result, not only the first but also the second metal coordination sphere displays nearly octahedral geometry. The Co···Co and Mg···Co distances range from 5.272 to 7.944 and from 5.278 to 7.936 Å, respectively. The shortest and the longest metal···metal separations add up to a value of the lattice parameter ‘*a*’, as both metals are situated on the twofold axis parallel to *x*-direction. Such alternating arrangement of the cationic and anionic species might indicate a nearly spherical charge distribution on each of the complex units, which is consistent with their first coordination sphere being close to a regular octahedron (vide infra). Apart from the electrostatic interactions, the $[\mathrm{Co^{II}(1,3\text{-}pdta)}]^{2-}$ and $[\mathrm{M^{II}(H_2O)_6}]^{2+}$ octahedra are hydrogen bonded to form a hydrogen-bond layer parallel to (1 0 0) lattice plane (Fig. 2(a)) in which the metal aqua ions act solely as donors to carboxylate oxygens [O(2), O(3) and O(4)] acting as acceptors. The solvent water molecules [O(4)W and O(5)W], situated in between the (1 0 0) layers, act as double donors and double acceptors and help to join the neighboring layers (Fig. 2(b)). This interlayer bonding is supplemented by hydrogen bonds from water molecules of $\mathrm{M^{II}}$ aqua complex to O(1) oxygen atoms from the G rings. This way the coordinated carboxylate oxygens act as single and the uncoordinated as double H-bond acceptors. No

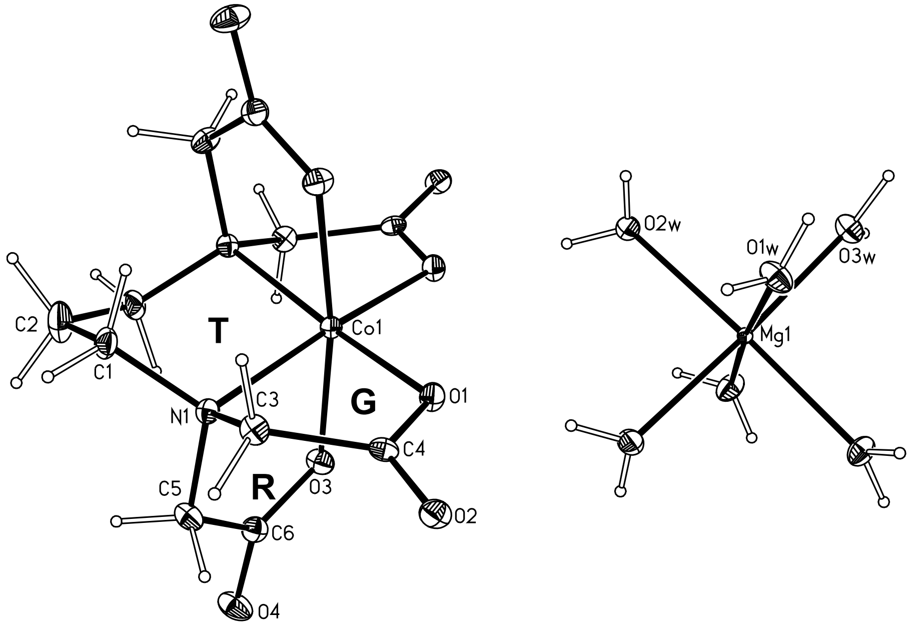


Fig. 1. The ORTEP drawing of the $[\mathrm{Co^{II}(1,3\text{-}pdta)}]^{2-}$ and $[\mathrm{Mg(H_2O)_6}]^{2+}$ octahedra. As the molecules are situated on a twofold symmetry axis, generation of the second half of the complex cation and anion requires the symmetry operation x, $0.5-y$, $0.5-z$.

