

bit the same configuration: that of the *trans* diastereomer.

The torsion angles for the sequences corresponding to C(10)—C(11)—C(15)—N(5) are 20.7, 32.9, 61.8 and 70.4°, respectively, indicating the angular rotation between the six- and five-membered rings of the four ligands. The relationship between ligand configuration and formation of complexes of this type would be an interesting topic for study.

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## Mononuclear and Binuclear Products from Bis(acetylacetonato)zinc and 1,4-Diazabicyclo[2.2.2]octane (Dabco)

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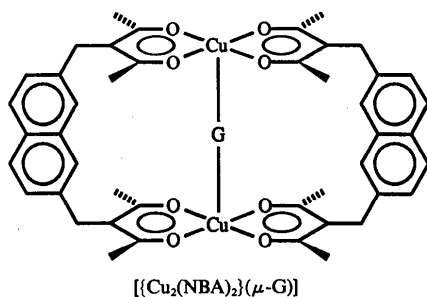
**Abstract.** The structures of two products formed from  $\text{Zn}(\text{acac})_2 \cdot \text{H}_2\text{O}$  ( $\text{acacH} = 2,4\text{-pentanedione}$ ) and Dabco (1,4-diazabicyclo[2.2.2]octane) are reported. In  $\text{CH}_2\text{Cl}_2$ , Dabco is chloroalkylated: *trans*-bis(1-chloromethyl-4-aza-1-azoniabicyclo[2.2.2]octane- $N^4$ )-bis(2,4-pentanedionato)zinc dichloride,  $[\text{Zn}(\text{Dabco-CH}_2\text{Cl})_2(\text{acac})_2]\text{Cl}_2$ , (I),  $\text{C}_{24}\text{H}_{42}\text{Cl}_4\text{N}_4\text{O}_4\text{Zn}$ ,  $M_r = 657.82$ , monoclinic,  $C2/m$ ,  $a = 20.724$  (3),  $b = 11.405$  (2),  $c = 6.595$  (1) Å,  $\beta = 104.78$  (1)°,  $V = 1507.3$  (9) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.449$ ,  $D_m = 1.44$  (2) Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 1.23$  mm<sup>-1</sup>,  $F(000) = 688$ ,  $T = 293$  K,  $R = 0.039$  for 1619 data with  $F_o^2 > 3\sigma(F_o^2)$  ( $R = 0.100$  for 2722 data with  $F_o^2 > 0$ ). The complex cation lies upon a  $2/m$  site and consists of two  $\text{N}(\text{CH}_2\text{CH}_2)_3\text{NCH}_2\text{Cl}^+$

(Dabco $\text{CH}_2\text{Cl}^+$ ) and two  $\text{acac}^-$  ligands in a *trans* arrangement about Zn. The Zn—O and Zn—N distances are 2.042 (2) and 2.400 (2) Å respectively. The cationic Dabco $\text{CH}_2\text{Cl}^+$  ligands in (I) appear to be produced by nucleophilic attack of Dabco on  $\text{CH}_2\text{Cl}_2$ . The reaction in benzene is more straightforward:  $\mu$ -(1,4-diazabicyclo[2.2.2]octane- $N^1, N^4$ )-bis[bis(2,4-pentanedionato)zinc] benzene solvate  $[\{\text{Zn}(\text{acac})_2\}_2(\mu\text{-Dabco})] \cdot \text{C}_6\text{H}_6$ , (II),  $\text{C}_{32}\text{H}_{46}\text{N}_2\text{O}_8\text{Zn}_2$ ,  $M_r = 717.50$ , triclinic,  $P\bar{1}$ ,  $a = 10.409$  (2),  $b = 11.327$  (1),  $c = 7.6915$  (6) Å,  $\alpha = 94.072$  (8),  $\beta = 99.830$  (9),  $\gamma = 102.83$  (1)°,  $V = 865.6$  (4) Å<sup>3</sup>,  $Z = 1$ ,  $D_x = 1.376$ ,  $D_m = 1.39$  (2) Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 1.466$  mm<sup>-1</sup>,  $F(000) = 376$ ,  $T = 295$  K,  $R = 0.034$  for 3141 data with  $F_o^2 > 3\sigma(F_o^2)$  ( $R = 0.087$  for 5028 data with  $F_o^2 > 0$ ). In the centrosymmetric  $[\{\text{Zn}(\text{acac})_2\}_2(\mu\text{-Dabco})]$  units in (II)

