Acta Cryst. (1972). **B28**, 667

The Crystal and Molecular Structure of Dichlorobis(antipyrine)zinc, $Zn(C_{11}H_{12}ON_2)_2Cl_2$

By Marina Biagini Cingi, Carlo Guastini, Amos Musatti and Mario Nardelli

Istituto di Chimica Generale ed Inorganica, Università degli Studi, Centro di Studio per la Strutturistica Diffrattometrica del C.N.R., Parma, Italy

(*Received* 11 *May* 1971)

Dichlorobis(antipyrine)zinc, $Zn(C_{11}H_{12}ON_2)_2Cl_2$, is monoclinic, $P2_1/c$: $a=9·35$ (1), $b=19·07$ (1), $c=13·88$ (1) Å, $\beta=100·2$ (0·3)°, $Z=4$. The crystal structure has been determined at room temperature from three-dimensional X-ray photographic data and refined by differential methods with anisotropic thermal parameters to a final R value of 8·3 %. Two oxygen atoms from two antipyrine molecules and two chlorine ions coordinate to zinc in a tetrahedral arrangement [Zn–O = 1·997 (4) and 2·019 (6) Å, Zn–Cl = 2·242 (4) and 2·249 (2) Å]. The pyrazolone and benzene rings are planar in both ligands but there is no conjugation between these rings as indicated by the internal rotation angles (49·9° and 73·6°) around the $N_{pyrazole}–C_{benzene}$ (1·429 and 1·438 Å) bond. Dichlorobis(antipyrine)cobalt(II) [$a=9·29$ (1), $b=18·92$ (1), $c=13·69$ (1) Å, $\beta=100·6$ (0·2)°] is isostructural with the zinc compound.

Introduction

As a part of a programme for studying metal complexes of ligands containing oxygen as donor atom, two isostructural complexes of antipyrine: $Zn(antip)_2Cl_2$ and $Co(antip)_2Cl_2$ (antip = 1-phenyl-2,3-dimethyl-5-pyrazolone = antipyrine) have been prepared. Crystals suitable for single-crystal X-ray analysis were obtained from aqueous solutions of the components and a three-dimensional X-ray analysis was carried out on the $Zn(antip)_2Cl_2$ adduct to study the type of metal-coordination and the influence of it, if any, on the antipyrine ligand.

Experimental

$Zn(antip)_2Cl_2$ gives colourless monoclinic prisms, elongated along [001]; their unit-cell constants, determined from rotation and Weissenberg photographs ($CuK\alpha, \lambda=1·5418$ Å), are as follows: $Zn(C_{11}H_{12}ON_2)_2Cl_2$, $M=512·7$, $a=9·35$ (1), $b=19·07$ (1), $c=13·88$ (1) Å; $\beta=100·2$ (3)°; $Z=4$; $V=2436$ Å^3; $D_m=1·43$, $D_x=1·40$ g.cm^{-3}; $\mu=36·6$ cm^{-1}; $F(000)=1056$. Space group $P2_1/c$ (from systematic absences).

Two series of integrated equi-inclination Weissenberg photographs (multiple film technique) were taken at room temperature along [100] up to the 8th and along [001] up to the 12th layers. 3239 independent reflexions were observed out of a possible 5552. The intensities were measured photometrically and corrected for Lorentz, polarization and spot shape effects. The sample used to collect data around [100] was a nearly spherical fragment with a mean radius of 0·02 cm, and that used for the photographs around [001] was a prism elongated along this axis with a mean radius of 0·01 cm, so the approximation was made of considering the first as a sphere and the second as a cylinder in calculating the absorption corrections. The data of both sets were correlated and put on a common scale by the least-squares procedure of Rollett & Sparks (1960) and the absolute scale was determined first by Wilson's method, then by comparison with the calculated values.

Structure determination and refinement

The structure was solved by the heavy-atom method using Patterson and Fourier techniques, and refined down to $R=9·0$% by several cycles of Booth differential synthesis with anisotropic thermal parameters determined from the electron density second derivatives (Nardelli & Fava, 1960). A final $F_o–F_c$ synthesis was suitable for locating all the hydrogen atoms; their coordinates are given in Table 1 with the electron density values, determined by differential synthesis.

Table 1. *Atomic fractional coordinates* ($\times 10^4$) *and corresponding* ϱ_0 *values for hydrogen atoms*

	x/a	y/b	z/c	ϱ_0
H(1)	2833	251	1667	0·7e.Å^{-3}
H(2)	−494	−1288	1977	0·5
H(3)	−2532	−1364	632	0·7
H(4)	−4609	−595	564	0·7
H(5)	−4644	2301	1895	1·0
H(6)	−2623	308	3245	1·1
H(7)	−1833	1417	1833	0·6
H(8)	−3171	4013	2072	0·9
H(9)	−2654	5183	2781	1·3
H(10)	−1569	5291	4519	0·8
H(11)	−992	4229	5518	0·8
H(12)	−1525	3081	4795	0·8
H(13)	−901	−1833	3633	0·7
H(14)	583	−1917	4167	0·7
H(15)	−403	−1603	4702	0·9
H(16)	2333	−1667	5417	0·9
H(17)	3667	−1167	5333	1·0
H(18)	3003	−1501	4583	0·6
H(19)	−6001	2833	1833	1·2
H(20)	−5607	2583	2833	1·4
H(21)	−5333	3333	2702	0·7
H(22)	−5233	2083	417	1·3
H(23)	−5333	1417	1250	0·5
H(24)	−4333	1417	583	0·6

