

On the Structures of Three Different Forms of Solid Cadmium Oxydiacetate Hydrate

CARL-ERIK BOMAN

Inorganic Chemistry I, Chemical Center,
University of Lund, P.O.B. 740, S-220 07 Lund,
Sweden

Two monoclinic phases of cadmium oxydiacetate hydrate, in the following called CDOXY I and CDOXY II, are formed simultaneously when aqueous solutions of equimolar amounts of cadmium nitrate and disodium oxydiacetate are evaporated slowly at room temperature. From solutions of the same composition an orthorhombic phase, called CDOXY III, precipitates at slightly elevated temperatures. Table 1 shows some relevant data for the three structures.

Three-dimensional X-ray intensity data were collected for CDOXY I and CDOXY II using non-integrated Weissenberg photographs, and for CDOXY III by means of an automatic linear single crystal diffractometer of type PAILRED. In all three cases $\text{CuK}\alpha$ radiation was used. The structure of CDOXY II is being reinvestigated by means of an automatic four-circle diffractometer of type CAD-4.

The positions of the cadmium atoms in the three structures were obtained from Patterson syntheses and the positions of the oxygen and carbon atoms could then be determined in the difference electron density maps. The structures were refined by least-squares methods to the R -values given in Table 1.

In the three cadmium oxydiacetate structures each cadmium atom is coordinated by seven oxygen atoms and the coordination polyhedra are somewhat distorted pentagonal bipyramids. The Cd—O distances, given in Tables 2 and 3, agree well with those published. A compilation of Cd—O distances in various cadmium compounds is given by Harrison and Trotter.¹

In the unit cell of CDOXY I two cadmium atoms, denoted Cd(1) and Cd(2), two ligands and seven water molecules are independent. Each Cd(1) atom is joined by two ligands to two other Cd(1) atoms and in this way infinite zigzag chains parallel to the b -axis are formed. Each Cd(1) atom is also bound to a Cd(2) atom by an oxygen bridge, which means that the pentagonal bipyramids have one vertex in common. The structure thus consists of broad chains which are held together by hydrogen bonds *via* the water molecules. A part of the structure is shown in Fig. 1. Two ligands are

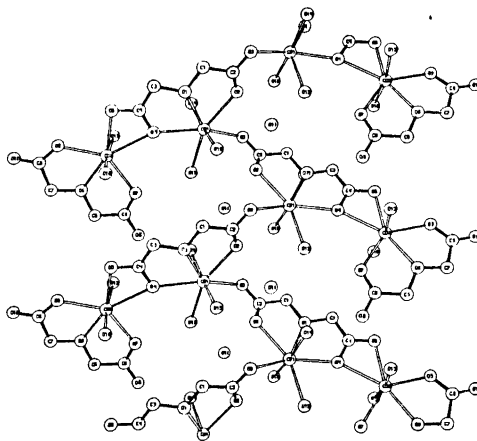


Fig. 1. Part of the structure of CDOXY I showing one of the broad chains parallel to the b -axis.

bound to each cadmium atom; those coordinated by Cd(1) are tridentate and monodentate and those by Cd(2) are tridentate and bidentate. The bidentate ligand forms a carboxylate chelate with a bite of 2.20(3) Å.

The structure of CDOXY II is composed of discrete units containing two cadmium atoms,

Table 1. Data for the three phases of cadmium oxydiacetate hydrate. (Oxy = $\text{O}(\text{CH}_2\text{COO})_2^{2-}$)

Phase	CDOXY I	CDOXY II	CDOXY III
Formula	$\text{CdOxy} \cdot 3\frac{1}{2}\text{H}_2\text{O}$	$\text{CdOxy} \cdot 3\text{H}_2\text{O}$	$\text{CdOxy} \cdot 3\text{H}_2\text{O}$
Space group	$P2_1/c$	$P2_1/c$	$P2_12_12_1$
$a/\text{Å}$	7.3215(11)	6.3848(7)	7.3934(7)
$b/\text{Å}$	7.3012(8)	10.2093(9)	8.8955(10)
$c/\text{Å}$	37.1411(38)	14.0470(16)	13.3536(15)
$\beta/^\circ$	90.673(11)	101.753(10)	—
Z	8	4	4
$V/\text{Å}^3$	1985.3	896.4	878.2
R -value	0.11	0.13	0.065
Number of independent reflexions	1800	800	550

Table 2. Coordination distances (Å) in CDOXY I with their estimated standard deviations. The oxygen atoms in one of the independent ligands are numbered 1–5 and in the other 6–10. The water oxygens are numbered 11–17. Oxygen atoms belonging to symmetry-related ligands are distinguished by the sign '.