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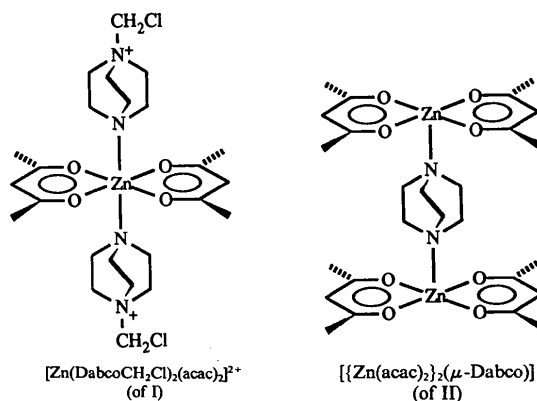
[Zn...Zn 6.8489 (3) Å], each metal atom is in a square-pyramidal environment, with a Dabco N atom at the apex; the Dabco moiety is disordered about the center of symmetry, and the two Zn(acac)<sub>2</sub> moieties are eclipsed. Zn—O distances range from 2.004 (2) to 2.030 (2) Å, and the Zn—N distance is 2.127 (2) Å.

**Introduction.** The cofacial binuclear complex Cu<sub>2</sub>(NBA)<sub>2</sub>\* (see scheme) recognizes and binds small guest molecules G (Maverick, Ivie, Waggenspack & Fronczek, 1990; Maverick, Buckingham, Yao, Bradbury & Stanley, 1986). We are currently preparing zinc analogs of these complexes as models for the active site of *E. coli* alkaline phosphatase (Coleman & Gettins, 1983). Because the β-diketone complexes of Zn have been less extensively studied than those of Cu, we first studied the reactions of Zn(acac)<sub>2</sub> (acacH = 2,4-pentanedione) with Dabco (1,4-diazabicyclo[2.2.2]octane). The structures of two of the products are reported herein. The first of these compounds is also of interest because it shows that Dabco is chloroalkylated by CH<sub>2</sub>Cl<sub>2</sub>, which is ordinarily considered an unreactive solvent.



**Experimental.** Both compounds were prepared by reaction of bis(acetylacetonato)zinc hydrate (Lippert & Truter, 1960) with Dabco in 2:1 molar ratio at room temperature. When the reagents were mixed in CH<sub>2</sub>Cl<sub>2</sub> and the solution was allowed to evaporate, feathery polycrystalline material was produced, along with a small quantity of colorless prisms which were suitable for X-ray analysis. <sup>1</sup>H NMR spectra suggested that the feathery and prismatic crystals were [Zn(acac)<sub>2</sub>](Dabco) and [{Zn(acac)<sub>2</sub>]<sub>2</sub>(μ-Dabco)] respectively. However, the structure determination shows that the prismatic crystals are actually *trans*-bis(1-chloromethyl-4-aza-1-azoniabicyclo[2.2.2]octane-*N*<sup>4</sup>)bis(2,4-pentanedionato)zinc dichloride, [Zn(DabcoCH<sub>2</sub>Cl)<sub>2</sub>(acac)<sub>2</sub>]Cl<sub>2</sub> [(I); see scheme of cation]. The major product in benzene solution, on the other hand, is [{Zn(acac)<sub>2</sub>]<sub>2</sub>(μ-

Dabco)].C<sub>6</sub>H<sub>6</sub> [(II); see scheme]. Colorless plate-shaped crystals of (II) suitable for X-ray analysis were obtained by layering a solution of the compound in benzene with hexanes.



Crystals were placed in random orientations in glass capillaries, which were mounted on an Enraf-Nonius CAD-4 diffractometer fitted with Mo *K*α source and graphite monochromator. Cell dimensions were determined by a least-squares fit to setting angles of 25 reflections having 10 < θ < 18°. ω-2θ scans were made at speeds ranging from 0.45 to 4.0° min<sup>-1</sup> to measure all significant data with approximately equal relative precision. Data reduction included corrections for background and Lorentz and polarization effects. Absorption corrections were based on ψ scans. For (II), the standard reflections increased in intensity by ca 1.8% during data collection, and a linear correction was applied. No such correction was necessary for (I). Additional data collection and refinement parameters are given in Table 1.

The space group for (I) was determined by systematic absences (*hkl*, *h* + *k* odd), and by successful refinement of a centrosymmetric model. The space group for (II) was determined by successful refinement of a centrosymmetric model. Initial solution was by Patterson and direct methods. Refinement was by full-matrix least squares based upon *F*, with weights  $w = 4F_o^2[\sigma^2(I) + (0.02F_o^2)^2]^{-1}$ , using the *Enraf-Nonius SDP/VAX Structure Determination Package* (Frenz, 1985), scattering factors of Cromer & Waber (1974) and anomalous coefficients of Cromer (1974). Non-H atoms were refined anisotropically; H atoms were located by Δ*F* synthesis and refined isotropically, except for the Dabco H atoms in (II). These were placed in calculated positions, with fixed isotropic displacement parameters; they, and the attached C atoms, were assigned populations of ½ to model the disorder about the center of symmetry. An extinction coefficient  $g = 2.6(7) \times 10^{-7}$  was refined for (II), where the correction factor

\* NBAH<sub>2</sub> = 2,7-naphthalenediylbis(methylene)bis(acetylacetonate), or 3,3'-[2,7-naphthalenediylbis(methylene)]bis(2,4-pentanedione).

