Synthesis, Crystal Structure and Hydrogen Bonding of μ -Hydroxo- μ -peroxo-bis[bis(ethylenediamine)cobalt(III)] squarate

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Abstract. Black-brown needle-shaped single crystals of $[\text{Co}_2(\text{en})_4(\text{O}_2)(\text{OH})][\text{C}_4\text{O}_4]_{1.5} \cdot 4\text{H}_2\text{O}$ (en = ethylenediamine) have been prepared in aqueous solution at room temperature. Space group $P\bar{1}$ (no.2) with $a = 800.20(8)$, $b = 1225.48(7)$, $c = 1403.84(9)$ pm, $\alpha = 100.282(5)$, $\beta = 94.515(7)$, $\gamma = 95.596(6)^\circ$. The Co^{3+} cations [Co(1), Co(2)] are coordinated in an octahedral manner by four nitrogen atoms stemming from the ethylenediamine molecules and two oxygen atoms each from a hydroxo group and a peroxo group, respectively. Both Co^{3+} coordination polyhedra are connected by a common corner and by the peroxo group leading to the binuclear $[(\text{en})_2\text{Co}(\text{O}_2)(\text{OH})\text{Co}(\text{en})_2]^{3+}$ cation. The squarate dianions, not bonded to Co^{3+} , and the $[(\text{en})_2\text{Co}(\text{O}_2)(\text{OH})\text{Co}(\text{en})_2]^{3+}$ cations are linked by hydrogen bonds forming a three-dimensional supramolecular network containing water molecules. Magnetic measurements reveal a diamagnetic behaviour indicating a low-spin electron configuration of Co^{3+} . The UV-Vis spectra shows two LMCT bands ($\pi^*(\text{O}_2^{2-}) \rightarrow d_\sigma^*(\text{Co}^{3+})$) at 274 and 368 nm and the d–d transition ($^1A_{1g} \rightarrow ^1T_{1g}$) at 542 nm. Thermoanalytical investigations in air show that the compound is stable up to 120 °C. Subsequent decomposition processes to cobalt oxide are finished at 460 °C.

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Keywords: Squarate; Cobalt; Ethylenediamine; Peroxo, Supramolecular network

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Introduction

Squaric acid (3,4-dihydroxycyclobut-3-ene-1,2-dione) belongs to the family of oxocarbon acids. The resonance stabilized squarate dianion ($\text{C}_4\text{O}_4^{2-}$) is able to act as monodentate or as bridging ligand to form one-, two-, and three-dimensional coordination polymers with interesting properties [1–10]. Early work has been done on compounds with $\text{MC}_4\text{O}_4 \cdot 2\text{H}_2\text{O}$ composition [11]. A preliminary crystal structure determination of cubic $\text{NiC}_4\text{O}_4 \cdot 2\text{H}_2\text{O}$ [12] was reported with obviously too small a unit cell and later it turned out that $\text{MC}_4\text{O}_4 \cdot 2\text{H}_2\text{O}$ occurs in a cubic and a triclinic modification which can serve as the host lattice of inclusion compounds with voids able to accommodate guest molecules like acetic acid [1, 13]. In combination with additional donor ligands numerous different structural features are available [14–21]. Although the coordinating manner of the squarate dianion was variable in different compounds, the C–C and C–O bond lengths were found to be rather uniform. Structural studies in particular with low

temperature neutron diffraction confirmed that the squarate dianion acts as a proton acceptor in hydrogen bonds preferably with those of its oxygen atoms that are weakly or not bond to metal cations [4, 22, 23]. Thus avoiding perturbation of its resonance stabilization. Supramolecular structures in which the squarate dianion acts merely as a counter ion were found using N-donor ligands [24–34]. Yesilel et al. [35] reports on the reaction of cobalt(II) squarate with ethylenediamine (en) at elevated temperature leading to a tris(ethylenediamine)cobalt(III) squarate, in which the squarate dianions act exclusively as counter ions and hydrogen bonds between the anions and the complex $[\text{Co}(\text{en})]^{3+}$ cations build up a three-dimensional supramolecular network. On the other hand the reaction between Co^{2+} and ethylenediamine in the presence of oxygen at room temperature or below leads to the binuclear cation $[(\text{en})_2\text{Co}(\text{O}_2)(\text{OH})\text{Co}(\text{en})_2]^{3+}$ [36,37]. Such binuclear peroxo- and hydroxo-bridged complex cobalt cations are obviously favoured and also available using e.g. dipyrityl, NH_3 , triethylenetetramine, and tris(2-aminoethyl)amine as N-donor ligands [38–41]. A few early single crystal structure determinations have been reported some decades ago containing the $[(\text{en})_2\text{Co}(\text{O}_2)(\text{OH})\text{Co}(\text{en})_2]^{3+}$ cation with iodide, perchlorate and dithionate-nitrate as counter anions [42–44].

