

Structures of Ethylenediaminetetraacetato(3–) Metal Complexes. I. Complexes with Co, Mg and Cd Metals

BY X. SOLANS AND M. FONT-BARDÍA

Dpto Cristalografía y Mineralogía, Universidad de Barcelona, Grand Via 585, 08007-Barcelona, Spain

M. AGUILÓ

Cristalografía, Fac. Químicas, Universidad de Barcelona, Pza Imperial Tarraco 1, Tarragona, Spain

AND M. AROSTEGUI AND J. OLIVA

Dpto Farmacia, Universidad de Barcelona, Diagonal 645, 08028-Barcelona, Spain

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Abstract. (I): Hexaaquacobalt(II) aqua[ethylenediaminetetraacetato(3–)]cobaltate(II) dihydrate, $[\text{Co}(\text{H}_2\text{O})_6][\text{Co}(\text{C}_{10}\text{H}_{13}\text{N}_2\text{O}_8)(\text{H}_2\text{O})_2 \cdot 2\text{H}_2\text{O}]$, $M_r = 935.4$, monoclinic, $C2/c$, $a = 13.842(3)$, $b = 9.402(2)$, $c = 27.936(4)$ Å, $\beta = 90.80(2)^\circ$, $V = 3635(2)$ Å³, $Z = 4$, $D_x = 1.709$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 1.512$ mm⁻¹, $F(000) = 1932$, $T = 288$ K. (II): Tetra-

aquabis{aqua[ethylenediaminetetraacetato(3–)]cadmium(II)-*O,O'*}cadmium(II) tetrahydrate, $[\text{Cd}\{\text{Cd}(\text{C}_{10}\text{H}_{13}\text{N}_2\text{O}_8)(\text{H}_2\text{O})_2(\text{H}_2\text{O})_4\} \cdot 4\text{H}_2\text{O}]$, $M_r = 1095.8$, monoclinic, $P2_1/c$, $a = 12.054(2)$, $b = 16.457(2)$, $c = 9.118(1)$ Å, $\beta = 91.11(2)^\circ$, $V = 1808.4(7)$ Å³, $Z = 2$, $D_x = 2.012$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 1.843$ mm⁻¹, $F(000) = 1092$, $T = 288$ K. $R = 0.054$

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(I) and 0.022 (II) for 2431 and 2901 observed reflections, respectively. From powder-diffraction patterns it is observed that the Mg complex is isostructural to the Co complex. Both structures consist of discrete $[M(H_2O)_6]^{2+}$ and $[M(Hedta)(H_2O)]^-$ ions, while the Cd complex consists of trimeric molecules, where the $[Cd(H_2O)_4]^{2+}$ moiety acts as a bridge between two $[Cd(Hedta)(H_2O)]^-$ units. The Co^{2+} ions and the Cd^{2+} ion of the $[Cd(H_2O)_4]^{2+}$ unit display a distorted octahedral coordination, while the Cd linked to the Hedta ligand displays a distorted pentagonal-bipyramidal coordination, being linked to four O and two N of the Hedta ligand and a water molecule. The Co linked to Hedta is coordinated to three O and two N of the Hedta and a water molecule.

Introduction. In preceding papers the crystal structure of ethylenediaminetetraacetato(4-) metal complexes has been studied (Solans, Font-Altaba & García-Oricain, 1985). A new systematic study has begun on complexes synthesized in more acid conditions. In order to determine the geometrical variations, crystal-structure determination of the title compounds has been carried out.

Experimental. Red prismatic crystals of (I) ($0.1 \times 0.1 \times 0.15$ mm); colourless tabular crystals of (II) ($0.1 \times 0.1 \times 0.008$ mm). Philips PW 1100 diffractometer. Unit-cell parameters from 25 reflections ($4 \leq \theta \leq 12^\circ$) and refined by least squares, graphite monochromator, Mo $K\alpha$ radiation, ω -scan technique, scan width 1° in (I) and 0.8° in (II), scan speed $0.03^\circ s^{-1}$. Three reflections every 2 h, significant intensity decay was not observed. In (I) 2554 reflections with $\theta \leq 25^\circ$, hkl range: -16 to 16 ; 0 to 11 ; 0 to 32 , respectively, 2431 with $I \geq 2.5\sigma(I)$, $R_{int} = 0.026$. In (II) 3124 reflections with $\theta \leq 25^\circ$, hkl range: -14 to 14 ; 0 to 19 ; 0 to 10 , respectively, 2901 with $I \geq 2.5\sigma(I)$, $R_{int} = 0.013$. Lp corrections, empirical absorption correction in (II), max. and min. transmission factor 0.86 and 0.81, respectively.