Table 1. Data collection and refinement parameters

	[Zn(DabcoCH <sub>2</sub> Cl) <sub>2</sub> (acac) <sub>2</sub> ]Cl <sub>2</sub> (I)	[[Zn(acac) <sub>2</sub> ] <sub>2</sub> (μ-Dabco)] <sub>2</sub> C <sub>6</sub> H <sub>6</sub> (II)
Crystal size (mm)	0.18 × 0.25 × 0.55	0.13 × 0.42 × 0.47
Transmission range	0.9680–0.9991	0.7209–0.9998
T (K)	293	295
θ range (°)	1–32	1–30
Reflections measured	–30 ≤ h ≤ 30	–14 ≤ h ≤ 14
	0 ≤ k ≤ 17	–15 ≤ k ≤ 15
	0 ≤ l ≤ 9	0 ≤ l ≤ 10
R <sub>int</sub>	0.027	—
Standard reflections	400, 040, 001	200, 020, 002
Unique reflections	2722 [1619, I > 3σ(I)]	5028 [3141, I > 3σ(I)]
Parameters refined	139	295
R (observed data)	0.039	0.034
R (all data)	0.100	0.087
wR	0.040	0.037
S	1.787	1.596
Δ/σ <sub>max</sub>	0.01	0.05
Max., min. Δρ (e Å <sup>-3</sup> )	0.61, –0.58	0.22, –0.22
Extinction	—	2.6 (7) × 10 <sup>-7</sup>

Table 2. Coordinates and equivalent isotropic displacement parameters

	x	y	z	U <sub>eq</sub> (Å <sup>2</sup> )*
[Zn(DabcoCH <sub>2</sub> Cl) <sub>2</sub> (acac) <sub>2</sub> ]Cl <sub>2</sub> (I)				
Zn	0	0	0	0.0341 (1)
O1	–0.03614 (7)	–0.1274 (1)	0.1588 (2)	0.0363 (4)
N1	0.1028 (1)	0	0.2689 (3)	0.0310 (6)
N2	0.2128 (1)	0	0.5593 (4)	0.0327 (6)
C1	0	–0.2921 (3)	0	0.0457 (9)
C2	–0.0330 (1)	–0.2369 (2)	0.1332 (3)	0.0399 (6)
C3	–0.0700 (1)	–0.3116 (2)	0.2553 (4)	0.0602 (8)
C4	0.0895 (2)	0	0.4751 (5)	0.053 (1)
C5	0.1535 (2)	0	0.6531 (4)	0.0456 (9)
C6	0.1426 (1)	–0.1042 (3)	0.2540 (4)	0.0603 (8)
C7	0.2082 (1)	–0.1075 (2)	0.4282 (4)	0.0558 (7)
C8	0.2744 (2)	0	0.7374 (5)	0.047 (1)
C11	↓	↓	0	0.0531 (2)
C12	0.34765 (5)	0	0.6503 (2)	0.1062 (6)
[[Zn(acac) <sub>2</sub> ] <sub>2</sub> (μ-Dabco)] <sub>2</sub> C <sub>6</sub> H <sub>6</sub> (II)				
Zn	0.78006 (2)	0.57665 (2)	0.82986 (3)	0.04965 (6)
O1	0.7180 (2)	0.6816 (2)	1.0082 (2)	0.0619 (5)
O2	0.8735 (2)	0.7310 (2)	0.7423 (2)	0.0638 (5)
O3	0.7519 (2)	0.4457 (2)	0.9911 (2)	0.0591 (5)
O4	0.8975 (1)	0.4899 (2)	0.7134 (2)	0.0578 (4)
N	0.6054 (2)	0.5300 (2)	0.6261 (2)	0.0458 (5)
C1	0.6791 (3)	0.8501 (3)	1.1670 (4)	0.103 (1)
C2	0.7399 (3)	0.7960 (2)	1.0267 (3)	0.0636 (7)
C3	0.8132 (3)	0.8738 (2)	0.9280 (4)	0.0711 (8)
C4	0.8723 (2)	0.8389 (2)	0.7916 (3)	0.0603 (7)
C5	0.9396 (3)	0.9348 (3)	0.6887 (4)	0.087 (1)
C6	0.7784 (3)	0.2776 (3)	1.1444 (4)	0.0826 (9)
C7	0.8074 (2)	0.3566 (2)	0.9999 (3)	0.0527 (6)
C8	0.8920 (2)	0.3283 (2)	0.8906 (3)	0.0545 (6)
C9	0.9322 (2)	0.3943 (2)	0.7551 (3)	0.0486 (6)
C10	1.0250 (3)	0.3504 (3)	0.6506 (3)	0.0721 (8)
C1D'	0.5091 (5)	0.4141 (5)	0.6517 (7)	0.079 (2)
C2D	0.5250 (5)	0.6216 (7)	0.6164 (7)	0.081 (2)
C3D	0.6364 (5)	0.5080 (5)	0.4488 (8)	0.083 (2)
C4D	0.3863 (6)	0.3778 (5)	0.5009 (7)	0.074 (2)
C5D	0.4013 (5)	0.5856 (5)	0.4666 (8)	0.083 (2)
C6D	0.5129 (5)	0.4715 (7)	0.2990 (7)	0.080 (2)
C1S	0.4934 (4)	0.0529 (4)	0.3472 (5)	0.114 (1)
C2S	0.5969 (4)	0.0974 (3)	0.4807 (5)	0.105 (1)
C3S	0.3953 (4)	–0.0459 (4)	0.3653 (5)	0.112 (1)