Herein, we report on the structure and further properties of a three-dimensional supramolecular network formed by hydrogen bonds between squarate dianions and binuclear $[(\text{en})_2\text{Co}(\text{O}_2)(\text{OH})\text{Co}(\text{en})_2]^{3+}$ cations.

Results and Discussion

There are two crystallographically independent Co^{3+} cations. Each Co^{3+} cation is coordinated in a slightly

distorted octahedral manner by four nitrogen atoms stemming from two crystallographically different ethylenediamine molecules, one oxygen atom from the hydroxo group [O(9)–H(33)] and one from the peroxo group [O(7)–O(8)]. The Co–N distances are between 193.3(2) and 199.4(2) pm and the Co–O bonds range from 187.3(2) to 191.9(2) pm (Tab. 1). The bond angles differ slightly from the ideal values of 180 and 90 ° (Tab. S1, supporting information). Both Co(1) and Co(2) polyhedra are connected by a common corner (O(9)) and a common peroxo group, leading to the binuclear [(en)₂Co(O₂)(OH)Co(en)₂]³⁺ cation. The octahedra are tilted against each other by 15.6 ° (Fig. 1). The O(7)–O(8) bond length is 146.4(2) pm and the Co(1)–O(7)–O(8)–Co(2) torsion angle is 61.2 ° indicating that the oxygen–oxygen group is a peroxo group. In contrast, the distance in a superoxo group is between 126 and 136 pm and the Co–O–O–Co group should be nearly planar [45,46,47]. Magnetic measurement at room temperature indicates that the compound is diamagnetic. Thus the Co³⁺ cations have a low-spin electron configuration.

Such binuclear cobalt(III) complex cations are often formed in the presence of amines and oxygen in alkaline solutions [36,37]. Furthermore, Springborg and Zehnder [48] report on the crystal structure of a rhodium(III)-trifluoromethanesulfonate complex containing the analogous binuclear cation [(en)₂Rh(O₂)(OH)Co(en)₂]³⁺.

Figure 1. (a) The coordination environment of Co³⁺ (Ellipsoids are given at 50% probability, arbitrary radii for hydrogen atoms). (b) Arrangement of the Co(1) and Co(2) coordination polyhedra.

Table 1. The Coordination Environment of Co³⁺.

bond lengths (pm)			
Co(1)–O(7)	187.3(2)	Co(2)–O(8)	187.5(2)
Co(1)–O(9)	191.9(2)	Co(2)–O(9)	191.7(2)
Co(1)–N(1)	196.5(2)	Co(2)–N(5)	195.9(2)
Co(1)–N(2)	199.4(2)	Co(2)–N(6)	198.3(2)
Co(1)–N(3)	193.3(2)	Co(2)–N(7)	193.6(2)
Co(1)–N(4)	196.2(2)	Co(2)–N(8)	195.8(2)
O(7)–O(8)	146.4(2)		

There are four crystallographically independent ethylenediamine molecules. The N–C distances vary only slightly between 147.3(4) and 148.2(4) pm. The C–C bond lengths in the molecules **II**, **III**, **IV** do not differ significantly among each other (149.9(4)–150.5(4) pm) (Tab. 2 and S2, supporting information). In contrast, molecule **I** has a shorter C–C bond length of 143.7(5) pm and the N–C–C angles are expanded up to 5 °. Due to the chelating coordination to Co³⁺ the ethylenediamine molecules adopt a synclinal conformation, as demonstrated in Fig. 2 for molecule **I**. The N–C–C–N torsions angles of the molecules **II**, **III**, **IV** are between 49.0 and 49.3 °, leading to N...N distances from 263.3(1) to 267.3(1) pm (Tab. 2). On the other hand a considerably smaller torsion angle of 44.2 ° is found in molecule **I**. The resulting larger repulsion between the amino groups in **I** due the smaller torsion angle and the shorter C–C bond is overcompensated by the larger N–C–C angles leading to a N(1)···N(2) distance of 267.7(1) pm.

