Structure of a Copper(II) Chloride–Nicotine Complex: Hexa-μ-chloro-μ₄-oxo-tetrakis[(nicotine)copper(II)]*

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Abstract. [$Cu_4Cl_6O(C_{10}H_{14}N_2)_4$], $M_r = 1131 \cdot 8$, monoclinic, $P2_1$, $a = 13 \cdot 117\,(3)$, $b = 13 \cdot 050\,(3)$, $c = 14 \cdot 067\,(3)$ Å, $\beta = 92 \cdot 50\,(2)°$, $V = 2405 \cdot 6\,(9)$ Å, $Z = 2$, $D_x = 1 \cdot 562$, $D_m = 1 \cdot 55\,(1)$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0 \cdot 71073$ Å, $\mu = 2 \cdot 18$ mm^{-1}, $F(000) = 1156$, $T = 293\,(1)$ K, $R = 0 \cdot 048$ for 2910 reflections. Each of the two asymmetric units consists of a central cluster containing an O atom, four Cu atoms, and six Cl atoms, with four nicotine molecules attached to the Cu atoms *via* the N atoms of the six-membered heterocyclic rings. The Cu atoms are tetrahedrally oriented about the O atom and are bridged by the six Cl atoms, which are approximately octahedral with respect to the cluster center. The Cu and coordinated N atoms lie along directions which correspond to four of the eight threefold axial directions of a regular octahedron. Each Cu atom lies at the center of a trigonal bipyramid, with the O atom and the nicotine N atom in the axial positions and three Cl atoms in the equatorial positions. Average distances are: Cu–N, $1 \cdot 977\,(10)$; Cu–O, $1 \cdot 908\,(8)$; Cu–Cl, $2 \cdot 396\,(4)$; Cu–Cu, $3 \cdot 115\,(2)$ Å. The configuration of the nicotine ligands is that of the *trans* diastereomer.

Introduction. Numerous adducts of alkaloids with metal salts have been reported, especially in the older literature. For example, nicotine [3-(1-methyl-2-pyrrolidinyl)pyridine] was reported to form molecular complexes with copper(II) chloride (Babak & Kagramanova, 1954; Prasad & Sharma, 1958). Published results were not always in agreement, but a simple stoichiometry, CuCl₂.nicotine, could be assumed. The elucidation of the structure of a representative sample became a matter of interest.

Experimental. The complex was formed by addition of an aqueous solution of nicotine to an acetone solution of copper(II) chloride dihydrate. The red-orange precipitate was recrystallized by slow evaporation of a chloroform solution. Density was measured by flotation in dichloromethane/carbon tetrachloride. Analysis: calculated for $C_{40}H_{56}$-

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* Nicotine is 3-(1-methyl-2-pyrrolidinyl)pyridine.

$Cl_6Cu_4N_8O$: C 42·45; Cl 18·5; H 4·99; N 9·90%; found: C42·19; Cl 19·5; H 4·97; N 9·78%.

The reflection intensities of a dark brown crystal (size not recorded) were measured at the Department of Chemistry, University of Texas, Austin, on an Enraf–Nonius CAD-4 diffractometer. Data reduction to the final intensity file was carried out at Enraf–Nonius, Bohemia, NY. Cell dimensions from setting angles of 25 reflections. 4616 reflections measured in $P1$, 42·9 h exposure time, two intensity standards measured every hour, 0·6% decay, no linear decay correction. Converted to monoclinic cell, no evidence of further cell reduction. ψ scan for empirical absorption correction, transmission factors 0·65–1·00. Maximum $\sin\theta/\lambda = 0·594$ Å^{-1}. Systematically absent reflections were rejected and the data set averaged for symmetry related reflections; 4420 remaining reflections, 1260 unobserved with $I > 3\sigma(I)$; h −15 to 15, k 0 to 15, l 0 to 16.

Intensity statistics strongly indicated $P2_1/m$ as the probable space group, and the composition of the complex was assumed to be $CuCl_2.C_{10}H_{14}N_2$, $Z = 8$, in accord with earlier reports. Attempts to solve the complicated Patterson map were unsuccessful, and trials with direct methods suggested that high symmetry of the copper chloride moiety was strongly affecting solution techniques. In the meantime, the program *NRCVAX* (Gabe, Lee & LePage, 1985) had been implemented and was used to generate an E map in $P2_1$ on which four symmetry unrelated Cu atoms were identified. 55 additional non-H atoms were located by successive passes of the *DIRDIF* system (Beurskens *et al.*, 1985). Only six of the eight postulated Cl atoms of the asymmetric unit could be identified as such on the Fourier map. Peak heights associated with the remaining two atoms indicated that these were O atoms, located approximately at the centers of the two tetrahedra of Cu atoms. The original assumed composition was incorrect; the complex is $Cu_4Cl_6O(C_{10}H_{14}N_2)_4$, $Z = 2$, and the refinement was continued on this basis.