\*U<sub>eq</sub> =  $\frac{1}{3}[a^2U_{11} + b^2U_{22} + c^2U_{33} + 2(aba^*b^*U_{12}\cos\gamma + aca^*c^*U_{13}\cos\beta + bcb^*c^*U_{23}\cos\alpha)]$ .

†C atoms labeled D were assigned  $\frac{1}{2}$  occupancy.

$(1 + gI_c)^{-1}$  was applied to  $F_c$ . Final R factors and residual electron densities are given in Table 1.

**Discussion.** Refined fractional coordinates and isotropic equivalent displacement parameters are listed in Table 2. Figs. 1 and 2 are ORTEP drawings

Table 3. Bond distances (Å) and bond angles (°)

See Figs. 1 and 2 for explanations of the symbols ', '' and \*.

[Zn(DabcoCH <sub>2</sub> Cl) <sub>2</sub> (acac) <sub>2</sub> ]Cl <sub>2</sub> (I)			
Zn—O1	2.042 (2)	N2—C5	1.509 (4)
Zn—N1	2.400 (2)	N2—C7	1.489 (3)
O1—C2	1.264 (3)	N2—C8	1.499 (4)
C1—C2	1.393 (3)	C4—C5	1.532 (4)
C2—C3	1.509 (4)	C6—C7	1.540 (3)
N1—C4	1.455 (4)	C8—C12	1.755 (4)
N1—C6	1.464 (3)		
O1—Zn—O1'	89.27 (6)	C1—C2—C3	118.6 (2)
O1—Zn—O1''	90.73 (6)	C4—N1—C6	107.9 (2)
O1—Zn—O1*	180	C6—N1—C6''	108.6 (2)
O1—Zn—N1	89.64 (5)	C5—N2—C7	107.4 (2)
O1—Zn—N1'	90.36 (5)	C5—N2—C8	107.4 (2)
N1—Zn—N1'	180	C7—N2—C7''	110.8 (2)
Zn—O1—C2	126.6 (1)	C7—N2—C8	111.7 (1)
Zn—N1—C4	110.2 (2)	N1—C4—C5	112.4 (3)
Zn—N1—C6	111.1 (1)	N2—C5—C4	108.8 (2)
C2—C1—C2'	126.3 (3)	N1—C6—C7	112.0 (2)
O1—C2—C1	125.6 (2)	N2—C7—C6	109.0 (2)
O1—C2—C3	115.8 (2)	C12—C8—N2	112.3 (2)
[[Zn(acac) <sub>2</sub> ] <sub>2</sub> (μ-Dabco)] <sub>2</sub> C <sub>6</sub> H <sub>6</sub> (II)			
Zn—Zn'	6.8489 (3)	C7—C8	1.388 (4)
Zn—O1	2.030 (2)	C8—C9	1.393 (3)
Zn—O2	2.023 (2)	C9—C10	1.499 (4)
Zn—O3	2.004 (2)	N—C1D	1.512 (6)
Zn—O4	2.011 (2)	N—C2D	1.469 (6)
Zn—N	2.127 (2)	N—C3D	1.471 (6)
O1—C2	1.259 (3)	C1D—C4D	1.531 (7)
O2—C4	1.258 (3)	C2D—C5D	1.532 (7)
O3—C7	1.269 (3)	C3D—C6D	1.530 (6)
O4—C9	1.260 (3)	C4D—N'	1.479 (6)
C1—C2	1.501 (5)	C5D—N'	1.427 (6)
C2—C3	1.389 (4)	C6D—N'	1.443 (6)
C3—C4	1.381 (4)	C1S—C2S	1.332 (5)
C4—C5	1.506 (4)	C2S—C3S	1.355 (6)
C6—C7	1.504 (4)	C3S—C1S'	1.371 (5)
O1—Zn—O2	88.55 (7)	O4—C9—C8	125.0 (2)
O1—Zn—O3	86.65 (7)	O4—C9—C10	116.7 (2)
O1—Zn—O4	161.09 (6)	C8—C9—C10	118.3 (2)
O1—Zn—N	100.18 (7)	Zn—N—C1D	112.2 (2)
O2—Zn—O3	157.45 (6)	Zn—N—C2D	114.1 (2)
O2—Zn—O4	87.66 (7)	Zn—N—C3D	112.7 (2)
O2—Zn—N	97.97 (7)	C1D—N—C2D	104.5 (3)
O3—Zn—O4	89.79 (7)	C1D—N—C3D	105.5 (3)
O3—Zn—N	104.57 (6)	C2D—N—C3D	107.2 (4)
O4—Zn—N	98.69 (6)	N—C1D—C4D	112.1 (4)
Zn—O1—C2	127.0 (2)	N—C2D—C5D	112.5 (4)
Zn—O2—C4	127.8 (2)	N—C3D—C6D	114.2 (4)
Zn—O3—C7	126.5 (2)	C1D—C4D—N'	109.6 (4)