Figure 2. (a) The ethylenediamine molecule **I** (Ellipsoids are given at 50% probability, arbitrary radii for hydrogen atoms). (b) Newman projection along C(7)–C(8).

There are two crystallographically independent squarate dianions (dianion of 3,4-dihydroxycyclobut-3-ene-1,2-dione). The centrosymmetric dianion **I** is almost planar with a maximum deviation from the best plane of 1.4 pm (C(1)) (Tab. S3, supporting information). The C–C bonds as well as the C–O bonds do not differ significantly from each other suggesting an unperturbed delocalization of the π -electrons. The carbon skeleton is orthogonal, therefore the dianion **I** possess a $4/mmm$ (D_{4h}) point group symmetry (Tab. 2 and S2, supporting information). The C–C bonds in the dianion **II** are between 144.8(4) and 147.3(4) pm and the C–O distances range from 124.1(4) to 126.6(3) pm. The C(5)–O(5) bond indicates a slightly stronger single-bond character similar to the relations found in the squaric acid

molecule [49]. However, the elongation of this bond is rather moderate since O(5) acts as a proton acceptor in four hydrogen bonds to the amino groups (Tab. 3). The dianion **II** is planar (max. deviation (O(4)): 4.5 pm) and can be described by the point group m (C_s) in good approximation.

Table 2. Bond Lengths (pm) of the Squarate Dianions and the Ethylenediamine molecules.

Squarate Dianions					
I					
C(1)-C(2)	144.4(4)	C(1)-C(2) ^{#1}	145.0(4)	C(1)-O(1)	125.3(3)
				C(2)-O(2)	124.9(4)
II					
C(3)-C(4)	147.3(4)	C(5)-C(6)	144.8(4)	C(4)-O(4)	124.1(4)
C(4)-C(5)	145.4(4)	C(3)-C(6)	146.1(4)	C(5)-O(5)	126.6(3)
		C(3)-O(3)	125.1(3)	C(6)-O(6)	124.6(4)
Ethylenediamine Molecules					
I					
C(7)-N(1)	147.3(4)	C(8)-N(2)	147.9(4)	C(7)-C(8)	143.7(5)
N(1)···N(2)	267.7(1)				
II					
C(9)-N(3)	147.8(3)	C(10)-N(4)	147.9(4)	C(9)-C(10)	150.5(4)
N(3)···N(4)	263.3(1)				
III					
C(11)-N(5)	148.1(3)	C(12)-N(6)	148.2(4)	C(11)-C(12)	149.9(4)
N(5)···N(6)	267.3(1)				
IV					
C(13)-N(7)	148.1(4)	C(14)-N(8)	147.8(4)	C(13)-C(14)	150.4(5)
N(7)···N(8)	263.3(1)				

Symmetry code. #1: -x; -y+1; -z+2.

The crystal structure of $[\text{Co}_2(\text{en})_4(\text{O}_2)(\text{OH})][\text{C}_4\text{O}_4]_{1.5} \cdot 4\text{H}_2\text{O}$ is shown in Fig. 3. The squarate dianions **I** are stacked along [001] in a ...AAA... sequence, whereas the dianions **II** have a ...ABAB sequence along the [010] direction (see also Fig. S2, supporting information). The distance between the nearest squarate dianions **II** is around 488 pm, therefore a π - π interaction between the aromatic systems cannot be ruled out [50]. A layer-like separation between the binuclear cations and the squarate dianions exists with respect to the [100] and [001] direction. The binuclear $[(\text{en})_2\text{Co}(\text{O}_2)(\text{OH})\text{Co}(\text{en})_2]^{3+}$ cations and the $\text{C}_4\text{O}_4^{2-}$ dianions are not connected by strong chemical bonds, but the structure is stabilized by hydrogen bonds. As seen in Fig. 4 the hydrogen bonds between the squarate dianions and the amino groups of the binuclear cations build up a three-dimensional network with small channels extending along [100] containing water molecules. Neighbouring $[(\text{en})_2\text{Co}(\text{O}_2)(\text{OH})\text{Co}(\text{en})_2]^{3+}$ cations are directly connected by hydrogen bonds between the peroxo oxygen atom O(7) and the amino group N(4), whereas the peroxo oxygen atom O(8) forms an intramolecular hydrogen bond to N(3). The bridging hydroxo group $[\text{O}(9)-\text{H}(33)]$ forms a weak hydrogen bond to the squarate oxygen atom O(4) (Tab. 3). Each squarate anion **I** links two $[(\text{en})_2\text{Co}(\text{O}_2)(\text{OH})\text{Co}(\text{en})_2]^{3+}$ cations, whereas anion **II** connects three binuclear cations by hydrogen bonds (Fig. S3, supporting information). Except O(2) all squarate oxygen atoms act as proton acceptors in hydrogen bonds to the amino groups. O(2) forms only a strong hydrogen bond to the water molecule O(w2). The water molecules O(w1), O(w2) and O(w3) act as proton acceptors in hydrogen bonds to the amino groups and as proton donors to the squarate oxygen atoms. The