Co atoms in (I) from Patterson synthesis. Cd atoms and coordination polyhedra of metals in (II) from direct-methods program MULTAN80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). The remaining non-H atoms in both structures from a weighted Fourier synthesis. Both structures refined by full-matrix least-squares methods (SHELX76, Sheldrick, 1976), $\sum w(|F_o| - |F_c|)^2$ minimized, $w = [\sigma^2(F_o) + k|F_o|^2]^{-1}$, $k = 0.0066$ in (I) and 0.0 in (II), f , f' and f'' from *International Tables for X-ray Crystallography* (1974). Non-H atoms refined anisotropically. 20 H of (I) from $\Delta\rho$ map, refined with an overall isotropic temperature factor. H atoms not located in (II). Final R 0.054 in (I) and 0.022 in (II), wR 0.058 and 0.027, respectively, for all observed reflections. Max. shift/e.s.d. = -0.34 for z of

H(12) in (I) and -0.22 for y of C(42) in (II). Max. and min. peaks in final $\Delta\rho$ map $0.4 e \text{ \AA}^{-3}$ 0.75 \AA from C(22) and $-0.4 e \text{ \AA}^{-3}$, respectively, for (I) and $0.5 e \text{ \AA}^{-3}$ 0.71 \AA from O(W1) and $-0.4 e \text{ \AA}^{-3}$, respectively, for (II). IBM-3083 computer.

Discussion. The atomic coordinates and equivalent isotropic thermal coefficients are listed in Table 1, selected bond lengths and angles of the two compounds in Table 2.* Fig. 1 shows a view of (II). From powder-diffraction patterns the Mg complex has been determined to be isostructural to the Co complex; its cell parameters are $a = 13.825$ (4), $b = 9.394$ (3), $c = 27.918$ (9) \AA , $\beta = 90.82$ (4) $^\circ$.

The structures of the title compounds differ from that of the non-protonated-edta Co complex (Candlish, Michael, Neal, Lingafelter & Rose, 1978), which consists of chains of alternate $[Co(H_2O)_4]^{2+}$ and $[Co(edta)]^{2-}$ ions bridged by edta ligands. The structure of the Co complex consists of discrete ions linked by van der Waals forces and hydrogen bonds. The Cd complex consists of trimeric molecules where the $[Cd(H_2O)_4]^{2+}$ ion acts as a bridge between two $[Cd(Hedta)(H_2O)]^-$ moieties, while the $[Cd(edta)Mn(H_2O)_4] \cdot 2H_2O$ crystal structure (Solans, Font-Altaba, Oliva & Herrera, 1985) consists of chains of alternate $[Cd(edta)]^{2-}$ moieties and $[Mn(H_2O)_4]^{2+}$ pairs.

The Co(1) ion is linked to two N and three O atoms of the Hedta ligand and water molecule, displaying a distorted octahedral coordination. The two N atoms, acetato O and the water molecule are in the equatorial plane. The apical Co—O(acetato) bond lengths [average value 2.075 (7) \AA] are shorter than the equatorial Co—O(acetato) length [2.114 (4) \AA], which was also observed in the Mn—Co complex of edta (Solans, Font-Altaba, Oliva & Herrera, 1983). The Co—N bond length alters according to the electronegative character of the *trans* ligand. The small N—Co—N [83.1 (2) $^\circ$] and N(1)—Co(1)—O(11) [78.3 (2) $^\circ$] bond angles produce larger O(W1)—Co(1)—O(11) [99.2 (2) $^\circ$] and O(W1)—Co(1)—N(2) [101.1 (2) $^\circ$] bond angles.