Zn—O4—C9	127.2 (2)	C2D—C5D—N'	110.5 (5)
O1—C2—C1	115.8 (2)	C3D—C6D—N'	108.7 (4)
O1—C2—C3	125.5 (3)	C4D—N'—C5D	108.6 (4)
C1—C2—C3	118.6 (3)	C4D—N'—C6D	108.0 (4)
C2—C3—C4	125.9 (3)	C4D—N'—Zn'	109.6 (2)
O2—C4—C3	125.0 (2)	C5D—N'—C6D	111.4 (4)
O2—C4—C5	115.8 (2)	C5D—N'—Zn'	109.0 (2)
C3—C4—C5	119.2 (2)	C6D—N'—Zn'	110.2 (2)
O3—C7—C6	115.7 (2)	C2S—C1S—C3S'	119.9 (4)
O3—C7—C8	125.7 (2)	C1S—C2S—C3S	120.2 (3)
C6—C7—C8	118.6 (2)	C2S—C3S—C1S'	119.9 (3)
C7—C8—C9	125.6 (2)		

(Johnson, 1976), showing the atom numbering; packing diagrams appear in Figs. 3 and 4. Bond distances and angles are presented in Table 3.\*

The structure of (I) consists of *trans*-octahedral [Zn(DabcoCH<sub>2</sub>Cl)<sub>2</sub>(acac)<sub>2</sub>]<sup>2+</sup> ions at 2/m sites and

\* Tables of H-atom coordinates and thermal parameters, distances and angles involving H atoms, anisotropic displacement parameters and structure-factor amplitudes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53060 (48 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

chloride ions on inversion centers. The central CH groups of the nearly planar [maximum deviation 0.071 (1) Å] acac moieties lie on the twofold axis; the atoms N1, N2, C4, C5, C8 and C12 lie in the mirror plane. Chlorine atom Cl2 exhibits a displacement ellipsoid elongated across the mirror (r.m.s. amplitude of vibration 0.456 Å); the C8—Cl2 distance, 1.755 (4) Å, is also slightly shorter than expected. These features may represent unresolved disorder; for example, models with Cl2 displaced slightly out of the mirror plane, or with the mirror plane completely removed (as in space group *C*<sub>2</sub>), may be more complete. However, because these models were expected to cause difficulties in refinement, they were not pursued. The chloride ion makes its closest approach to the chloromethyl group in the DabcoCH<sub>2</sub>Cl<sup>+</sup> ligand [Cl1...C8 3.440 (2), Cl1...H8 2.58 (2) Å]. The closest intermolecular contact is between the coordinated O atom and the DabcoCH<sub>2</sub>Cl<sup>+</sup> moiety in an adjacent molecule [O1...C4 3.244 (3), O1...H4 2.69 (3) Å]. The cationic DabcoCH<sub>2</sub>Cl<sup>+</sup> ligands in this structure have apparently been formed by nucleophilic attack of Dabco on the CH<sub>2</sub>Cl<sub>2</sub> solvent. We have recently shown that other amines, such as 2-(aminomethyl)pyridine, can attack CH<sub>2</sub>Cl<sub>2</sub> in a similar fashion (Maverick, Ivie & Fronczek, 1990).