N(4)-H(23) group forms a three-center hydrogen bond to O(w2) and O(7) [51]. O(w4) builds only a hydrogen bond to O(w3). Apart from that, the water molecules do not form any hydrogen bonds among themselves.

< Figure 3 >

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< Figure 4 >

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Table 3. Hydrogen bonds.

	N···O Distance (pm)	N-H···O Angle (°)
N(1)-H(17)···O(w1)	301.6	164
N(1)-H(18)···O(5)	343.3	163
N(2)-H(19)···O(4)	295.3	156
N(2)-H(20)···O(3)	317.1	135
N(3)-H(21)···O(5)	285.5	143
N(3)-H(22)···O(8) ^a	277.9	122
N(4)-H(23)···O(w1)	326.7	143
N(4)-H(23)···O(7) ^b	310.6	136
N(4)-H(24)···O(w2)	298.0	156
N(5)-H(25)···O(1)	281.2	156
N(5)-H(26)···O(5)	319.7	156
N(6)-H(27)···O(6)	288.5	163
N(6)-H(28)···O(w3)	298.5	163
N(7)-H(29)···O(5)	288.3	155
N(7)-H(30)···O(7)	274.8	124
N(8)-H(31)···O(1)	289.9	155
N(8)-H(32)···O(w3)	293.4	156
	O···O Distance (pm)	O-H···O Angle (°)
O(9)-H(33)···O(4)	291.9	165
O(w1)-H(34)···O(8)	274.4	162
O(w1)-H(35)···O(2)	277.3	178
O(w2)-H(36)···O(3)	293.2	141
O(w3)-H(38)···O(w4)	273.1	170
O(w3)-H(39)···O(6)	268.0	171
O(w4)-H(41)···O(1)	305.8	161

a) intramolecular; b) intermolecular

TGA/DTA studies (Fig. 5) were carried out in air from room temperature to 1000 °C at a heating rate of 10 K min⁻¹. The compound is stable up to 120 °C. A following endothermic weight loss of 19.7 % up to 210 °C corresponds well to the loss of four water molecules, one OH-, and one peroxy group per formula unit (calc. 18.7 %). Strong exothermic processes lead to a complete decomposition up to 460 °C. The total mass loss is 74.0 % indicating the formation of Co₃O₄ (calc. 75.2 %). An endothermic weight loss of 2.4 % at 946 °C is caused by the partial formation of CoO. The present compound is significantly more thermally stable than the [Co(en)₃][C₄O₄]_{1.5}·6H₂O and [Co(NO₃)(bipy)₂][C₄O₄]_{0.5}·4H₂O (bipy = 2,2'-bipyridine) complexes which start to decompose between 50 and 60 °C [24,35].

Figure 5. Thermal analysis of [Co₂(en)₄(O₂)(OH)][C₄O₄]_{1.5}·4H₂O.

The IR spectrum is shown in Fig. 6. O–H and N–H stretching vibrations are represented at 3372, 3204, 3142, and 3081 cm⁻¹. Bands at 2968, 2940, and 2893 cm⁻¹ reflect the C–H stretching modes from the ethylenediamine molecules. The H–O–H bending mode causes a weak and broad band at 1652 cm⁻¹. The sharp band at 1592 cm⁻¹ can be assigned to the C=C conjugation system [52,53]. The intensive absorption at 1483 and 1450 cm⁻¹ is due the C–O stretching vibration coupled with the C–C mode. The absorption band at 1049 cm⁻¹ is due the C–C vibration [35,53]. The weak band at 889 cm⁻¹ is mainly caused by the peroxy group [54,55].

