

The apical Cu—Cl distances [2.254 (2) and 2.242 (2) Å] of the present bipyramidal complex are very close to the equatorial Cu—Cl distances [2.228 (2) and 2.214 (2) Å] of the octahedral Cu<sup>II</sup>-12-crown-4 complex (van Remoortere, Boer & Steiner, 1975). The equatorial Cu—O distances observed (2.240–2.337 Å) are much longer than those [2.113 (3) and 2.128 (3) Å] of the octahedral complex, and rather similar to those of the apical Cu—O distances [2.343 (4) and 2.403 (3) Å] in the octahedral complex. These observations are consistent with previous proposals derived from ESR studies, that is, the ground

state of the present complex is  $3d_{z^2}$  and that of the octahedral complex is  $3d_{x^2-y^2}$  or  $3d_{xy}$  (Ishizu *et al.*, 1980).

The effective radii of Mg<sup>II</sup> (0.86 Å), Co<sup>II</sup> (0.88 Å) and Cu<sup>II</sup> (0.87 Å) for octahedral coordination are very similar (Shannon & Prewitt, 1969). These values indicate that these ions fit the cavity (diameter: 1.7–2.2 Å) of this crown ring well. Therefore, similar radii will also be maintained for the pentagonal-bipyramidal coordination.

The molecular packing between Cl(1) and carbon in CHCl<sub>3</sub> [3.343 (8) Å] is slightly closer than the sum of the ordinary van der Waals radii (Fig. 3).

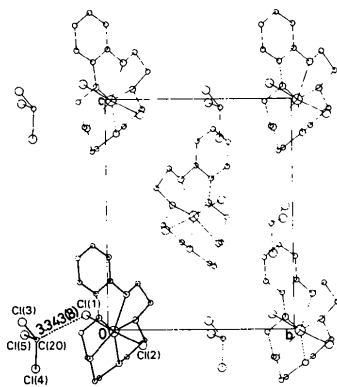


Fig. 3. The crystal structure projected along the *a* axis. The projection is limited between  $x = 0$  and  $0.52$ .

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## Structure of *cis*-Bis(acetylacetonato)diaquacalcium Monohydrate, [Ca(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>].H<sub>2</sub>O

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**Abstract.**  $M_r = 292.34$ ,  $Pnbn$ ,  $a = 5.260$  (2),  $b = 13.683$  (3),  $c = 20.062$  (7) Å,  $V = 1443.8$  (9) Å<sup>3</sup>,  $Z = 4$ ,  $D_m$  (295 K) = 1.33,  $D_x$  (85 K) = 1.34 g cm<sup>-3</sup>, Mo  $K\alpha$  radiation,  $\lambda = 0.71069$  Å,  $\mu = 4.30$  cm<sup>-1</sup>,  $T = 85$  K,  $R = 0.048$ , 1290 unique observed reflections, recrystallized from water. The complex possesses twofold symmetry and *cis* coordination of the two water molecules with Ca—O 2.356 (2) Å. Two bidentate acetylacetonate ligands complete the octahedral coordination about the Ca<sup>2+</sup> ion with Ca—O 2.336 (2)

and 2.320 (2) Å. An additional water molecule is also present in the lattice and is hydrogen bonded to the complexes.

**Introduction.** During our study of the electronic, vibrational, and magnetic-resonance spectra of various closed-shell metal acetylacetonate (acac) complexes, we found it necessary to obtain the crystal and molecular structure of the title compound. Solution of this structure adds another member to the diverse group of structures found for  $[M^{II}(\text{acac})_2L_n]$  compounds.