Cd(1)–O(15)	2.27(2)
Cd(1)–O(3)'	2.30(2)
Cd(1)–O(14)	2.30(2)
Cd(1)–O(12)	2.32(3)
Cd(1)–O(1)	2.38(2)
Cd(1)–O(2)	2.41(2)
Cd(1)–O(4)	2.41(2)

Cd(2)–O(9)	2.30(2)
Cd(2)–O(5)	2.31(2)
Cd(2)–O(6)	2.31(2)
Cd(2)–O(13)	2.31(2)
Cd(2)–O(7)	2.33(2)
Cd(2)–O(16)	2.35(2)
Cd(2)–O(4)	2.49(2)

Table 3. Coordination distances (Å) in CDOXY II and CDOXY III with their estimated standard deviations. The oxygen atoms in the ligand are numbered 1–5 and the water oxygens are numbered 6–8. Oxygen atoms belonging to different ligands are distinguished by the signs ' and ''.

CDOXY II

Cd–O(6)	2.26(2)
Cd–O(1)	2.33(2)
Cd–O(8)	2.33(2)
Cd–O(2)	2.34(2)
Cd–O(4)'	2.34(2)
Cd–O(7)	2.36(2)
Cd–O(4)	2.45(2)

CDOXY III

Cd–O(5)	2.26(1)
Cd–O(2)'	2.30(1)
Cd–O(6)	2.31(1)
Cd–O(3)''	2.36(1)
Cd–O(7)	2.36(1)
Cd–O(1)'	2.47(1)
Cd–O(4)	2.63(1)

two ligands and six water molecules. In these units, which are almost planar, except for the four oxygen atoms at the apices of the pentagonal bipyramids, the two cadmium atoms are held together by two oxygen bridges. In this structure the pentagonal bipyramids share an edge in the pentagonal base. The structure is shown in Fig. 2. The separate units are

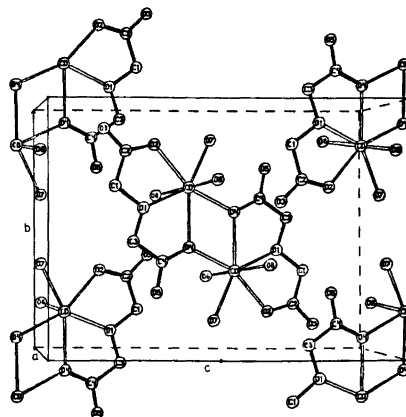


Fig. 2. The crystal structure of CDOXY II.

joined by hydrogen bonds *via* water molecules to a three-dimensional network. Two ligands are coordinated by each cadmium atom, one being tridentate and the other monodentate.

CDOXY III has a layer structure, which is shown in Fig. 3. The layers are held together

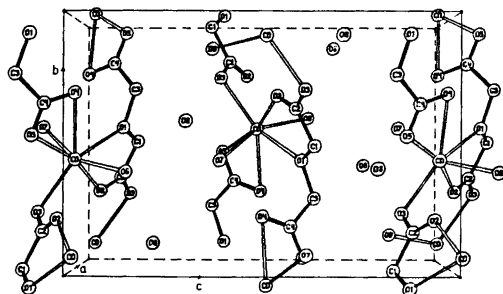


Fig. 3. The crystal structure of CDOXY III.

by an extensive hydrogen bond system in which the water molecules are involved. In this structure there are no oxygen bridges between cadmium atoms, the pentagonal bipyramids being linked up by the ligand. Three ligands are bound to each cadmium atom, two of which are bidentate and the third monodentate. One of the bidentate ligands forms a carboxylate chelate with a bite of 2.15(2) Å.