Figure 6. IR spectrum of [Co₂(en)₄(O₂)(OH)][C₄O₄]_{1.5}·4H₂O.

The diffuse reflectance UV-Vis spectrum (Fig. 7) of [Co₂(en)₄(O₂)(OH)][C₄O₄]_{1.5}·4H₂O shows three bands centered at 274 (band I), 368 (band II), and 542 nm (band III). As mentioned above, Co³⁺ possess a low-spin electron configuration, therefore the ground state is ¹A_{1g} based on the Tanabe-Sugano diagram [56] for a d⁶-system in an octahedral crystal field. The absorption band at 542 nm can be assigned to the d–d transition of ¹A_{1g}(D) → ¹T_{1g}(D) [57]. According to Gray and Lever [58] as well as Pickens and Martel [57] the stronger bands at 274 and 368 nm are mainly caused by ligand-to-metal-charge-transfer (LMCT) transitions from π*(O₂²⁻) to d_g*(Co³⁺). The absence of a metal-to-ligand-charge transfer (MLCT) band above 600 nm, which is usually found in μ-superoxo-dicobalt(III) complexes [58], prove the formation of a peroxy bridge in the binuclear [(en)₂Co(O₂)(OH)Co(en)₂]³⁺ cation.

Figure 7. UV-Vis spectrum (diffuse reflectance) of [Co₂(en)₄(O₂)(OH)][C₄O₄]_{1.5}·4H₂O. The sample was diluted with MgO. (F(R) = Kubelka-Munk-function)

Conclusions

In summary, we reported on the synthesis and crystal structure of a Co(III)-squarate featured by a hydroxo and peroxy bridged binuclear Co³⁺ complex cation. Hydrogen bonds between the Co³⁺ complex cations and the squarate dianions lead to a three-dimensional supramolecular network with small channel-like openings. These openings accommodate water molecules. The Co³⁺ cations possess a low-spin electron configuration. The UV-Vis spectra confirmed the formation of a peroxy group and shows two LMCT bands and the d–d transition between the ground state ¹A_{1g} and the ¹T_{1g} term. The compound is thermally stable up to 120 °C.

Experimental Section

Single crystals of [Co₂(en)₄(O₂)(OH)][C₄O₄]_{1.5}·4H₂O were synthesized in aqueous solution. 10 ml of a 0.1M Co(NO₃)₂ solution were mixed with 0.06 g ethylenediamine. Then a solution

of 10 ml 0.1M sodium squarate was added. The resulting solution was kept for some days at room temperature. Afterwards, the solution was overlayed with acetone and after 4 days black-brown needles were formed.

Results of elemental analysis: (Mw 647.41) C 25.94 (calcd. 25.97); H 6.42 (6.38); N 16.98 (17.31)%.

IR-ATR (cm^{-1}): 3372(m), 3204(s), 3142(s), 3081(s) 2968(m) 2940(m), 2893(m), 1652(w,br), 1592(m), 1483(s), 1450(s), 1370(w), 1324(w), 1284(w), 1218(w), 1158(w), 1132(w), 1090(w), 1049(m), 1002(m), 889(w), 787(w), 671(m).

ATR Fourier transformed infrared (IR-ATR) measurements were carried out at room temperature using a Bio-rad FTS 25. Thermoanalytic measurements were performed in flowing air using a Netzsch STA429 device. Magnetic measurements at room temperature were carried out with a SQUID magnetometer (Quantum Design, MPMS2). The diffuse reflectance UV-Vis spectrum was obtained using a Perkin Elmer UV-Vis spectrometer Lambda 19. X-ray single crystal structure determination was performed on a Siemens P4 four-circle diffractometer (MoK α , graphite monochromator) in a theta range up to 25.00°. Numerical absorption corrections have been applied. The phase problem was solved by direct methods. Full matrix least squares refinement employing $|F|^2$ made use of the SHELXTL program suite [59]. Some of the hydrogen atoms have been placed into calculated positions, further hydrogen atom positions could be taken from Difference Fourier maps. They were allowed to refine with a common isotropic displacement parameter. Crystallographic data are given in Table 4.