Table 2
Average metal–ligand bond distances (Å) and angles (°) for $[Co^{II}(1,3\text{-pdta})]^{2-}$ units and metal–water bond distances and valency angles for $[Co(H_2O)_6]^{2+}$ and $[Mg(H_2O)_6]^{2+}$ units, as observed in **2** and **3**

Co(1)–O(1)	2.055(2)	Co1–O3	2.111(2)
Co(1)–N(1)	2.142(2)		
O(1)–Co(1)–O(1) [a]	101.7(1)	O3–Co1–N1 [a]	93.96(8)
O(1)–Co(1)–N(1)	81.85(8)	O1–Co1–O3	93.77(8)
O(1)–Co(1)–N(1) [a]	171.42(8)	O3–Co1–N1	80.48(8)
N(1)–Co(1)–N(1) [a]	95.7(1)	O3–Co1–O3 [a]	171.8(1)
O(1)–Co(1)–O(3) [a]	91.43(6)		
Co(2)–O(1)W/Mg(1)–O(1)W	2.094(1)/2.052(2)		
Co(2)–O(2)W/Mg(1)–O(2)W	2.079(1)/2.069(2)		
Co(2)–O(3)W/Mg(1)–O(3)W	2.073(1)/2.070(2)		
O(1)W–Co(2)–O(1)W [a]/O(1)W–Mg(1)–O(1)W [a]	175.14(7)/175.2(1)		
O(1)W–Co(2)–O(3)W [a]/O(1)W–Mg(1)–O(3)W [a]	87.08(5)/87.66(7)		
O(1)W–Co(2)–O(3)W/O(1)W–Mg(1)–O(3)W	89.60(5)/89.09(7)		
O(3)W–Co(2)–O(3)W [a]/O(3)W–Mg(1)–O(3)W [a]	93.91(7)/94.20(9)		
O(1)W–Co(2)–O(2)W/O(1)W–Mg(1)–O(2)W	91.57(5)/91.54(7)		
O(2)W–Co(2)–O(3)W/O(2)W–Mg(1)–O(3)W	88.54(5)/88.56(6)		
O(1)W–Co(2)–O(2)W [a]/O(1)W–Mg(1)–O(2)W [a]	91.90(5)/91.87(7)		
O(2)W–Co(2)–O(3)W [a]/O(2)W–Mg(1)–O(3)W [a]	177.19(5)/177.11(7)		
O(2)W–Co(2)–O(2)W [a]/O(2)W–Mg(1)–O(2)W [a]	89.05(8)/88.7(1)		

[a] Symmetry code: $x,\ -y+0.5,\ -z+0.5$.

carboxylate bridges, commonly present in the crystal structures of Co^{II}-edta-type and M^{III}-1,3-pdta complexes [22], are observed.

3.2. Structural parameters correlating geometry of six-coordinate Co^{II}-edta-type complexes

The metal ion surrounded by six ligands is usually considered in terms of distortions from either an octahedral or trigonal-prismatic configuration. The parameters used here for describing the distortion of six-coordinate Co^{II}-edta-type complexes **2**–**9** are twist angle (Φ) [28] and the mean deviation from octahedral angles (average (ΔO_h)), Table 3. The Co^{II}-edta-type complexes **2**, **3**, **5** [8] and **9** [8] are hexadentate, whereas **4**, [29] **6**, [30] **7** [31] and **8** [32] are pentadentate complexes in which monodentate ligand (H_2O) displaces in-plane (G) glycinate ring of edta. Both parameters (Φ and av. (ΔO_h)) reflect well the varieties in distortion of six-coordinate Co^{II}-edta-type complexes **2**–**9**, and a decrease of Φ with an increase of the mean deviation from octahedral angles (Table 3).