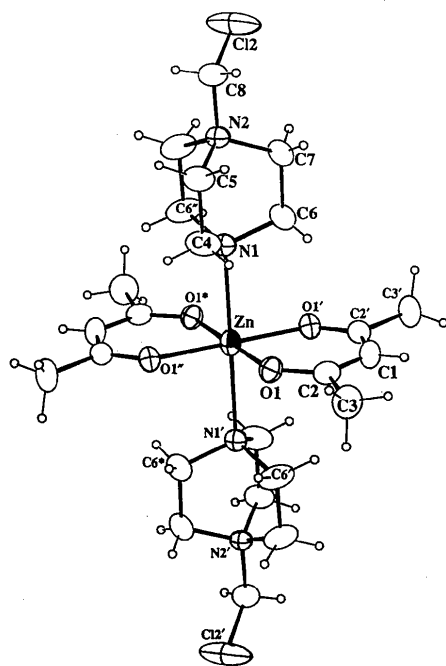


Fig. 1. ORTEP drawing (Johnson, 1976) of [Zn(DabcoCH<sub>2</sub>Cl)<sub>2</sub>(acac)<sub>2</sub>]<sup>2+</sup>, the cation in (I), representing H atoms by circles of arbitrary radius and other atoms by 40% probability ellipsoids. The symbols ', ', and \* indicate the symmetry operations 2, *m*, and  $\bar{1}$  respectively.

In (II), the binuclear [{Zn(acac)<sub>2</sub>]<sub>2</sub>(μ-Dabco)] unit [Zn...Zn' 6.8489 (3) Å] and the benzene solvent molecule possess inversion symmetry. The environment about the Zn atoms is square pyramidal, with the Zn atom displaced 0.363 (1) Å out of the least-squares plane of the four O atoms. The two unique acac<sup>-</sup> moieties (O1, O2, C1—C5; O3, O4, C6—C10) are nearly planar, with maximum deviations 0.044 (3) and 0.024 (3) Å respectively, and the two least-squares planes make an angle of 30.1 (2)°. Although the Zn(acac)<sub>2</sub> moiety possesses approximate local *mm*2 (*C*<sub>2v</sub>) symmetry, the μ-Dabco moiety is rotated about its N...N axis so as not to conform to either of these local mirrors [the O4—Zn—N—C3D torsion angle, for example, is -27.5 (3)°]. Because Dabco lacks a center of symmetry, the μ-Dabco moiety in this structure must be disordered, with its C and H atoms required to have ½ occupancy. (We attempted to refine an ordered model for this structure in space group *P*<sub>1</sub>; however, this led to convergence difficulties, correlation coefficients greater than 0.8 and variations approaching 0.2 Å in chemically equivalent bond lengths.) The benzene molecule (atoms C1S—C3S and H1S—H3S) is near the μ-Dabco moiety (C2S...H52D 3.03 Å). The closest contacts between adjacent [{Zn(acac)<sub>2</sub>]<sub>2</sub>(μ-Dabco)] molecules are O2...C10 [ $\bar{x}, 1 - y, 1 - z$ ; 3.497 (3) Å] and O4...C7 [ $\bar{x}, 1 - y, \bar{z}$ ; 3.477 (2) Å].

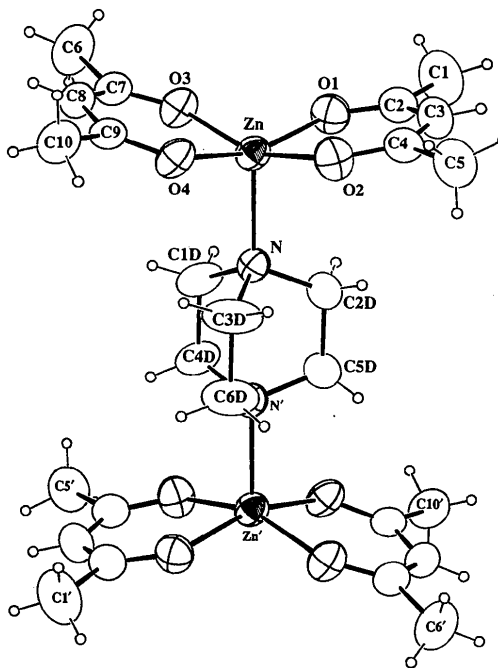


Fig. 2. ORTEP drawing (Johnson, 1976) of [{Zn(acac)<sub>2</sub>]<sub>2</sub>(μ-Dabco)], the binuclear complex of (II), representing H atoms by circles of arbitrary radius and other atoms by 40% probability ellipsoids. The primes represent atoms related by the crystallographic inversion center. Only one of the two inversion-related Dabco orientations is shown.