Least-squares refinement on F, block-diagonal approximation, isotropic and anisotropic thermal parameters. The positions of the 20 H atoms of the

pyridine rings were calculated; the remainder, except for those of the methyl groups, were located on a difference Fourier map or by superposition of a model on a scaled projection. H atoms of the CH_3 groups could not be identified. Final block-diagonal refinement, with H atoms fixed, using 2910 reflections (242 low-intensity reflections with $\Delta F/F > 0.3$ and eight reflections of low θ with $|F_o| \ll |F_c|$ omitted), anomalous dispersion for Cu, and $B = 5.0\,\text{Å}^2$ for H atoms, converged at $R = 0.048$, $w = 1/\sigma^2(F_o)$, $wR = 0.038$. $(\Delta/\sigma)_{av} = 0.11$, $(\Delta/\sigma)_{max} = 0.54$, $S = 1.65$ with 531 variables. Final difference map, with $\Delta F(000) = 12$, showed max. and min. peaks of 0.77 and $-0.81\,\text{e\,Å}^{-3}$. No systematic errors as functions of $\sin\theta$ or F_o. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). National Research Council of Canada programs (Ahmed, 1973) used for most refinement calculations; *ORTEP*II (Johnson, 1976) for the thermal-ellipsoid plots.

Discussion. Final positional parameters of non-H atoms are given in Table 1,* and principal bond distances and angles in Table 2. The asymmetric molecule is shown in projection in Fig. 1; the thermal-ellipsoid plots of the central cluster and one of the nicotine ligands in Fig. 2. H atoms are omitted for clarity.

The molecule has an O atom at the center of a tetrahedron of Cu atoms, which is itself centered in a slightly distorted octahedron of Cl atoms. This octahedron is in turn surrounded tetrahedrally by the four pyridine N atoms of the nicotine ligands, in parallel orientation with the Cu tetrahedron. The Cu atoms are bridged by the six Cl atoms. The net effect is to place each Cu atom at the center of a quasi-trigonal bipyramid (t.b.p.); the four bipyramids have six edges in common. The central O atom and the pyridine N atoms are in the axial positions, the bridging Cl atoms in equatorial positions. This type of cluster structure was first reported by Bertrand & Kelley (1966) and Bertrand (1967) in $Cu_4Cl_6O(TPPO)_4$; by Kilbourn & Dunitz (1967) in $Cu_4Cl_6O(py)_4$; by Bertrand & Kelley (1969) in $[(CH_3)_4N_4Cu_4OCl_{10}]$; and by Gill & Sterns (1970) in $Cu_4Cl_6O(2\text{-mepy})_4$. Additional structures have been reported since and the references to these are given in the comprehensive paper of Norman, Rose & Stenkamp (1989), which also reports the structure of

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, ring-bond distances and angles not in Table 2, planes data, dihedral and torsion angles and a stereoview have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53025 (60 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional atomic coordinates and equivalent isotropic temperature factors*

