Crystal and Molecular Structure of Cadmium(II) Cyanoacetate

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Crystals of the title compound are monoclinic, a = 4·465(1), b = 10·262(2), c = 17·567(5) Å, β = 95·44(2)° Z = 4, space group $P2_1/n$. The structure was determined from X-ray diffractometer data by Patterson and Fourier syntheses, and refined by full-matrix least-squares calculations to R 0·046 for 1656 observed reflections. The cadmium is co-ordinated to one nitrogen and five oxygen atoms in distorted octahedral geometry. Each of the two independent cyanoacetate ligands co-ordinates to three symmetry-related cadmium atoms to give a three-dimensional polymeric lattice. One ligand co-ordinates through two oxygen atoms, one of which is also bridging, while the other co-ordinates through two oxygen atoms and the nitrogen atom. In common with many other acetates, the metal atom is not chelated, the ligands acting as bridging molecules.

THE structures of many metal acetates have been reported,[1] and although chelation by the acetate group has been observed,[2-5] in most cases the ligand has been found to behave as a bridging entity to yield dimeric structures, many being of the copper(II) acetate dihydrate type,[6-10] and some higher polymers,[11-13] the latter appearing to be favoured by metals which attain higher co-ordination numbers. Much less work has been carried out with carboxylic acids having more than one functional group, the interest in this field centring on whether the co-ordination behaviour of the carboxy-group is modified by the dual functionality and geometry of the ligand, and whether unusual modes of polymerisation result from the increase in possible co-ordination sites. The alkoxy-acetates of metals such as copper(II) [14,15] and nickel(II) [16] have been shown to contain unidentate carboxy-groups, the ligand being bidentate through the alkoxy oxygen atom to give a five-membered chelate ring. Similar behaviour has been noted in some hydroxy-acetates.[14] The free oxygen atom of the acetate group in these compounds is involved in hydrogen bonding and in some cases [14] forms a weak Cu–O bond, but di- or poly-meric lattices through bridged, co-ordinating atoms are not so common as in the acetates. The hydrated copper(II) complex with succinic acid,[17] however, is polymeric, each unit containing carboxylate bridges of the copper acetate dimer type. Polymeric structures have also been predicted [17,18] for some other copper(II)–dicarboxylic acid complexes. The only studies with metal cyanoacetates have involved spectroscopic [19] and magnetic [19,20] measurements of the copper(II) compound. Although the two investigations appear to have been, separately, on the hydrated and anhydrous forms, the conclusions are similar in that an oligomeric or polymeric structure has been proposed.

The preparation and X-ray structural study of a number of cadmium(II) complexes with carboxylic acids with two functional groups, and with dicarboxylic acids has been undertaken in the hope that cadmium, which is known in some compounds to achieve a co-ordination number of eight,[21,22] would yield interesting polymeric structures. An e.s.r. study [23] of copper(II) and mercury(II)-doped cadmium compounds is also in progress and accurate structural data should facilitate these investigations.

EXPERIMENTAL

Cadmium(II) cyanoacetate was prepared by warming a solution of cyanoacetic acid with a slight stoicheiometric excess of cadmium carbonate in suspension in water. Crystals were obtained on cooling. Crystals from aqueous solution were colourless plates, elongated in the a direction, with the {011} faces well developed. Space group and preliminary unit-cell dimensions were determined from precession and Weissenberg photographs. Accurate unit-cell parameters were obtained later from a least-squares treatment of the 2θ values of 18 general hkl reflections, measured on a General Electric XRD 6 diffractometer.

Crystal Data.—$C_6H_4CdN_2O_4$, M = 280·5, Monoclinic, a = 4·465(1), b = 10·262(2), c = 17·567(5), β = 95·44(2)°, U = 801·3 Å^3, Z = 4, D_c = 2·32, $F(000)$ = 536. Mo-K_α radiation, λ = 0·71069 Å, μ(Mo-K_α) = 26·8 cm^{-1}. Space group $P2_1/n$ from systematic absences: $0k0$ when k is odd, $h0l$ when $h + l$ is odd.