By adding the contributions of the hydrogen atoms to the structure factors (assuming the isotropic temperature factors of the carbon atoms to which the hydrogens are attached), the residual error indices, R and R', improved to 8·3% and 11·9% respectively, (R for observed reflexions only, R' assuming $F_o=\frac{1}{2}F_{\min}$ when $F_c\geq F_{\min}$ for unobserved reflexions; multiplicities not considered).

In Table 2 the final atomic parameters with their e.s.d.'s (Cruickshank, 1949, 1950, 1956) and the ratios between the e.s.d.'s and the coordinate shifts are quoted. Observed and calculated structure factors are

Table 2. *Final atomic fractional coordinates* ($\times 10^4$), *thermal parameters* ($\times 10\times 8\pi^2$ Å^2) *with e.s.d.'s and ratios* (*e.s.d.*)/(*coordinate shift*)

	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	$\|r(x)\|$	$\|r(y)\|$	$\|r(z)\|$
Zn	1247 (1)	1639 (0)	3230 (1)	25 (0)	26 (0)	38 (1)	0 (0)	1 (1)	0 (1)	3	4	2
Cl(1)	1553 (2)	1644 (1)	1659 (1)	38 (1)	34 (0)	44 (2)	0 (1)	11 (2)	−2 (2)	21	8	8
Cl(2)	3227 (2)	1778 (1)	4388 (2)	30 (1)	46 (1)	53 (2)	−6 (1)	−11 (1)	−2 (2)	19	∞	5
O(1)	155 (5)	767 (2)	3430 (3)	29 (3)	24 (1)	42 (5)	−1 (3)	0 (5)	2 (4)	6	6	1
O(2)	−332 (5)	2331 (2)	3382 (3)	26 (3)	25 (1)	31 (4)	5 (3)	−2 (4)	−3 (4)	24	4	5
N(1)	543 (7)	−1010 (3)	3942 (4)	27 (3)	26 (2)	29 (5)	4 (4)	2 (5)	2 (5)	6	2	11
N(2)	−229 (6)	−429 (2)	3502 (4)	24 (3)	20 (1)	29 (4)	0 (3)	1 (4)	−2 (4)	3	∞	3
N(3)	−3870 (5)	2680 (2)	2194 (4)	20 (3)	28 (2)	30 (4)	1 (3)	1 (4)	−5 (4)	9	23	13
N(4)	−2647 (6)	2799 (2)	2939 (4)	22 (3)	20 (1)	29 (4)	−2 (3)	0 (4)	−4 (4)	7	2	3
C(1)	609 (7)	173 (3)	3779 (5)	23 (3)	22 (2)	28 (5)	1 (4)	2 (5)	−2 (5)	15	16	8
C(2)	1869 (8)	−51 (3)	4433 (5)	28 (4)	26 (2)	29 (5)	1 (4)	3 (6)	2 (5)	15	∞	3
C(3)	1761 (8)	−768 (3)	4523 (5)	30 (4)	29 (2)	21 (5)	3 (5)	5 (6)	−1 (5)	6	4	8
C(4)	−1415 (8)	−494 (3)	2702 (5)	28 (4)	25 (2)	20 (4)	−4 (4)	2 (5)	−1 (4)	3	3	17
C(5)	−1377 (9)	−972 (4)	1952 (6)	31 (4)	37 (2)	36 (6)	−5 (4)	5 (6)	−8 (5)	12	3	10
C(6)	−2561 (12)	−1013 (3)	1175 (6)	49 (6)	46 (2)	38 (7)	−14 (5)	5 (8)	−5 (6)	61	3	9
C(7)	−3753 (10)	−574 (4)	1143 (7)	45 (4)	41 (3)	52 (9)	−15 (5)	−6 (7)	3 (7)	8	8	2
C(8)	−3759 (9)	−82 (4)	1907 (8)	34 (3)	42 (3)	52 (8)	−5 (5)	−5 (7)	4 (8)	6	5	6
C(9)	−2616 (9)	−51 (3)	2694 (7)	25 (3)	32 (2)	49 (8)	−3 (4)	2 (7)	1 (6)	∞	11	2
C(10)	−1585 (6)	2304 (3)	2847 (5)	20 (3)	20 (2)	32 (6)	2 (4)	4 (6)	1 (5)	5	∞	3
C(11)	−2220 (6)	1841 (3)	2084 (5)	26 (4)	26 (2)	34 (5)	1 (4)	2 (6)	−6 (5)	9	5	8
C(12)	−3619 (8)	2076 (3)	1713 (5)	24 (4)	25 (2)	31 (5)	3 (4)	1 (5)	−8 (5)	14	∞	4
C(13)	−2381 (7)	3480 (3)	3378 (4)	22 (3)	20 (1)	25 (5)	−1 (4)	5 (5)	−1 (4)	12	13	7
C(14)	−2716 (8)	4073 (3)	2780 (6)	25 (4)	21 (2)	34 (7)	1 (4)	11 (7)	2 (5)	40	2	7
C(15)	−2409 (8)	4735 (3)	3213 (7)	33 (5)	27 (2)	38 (7)	0 (5)	9 (7)	1 (6)	22	15	6
C(16)	−1792 (9)	4792 (2)	4207 (6)	32 (3)	32 (2)	42 (8)	−7 (4)	11 (7)	−4 (5)	91	2	5
C(17)	−1462 (10)	4191 (3)	4788 (6)	48 (6)	33 (2)	31 (6)	−6 (5)	6 (7)	−4 (6)	3	8	8
C(18)	−1772 (8)	3526 (3)	4365 (5)	33 (4)	31 (2)	27 (5)	−1 (4)	3 (6)	−1 (5)	3	3	6
C(19)	−242 (9)	−1659 (3)	4070 (7)	48 (6)	29 (2)	56 (11)	−6 (6)	7 (10)	5 (8)	31	5	2
C(20)	2794 (11)	−1278 (5)	5141 (6)	47 (7)	41 (5)	37 (6)	13 (8)	−4 (8)	6 (8)	36	4	4
C(21)	−5319 (8)	2916 (3)	2339 (7)	26 (4)	42 (3)	54 (9)	2 (6)	8 (8)	−6 (7)	4	∞	4
C(22)	−4740 (8)	1769 (4)	919 (5)	38 (5)	37 (2)	43 (5)	5 (5)	−11 (6)	−17 (5)	3	6	1