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

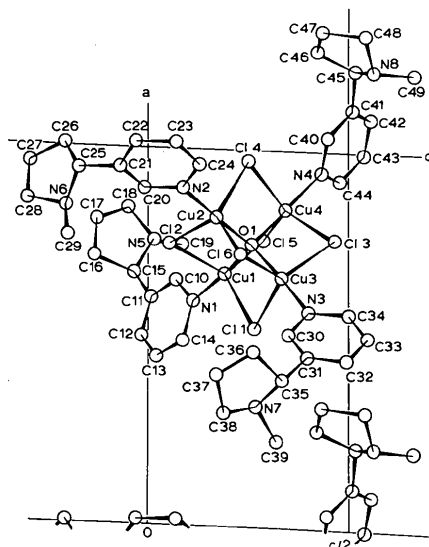|	x	y†	z	$B_{eq}(\text{Å}^2)$
Cu(1)	0.66536 (10)	0.30602 (12)	0.19019 (9)	2.97
Cu(2)	0.81601 (13)	0.48854 (13)	0.17154 (9)	2.85
Cu(3)	0.65962 (10)	0.48830 (13)	0.33245 (9)	2.86
Cu(4)	0.84194 (10)	0.33560 (11)	0.34199 (9)	2.97
Cl(1)	0.5236 (2)	0.3868 (3)	0.2654 (2)	4.51
Cl(2)	0.7422 (3)	0.3801 (3)	0.0540 (2)	4.79
Cl(3)	0.7642 (2)	0.4358 (2)	0.4651 (2)	3.64
Cl(4)	0.9668 (2)	0.4255 (3)	0.2512 (2)	5.08
Cl(5)	0.7582 (3)	0.1870 (2)	0.2872 (2)	5.48
Cl(6)	0.7202 (2)	0.6293 (2)	0.2317 (2)	4.09
O(1)	0.7466 (5)	0.4088 (5)	0.2599 (4)	2.22
N(1)	0.5893 (7)	0.2080 (7)	0.1123 (6)	3.57
N(2)	0.8923 (7)	0.5815 (7)	0.0849 (6)	3.98
N(3)	0.5696 (7)	0.5848 (7)	0.4025 (6)	3.41
N(4)	0.9420 (7)	0.2730 (7)	0.4302 (6)	3.34
N(5)	0.7522 (8)	-0.0445 (9)	0.0158 (8)	6.77
N(6)	0.8336 (10)	0.5918 (10)	-0.2084 (6)	7.56
N(7)	0.3197 (8)	0.7454 (8)	0.2690 (7)	5.19
N(8)	1.2114 (8)	0.4118 (8)	0.5628 (7)	5.28
C(10)	0.6426 (9)	0.1329 (9)	0.0716 (8)	3.82
C(11)	0.5973 (8)	0.6420 (9)	0.0062 (8)	3.52
C(12)	0.4956 (11)	0.0698 (12)	-0.0160 (10)	6.16
C(13)	0.4419 (11)	0.1489 (12)	0.0243 (11)	7.86
C(14)	0.4869 (10)	0.2157 (11)	0.0868 (10)	6.06
C(15)	0.6598 (9)	-0.0197 (12)	-0.0374 (8)	5.19
C(16)	0.7011 (12)	0.0161 (14)	-0.1358 (11)	8.67
C(17)	0.8003 (14)	-0.0128 (21)	-0.1342 (16)	16.36
C(18)	0.8337 (12)	-0.0721 (14)	-0.0506 (12)	9.81
C(19)	0.7378 (17)	-0.1166 (14)	0.0910 (12)	11.84
C(20)	0.8875 (9)	0.5720 (9)	-0.0086 (7)	3.43
C(21)	0.9421 (9)	0.6328 (10)	-0.0690 (9)	4.72
C(22)	1.0075 (10)	0.7061 (9)	-0.0305 (9)	4.51
C(23)	1.0113 (10)	0.7139 (9)	0.0688 (9)	5.14
C(24)	0.9554 (10)	0.6527 (9)	0.1268 (9)	4.58
C(25)	0.9341 (13)	0.6224 (12)	-0.1744 (9)	7.66
C(26)	0.9999 (14)	0.5367 (16)	-0.2093 (11)	11.55
C(27)	0.9490 (14)	0.4925 (16)	-0.2947 (11)	10.90
C(28)	0.8479 (13)	0.5522 (13)	-0.3002 (9)	8.25
C(29)	0.7532 (17)	0.6699 (14)	-0.2040 (12)	11.85
C(30)	0.5091 (8)	0.6520 (9)	0.3520 (8)	3.57
C(31)	0.4518 (9)	0.7236 (9)	0.3960 (8)	4.10
C(32)	0.4502 (9)	0.7276 (10)	0.4938 (8)	4.42
C(33)	0.5094 (9)	0.6582 (10)	0.5460 (8)	4.53
C(34)	0.5671 (9)	0.5886 (10)	0.4993 (7)	3.99
C(35)	0.3928 (10)	0.7995 (11)	0.3308 (8)	5.87
C(36)	0.4605 (12)	0.8626 (12)	0.2625 (10)	7.56
C(37)	0.4005 (14)	0.8617 (15)	0.1723 (10)	9.94
C(38)	0.3021 (11)	0.8134 (13)	0.1895 (9)	7.51
C(39)	0.2258 (12)	0.7104 (13)	0.3166 (11)	7.69
C(40)	1.0355 (8)	0.3133 (9)	0.4465 (8)	3.52
C(41)	1.1079 (8)	0.2682 (9)	0.5076 (8)	3.72
C(42)	1.0828 (10)	0.1785 (10)	0.5525 (8)	4.77
C(43)	0.9908 (10)	0.1367 (11)	0.5359 (8)	5.22
C(44)	0.9224 (10)	0.1849 (10)	0.4775 (8)	4.30
C(45)	1.2152 (10)	0.3145 (10)	0.5150 (8)	5.17
C(46)	1.2630 (10)	0.3430 (14)	0.4196 (9)	7.10
C(47)	1.3156 (16)	0.4463 (15)	0.4321 (13)	12.77
C(48)	1.3086 (11)	0.4589 (13)	0.5413 (13)	7.84
C(49)	1.2059 (12)	0.4005 (10)	0.6655 (10)	6.48