A crystal was cut to give a parallelepiped of side *ca.* 0·5

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mm for unit-cell refinement and data collection. The a^* direction of the crystal was set coincident with the instrument ϕ axis of a Datex-automated General Electric XRD 6 diffractometer, and all reflections with $2\theta(\text{Mo-}K_\alpha) \leqslant 55°$ were measured, by use of a θ—2θ scan at 2° min^{-1} in 2θ. A total of 1826 independent reflections was measured; 170 of these had intensities $< 3\sigma(I)$ above background, [$\sigma(I)$ is defined by: $\sigma^2(I) = S + B + (0{\cdot}05S)^2$, where S = scan count and B = background], and were treated as unobserved. A check and scaling reflection was measured every 50 reflections; throughout data collection its value dropped by a maximum of 5%. Lorentz and polarisation corrections were applied and relative structure factors derived. No absorption correction was made.

Structure Solution and Refinement.—The cadmium position was apparent in a three-dimensional Patterson synthesis, and from a Fourier synthesis, calculated with the structure factors phased by the cadmium, the remaining carbon, nitrogen, and oxygen atoms were placed. All the positional and isotropic thermal parameters were refined, by full-matrix least-squares methods, to a conventional R value of 0·082 after two cycles. One further cycle, with all the atoms treated anisotropically, yielded R 0·062. At this stage a difference Fourier indicated sites for the four hydrogen atoms, the positions coinciding with those calculated for methylene hydrogen atoms on the two carbon atoms concerned. The hydrogen atoms were included in subsequent structure-factor calculations, but their positional and thermal parameters (B_{iso} 5·0 Å^2) remained fixed during refinement. Three more cycles of anisotropic refinement, with the cadmium scattering factor corrected for the real and imaginary components of anomalous dispersion, reduced R to 0·046. During the final cycle no parameter shift was $> 0{\cdot}2\sigma$. A weighting scheme with the form $w = [A + B|F_o| + C|F_o|^2 + D|F_o|^3]^{-1}$ was employed during the final stages, with $A = 3{\cdot}80$, $B = -0{\cdot}28$, $C = -0{\cdot}009$, and $D = 0{\cdot}00004$. At convergence R' was 0·059. Final positional and thermal parameters are given in Tables 1 and 2. Measured and calculated structure factors are listed in Supplementary Publication No. SUP 20865 (18 pp., 1 microfiche).†

TABLE 1

Final positional parameters ($\times 10^4$), with standard deviations in parentheses

Atoms	x	y	z
Cd	3242·0(8)	5441·4(4)	4033·4(2)
O(1)	7215(9)	4191(4)	4717(2)
O(2)	10 908(10)	3489(4)	4043(3)
O(3)	10 720(11)	6868(5)	3267(3)
O(4)	7134(12)	6929(5)	4057(3)
N(1)	11 089(18)	178(7)	3994(5)
N(2)	9791(14)	9509(5)	2050(3)
C(1)	8726(12)	3310(5)	4424(3)
C(2)	7643(16)	1931(7)	4520(5)
C(3)	9596(18)	946(7)	4224(4)
C(4)	8277(14)	7268(6)	3473(4)
C(5)	6520(13)	8250(7)	2941(4)
C(6)	8371(14)	8950(6)	2445(3)
H(1)	9530	6840	780
H(2)	7500	6750	−110
H(3)	5470	8390	3280
H(4)	4870	7720	2590

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† For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue.

DISCUSSION

Structural details are shown in Figure 1. The co-ordination geometry around the cadmium atom is shown in Figure 2, in which atoms not bonded to Cd are omitted for clarity. Bond lengths and angles are presented in Tables 3 and 4, respectively, while some mean planes are given in Table 5.

TABLE 2

Final anisotropic thermal parameters (Å^2 × 10^3),* with standard deviations in parentheses

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cd	25·6(3)	27·3(3)	21·5(3)	1·4(2)	4·0(2)	1·3(2)
O(1)	28(2)	34(2)	19(2)	6(2)	2(2)	2(2)
O(2)	33(2)	34(2)	34(2)	1(2)	5(2)	−3(2)
O(3)	33(3)	44(3)	54(3)	6(2)	6(2)	16(2)
O(4)	42(3)	45(3)	27(2)	−13(2)	−3(2)	11(2)
N(1)	58(4)	42(4)	59(4)	9(3)	4(4)	−9(3)
N(2)	36(3)	44(3)	29(3)	0(2)	1(2)	9(2)
C(1)	22(3)	29(3)	22(3)	4(2)	−4(2)	2(2)
C(2)	35(4)	31(3)	59(5)	−3(3)	12(3)	−2(3)
C(3)	49(4)	28(3)	43(4)	−5(3)	4(3)	−4(3)
C(4)	27(3)	32(3)	34(3)	−7(2)	−4(2)	6(3)
C(5)	21(3)	43(3)	30(3)	4(2)	3(2)	13(3)
C(6)	29(3)	35(3)	28(3)	0(2)	−4(2)	7(2)

* In the form: $\exp[-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl)]$.