The protonation of O(41) produces a C(41)—O(41) [1.317 (8) \AA] bond length larger than that observed for C(41)—O(42) [1.194 (7) \AA], while the remaining C—O bond lengths show intermediate values [average value 1.26 (1) \AA].

Co(2) is linked to six O atoms of hydrate water molecules with Co—OW lengths in the range 1.970 (9)— 2.123 (5) \AA . The variation of Co—OW bond lengths can be assigned to different roles of the aqueous molecules, the longest Co—OW being that with the

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and all bond distances and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43560 (31 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

greatest number of O(acetato) hydrogen-bonded to the water molecule.

In structure (II), the Cd(1) ion is coordinated to two N and four O of the Hedta ligand and a water molecule, displaying a distorted pentagonal-bipyramidal coordination, with O(11) and O(31) in the apical sites. It has not been possible to determine the H-atom positions from a difference synthesis, but the protonated O(acetato) moiety must be assigned to O(22) according to C—O(acetato) bond lengths and hydrogen bonds. As in the Co complex, the C(21)—O(21) length is 1.178 (5) Å, while that of C(21)—O(22) is 1.304 (4) Å and the average value for the remaining C—O lengths is 1.26 (2) Å.

Table 1. Final atomic coordinates ($\times 10^4$, for Co and Cd $\times 10^5$) and equivalent isotropic thermal coefficients for structures (I) and (II)

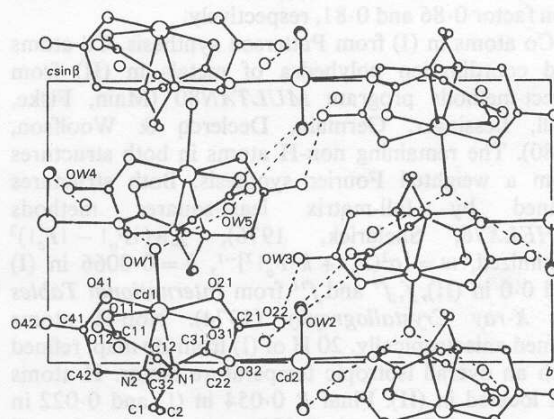
$$B_{eq} = \frac{3}{2} \pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