† In this space group atoms may be shifted freely along the *b* axis.

the 1-methylimidazole complex and discusses the variations in bond distances and angles that have been observed. The amount of distortion from the symmetric t.b.p. (as in the triphenylphosphine oxide complex) varies, presumably dependent on the symmetry and packing requirements of the ligands, unequal bond energies (O *vs* the ligand bonding atom) and intermolecular effects.

In the nicotine complex there is little indication of displacement towards a rectangular pyramid. The average of the axial O—Cu—N angles is 175.2 (3)°; that of the equatorial Cl—Cu—Cl angles is

Table 2. *Selected bond distances* (Å) *and angles* (°)

Cu(1)—Cu(2)	3·113 (2)	Cu(2)—Cu(3)	3·120 (2)
Cu(1)—Cu(3)	3·112 (2)	Cu(2)—Cu(4)	3·127 (2)
Cu(1)—Cu(4)	3·105 (2)	Cu(3)—Cu(4)	3·111 (2)
Cu(1)—Cl(1)	2·421 (3)	Cu(3)—Cl(1)	2·383 (4)
Cu(1)—Cl(2)	2·406 (3)	Cu(3)—Cl(3)	2·368 (3)
Cu(1)—Cl(5)	2·369 (4)	Cu(3)—Cl(6)	2·475 (3)
Cu(1)—O(1)	1·951 (7)	Cu(3)—O(1)	1·876 (7)
Cu(1)—N(1)	1·933 (9)	Cu(3)—N(3)	2·013 (9)
Cu(2)—Cl(2)	2·352 (4)	Cu(4)—Cl(3)	2·430 (3)
Cu(2)—Cl(4)	2·377 (4)	Cu(4)—Cl(4)	2·423 (4)
Cu(2)—Cl(6)	2·401 (4)	Cu(4)—Cl(5)	2·343 (4)
Cu(2)—O(1)	1·886 (7)	Cu(4)—O(1)	1·919 (7)
Cu(2)—N(2)	2·016 (9)	Cu(4)—N(4)	1·946 (9)
N(1)—C(10)	1·346 (15)	N(3)—C(30)	1·362 (14)
N(1)—C(14)	1·379 (16)	N(3)—C(34)	1·364 (13)
C(11)—C(15)	1·514 (18)	C(31)—C(35)	1·536 (18)
C(15)—N(5)	1·433 (16)	C(35)—N(7)	1·449 (16)
N(5)—C(18)	1·494 (20)	N(7)—C(38)	1·438 (18)
N(5)—C(19)	1·434 (21)	N(7)—C(39)	1·499 (18)
N(2)—C(20)	1·320 (14)	N(4)—C(40)	1·345 (14)
N(2)—C(24)	1·361 (15)	N(4)—C(44)	1·359 (15)
C(21)—C(25)	1·488 (17)	C(41)—C(45)	1·531 (17)
C(25)—N(6)	1·439 (21)	C(45)—N(8)	1·439 (16)
N(6)—C(28)	1·411 (16)	N(8)—C(48)	1·459 (18)
N(6)—C(29)	1·470 (24)	N(8)—C(49)	1·457 (17)
O(1)—Cl(1)	2·944 (8)	O(1)—Cl(4)	2·904 (8)
O(1)—Cl(2)	2·919 (7)	O(1)—Cl(5)	2·923 (8)
O(1)—Cl(3)	2·907 (7)	O(1)—Cl(6)	2·923 (7)