We have compared our complexes with related species in the literature in the following respects: distances from Zn to the apical N and  $\beta$ -diketonato O atoms, and the dihedral angle between the two  $\beta$ -diketonato planes (for five-coordinate structures). The largest difference in bond lengths between (I) and (II) is in the Zn—N bond, which is nearly 0.3 Å longer in the six-coordinate complex (I). It is also substantially longer than the corresponding Zn—L bonds in two other *trans*-L<sub>2</sub>( $\beta$ -diketonato)<sub>2</sub>Zn structures: *trans*-bis[1,3-di(2-hydroxyphenyl)-1,3-propanedionato]bis(ethanol)zinc [2.174 (6) and 2.180 (6) Å; Solans, Font-Altaba, Brioso, Llobet, Teixidor & Casabo (1983)] and *trans*-diaquabis(hexafluoroacetylacetonato)zinc [2.099 (7) and 2.157 (5) Å; Adams, Allen, Rychlewska & Hodgson (1986)]. The Zn—N bond in (I) may be unusually long because the cationic DabcoCH<sub>2</sub>Cl<sup>+</sup> ligand is a poorer electron donor than unsubstituted Dabco.

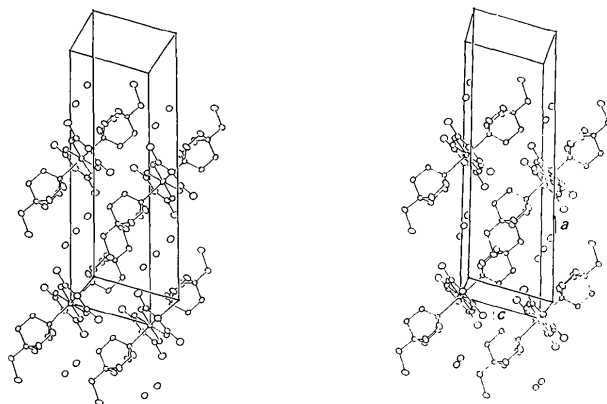


Fig. 3. ORTEP stereodrawing (Johnson, 1976), viewed approximately parallel to **b**, of the unit cell of [Zn(DabcoCH<sub>2</sub>Cl)(acac)<sub>2</sub>]Cl<sub>2</sub> (I). Hydrogen atoms are omitted for clarity.

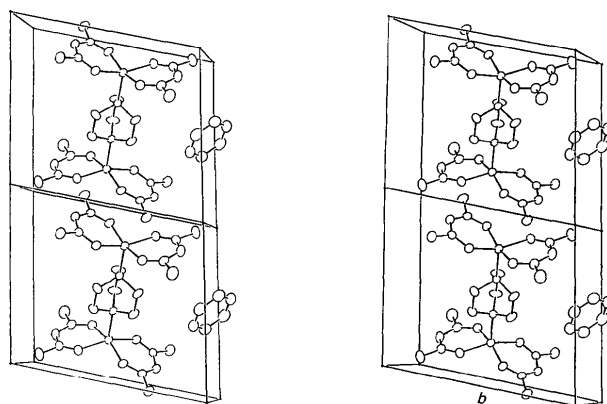


Fig. 4. ORTEP stereodrawing (Johnson, 1976), viewed approximately parallel to **b**, of two unit cells of [Zn(acac)<sub>2</sub>]<sub>2</sub>( $\mu$ -Dabco).C<sub>6</sub>H<sub>6</sub> (II). Hydrogen atoms are omitted for clarity. Only one of the two Dabco orientations is shown.

The structure of (II) can also be compared with those of other five-coordinate Zn complexes. The apical Zn—N bond in (II) [2.127 (2) Å] is considerably longer than the apical Zn—O bonds in [Zn(acac)<sub>2</sub>].H<sub>2</sub>O [2.00 (2) Å; Montgomery & Lingafelter (1963)] and bis(benzoylacetonato)(ethanol)zinc {[Zn(bzac)<sub>2</sub>].C<sub>2</sub>H<sub>5</sub>OH, 2.068 (7) Å; Belford, Chasteen, Hitchman, Hon, Pfluger & Paul (1969)}.