	x	y	z	$B_{eq}(\text{Å}^2)$
Structure (I)				
Co(1)	32386 (4)	37892 (6)	38794 (2)	1.51 (3)
N(1)	4208 (3)	5555 (4)	3805 (1)	1.7 (2)
C(1)	3961 (4)	6573 (6)	4188 (2)	2.5 (2)
C(2)	2876 (4)	6689 (5)	4232 (2)	2.2 (2)
N(2)	2462 (3)	5273 (4)	4355 (2)	1.7 (2)
O(11)	4443 (2)	2812 (4)	3559 (1)	2.2 (1)
C(11)	5224 (4)	3508 (5)	3615 (2)	2.0 (2)
C(12)	5179 (4)	4918 (6)	3866 (2)	2.2 (2)
O(21)	6031 (2)	3054 (4)	3480 (1)	2.6 (2)
O(22)	2701 (3)	4610 (4)	3234 (1)	2.3 (1)
C(21)	3205 (4)	5572 (6)	3054 (2)	2.1 (2)
C(22)	4083 (5)	6139 (6)	3324 (3)	2.6 (2)
O(31)	3024 (3)	6123 (4)	2653 (2)	3.1 (2)
O(32)	3721 (2)	3108 (4)	4542 (1)	2.1 (1)
O(33)	3372 (3)	3653 (5)	4919 (2)	1.5 (2)
C(32)	2677 (4)	4879 (6)	4862 (2)	2.1 (2)
O(32)	3579 (3)	3243 (4)	5329 (1)	2.4 (2)
O(41)	-145 (3)	5892 (5)	4441 (2)	2.9 (2)
C(41)	775 (4)	6199 (5)	4512 (2)	2.1 (2)
C(42)	1416 (3)	5185 (5)	4238 (2)	1.9 (2)
O(42)	1057 (3)	7202 (5)	4735 (2)	3.6 (2)
O(43)	2279 (3)	2124 (4)	3840 (2)	2.6 (2)
O(44)	-2540 (3)	5144 (5)	-1776 (2)	3.2 (2)
Co(2)	0	49481 (10)	125506 (26)	1.4 (1)
O(51)	-1006 (3)	6526 (5)	2327 (2)	3.1 (2)
O(52)	1030 (3)	3439 (5)	2732 (2)	2.9 (2)
O(53)	-534 (3)	5029 (4)	3200 (2)	2.5 (2)
Structure (II)				
Cd(2)	0	0	50000	3.73 (2)
Cd(1)	22012 (2)	22202 (1)	16796 (3)	3.11 (2)
OW(1)	2028 (2)	2117 (1)	4127 (4)	3.3 (1)
N(1)	957 (3)	2513 (2)	-369 (4)	2.7 (1)
C(1)	1353 (2)	2109 (2)	-1715 (5)	3.3 (2)
C(2)	2626 (4)	2200 (2)	-1757 (4)	3.8 (2)
N(2)	3193 (2)	1882 (2)	-470 (4)	3.5 (1)
O(11)	892 (2)	1181 (1)	1411 (3)	3.7 (1)
C(11)	-56 (3)	1381 (2)	828 (4)	3.0 (1)
O(12)	-924 (2)	993 (2)	1011 (4)	5.3 (2)
C(12)	-159 (3)	2157 (2)	-4 (5)	3.7 (2)
C(22)	886 (3)	3425 (2)	-464 (5)	3.4 (2)
C(21)	962 (3)	3780 (2)	1140 (5)	3.2 (2)
O(21)	1110 (2)	3363 (1)	2176 (3)	3.7 (1)
O(22)	753 (2)	4557 (1)	1171 (4)	4.8 (1)
C(32)	4340 (3)	2261 (2)	-330 (5)	2.7 (1)
C(31)	4266 (3)	3122 (2)	321 (4)	3.6 (2)
O(31)	3507 (2)	3279 (1)	1239 (4)	4.6 (1)
O(32)	5013 (2)	3593 (2)	-53 (4)	5.3 (1)
O(41)	3454 (2)	1161 (1)	2201 (3)	3.6 (1)
O(42)	3930 (2)	-32 (1)	1271 (4)	4.7 (1)
C(41)	3582 (3)	706 (2)	1118 (6)	3.9 (2)
C(42)	3348 (4)	989 (2)	-413 (6)	5.4 (2)
OW(2)	3627 (2)	4989 (2)	1681 (4)	5.6 (2)
OW(3)	6348 (3)	4966 (2)	1838 (5)	6.0 (2)
OW(4)	3212 (2)	725 (2)	5729 (4)	4.8 (1)
OW(5)	1931 (3)	3588 (2)	5469 (4)	5.7 (2)

Table 2. Selected bond lengths (Å) and angles (°)

