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Zinc Complex of 1,2,3,7,8,12,13,17,18,19-Decamethylbiladiene-*a,c*

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Abstract. $C_{58}H_{68}N_8Zn_2$, tetragonal, $P4_32_12$, $a = b =$ 12·837 (1), $c =$ 26·498 (2) Å, $M_r =$ 1008·0, $Z = 4$, $D_x =$ 1·32 Mg m^{-3}. The compound is dimeric containing two distorted tetrahedral Zn atoms and two quadridentate biladiene-*a,c* ligands in a ridge–tile conformation. Twofold symmetry is observed, with the Zn atoms positioned on a crystallographic diad axis. Bonding in the individual pyrromethene units is similar to that in pyrromethene metal complexes. $R =$ 0·052 for 2032 independent reflexions.

Introduction. Biladiene-*a,c*–metal complexes are important intermediates in the preparation of tetrapyrrole macrocycles (Johnson, 1975). Their cyclization behaviour is not, however, well understood (Gossauer & Engel, 1978). Whereas the Ni, Co and Pd complexes of decamethylbiladiene-*a,c* yield tetrahydrocorrin–metal complexes upon cyclization, the analogous Cu complex gives rise to a metalloporphyrin upon ring closure. For the Zn complex no cyclization has been reported previously. These species are also of interest because of their potential structural similarity to metal complexes of the naturally occurring bile pigment, bilirubin. However, no molecular structure of a metal–biladiene-*a,c* complex has previously been determined by X-ray analysis. This paper presents the X-ray structure of the Zn complex (1) of decamethylbiladiene-*a,c*. A preliminary report of the synthesis and structure of (1) has appeared (Sheldrick & Engel, 1980).

Cell dimensions were determined by a least-squares fit to settings for 15 reflexions $\pm(hkl)$ measured on a Syntex $P2_1$ diffractometer (Cu $K\alpha$ radiation, $\lambda =$ 1·54178 Å). Data collection was carried out in the θ–2θ mode ($2\theta \le 135°$) with graphite-monochromated Cu $K\alpha$ radiation. Intensities were corrected empirically for absorption [μ(Cu $K\alpha$) = 1·64 mm^{-1}]. After application of the observation criterion $F \ge 3{\cdot}0\sigma(F)$, 2032 independent reflexions were retained for use in the structure analysis. The structure was solved

Table 1. *Positional parameters* ($\times 10^4$) *for the non-hydrogen atoms*

$$U_{eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq} (Å^2)
Zn(2)	−1065 (1)	−1065 (1)	10000	52
Zn(1)	1172 (0)	1172 (0)	10000	51
N(21)	2355 (3)	1204 (3)	9573 (2)	56
C(1)	3306 (4)	1235 (4)	9707 (2)	70
C(2)	3898 (4)	1326 (4)	9271 (3)	72
C(3)	3299 (5)	1333 (4)	8865 (2)	73
C(4)	2323 (5)	1270 (4)	9048 (2)	64
C(5)	1457 (5)	1315 (4)	8785 (2)	63
N(22)	197 (3)	1258 (3)	9449 (1)	51
C(6)	511 (5)	1289 (4)	8942 (2)	60
C(7)	−326 (6)	1372 (4)	8633 (2)	70
C(8)	−1118 (5)	1383 (4)	8940 (2)	66
C(9)	−782 (4)	1318 (4)	9437 (2)	55
C(10)	−1410 (4)	1415 (4)	9882 (2)	78
N(23)	−1136 (3)	41 (3)	10466 (1)	49
C(11)	−1185 (4)	999 (4)	10388 (2)	56
C(12)	−1131 (4)	1520 (4)	10848 (2)	65
C(13)	−1071 (4)	854 (4)	11219 (2)	63
C(14)	−1071 (4)	−88 (4)	10997 (2)	56
C(15)	−1052 (4)	−972 (5)	11226 (2)	60
N(24)	−1082 (3)	−2094 (3)	10517 (2)	59
C(16)	−1055 (4)	−1884 (4)	11032 (2)	59
C(17)	−1041 (4)	−2794 (5)	11301 (2)	81
C(18)	−1051 (4)	−3523 (5)	10936 (3)	77
C(19)	−1078 (4)	−3060 (4)	10467 (2)	69
C(11)′	3597 (5)	1146 (6)	10238 (2)	87
C(21)	4983 (5)	1441 (5)	−726 (3)	113
C(31)	3569 (6)	1380 (5)	−1692 (2)	105
C(71)	−288 (7)	1415 (6)	−1943 (2)	118
C(81)	−2170 (5)	1453 (5)	−1212 (3)	106
C(121)	−1179 (5)	2606 (5)	10886 (3)	94
C(131)	−1012 (5)	1072 (6)	11775 (2)	93
C(171)	−1028 (6)	−2914 (7)	11863 (3)	120
C(181)	−1072 (6)	−4591 (5)	11040 (3)	113
C(191)	−1088 (6)	−3534 (5)	−48 (3)	98