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**Experimental.** Colorless plates obtained by slow evaporation of an aqueous solution of the complex, which was originally prepared following the general method of Chalmers & Umar (1968); density measured by flotation in  $C_2H_2Br_4/CCl_4$ , crystal selected was a plate  $0.575 \times 0.400 \times 0.125$  mm, mounted on a Syntex  $P2_1$  diffractometer with the longest dimension parallel to the  $\phi$  axis, cell dimensions determined from a least-squares fit of ten reflections with  $17^\circ < 2\theta < 26^\circ$ , determination of space group based upon systematic absences ( $Ok\bar{l}$ ,  $k = 2n$ ;  $h0l$ ,  $h + l = 2n$ ;  $hk0$ ,  $k = 2n$ ); equivalent positions for the centrosymmetric space group  $Pbn\bar{b}$  ( $a\bar{c}b$  setting of No. 56) are  $x, y, z$ ;  $\frac{1}{2}-x, y, \frac{1}{2}-z$ ;  $\frac{1}{2}+x, \frac{1}{2}-y, -z$ ;  $-x, \frac{1}{2}-y, \frac{1}{2}+z$ ; no absorption correction (range of absorption correction factors 1.1 to 1.3); data collected to  $2\theta_{\max} = 55^\circ$  in the positive quadrant with maximum  $h, k, l$  of 7, 18, 27; two check reflections measured every 100 reflections displayed less than a 2% average fluctuation throughout data collection; a total of 1945 unique data measured, 655 considered unobserved [ $I < 2\sigma(I)$ ]; structure solved by direct methods, all atoms (including H atoms) located on Fourier and difference Fourier maps, blocked-cascade least-squares refinement (based on  $F$ ), anisotropic thermal parameters for non-hydrogen atoms and isotropic thermal parameters for H atoms; refinement converged to  $R_w = 0.039$  with  $w = 1/\sigma^2(F_o)$ ,  $S = 1.33$ , a ratio of maximum least-squares shift to error of 0.14 for the  $z$  coordinate of C(3) in the final refinement cycle and an average ratio of shift to error of 0.03; maximum and minimum heights of 0.74 and  $-0.70 e \text{ \AA}^{-3}$  in the final difference Fourier synthesis;  $F(000) = 623.95$ ; atomic scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974); computer programs from the *SHELXTL* (version 3) package.

**Discussion.** Final atomic coordinates and equivalent isotropic thermal parameters are presented in Table 1.\*

A perspective drawing of the  $[Ca(acac)_2(H_2O)_2]$  complex is presented in Fig. 1. Bond distances and angles are given in Table 2. A horizontal twofold axis passes through the Ca atom. A different twofold axis passes through O(3) of the lattice water molecule. Although the coordination about Ca is essentially octahedral, rather severe deviations from idealized angles are evident. In part, these stem from the acute bite angle of  $76.2^\circ$  of the acac ligand. However, in addition to this there is a large angle of  $102.3^\circ$  between the coordinated water molecules. The four O atoms O(2), O(2<sup>i</sup>), O(4) and O(4<sup>i</sup>), form a tetrahedrally distorted plane with deviations from the least-squares

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters ( $\text{\AA}^2 \times 10^3$ )

$$U_{eq} = (U_{11} + U_{22} + U_{33})/3.$$

	$x$	$y$	$z$	$U_{eq}$
Ca	0.2500	0.2821 (1)	0.2500	13 (1)
O(1)	0.5409 (3)	0.2795 (1)	0.3380 (1)	16 (1)
O(2)	0.1153 (3)	0.4081 (1)	0.3189 (1)	16 (1)
O(3)	-0.2500	0.5115 (2)	0.2500	19 (1)
O(4)	-0.0270 (4)	0.1742 (2)	0.3057 (1)	18 (1)
C(1)	0.5454 (5)	0.3222 (2)	0.3946 (1)	15 (1)
C(2)	0.3860 (5)	0.4005 (2)	0.4134 (1)	16 (1)
C(3)	0.1898 (5)	0.4413 (2)	0.3748 (1)	13 (1)
C(4)	0.7365 (7)	0.2846 (2)	0.4444 (1)	19 (1)
C(5)	0.0542 (6)	0.5307 (2)	0.4011 (1)	20 (1)
H(2)	0.413 (5)	0.428 (2)	0.459 (1)	10 (6)
H(4A)	0.721 (5)	0.318 (2)	0.490 (1)	26 (7)
H(4B)	0.714 (5)	0.215 (2)	0.452 (1)	25 (7)
H(4C)	0.906 (5)	0.294 (2)	0.432 (1)	24 (8)
H(5A)	-0.129 (5)	0.522 (2)	0.399 (1)	32 (8)
H(5B)	0.095 (5)	0.546 (2)	0.452 (1)	29 (8)
H(5C)	0.101 (5)	0.582 (2)	0.379 (1)	30 (8)
H(8)	-0.153 (5)	0.480 (2)	0.272 (1)	29 (9)
H(9)	-0.162 (7)	0.204 (2)	0.324 (1)	72 (13)
H(10)	-0.071 (7)	0.125 (2)	0.298 (2)	70 (15)