Auf der Heyde & Nassimbeni (1984) described a classification method for five-coordinate structures, to give a quantitative measure of the placement of these structures between the 'square-pyramidal' and 'trigonal-bipyramidal' extremes. This approach is based on the dihedral angles spanned by the five ligands around Zn. In [Zn(acac)<sub>2</sub>]<sub>2</sub>( $\mu$ -Dabco), the sum of the absolute values of the deviations from ideal square-planar dihedral angles is 15.5°; whereas the corresponding value for deviation from ideal trigonal-bipyramidal geometry is 206.8°. The sum of these values, 222.3°, is close to that expected if the complex lies on the Berry pseudorotation coordinate (Berry, 1960). According to this procedure, the geometry of [Zn(acac)<sub>2</sub>]<sub>2</sub>( $\mu$ -Dabco) is 93% square pyramidal. This may be compared with [Zn(acac)<sub>2</sub>].H<sub>2</sub>O, 82% square pyramidal (Montgomery & Lingafelter, 1963) and [Zn(bzac)<sub>2</sub>].C<sub>2</sub>H<sub>5</sub>OH, 18% square pyramidal (Belford, Chasteen, Hitchman, Hon, Pfluger & Paul, 1969).

The metal coordination environment in the five-coordinate structures is relatively flexible, as judged by the dihedral angles between the  $\beta$ -diketonato planes: 30.1 (2)° in (II); 39.2° in [Zn(acac)<sub>2</sub>].H<sub>2</sub>O (Montgomery & Lingafelter, 1963) and 14.0° in [Zn(bzac)<sub>2</sub>].C<sub>2</sub>H<sub>5</sub>OH (Belford, Chasteen, Hitchman, Hon, Pfluger & Paul, 1969). In a copper(II) complex closely related to (II), [Cu(hexafluoroacetylacetonato)<sub>2</sub>]<sub>2</sub>( $\mu$ -pyrazine) (Belford, Fenton & Truter, 1974), the corresponding angle is 26.1°.

Experiments directed toward cofacial binuclear analogs of (II) are now in progress. If the Zn...Zn distance in [Zn<sub>2</sub>(NBA)<sub>2</sub>]( $\mu$ -Dabco) is similar to that in (II), this will represent a substantial contraction relative to the distances in [Cu<sub>2</sub>(NBA)<sub>2</sub>]( $\mu$ -G) [G = Dabco, 7.403 (4) Å (Maverick, Buckingham, Yao, Bradbury & Stanley, 1986); G = 2,5-dimethylpyrazine, 7.596 (2) and 7.559 (1) Å (Maverick, Ivie, Waggenspack & Fronczek, 1990)]. The shorter metal-metal distance in the Zn complex could easily be accommodated by bending the acac moieties in the bridging ligands closer together, which would make the environment about Zn more pyramidal. An arene-CH<sub>2</sub>-acac bond angle of 115.7° would be small enough to bring the Zn atoms to within 6.85 Å of each other. This is well within the range of arene-CH<sub>2</sub>-acac bond angles we have observed in cofacial binuclear complexes [113.9 (4)-

118·4 (4)°; Bradbury, Hampton, Martone & Maverick, 1989; Maverick, Ivie, Waggenpack & Fronczek, 1990] and the range of arene-CH<sub>2</sub>-arene angles in ten diarylmethane structures (112·5–119·2°; Barnes, Paton, Damewood & Mislow, 1981).

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## Bis(oxo-5 proline)platinate(II) de Sodium Dihydrate\*

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**Abstract.** Na<sup>+</sup>[Pt(C<sub>10</sub>H<sub>11</sub>N<sub>2</sub>O<sub>6</sub>)<sub>2</sub>]<sup>-</sup>·2H<sub>2</sub>O, *M<sub>r</sub>* = 509·3, monoclinic, *P*2<sub>1</sub>, *a* = 4·1665 (7), *b* = 10·770 (2), *c* = 16·139 (2) Å, β = 90·08 (1)°, *V* = 724·2 (3) Å<sup>3</sup>, *Z* = 2, *D<sub>x</sub>* = 2·34 Mg m<sup>-3</sup>, λ(Mo *K*α) = 0·7107 Å, μ = 9·86 mm<sup>-1</sup>, *F*(000) = 484, *T* = 294 (1) K, *R* = 0·036 for 1903 independent reflections. The Pt atom displays square-planar coordination. It is linked to two 5-oxoproline molecules. The anion is almost planar and its geometry is similar to that of the same anion in the potassium compound previously described [Viossat, Rodier, Nguyen-Huy Dung &

Guillard (1986). *Acta Cryst.* **C42**, 659–662]. The amide function takes the tautomeric iminoalcohol form. The Na<sup>+</sup> cation, the two water molecules and two O atoms of the anion are subjected to statistical disorder. Each of them may occupy two positions with an occupancy factor of 50%. There is a relationship between occupied sites. O atoms coordinated to the Na<sup>+</sup> ion build either a distorted octahedron or a trigonal bipyramid. Numerous interatomic distances O(water)···O show evidence for hydrogen bonds.

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**Introduction.** L'étude structurale du bis(oxo-5 proline)platinate(II) de sodium dihydrate a été entreprise dans le cadre de la préparation et de l'étude des