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Table 2. *Bond lengths* (Å) *and angles* (°)

N(23)–Zn(2)	1·970 (4)	N(24)–Zn(2)	1·976 (4)
N(21)–Zn(1)	1·991 (4)	N(22)–Zn(1)	1·992 (4)
C(1)–N(21)	1·364 (8)	C(4)–N(21)	1·394 (6)
C(2)–C(1)	1·422 (9)	C(11)′–C(1)	1·469 (9)
C(3)–C(2)	1·359 (9)	C(21)–C(2)	1·510 (9)
C(4)–C(3)	1·437 (10)	C(31)–C(3)	1·527 (9)
C(5)–C(4)	1·388 (9)	C(6)–C(5)	1·374 (10)
C(6)–N(22)	1·413 (6)	C(9)–N(22)	1·358 (7)
C(7)–C(6)	1·424 (9)	C(8)–C(7)	1·365 (9)
C(71)–C(7)	1·530 (8)	C(9)–C(8)	1·400 (8)
C(81)–C(8)	1·513 (10)	C(10)–C(9)	1·470 (8)
C(11)–C(10)	1·492 (8)	C(11)–N(23)	1·343 (7)
C(14)–N(23)	1·422 (6)	C(12)–C(11)	1·420 (9)
C(13)–C(12)	1·350 (8)	C(121)–C(12)	1·508 (8)
C(14)–C(13)	1·432 (8)	C(131)–C(13)	1·505 (8)
C(15)–C(14)	1·365 (8)	C(16)–C(15)	1·362 (8)
C(16)–N(24)	1·397 (6)	C(19)–N(24)	1·342 (7)
C(17)–C(16)	1·447 (9)	C(18)–C(17)	1·396 (10)
C(171)–C(17)	1·501 (9)	C(19)–C(18)	1·400 (10)
C(181)–C(18)	1·503 (9)	C(191)–C(19)	1·515 (9)