Further details concerning the crystal structure analysis have been deposited with Cambridge Crystallographic Data Centre, The Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK, Fax +(1223)336-033, e-mail data_request@ccdc.cam.ac.uk, www.ccdc.cam.ac.uk/data_request.cif under CCDC 1456628.

Table 4. Crystallographic Data.

Empirical formula	C ₁₄ H ₄₁ N ₈ Co ₂ O ₁₃
Crystal system	triclinic
Space group	<i>P</i> $\bar{1}$ (no.2)
Lattice constants	<i>a</i> = 800.20(8) pm <i>b</i> = 1225.48(7) pm <i>c</i> = 1403.84(9) pm α = 100.282(5)° β = 94.515(7)° γ = 95.596(6)°
Cell volume	1.3416(2) nm ³
Formulas in unit cell	2
Formula weight	647.41 g/mol
Density (calc.)	1.603 g/cm ³
Wavelength	71.073 pm
Absorption coefficient	1.310 mm ⁻¹
Numerical absorption correction	min./max. transmittance
Temperature	293(2) K
Crystal size (mm)	1.0 x 0.18 x 0.12
F (000)	678
Θ -range	2.03° – 25.00°
Limiting indices	h -1/+9; k -14/+14; l -16/+16
Reflections collected	5821
Independent reflections	4715 (R_{int} = 0.0137)

Structure solution	Direct methods
Structure refinement	Full-matrix least-squares on $ F ^2$
Refined parameters	364
Final mean shift/esd	-0.008
Goodness-of-fit on $ F ^2$	1.706
Residuals (all data)	R_1 = 0.0409, wR_2 = 0.0679
Max. features in last difference Fourier synthesis	697 and -457 e·nm ⁻³

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Figure 3. Crystal structure of $\text{Co}_2(\text{en})_4(\text{O}_2)(\text{OH})[\text{C}_4\text{O}_4]_{1.5} \cdot 4\text{H}_2\text{O}$. The squarate dianion **I** is drawn with open bonds. C–H bonds are omitted for clarity.

Figure 4. Hydrogen bonds (red lines) between the binuclear cations and the squarate dianions in $\text{Co}_2(\text{en})_4(\text{O}_2)(\text{OH})[\text{C}_4\text{O}_4]_{1.5} \cdot 4\text{H}_2\text{O}$ viewed along $[100]$. The squarate dianion **I** is drawn with open bonds. Hydrogen atoms are omitted for clarity.

Roberto Köferstein and Christian Robl* Page No. – Page No.

Synthesis, Crystal Structure and Hydrogen Bonding of μ -Hydroxo- μ -peroxo-bis[bis(ethylenediamine)cobalt(III)] squarate

$[\text{Co}_2(\text{en})_4(\text{O}_2)(\text{OH})][\text{C}_4\text{O}_4]_{1.5} \cdot 4\text{H}_2\text{O}$ (en = ethylenediamine) has been synthesized and structurally characterized. The squarate dianions and the $[(\text{en})_2\text{Co}(\text{O}_2)(\text{OH})\text{Co}(\text{en})_2]^{3+}$ cations are linked by hydrogen bonds forming a supramolecular network containing water molecules.

Supporting Information:

Synthesis, Crystal Structure and Hydrogen Bonding of μ -Hydroxo- μ -peroxo-bis[bis(ethylenediamine)cobalt(III)] squarate

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Table S1. The Coordination Environment of Co³⁺

Bond angles (°)			
O(7)-Co(1)-O(9)	87.99(8)	O(8)-Co(2)-N(7)	89.06(9)
O(9)-Co(1)-N(3)	93.43(9)	O(8)-Co(2)-N(5)	90.89(9)
O(9)-Co(1)-N(4)	175.14(10)	N(7)-Co(2)-N(5)	176.68(10)
O(7)-Co(1)-N(1)	90.87(9)	O(9)-Co(2)-N(8)	173.37(10)
N(3)-Co(1)-N(1)	176.86(10)	N(8)-Co(2)-N(5)	91.61(10)
O(7)-Co(1)-N(2)	175.15(10)	O(9)-Co(2)-N(6)	90.33(9)
N(3)-Co(1)-N(2)	94.13(11)	N(5)-Co(2)-N(6)	85.37(10)
N(1)-Co(1)-N(2)	85.10(11)	O(8)-Co(2)-O(9)	88.72(8)
O(7)-Co(1)-N(3)	90.04(9)	O(9)-Co(2)-N(7)	89.14(9)
O(7)-Co(1)-N(4)	87.39(9)	O(9)-Co(2)-N(5)	94.18(9)
N(3)-Co(1)-N(4)	85.06(10)	O(8)-Co(2)-N(8)	87.97(9)
O(9)-Co(1)-N(1)	89.61(10)	N(7)-Co(2)-N(8)	85.07(10)
N(4)-Co(1)-N(1)	91.98(11)	O(8)-Co(2)-N(6)	176.07(10)
O(9)-Co(1)-N(2)	89.28(9)	N(7)-Co(2)-N(6)	94.74(10)
N(4)-Co(1)-N(2)	95.43(10)	N(8)-Co(2)-N(6)	93.36(10)
O(8)-O(7)-Co(1)	109.33(12)	O(7)-O(8)-Co(2)	109.47(13)
		Co(2)-O(9)-Co(1)	115.82(9)