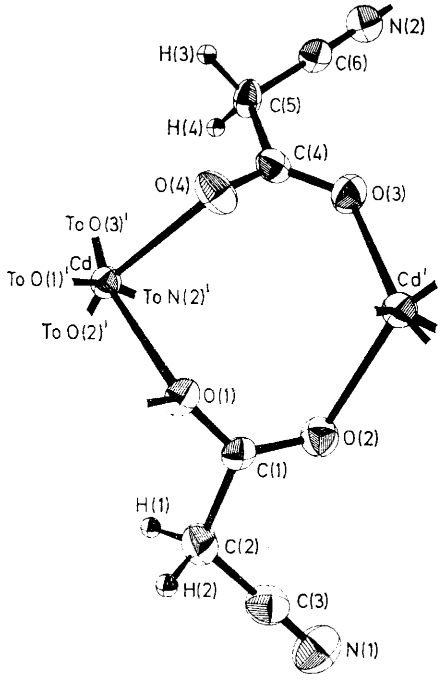

FIGURE 1 Perspective view of cadmium(II) cyanoacetate. All non-hydrogen atoms are represented by 50% probability, thermal ellipsoids

The cadmium atom is six-co-ordinate, through five oxygen atoms and one nitrogen, and the co-ordination geometry is best described as a distorted octahedron (Figure 2). The atoms O(1), O(2′), O(3′), O(4) form a plane (Table 5), from which the maximum atom displacement is 0·019 Å, while the Cd atom lies 0·19 Å above this plane in the direction of O(1). In this structure, therefore, the Cd atom does not achieve one of its higher co-ordination numbers, but distorted or irregular octahedra have been reported for some other cadmium compounds.[24-26] Over a period of a few months the compound does take up moisture from the atmosphere to a noticeable extent, and the water could, therefore, co-ordinate to the Cd to increase its co-ordination number, although there is no definite evidence for this.

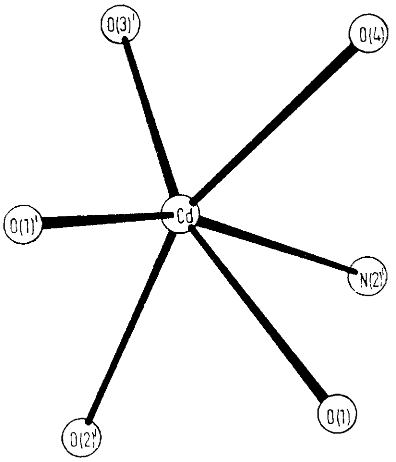

FIGURE 2 Perspective view showing the co-ordination geometry around the cadmium atom

TABLE 3

Bond distances (Å), with standard deviations in parentheses

Cd–O(1)	2·415(4)	C(3)–N(1)	1·132(10)
Cd–O(1')	2·256(4)	C(4)–O(3)	1·250(8)
Cd'–O(2)	2·259(4)	C(4)–O(4)	1·238(8)
Cd'–O(3)	2·223(5)	C(4)–C(5)	1·538(8)
Cd–O(4)	2·310(5)	C(5)–C(6)	1·447(8)
Cd–N(2)	2·372(6)	C(6)–N(2)	1·139(9)
C(1)–O(1)	1·267(7)	C(2)–H(1)	1·06
C(1)–O(2)	1·247(7)	C(2)–H(2)	1·06
C(1)–C(2)	1·510(9)	C(5)–H(3)	1·05
C(2)–C(3)	1·462(10)	C(5)–H(4)	1·06