N(24)–Zn(2)–N(23)	97·2 (2)	N(22)–Zn(1)–N(21)	98·0 (2)
C(1)–N(21)–Zn(1)	130·2 (4)	C(4)–N(21)–Zn(1)	122·9 (4)
C(4)–N(21)–C(1)	106·8 (5)	N(21)–Zn(1)–N(21)′	106·7 (3)
C(2)–C(1)–N(21)	110·3 (5)	C(11)′–C(1)–N(21)	120·8 (5)
C(11)′–C(1)–C(2)	128·9 (6)	C(3)–C(2)–C(1)	107·0 (6)
C(21)–C(2)–C(1)	125·4 (6)	C(31)–C(2)–C(3)	127·5 (6)
C(4)–C(3)–C(2)	107·8 (5)	C(31)–C(3)–C(2)	128·2 (7)
C(31)–C(3)–C(4)	124·0 (6)	C(3)–C(4)–N(21)	108·1 (5)
C(5)–C(4)–N(21)	122·1 (5)	C(5)–C(4)–C(3)	129·7 (5)
C(6)–C(5)–C(4)	132·1 (5)	C(6)–N(22)–Zn(1)	119·4 (4)
C(9)–N(22)–Zn(1)	134·2 (3)	C(9)–N(22)–C(6)	106·4 (4)
N(22)–C(6)–C(5)	125·5 (5)	C(7)–C(6)–C(5)	126·9 (5)
C(7)–C(6)–N(22)	107·4 (5)	C(8)–C(7)–C(6)	108·2 (5)
C(71)–C(7)–C(6)	123·3 (7)	C(71)–C(7)–C(8)	128·5 (7)
C(9)–C(8)–C(7)	107·1 (6)	C(81)–C(8)–C(7)	127·9 (6)
C(81)–C(8)–C(9)	125·1 (6)	C(8)–C(9)–N(22)	111·0 (5)
C(10)–C(9)–N(22)	125·2 (5)	C(10)–C(9)–C(8)	123·5 (5)
C(11)–C(10)–C(9)	124·2 (5)	C(11)–N(23)–Zn(2)	132·3 (4)
C(14)–N(23)–Zn(2)	121·3 (3)	C(14)–N(23)–C(11)	106·3 (4)
N(23)–Zn(2)–N(23)′	118·0 (2)	N(23)–C(11)–C(10)	122·0 (5)
C(12)–C(11)–C(10)	126·0 (5)	C(12)–C(11)–N(23)	111·4 (5)
C(13)–C(12)–C(11)	106·4 (5)	C(121)–C(12)–C(11)	124·1 (6)
C(121)–C(12)–C(13)	129·4 (6)	C(14)–C(13)–C(12)	108·8 (5)
C(131)–C(13)–C(12)	125·4 (6)	C(131)–C(13)–C(14)	125·8 (5)
C(13)–C(14)–N(23)	106·9 (5)	C(15)–C(14)–N(23)	123·6 (5)
C(15)–C(14)–C(13)	129·4 (5)	C(16)–C(15)–C(14)	131·5 (4)
C(16)–N(24)–Zn(2)	121·8 (4)	C(19)–N(24)–Zn(2)	130·4 (4)
C(19)–N(24)–C(16)	107·7 (5)	N(24)–Zn(2)–N(24)′	117·6 (3)
N(24)–C(16)–C(15)	124·2 (5)	C(17)–C(16)–C(15)	128·4 (5)
C(17)–C(16)–N(24)	107·4 (5)	C(18)–C(17)–C(16)	106·8 (5)
C(171)–C(17)–C(16)	125·8 (6)	C(171)–C(17)–C(18)	127·5 (7)
C(19)–C(18)–C(17)	106·5 (6)	C(181)–C(18)–C(17)	125·6 (7)
C(181)–C(18)–C(19)	127·8 (7)	C(18)–C(19)–N(24)	111·5 (5)
C(191)–C(19)–N(24)	121·4 (5)	C(191)–C(19)–C(18)	127·1 (5)
N(22)–Zn(1)–N(22)′	128·2 (2)	N(23)–Zn(2)–N(24)′	114·1 (2)
N(21)–Zn(1)–N(22)′	112·5 (2)		

by Patterson and difference syntheses and refined by blocked full-matrix least squares with anisotropic temperature factors for the non-hydrogen atoms. The H atoms on C(5), C(10) and C(15) were refined with a group isotropic temperature factor under the bond-length constraint d(C–H) = 1·08 ± 0·02 Å. The methyl H atoms, which were also assigned group isotropic temperature factors, were refined as part of rigid methyl groups. Terminal values of R_w and R were respectively 0·049 and 0·052. The weights were given by $w = k[\sigma^2(F_o) + 0{\cdot}0002F_o^2]^{-1}$. Complex neutral-atom scattering factors were employed (Cromer & Waber, 1965; Cromer & Liberman, 1970). Table 1 lists the final non-hydrogen atom coordinates, Table 2 bond distances and angles.* Calculations were carried out with *SHELX* (Sheldrick, 1976) and local programs. Fig. 1 was drawn with *RSPLOT* (W. S. Sheldrick).

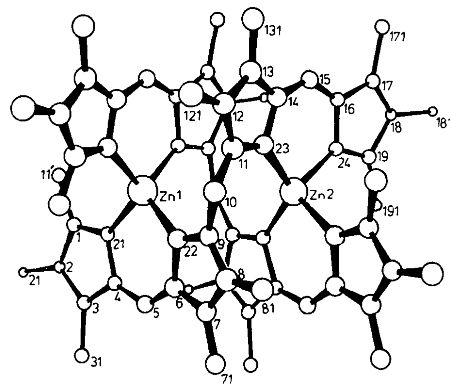

Fig. 1. The molecule of (1) in perspective.