Table S2. Bond angles (°) in the Squarate Dianions and Ethylenediamine Molecules

Squarate Dianions					
I					
O(1)-C(1)-C(2)	133.5(3)	O(2)-C(2)-C(1) ^{#1}	135.9(3)	C(2)-C(1)-C(2) ^{#1}	90.3(3)
O(1)-C(1)-C(2) ^{#1}	136.2(3)	O(2)-C(2)-C(1)	134.3(3)	C(1)-C(2)-C(1) ^{#1}	89.7(3)
II					
O(3)-C(3)-C(6)	134.8(3)	O(6)-C(6)-C(5)	134.5(3)	C(6)-C(3)-C(4)	89.9(2)
O(3)-C(3)-C(4)	135.3(3)	O(6)-C(6)-C(3)	135.7(3)	C(5)-C(4)-C(3)	88.1(2)
O(4)-C(4)-C(5)	134.5(3)	O(5)-C(5)-C(6)	134.8(3)	C(6)-C(5)-C(4)	91.2(2)
O(4)-C(4)-C(3)	136.3(3)	O(5)-C(5)-C(4)	133.9(3)	C(5)-C(6)-C(3)	89.8(2)
Ethylenediamine Molecules					
I		II		III	
C(8)-C(7)-N(1)	109.8(3)	N(3)-C(9)-C(10)	105.9(2)	N(5)-C(11)-C(12)	107.3(3)
C(7)-C(8)-N(2)	111.0(3)	N(4)-C(10)-C(9)	107.5(2)	N(6)-C(12)-C(11)	108.0(3)
IV					
N(7)-C(13)-C(14)	106.6(2)				
N(8)-C(14)-C(13)	106.9(2)				

Symmetry code. #1: -x;-y+1;-z+2

Table S3. Deviation from the best plane of the squarate dianions

I
Plane: C(1), C(2), O(1), O(2), C(1) ^{#1} , C(2) ^{#1} , O(1) ^{#1} , O(2) ^{#1}
Deviation from the best plane (pm): C(1): 1.36, C(2): -0.43, O(1): -0.61, O(2): 0.20, C(1) ^{#1} : -1.36, C(2) ^{#1} : 0.43, O(1) ^{#1} : 0.61, O(2) ^{#1} : -0.20.
Average deviation: 0.65 pm
II
Plane: C(3), C(4), C(5), C(6), O(3), O(4), O(5), O(6)
Deviation from the best plane (pm): C(3): -1.73, C(4): -1.11, C(5): -2.59, C(6): -0.23, O(3): -1.57, O(4): 4.45, O(5): -1.30, O(6): 4.07.
Average deviation: 2.13 pm
Symmetry code. #1: -x;-y+1;-z+2

Figure S1. Newman projections of the ethylenediamine molecules. (a) molecule **II** along C(9)–C(10), (b) molecule **III** along C(11)–C(12), and (c) molecule **IV** along C(13)–C(14).

Figure S2. Stacking of the squarate dianion **II** in $[\text{Co}_2(\text{en})_4(\text{O}_2)(\text{OH})][\text{C}_4\text{O}_4]_{1.5} \cdot 4\text{H}_2\text{O}$.

Figure S3. Hydrogen bonds between the $[(en)_2Co(O_2)(OH)Co(en)_2]^{3+}$ cations and the squarate dianions I (a) and II (b). Hydrogen atoms are omitted for clarity.