The investigated complexes **2** and **3** containing flexible cobalt(II)-1,3-propanediamine ring system show the lowest degree of distortion from octahedral configuration of all other complexes considered (av. (ΔO_h) and Φ amount to 6.4° and 56.8°, respectively). The other two hexadentate complexes **5** and **9** are twisted much more away from octahedral toward trigonal-prismatic configuration and the mean deviations from octahedral angles are equal to 10.1° (for **5**) and 16.7° (for **9**). For those complexes (**2**, **3**, **5** and **9**) that contain ligands differing only in the structure of diamine chain (1,3-pdta, edta and *o*-phdta; *o*-phdta is *o*-phenylenediaminetetraacetate ion) the twist angle (Φ) decreases in order 56.8° (**2** and **3**) $>41.8°$ (**5**) $>20.7°$ (**9**) with increasing rigidity of the diamine part. The pentadentate complex anion $[Co^{II}(Hedta)(H_2O)]^-$ (**6**) shows almost the same degree of distortion from ideal octahedron as its hexadentate congener $[Co^{II}(edta)]^{2-}$ (**5**) as indicated by twist angles of 40.7° and 41.8°, respectively. Nevertheless, somewhat lower degree of distortion was found in pentadentate complex anion $[Co^{II}(edta)(H_2O)]^{2-}$ (**4**) for which the twist angle is 47.7°, Table 3. The variation in distortion found for **4** and **6** may arise from differences in their crystal packing. While **4** is a crystalline three-dimensional polymer, where the Co ions, belonging to three different units (CoN_2O_4, CoO_4 and CoO_6), are bridged by carboxylate groups from the edta ligand, in the crystal structure of **6** the $[Co^{II}Hedta(H_2O)]^-$ anions are bridged by carboxylate groups to the Sr cations to form two-dimensional polymeric structure. Unusually high octahedral distortion was found in pentadentate complexes **7** and **8** for which the average twist angles amount to 27.6° and 26.5°, respectively. The reason for this lies in the fact that in **7** and **8** one of the ligand arms is dissociated, but not completely, so one of the oxygen atoms from this arm is still at a distance of 2.7 Å from Co^{II} ion. Thus, these types of compounds can be treated as $6+1$ coordinate complexes [31,32].

3.3. Electronic absorption spectra of cobalt(II) complexes

The electronic absorption spectra of $[M^{II}(H_2O)_6][Co^{II}(1,3\text{-pdta})]\cdot 2H_2O$ complexes ($M^{II}=$ Ba