Structure (I)		Structure (II)	
N(1)—Co(1)	2.146 (5)	OW(1)—Cd(1)	2.252 (3)
N(2)—Co(1)	2.215 (5)	O(11)—Cd(1)	2.337 (2)
O(11)—Co(1)	2.114 (4)	N(1)—Cd(1)	2.421 (3)
O(21)—Co(1)	2.088 (4)	O(21)—Cd(1)	2.345 (2)
O(31)—Co(1)	2.062 (4)	N(2)—Cd(1)	2.381 (3)
OW(1)—Co(1)	2.055 (4)	O(31)—Cd(1)	2.387 (2)
OW(3)—Co(2)	2.123 (5)	O(41)—Cd(1)	2.349 (3)
OW(4)—Co(2)	2.070 (5)	O(32)—Cd(2)	2.316 (3)
OW(5)—Co(2)	1.970 (9)	OW(2)—Cd(2)	2.278 (2)
OW(3)—Cd(2)	2.312 (3)		
N(2)—Co(1)—N(1)	83.1 (2)	N(2)—Cd(1)—N(1)	74.1 (1)
O(11)—Co(1)—N(1)	78.3 (2)	N(1)—Cd(1)—O(11)	69.9 (1)
O(11)—Co(1)—N(2)	156.9 (2)	N(2)—Cd(1)—O(11)	95.3 (1)
O(21)—Co(1)—N(1)	81.2 (2)	O(21)—Cd(1)—N(1)	69.4 (1)
O(21)—Co(1)—N(2)	96.6 (2)	N(2)—Cd(1)—O(21)	129.7 (1)
O(21)—Co(1)—O(11)	93.9 (2)	O(21)—Cd(1)—O(11)	103.1 (1)
O(31)—Co(1)—N(1)	97.6 (2)	O(31)—Cd(1)—O(11)	97.2 (1)
O(31)—Co(1)—N(2)	79.1 (2)	O(31)—Cd(1)—N(2)	71.9 (1)
O(31)—Co(1)—O(11)	89.9 (2)	O(31)—Cd(1)—O(21)	164.3 (1)
O(31)—Co(1)—O(21)	175.6 (2)	O(31)—Cd(1)—O(21)	79.7 (1)
OW(1)—Co(1)—N(1)	171.3 (2)	N(1)—Cd(1)—OW(1)	135.3 (1)
OW(1)—Co(1)—N(2)	101.1 (2)	N(2)—Cd(1)—OW(1)	148.8 (1)
OW(1)—Co(1)—O(11)	99.2 (2)	O(11)—Cd(1)—OW(1)	88.5 (1)
OW(1)—Co(1)—O(21)	90.8 (2)	O(21)—Cd(1)—OW(1)	78.8 (1)
OW(1)—Co(1)—O(31)	90.7 (2)	O(31)—Cd(1)—OW(1)	107.2 (1)
OW(4)—Co(2)—OW(3)	176.5 (4)	O(41)—Cd(1)—OW(1)	79.4 (1)
OW(5)—Co(2)—OW(3)	89.5 (2)	O(41)—Cd(1)—O(11)	84.8 (1)
OW(5)—Co(2)—OW(4)	93.9 (4)	O(41)—Cd(1)—N(1)	133.6 (1)
OW(1)...O(32 ⁱ)	2.644 (8)	O(41)—Cd(1)—O(21)	156.5 (1)
OW(1)...O(2 ⁱⁱ)	2.754 (8)	O(41)—Cd(1)—N(2)	70.2 (1)
OW(2)...O(12 ⁱⁱⁱ)	2.708 (8)	O(41)—Cd(1)—O(31)	98.8 (1)
OW(2)...O(22 ^{iv})	2.796 (8)	O(32)—Cd(2)—OW(2)	90.7 (1)
OW(3)...O(12 ^v)	2.673 (8)	O(32)—Cd(2)—OW(3)	89.2 (1)
OW(3)...O(22 ^{vi})	2.820 (8)	OW(2)—Cd(2)—OW(3)	91.2 (1)
OW(4)...O(22 ^{vii})	2.766 (8)	OW(1)...OW(5 ^{viii})	2.716 (4)
OW(5)...O(11 ^{viii})	2.802 (8)	OW(1)...O(31 ^{ix})	2.809 (4)
OW(5)...O(22 ^{ix})	2.783 (9)	OW(2)...O(11 ^x)	2.679 (4)
O(41)...O(31 ^x)	2.627 (8)	OW(3)...O(12 ^x)	2.646 (4)
		OW(3)...OW(4 ^{xi})	2.730 (5)
		OW(5)...O(12 ^{xi})	2.712 (4)
		O(22)...O(42 ^{xii})	2.452 (4)

Symmetry code: (i) $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$; (ii) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; (iii) $x - 1, 1 - y, z - \frac{1}{2}$; (iv) $-x, 1 - y, -z$; (v) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$; (vi) $-x, y, \frac{3}{2} - z$; (vii) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{3}{2} - z$; (viii) $x - \frac{1}{2}, y + \frac{1}{2}, z$; (ix) $x, 1 - y, z + \frac{1}{2}$; (x) x, y, z ; (xi) $x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} + z$; (xii) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$.



Cd(2) is located on an inversion centre and it is coordinated to four *OW* molecules and two O(acetato). As in the Co complex the longest Cd—*OW* length corresponds to that involving the *OW* with the greatest number of hydrogen bonds.

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