Cu(2)—Cu(1)—Cu(3)	60·17 (4)	Cu(1)—Cu(3)—Cu(2)	59·94 (4)
Cu(2)—Cu(1)—Cu(4)	60·38 (4)	Cu(1)—Cu(3)—Cu(4)	59·87 (4)
Cu(3)—Cu(1)—Cu(4)	60·06 (4)	Cu(2)—Cu(3)—Cu(4)	60·23 (4)
Cu(1)—Cu(2)—Cu(3)	59·89 (4)	Cu(1)—Cu(4)—Cu(2)	59·94 (4)
Cu(1)—Cu(2)—Cu(4)	59·68 (4)	Cu(1)—Cu(4)—Cu(3)	60·07 (4)
Cu(3)—Cu(2)—Cu(4)	59·74 (4)	Cu(2)—Cu(4)—Cu(3)	60·03 (4)
Cu(1)—O(1)—Cu(2)	108·5 (3)	Cu(2)—O(1)—Cu(3)	112·1 (3)
Cu(1)—O(1)—Cu(3)	108·8 (3)	Cu(2)—O(1)—Cu(4)	110·5 (3)
Cu(1)—O(1)—Cu(4)	106·7 (3)	Cu(3)—O(1)—Cu(4)	110·1 (3)
Cl(1)—Cu(1)—Cl(2)	122·0 (1)	Cl(1)—Cu(3)—Cl(3)	123·3 (1)
Cl(2)—Cu(1)—Cl(5)	120·0 (1)	Cl(3)—Cu(3)—Cl(6)	118·5 (1)
Cl(5)—Cu(1)—Cl(1)	114·8 (1)	Cl(6)—Cu(3)—Cl(1)	116·1 (1)
Cl(2)—Cu(2)—Cl(4)	115·6 (1)	Cl(3)—Cu(4)—Cl(4)	115·4 (1)
Cl(4)—Cu(2)—Cl(6)	122·4 (1)	Cl(4)—Cu(4)—Cl(5)	123·0 (1)
Cl(6)—Cu(2)—Cl(2)	120·2 (1)	Cl(5)—Cu(4)—Cl(3)	118·3 (1)
Cl(1)—Cu(1)—N(1)	98·6 (3)	Cl(1)—Cu(3)—N(3)	95·5 (3)
Cl(2)—Cu(1)—N(1)	92·2 (3)	Cl(3)—Cu(3)—N(3)	97·3 (3)
Cl(5)—Cu(1)—N(1)	97·6 (3)	Cl(6)—Cu(3)—N(3)	91·4 (3)
Cl(1)—Cu(1)—O(1)	83·9 (2)	Cl(1)—Cu(3)—O(1)	86·6 (2)
Cl(2)—Cu(1)—O(1)	83·4 (2)	Cl(3)—Cu(3)—O(1)	85·6 (2)
Cl(5)—Cu(1)—O(1)	84·6 (2)	Cl(6)—Cu(3)—O(1)	83·2 (2)
O(1)—Cu(1)—N(1)	175·6 (3)	O(1)—Cu(3)—N(3)	174·6 (3)
Cl(2)—Cu(2)—N(2)	97·9 (3)	Cl(3)—Cu(4)—N(4)	93·7 (3)
Cl(4)—Cu(2)—N(2)	93·9 (3)	Cl(4)—Cu(4)—N(4)	95·0 (3)
Cl(6)—Cu(2)—N(2)	92·0 (3)	Cl(5)—Cu(4)—N(4)	99·0 (3)
Cl(2)—Cu(2)—O(1)	86·3 (2)	Cl(3)—Cu(4)—O(1)	83·0 (2)
Cl(4)—Cu(2)—O(1)	85·1 (2)	Cl(4)—Cu(4)—O(1)	83·1 (2)
Cl(6)—Cu(2)—O(1)	85·1 (2)	Cl(5)—Cu(4)—O(1)	86·0 (2)
O(1)—Cu(2)—N(2)	175·7 (3)	O(1)—Cu(4)—N(4)	174·9 (3)
C(10)—N(1)—C(14)	117·4 (10)	C(30)—N(3)—C(34)	117·3 (9)
C(10)—C(11)—C(15)	120·6 (10)	C(30)—C(31)—C(35)	116·4 (10)
C(11)—C(15)—N(5)	114·4 (10)	C(31)—C(35)—N(7)	110·3 (10)
C(15)—N(5)—C(18)	109·9 (11)	C(35)—N(7)—C(38)	104·2 (10)
C(15)—N(5)—C(19)	113·4 (12)	C(35)—N(7)—C(39)	114·6 (10)
C(20)—N(2)—C(24)	119·8 (10)	C(40)—N(4)—C(44)	116·0 (9)
C(20)—C(21)—C(25)	122·9 (12)	C(40)—C(41)—C(45)	118·6 (10)
C(21)—C(25)—N(6)	112·4 (12)	C(41)—C(45)—N(8)	109·2 (10)
C(25)—N(6)—C(28)	104·4 (12)	C(45)—N(8)—C(48)	103·1 (10)
C(25)—N(6)—C(29)	116·2 (12)	C(45)—N(8)—C(49)	112·2 (10)