Table 2. Bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ )

Ca—O(1)	2.336 (2)	C(2)—H(2)	1.00 (2)
Ca—O(2)	2.320 (2)	C(4)—H(4A)	1.03 (2)
Ca—O(4)	2.356 (2)	C(4)—H(4B)	0.96 (3)
C(1)—O(1)	1.278 (3)	C(4)—H(4C)	0.94 (3)
C(1)—C(2)	1.411 (4)	C(5)—H(5A)	0.97 (3)
C(1)—C(4)	1.508 (4)	C(5)—H(5B)	1.06 (2)
C(3)—O(2)	1.273 (3)	C(5)—H(5C)	0.88 (2)
C(3)—C(2)	1.405 (4)	O(3)—H(8)	0.81 (2)
C(3)—C(5)	1.511 (4)	O(4)—H(9)	0.89 (3)
		O(4)—H(10)	0.73 (4)
H(8)...O(2)	1.95 (4)	O(3)...O(2)	2.757 (3)
H(9)...O(1 <sup>ii</sup> )	1.90 (4)	O(4)...O(1 <sup>ii</sup> )	2.767 (3)
H(10)...O(3 <sup>iii</sup> )	2.06 (4)	O(4)...O(3 <sup>iii</sup> )	2.754 (3)
O(1)—Ca—O(1 <sup>i</sup> )	178.3 (1)	C(2)—C(1)—O(1)	124.9 (2)
O(1)—Ca—O(2)	76.2 (1)	C(2)—C(3)—O(2)	124.8 (2)
O(1)—Ca—O(4)	92.1 (1)	C(1)—C(2)—C(3)	126.2 (2)
O(1)—Ca—O(4 <sup>i</sup> )	86.8 (1)	O(1)—C(1)—C(4)	116.4 (2)
O(2)—Ca—O(1 <sup>i</sup> )	105.1 (1)	C(2)—C(1)—C(4)	118.5 (2)
O(2)—Ca—O(2)	84.0 (1)	O(2)—C(3)—C(5)	116.8 (2)
O(2)—Ca—O(4 <sup>i</sup> )	159.5 (1)	C(2)—C(3)—C(5)	118.5 (2)
O(2)—Ca—O(4)	89.7 (1)	O(3)—H(8)...O(2)	173 (1)
O(4)—Ca—O(4 <sup>i</sup> )	102.4 (1)	O(4)—H(9)...O(1 <sup>ii</sup> )	165 (1)
Ca—O(1)—C(1)	132.6 (2)	O(4)—H(10)...O(3 <sup>iii</sup> )	160 (1)
Ca—O(2)—C(3)	134.1 (2)		

Symmetry code: (i)  $\frac{1}{2}-x, y, \frac{1}{2}-z$ ; (ii)  $-1+x, y, z$ ; (iii)  $-\frac{1}{2}-x, -\frac{1}{2}+y, z$ .