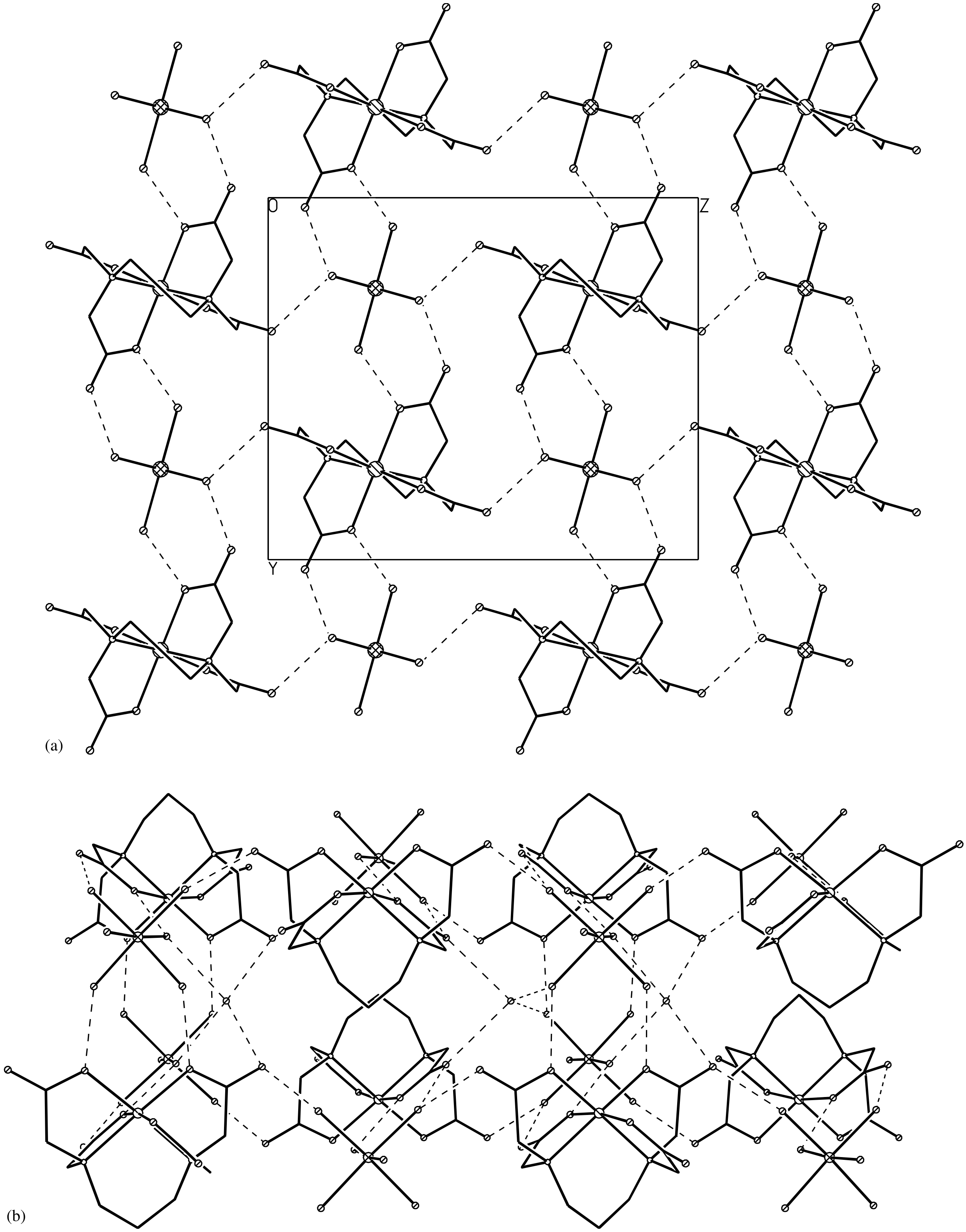


Fig. 2. Illustration of the preferential mode of packing of metal(II) 1,3-pdta complexes. (a) View of the (1 0 0) layer shows alternating complex cations and anions connected by hydrogen bonds. (b) View along [0 1 0] direction illustrates the role of uncoordinated water molecules in forming hydrogen bonds in between the (1 0 0) layers.

Table 3
Structural parameters correlating geometry of six-coordinate Co^{II}-edta-type complexes

Complex	Φ [a] (°)	(ΔO_h) (°)	Reference
[Co(H$_2$O)$_6$][Co^{II}(1,3-pdta)]·2H$_2$O (**2**)	56.8	6.4	This work
[Mg(H$_2$O)$_6$][Co^{II}(1,3-pdta)]·2H$_2$O (**3**)	56.8	6.4	This work
[Co$_2^{II}$ (edta)(H$_2$O)$_2$] (**4**)	47.7	7.1	[29]
[Co^{II}(H$_2$O)$_4$Co^{II}(edta)]·2H$_2$O (**5**)	41.8	10.1	[8]
Sr[Co^{II}(Hedta)(H$_2$O)]$_2$·4H$_2$O (**6**)	40.7	10.3	[30]
Ca[Co^{II}(edta)(H$_2$O)]·4H$_2$O (**7**)	27.6	15.5	[31]
[Sr(H$_2$O)$_3$Co^{II}(edta)(H$_2$O)]·H$_2$O (**8**)	26.5	15.8	[32]
Na$_2$[Co^{II}(H$_2$O)$_6$][Co^{II}(*o*-phdta)]$_2$·4H$_2$O (**9**)	20.7	16.7	[8]

[a] Φ (calculated applying the method 1 reported in Ref. [28]) is the average value of the three pseudotorsion angles that are measured along the line joining the centroids of two nearly parallel triangular faces of the octahedron and adopt the absolute values in the range 0–60°.