TABLE 4

Bond angles°, with standard deviations in parentheses

O(1)–Cd–O(1')	74·6(2)	Cd–O(1)–C(1)	124·9(3)
O(1)–Cd–O(2')	81·0(2)	Cd'–O(2)–C(1)	121·3(4)
O(1)–Cd–O(3')	163·3(2)	O(1)–C(1)–O(2)	125·9(5)
O(1)–Cd–O(4)	80·0(2)	O(1)–C(1)–C(2)	115·7(5)
O(1)–Cd–N(2')	82·8(2)	O(2)–C(1)–C(2)	118·3(5)
O(1')–Cd–O(2')	93·2(2)	C(1)–C(2)–C(3)	113·6(6)
O(1')–Cd–O(3')	113·1(2)	C(2)–C(3)–N(1)	179·5(8)
O(1')–Cd–O(4)	90·6(2)	Cd'–O(3)–C(4)	116·5(4)
O(1')–Cd–N(2')	157·3(2)	Cd–O(4)–C(4)	123·9(3)
O(2')–Cd–O(3')	112·4(2)	O(3)–C(4)–O(4)	126·0(6)
O(2')–Cd–O(4)	158·8(2)	O(3)–C(4)–C(5)	116·5(6)
O(2')–Cd–N(2')	81·7(2)	O(4)–C(4)–C(5)	117·5(6)
O(3')–Cd–O(4)	85·0(2)	C(4)–C(5)–C(6)	113·8(2)
O(3')–Cd–N(2')	89·1(2)	C(5)–C(6)–N(2)	179·0(7)
O(4)–Cd–N(2')	86·9(2)	Cd–N(2')–C(6')	164·3(5)

The two cyanoacetate ligands co-ordinate differently to the metal atom. One of them is bidentate, through O(1) and O(2), to bridge cadmium atoms separated by one unit translation in the *a* direction, while atom O(1) is trigonal and bridges to a centrosymmetrically related cadmium (Cd''). The other ligand is terdentate, the carboxy-group bridging cadmium atoms in the *a* direction, while atom N(2) co-ordinates screw related Cd atoms in the *b* direction. Each ligand is, therefore, bonded to three cadmium atoms to give an infinite, three-dimensional polymer (Figure 3).

TABLE 5

Equations of some least-squares mean planes (X, Y, Z, in Å based on orthogonal co-ordinate system a, b, c^*), and distances (Å) of atoms from the planes in square brackets

Plane (1): O(1), O(2), C(1), C(2)

$$-0{\cdot}5338X + 0{\cdot}0716Y - 0{\cdot}8425Z + 7{\cdot}9459 = 0$$

[O(1) 0·003, O(2) 0·004, C(1) −0·016, C(2) 0·008, Cd 1·988]

Plane (2): O(3), O(4), C(4), C(5)

$$-0{\cdot}4277X - 0{\cdot}7512Y - 0{\cdot}5028Z + 9{\cdot}9830 = 0$$

[O(3) 0·002, O(4) 0·002, C(4) −0·006, C(5) 0·002, Cd 1·910]

Plane (3): O(1), O(2), C(1)—(3), N(1)

$$-0{\cdot}5326X + 0{\cdot}0291Y - 0{\cdot}8459Z + 8{\cdot}1278 = 0$$

[O(1) −0·022, O(2) 0·016, C(1) 0·000, C(2) 0·083, C(3) 0·000, N(1) −0·057]

Plane (4): O(3), O(4), C(4)—(6), N(2)

$$-0{\cdot}3992X - 0{\cdot}6425Y - 0{\cdot}6540Z + 10{\cdot}0276 = 0$$

[O(3) 0·088, O(4) −0·164, C(4) 0·038, C(5) 0·277, C(6) 0·019, N(2) −0·176]

Plane (5): O(1)—(4)

$$-0{\cdot}6078X - 0{\cdot}2851Y - 0{\cdot}7411Z + 8{\cdot}8163 = 0$$

[O(1) −0·004, O(2) 0·004, O(3) −0·005, O(4) 0·006]

Plane (6):* O(1), O(2'), O(3'), O(4)

$$0{\cdot}4389X - 0{\cdot}3399Y - 0{\cdot}8318Z + 7{\cdot}2354 = 0$$

[O(1) −0·019, O(2') 0·015, O(3') −0·015, O(4) 0·019]

Plane (7):* Cd, Cd'', O(1), C(1)

$$0{\cdot}6768X + 0{\cdot}7342Y - 0{\cdot}0540Z - 4{\cdot}2650 = 0$$

[Cd −0·021, Cd'' −0·024, O(1) 0·096, C(1) −0·051]

* Cd'' at $1 - x$, $1 - y$, $1 - z$; O(2') and O(3') at $-1 + x$, y, z.