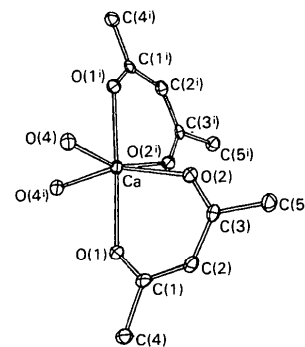


Fig. 1. A drawing of  $[Ca(acac)_2(H_2O)_2]$  showing the atom numbering scheme and anisotropic thermal ellipsoids at the 50% level.

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38198 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

plane of  $+0.40(1)$ ,  $-0.40(1)$ ,  $-0.33(1)$ , and  $+0.33(1)$  Å, respectively. The remaining O atoms are above and below this plane with  $O(1^1)-Ca-O(1) = 178.3^\circ$ . The puckering in the equatorial plane of the Ca complex may arise from non-bonded repulsions between the *cis*-coordinated water molecules. However, it may also be due to restrictions imposed by the strong intermolecular hydrogen bonding.

As can be seen by the interactions depicted in Fig. 2, a network of hydrogen bonding links molecules together in the *ab* plane. Each lattice water molecule is hydrogen bonded to four complexes. These hydrogen bonds are of two types: (1) between the O atom of the lattice water molecule and one of the H atoms of the coordinated water molecule and (2) between the H atom of the lattice water molecule and one of the O atoms of the acetylacetonate ligand. A third type of hydrogen bond is between the other O atom of acetylacetonate and the second H atom of a coordinated water molecule in an adjacent complex.

The only reported structure that contains Ca and an acetylacetonate-derived ligand is that of  $[Ca\{(C_6H_5CO)_2CH\}_2] \cdot \frac{1}{2}C_2H_5OH$  (Hollander, Templeton & Zalkin, 1973). A number of Ca—O distances varying between 2.256 (2) and 2.508 (2) Å were found. These bracket those found in this study.

Table 3 presents a comparison with the structures of the Be, Zn, Mg, Cd and Ca acac complexes. The broad range of effective ionic radii in this series not only has a striking effect on the *M*—O distances, but also is reflected in the increase in coordination number and decrease in the ring OMO angle from  $107(1)^\circ$  in

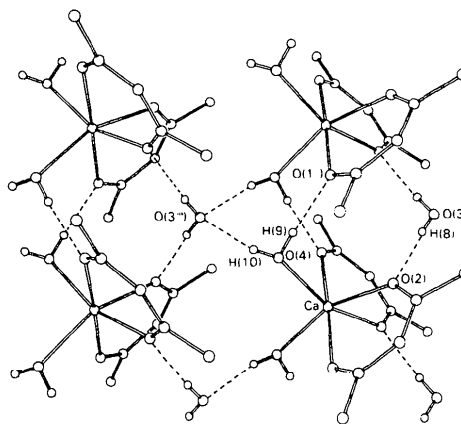


Fig. 2. Intermolecular hydrogen bonding in the *ab* plane. The smaller circles are H atoms of lattice and coordinated water molecules.

$[Be(acac)_2]$  (Stewart & Morosin, 1975) to  $76.2(1)^\circ$  in  $[Ca(acac)_2(H_2O)_2] \cdot H_2O$ .

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Table 3. Bond distances (Å), bond angles ( $^\circ$ ) and ionic radii (Å) of group II acetylacetonate complexes