(**1**), Co (**2**) and Mg (**3**)) are reported in Fig. 3. The corresponding numerical data for [Co^{II}(H$_2$O)$_6$]$^{2+}$, [Co^{II}(edta)]$^{2-}$ and [Co^{II}(*o*-phdta)]$^{2-}$ [8] are also given in Table 4. As we can see absorption spectra of **1** and **3** are almost the same in the shape and position of the absorption maxima, while the spectrum of complex **2** is slightly different. These differences, manifested through the absorbance intensity and number of the absorption maxima, should be contributed to the presence of [Co^{II}(H$_2$O)$_6$]$^{2+}$ counter cation in complex **2**. The electronic absorption spectra of [Co^{II}(1,3-pdta)]$^{2-}$ complexes with C_2 symmetry and Co^{II}–N$_2$O$_4$ chromophore of the ligand field are similar in the multiplicity and band positions with those for octahedral [Co^{II}(H$_2$O)$_6$]$^{2+}$ complex with O_h symmetry. However, as we can see from Table 4, the absorption spectra of [Co^{II}(edta)]$^{2-}$ and [Co^{II}(*o*-phdta)]$^{2-}$ with the same Co^{II}–N$_2$O$_4$ chromophore as the [Co^{II}(1,3-pdta)]$^{2-}$ system, exhibit higher multiplicity and clear bands separation [8]. This can be explained through by the fact that less strained [Co^{II}(1,3-pdta)]$^{2-}$ system with flexible cobalt(II)-1,3-propanediamine six-membered ring is much closer to the ideal octahedral configuration than [Co^{II}(edta)]$^{2-}$ and [Co^{II}(*o*-phdta)]$^{2-}$ complexes. The latter statement has been clearly demonstrated in Table 3 and discussed in previous parts of text.

4. General conclusions

We have found a very simple synthetic method for the preparation of new hexadentate cobalt(II) complexes of the general formula [M^{II}(H$_2$O)$_6$][Co^{II}(1,3-pdta)]·2H$_2$O (M^{II} = Ba (**1**), Co (**2**) and Mg (**3**)) (where 1,3-pdta represents the 1,3-propanediaminetetraacetate ion). Particularly, this method is very useful for the preparation of [Co^{II}(1,3-pdta)]$^{2-}$ complexes in water solutions and in the presence of oxygen from the air.

The crystal structure analyses of [M^{II}(H$_2$O)$_6$][Co^{II}(1,3-pdta)]·2H$_2$O (M^{II} = Mg and Co) complexes confirmed that the [Co^{II}(1,3-pdta)]$^{2-}$ system, with flexible cobalt(II)-1,3-propanediamine six-membered ring, is much closer to the ideal octahedral configuration than the [Co^{II}(edta)]$^{2-}$ and [Co^{II}(*o*-phdta)]$^{2-}$ complexes. This observation should provide an explanation for the low resolution and less multiplicity of the electronic absorption spectra of these complexes as compared with those for edta and *o*-phdta Co^{II} complexes.