Discussion. The complex adopts a dimeric structure with two distorted tetrahedral Zn atoms and two quadridentate biladiene-*a,c* ligands. This structure is similar to that proposed on the basis of mass-spectral evidence for an analogous biladiene-*a,c* Co complex (Dolphin, Harris, Huppatz, Johnson & Kay, 1966). Twofold symmetry is observed for the molecule with the two Zn atoms positioned on the crystallographic diad axis $x,x,1{\cdot}0$. The biladiene-*a,c* ligands adopt a ridge–tile conformation similar to that in bilirubin (Bonnett, Davies & Hursthouse, 1976), mesobilirubin (Becker & Sheldrick, 1978) and biladiene-*a,c* dihydrobromide (Engel & Struckmeier, 1979). Complex formation leads to a pronounced narrowing of the interplanar angle between the two *syn-Z* pyrromethene units in (1) compared to the above compounds. Thus, the interplanar angle in (1) is only 88·8° but respectively 98, 104 and 107° in bilirubin, mesobilirubin and biladiene-*a,c* dihydrobromide. The individual pyrromethene units in (1) display contrasting degrees of twist with respect to the central methylene bridge at C(10). The dihedral angles δ_1 and δ_2 (as defined by Sheldrick, Becker & Engel, 1978) are respectively 30·7 and 61·7°. In addition, the N–Zn bonds to Zn(1) of 1·991 (4) and 1·992 (4) Å are significantly longer than those of 1·970 (4) and 1·976 (4) Å to Zn(2).

The bond-length distribution in the pyrromethene units is symmetrical and similar to that observed in

* Lists of structure factors, anisotropic thermal parameters and H atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35632 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

other pyrromethene derivatives (Sheldrick, Borkenstein, Struckmeier & Engel, 1978). The shortness of the outer N—C bonds [average 1·35 (1) Å] in comparison to the inner N—C bonds [average 1·41 (1) Å] is explicable in terms of valence tautomers. On this basis, the former bond possesses a formal bond order of 1·5, the latter of 1·0.

The dimeric structure of (1) is considerably less strained than a cyclic monomer would be. It has, however, been suggested that a cyclic monomeric biladiene-*a,c*–metal complex is formed in the initial stages of the cyclization of biladienes-*a,c* (Johnson, 1975). If such dimeric complexes, as observed for (1), are of significance in solution, this would provide support for the hypothesis (Fuhrhop, 1978) that any template effect of the metal cation is relatively unimportant in the base-catalysed cyclization behaviour of biladienes-*a,c*. It appears that a metal cation must be capable of accepting an electron pair if ring closure is to occur. The Zn^{2+} cation cannot function as an electron sink and so no cyclization is observed in its case.

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Bis(azobenzenido)dicarbonylosmium(II)

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Abstract. $C_{26}H_{18}N_4O_2Os$, $[Os(CO)_2(C_6H_4NNC_6H_5)_2]$, monoclinic, $P2_1/c$, $a = 10·746$ (3), $b = 12·516$ (4), $c = 17·136$ (5) Å, $\beta = 90·63$ (2)°, $U = 2304·6$ Å^3, $Z = 4$, $D_c = 1·754$ Mg m^{-3}, μ(Mo $K\alpha$) = 5·54 mm^{-1}; final $R = 0·033$ for 3433 unique diffractometer data. The Os^{II} atom displays slightly distorted octahedral coordination geometry. The two CO ligands are *cis* with respect to each other. The azobenzenido ligands have undergone *ortho* metallation, and are arranged such that the coordinated N atom of one ligand is *trans* to the coordinated C atom of the other.

Introduction. The reaction of $Os_3(CO)_{12}$ with azobenzene in refluxing octane affords two major products and a number of low-yield minor products. One of the major products has been characterized as $[HOs_5(CO)_{13}(C_6H_5NC_6H_4N)]$ (Dawoodi, Mays & Raithby, 1980). To establish the molecular structure of the other, which was obtained as red-orange crystals by recrystallization from warm hexane after separation from the reaction mixture by thin-layer chromatography (10% CH_2Cl_2/hexane eluant), this X-ray analysis was undertaken.

4173 intensities were measured for $3·0 < 2\theta \leq 55·0°$ on a Stoe four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation, an ω–θ scan technique, and a crystal 0·32 × 0·29 × 0·27 mm. Lp corrections and a semi-empirical absorption correction based on a pseudo-ellipsoid model with 334 azimuthal scan data from 9 independent reflections were applied;

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