Complex	Effective ionic radius*	Geometry	<i>M</i> —O(acac)	<i>M</i> —O(H <sub>2</sub> O)	Ring OMO	MOC	Reference
$[Be(acac)_2]$	0.27	Tetrahedral	1.62 (2) av.		107 (1) av.	122 (1) av.	(a)
$[Zn(acac)_2]$	0.60	Tetrahedral	1.942 (6)		97.2 (13)	122.9 (10)	(b)
$[Zn(acac)_2(H_2O)]$	0.68	Distorted tetragonal pyramid	2.02 (2) av.	2.00 (2)	88.2 (8) av.	128.1 (1.3) av.	(c)
$[Zn(acac)_2]_3$	0.68	Trigonal bipyramid	2.03 (4) av.		89.6 (11) av.		(d)
	0.75	Octahedral	2.10 (5) av.		87.1 (1)		
$[Mg(acac)_2(H_2O)_2]$	0.72	<i>trans</i> -Octahedral	2.040 (4) 2.027 (4) av.	2.148 (4)	89.02 (2)	124.0 (4) 125.3 (4)	(e)
$[Cd(acac)_2]$	0.95	Octahedral	2.235 (15) av. 2.334 (4) av.		83 (3) av.	130.4 (5) 126.9 (5)	(f)
$[Ca(acac)_2(H_2O)_2] \cdot H_2O$	1.00	<i>cis</i> -Octahedral	2.336 (2) 2.320 (2)	2.356 (2)	76.2 (1)	132.6 (2) 134.1 (2)	(g)

References: (a) Stewart & Morosin (1975). (b) Shibata & Ohta (1981). (c) Montgomery & Lingafelter (1963). (d) Bennett, Cotton & Eiss (1968). (e) Morosin (1967). (f) Maslen, Greaney, Raston & White (1975). (g) This work.

\* Huheey (1972) (coordination number of the ion is taken into account).

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## Bis[bis(diethylamino)glyoximato]nickel(II), $C_{20}H_{42}N_8NiO_4$

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**Abstract.**  $M_r = 517.3$ , monoclinic, space group  $P2_1/a$ ,  $a = 15.760$  (2),  $b = 11.792$  (3),  $c = 7.297$  (1) Å,  $\beta = 99.10$  (1)°,  $V = 1339.0$  (7) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.28$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 0.765$  mm<sup>-1</sup>,  $F(000) = 556$ . Final  $R = 0.068$  for 1809 observed reflections. The Ni atom is located on an inversion centre, and displays a square-planar coordination. The bis(diaminoglyoximato)nickel(II) moiety is nearly planar, and the displacement of ethyl groups from this plane is a result of steric effects.

**Introduction.** Synthesis of compounds with possible metal...metal or metal...ligand contacts is presently being carried out by the Department of Chemistry of the National University of Colombia. In order to elucidate the configuration of the title compound, X-ray analysis was performed.

**Experimental.** Red elongated prisms, Philips PW-1100 diffractometer, Mo  $K\alpha$ , graphite monochromator,  $\omega$ -scan technique, 1819 independent with  $\theta \leq 25^\circ$ , 1809

with  $I \geq 2.5\sigma(I)$ , Lp correction, absorption ignored; direct methods (*MULTAN* 80; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980), anisotropic full matrix (*SHELX* 76; Sheldrick, 1976), anomalous scattering factors for all atoms (*International Tables for X-ray Crystallography*, 1974), H (from  $\Delta F$  synthesis) overall isotropic temperature factor, final  $R = 0.068$ ,  $R_w = 0.077$ ,  $w = [\sigma^2(F) + 0.0026|F|^2]^{-1}$ ; Digital VAX-750.

**Discussion.** Atomic parameters are given in Table 1; † atom numbering, bond distances and angles in Fig. 1.

The crystal structure consists of discrete molecules linked by van der Waals interactions in layers parallel to (001). The shortest Ni...Ni and Ni...N(Et)<sub>2</sub> lengths are 7.30 and 6.11 Å. The shortest intramolecular distance Ni...H(C43<sup>i</sup>) (where  $i = x, y, z + 1$ ) [3.04 (8) Å] is comparable to Ni...N [3.478 (3)] obtained by Endres (1979) in bis(oxamide ox-

\* This paper reports part of the research work undertaken to satisfy the requirements for this author's Master Thesis. Present address: Departamento de Química, Universidad Francisco de Paula, Santander, Colombia.

† Lists of structure factors, anisotropic thermal parameters and a complete list of distances and angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38225 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.