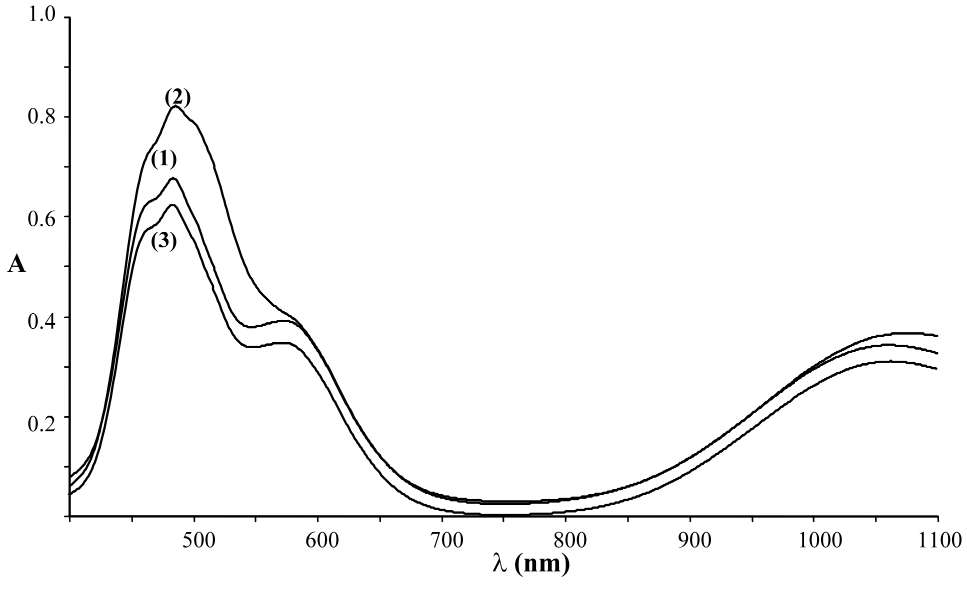


Fig. 3. Electronic absorption spectra of [Ba(H$_2$O)$_6$][Co^{II}(1,3-pdta)]·2H$_2$O (**1**), [Co^{II}(H$_2$O)$_6$][Co^{II}(1,3-pdta)]·2H$_2$O (**2**) and [Mg(H$_2$O)$_6$][Co^{II}(1,3-pdta)]·2H$_2$O (**3**).

Table 4
Electronic absorption data of cobalt(II) complexes

Complex	Absorption		
	λ (nm)	ε (M^{-1} cm^{-1})	
$[Co^{II}(H_2O)_6]^{2+}$	1234.0	1.4	$^4T_{1g} \rightarrow {}^4T_{2g}$
	625.0	0.3	$^4T_{1g} \rightarrow {}^4A_{2g}$
	515.0	4.9	$^4T_{1g} \rightarrow {}^4T_{1g}(P)$
	462.0(sh)		
$[Co^{II}(edta)]^{2-}$	1090.0	8.2	
	617.0	2.6	
	514.0	12.3	
	485.0	13.3	
	467.0	14.1	
$Na_2[Co^{II}(o\text{-phdta})]\cdot 3H_2O$	1030.0	6.2	
	614.0	1.7	
	515.0	9.1	
	485.0	9.1	
	457.0	10.4	
$[Ba(H_2O)_6][Co^{II}(1,3\text{-pdta})]\cdot 2H_2O$ (**1**)	1060.7	6.9	
	573.9	7.8	
	483.0	13.5	
	460.0(sh)	12.4	
$[Co^{II}(H_2O)_6][Co^{II}(1,3\text{-pdta})]\cdot 2H_2O$ (**2**)	1074.3	7.3	
	581.0(sh)	7.9	
	497.5(sh)	15.9	
	485.1	16.4	
	462.2(sh)	14.5	
$[Mg(H_2O)_6][Co^{II}(1,3\text{-pdta})]\cdot 2H_2O$ (**3**)	1062.8	6.6	
	572.5	7.3	
	483.0	12.9	
	460.0(sh)	11.7	

Absorption data for $[Co^{II}(H_2O)_6]^{2+}$, $[Co^{II}(edta)]^{2-}$ and $Na_2[Co^{II}(o\text{-phdta})]\cdot 3H_2O$ complexes were taken from Ref. [8].

As it follows from this study and from previous observations, all investigated crystals of transition metal(II) complexes with six-coordinated 1,3-pdta ligand and divalent counter cations: $[M^{II}(H_2O)_6][Cu^{II}(1,3\text{-pdta})]\cdot 2H_2O$ ($M^{II} = Mg$ [15] and Mn [16]), $[Mg(H_2O)_6][Ni^{II}(1,3\text{-pdta})]\cdot 2H_2O$ [17], and $[M^{II}(H_2O)_6][Co^{II}(1,3\text{-pdta})]\cdot 2H_2O$ ($M^{II} = Mg$ and Co), are isomorphic. This indicates that there is only one way of molecular organization in the solid state that is favored by the hexadentate 1,3-pdta-metal(II) complexes. Characteristic for this type of packing is the alternating arrangement of complex cations and anions leading to approximately octahedral surrounding in the second coordination sphere of the metal. This can be achieved because the first coordination sphere of both metals shows nearly ideal octahedral geometry and thus nearly spherical charge distribution, and the complex ions form discrete units not connected by carboxylate bridges. As a result, the packing is mostly governed by electrostatic forces.

5. Supplementary data

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre and allocated the deposition numbers CCDC 200453 and 200454 for compounds **2** and **3**, respectively. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.uk or www: http://www.ccdc.cam.ac.uk) and are available on request.

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