The estimated standard deviations of the ligand atoms are larger than for the atoms in the cluster; the atoms in the five-membered rings were the most difficult to locate. The four nicotine molecules exhi-

Fig. 1. Projection of an asymmetric unit of hexa-μ-chloro-μ_4-oxo-tetrakis[(nicotine)copper(II)] as viewed along the *b* axis.

(*a*)

(*b*)
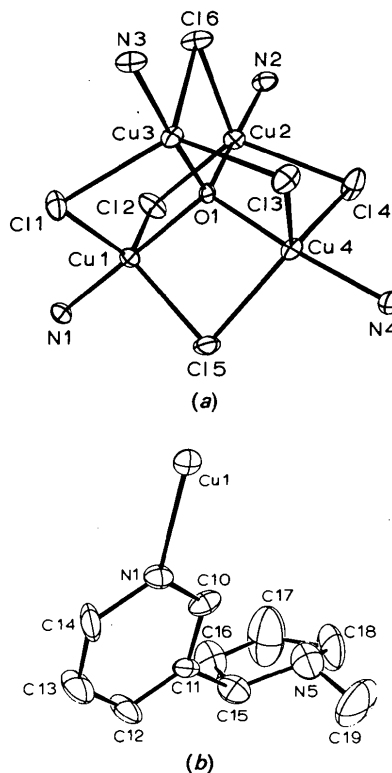
Fig. 2. Thermal-ellipsoid plots of hexa-μ-chloro-μ_4-oxo-tetrakis [(nicotine)copper(II)]. (*a*) The central $Cu_4OCl_6N_4$ cluster. (*b*) The nicotine ligand associated with Cu(1); plots of the other 3 ligands are similar.

119·1 (1)°. There is variation between the individual t.b.p.'s, with a parallelism in the distances associated with the pair Cu(1)—Cu(4) and with the pair Cu(2)—C(3), which accompany a reversal in orientation of the t.b.p.'s with respect to the *b* axis. Each Cu atom is within ±0·25 Å of the mean equatorial plane of the corresponding t.b.p., and the O atom is within ±0·02 Å of the three mean octahedral planes. The dihedral angles are within the ranges expected for a t.b.p. (Holmes, 1984; Haendler, 1989).

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 $Zn(acac)_2.H_2O$ (acacH = 2,4-pentanedione) and Dabco (1,4-diazabicyclo[2.2.2]octane) are reported. In CH_2Cl_2, Dabco is chloroalkylated: *trans*-bis(1-chloromethyl-4-aza-1-azoniabicyclo[2.2.2]octane-N^4)-bis(2,4-pentanedionato)zinc dichloride, [Zn(Dabco-$CH_2Cl)_2(acac)_2]Cl_2$, (I), $C_{24}H_{42}Cl_4N_4O_4Zn$, $M_r = 657·82$, 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^3, $Z = 2$, $D_x = 1·449$, $D_m = 1·44 (2)$ Mg m^{-3}, $\lambda(Mo\ K\alpha) = 0·71073$ Å, $\mu = 1·23$ mm^{-1}, $F(000) = 688$, $T = 293$ 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 $N(CH_2CH_2)_3NCH_2Cl^+$ ($DabcoCH_2Cl^+$) and two 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 $DabcoCH_2Cl^+$ ligands in (I) appear to be produced by nucleophilic attack of Dabco on CH_2Cl_2. The reaction in benzene is more straightforward: μ-(1,4-diazabicyclo[2.2.2]octane-N^1,N^4)-bis[bis(2,4-pentanedionato)zinc] benzene solvate [{Zn(acac)_2}_2(\mu-Dabco)].C_6H_6, (II), $C_{32}H_{46}N_2O_8Zn_2$, $M_r = 717·50$, 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^3, $Z = 1$, $D_x = 1·376$, $D_m = 1·39 (2)$ Mg m^{-3}, $\lambda(Mo\ K\alpha) = 0·71073$ Å, $\mu = 1·466$ mm^{-1}, $F(000) = 376$, $T = 295$ 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 [{Zn(acac)_2}_2(\mu-Dabco)] units in (II)

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