The oxydiacetate ion is planar in CDOXY II and almost planar in CDOXY I. In CDOXY III the two ligand halves about the ether oxygen are planar but form an angle of 85.5°. This was the first structure to be determined in which the oxydiacetate ion is not planar. It has later been found that this is also the case in the monoclinic phase of oxydiacetic acid.²

The three cadmium oxydiacetate hydrate structures can be compared with the structure of cadmium diacetate dihydrate, which has recently been determined.¹ In this compound the coordination about cadmium is also seven-fold although the coordination polyhedron is a square base-trigonal cap. Both acetate groups are bidentate forming carboxylate chelates and one oxygen is also in a bridging position in such a way that infinite cadmium-oxygen spirals are formed.

The cadmium oxydiacetate hydrate structures will be described in detail in forthcoming publications.

1. Harrison, W. and Trotter, J. *J. Chem. Soc. D* (1972) 956.
2. Herbertsson, H. and Boman, C.-E. *Acta Chem. Scand.* 27 (1973) 2234.

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Titrimetric Determination of Acidity and pK Values of Humic Acid

OLE K. BORGGÅRD

Royal Veterinary and Agricultural University,
Department of Soils and Agricultural Chemistry,
DK-1871 Copenhagen, Denmark

COOH and phenolic OH groups in humic acid are responsible for the cation exchange capacity and complexing ability of soil humic acid. Therefore, several methods have been proposed for the determination of the amounts (expressed as mequiv./g humic acid) of each of these groups.^{1,2} The COOH content is normally estimated by the calcium acetate method or by decarboxylation and the phenolic OH is estimated as the difference between total acidity (determined by the $Ba(OH)_2$ method) and the COOH content.^{1,2} As humic acid is a polyelectrolyte the individual carboxylic acids and phenols have different acid dissociation constants. These dissociation constants fall, however, in groups each associated with an average dissociation constant (denoted $p\bar{K}$).^{3,4}

This note presents a titrimetric method for the estimation of the amounts of COOH and phenolic OH and the $p\bar{K}$ values of these groups in humic acid.

It has been shown that the titration of humic acid ought to be carried out as fast as a normal acid-base titration.⁵ Therefore, it seems possible

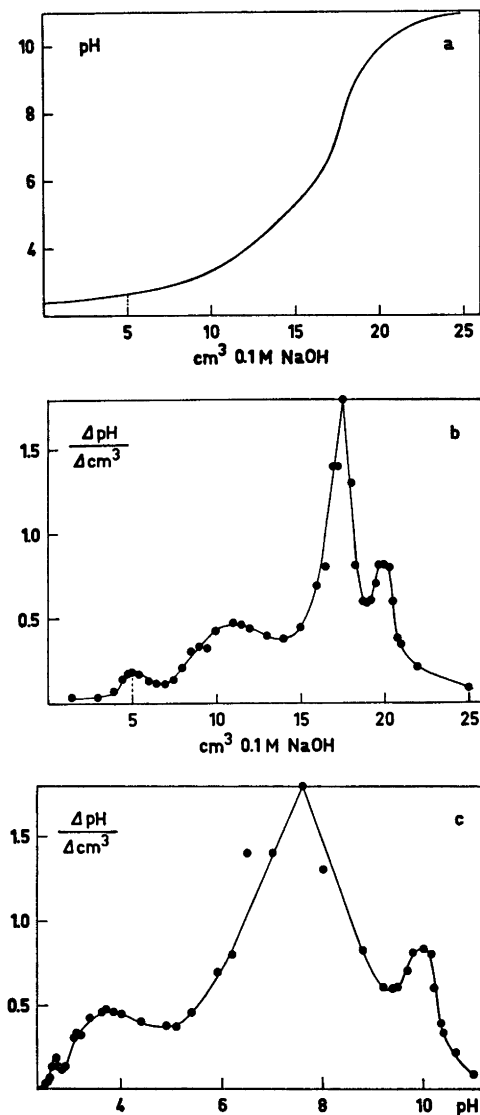


Fig. 1. The titration of 0.2 g Skarild A₁ humic acid. a. The original titration curve. b. $\Delta pH/\Delta cm^3$ plotted against cm^3 0.1 M NaOH. c. $\Delta pH/\Delta cm^3$ plotted against pH.

to determine the amounts of COOH and phenolic OH and the $p\bar{K}$ values from a simple titration. The inflection points of the titration curve are, however, blurred. This problem is overcome by differentiation of the titration curve.

Humic acid from four soil samples were tested. The soils are described elsewhere⁵ as is the extraction procedure. The titrations were