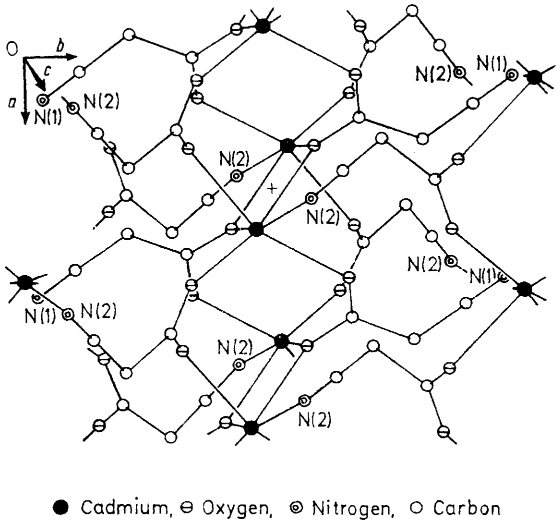

FIGURE 3 Diagram to show the lattice packing and polymeric structure (+ is at $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$)

The Cd–O distances vary from 2·223 [Cd'–O(3)] to

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2·415 Å [Cd–O(1)], which is well within the range reported for other cadmium compounds.[1,4] As has been found in other bridged structures,[4,5] the trigonal oxygen atom O(1) is involved in one long (2·415 Å), and one short (2·256 Å), metal–oxygen bond, and although C(1)–O(1) (1·267 Å) is longer than any of the other carbon–oxygen bonds, this lengthening is not necessarily a result of a weaker bond formed by a bridging atom, since an sp^2 hybridised oxygen need not lose any π-bonding ability in such a situation.[5] That the atoms C(1), O(1), Cd, Cd″ lie close to a plane and the relevant O(1) angles are not far from 120°, supports this sp^2 postulate. C(4)–O(3) (1·250 Å) is longer than C(4)–O(4) (1·238 Å), even though O(3) and O(4) are not, individually, involved in bridging. The Cd–O and C–O differences are more likely to be due to steric packing constraints in the complex polymeric lattice, than inherent chemical variations.

The Cd–N(2′) distance (2·372 Å) is close to those reported for bis(hydrazinecarboxylato-*N′O*)cadmium,[27] where the cadmium–nitrogen distances are 2·40 and 2·38 Å for the hydrated and anhydrous compounds, respectively. The closest approach to cadmium by N(1) is 4·954(7) Å, an obviously non-bonded distance. It is perhaps surprising, therefore, that the –C≡N distances in each ligand are nearly identical, and this suggests that a lone pair, which is non-bonding in the cyanide group, is involved in the dative bond from N(2) to cadmium. The different environments of the –C≡N groups are indicated well by the i.r. spectrum, which exhibits a pair of strong absorption bands at 2291 and 2263 cm^{-1}, and this supports the proposed structure for copper(II) cyanoacetate[19] in which a single Cu–N bond has been suggested and which yields i.r. absorption bands at 2285 and 2270 cm^{-1}.

In each of the cyanoacetate ligands, the acetate groups are very nearly planar, as expected. The ligand bites are 2·238 [O(1)–O(2)] and 2·217 Å [O(3)–O(4)], and close to the values found in unidentate acetates[14-16] and acetic acid itself,[28-30] indicating low strain in the moiety. The bite of chelated acetates is often smaller, *e.g.* 2·139 in acetato(dimethyl)indium(III),[5] and 2·189 and 2·196 Å in cadmium diacetate dihydrate.[4] The ligand O(1), O(2), C(1)—(3), N(1) is close to planar and bond lengths and angles are as expected. The other ligand is far from planar and this is almost certainly due to the coordination of atom N(2). The cyano-group is linearly rigid and the acetato-moiety is planar and rigid, factors contributing toward the unusually long and short C(4)–C(5) (1·538 Å) and C(5)–C(6) (1·447 Å) bonds.

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