Table 3. *Bond lengths and angles*

(i) In the coordination polyhedron

Zn–Cl(1)	2·249 (2) Å	Zn–O (1)	1·997 (4) Å
Zn–Cl (2)	2·243 (4)	Zn–O(2)	2·019 (6)
Cl(1)–Zn–Cl(2)	117·6 (1)°	Cl (2)–Zn–O(1)	112·1 (1)°
Cl(1)–Zn–O(1)	107·2 (1)	Cl(2)–Zn–O(2)	112·0 (1)
Cl(1)–Zn–O(2)	108·7 (1)	O(1)–Zn–O(2)	97·4 (2)

(ii) In the organic molecules

O(1)–C(1)	1·27 (1) Å	O(2)–C(10)	1·27 (1) Å
N(1)–N(2)	1·40 (1)	N(3)–N(4)	1·42 (1)
N(1)–C(3)	1·35 (1)	N(3)–C(12)	1·37 (1)
N(1)–C(19)	1·47 (1)	N(3)–C(21)	1·47 (1)
N(2)–C(1)	1·40 (1)	N(4)—C(10)	1·39 (1)
N(2)–C(4)	1·43 (1)	N(4)—C(13)	1·44 (1)
C(1)–C(2)	1·42 (1)	C(10)–C(11)	1·42 (1)
C(2)–C(3)	1·38 (1)	C(11)–C(12)	1·39 (1)
C(3)–C(20)	1·52 (1)	C(12)–C(22)	1·50 (1)
C(4)–C(5)	1·39 (1)	C(13)–C(14)	1·40 (1)
C(4)–C(9)	1·40 (1)	C(13)–C(18)	1·39 (1)
C(5)–C(6)	1·40 (1)	C(14)–C(15)	1·41 (1)
C(6)–C(7)	1·39 (1)	C(15)–C(16)	1·40 (1)
C(7)–C(8)	1·42 (1)	C(16)–C(17)	1·40 (1)
C(8)–C(9)	1·39 (1)	C(17)–C(18)	1·41 (1)

Table 3 (*cont.*)

N(2)-N(1)-C(3)	107·7 (5)°	N(4)—N(3)—C(12)	107·6 (5)°
N(2)-N(1)-C(19)	119·3 (6)	N(4)—N(3)—C(21)	119·6 (5)
C(3)-N(1)-C(19)	127·0 (6)	C(12)-N(3)—C(21)	124·2 (6)
N(1)-N(2)-C(1)	107·9 (5)	N(3)—N(4)—C(10)	108·8 (5)
N(1)-N(2)-C(4)	122·6 (5)	N(3)—N(4)—C(13)	120·6 (5)
C(1)-N(2)-C(4)	127·0 (5)	C(10)-N(4)—C(13)	125·4 (5)
O(1)-C(1)-N(2)	119·4 (6)	O(2)—C(10)-N(4)	121·2 (5)
O(1)-C(1)-C(2)	133·8 (6)	O(2)—C(10)-C(11)	132·7 (5)
N(2)-C(1)-C(2)	106·8 (5)	N(4)—C(10)-C(11)	106·2 (5)
C(1)-C(2)-C(3)	106·9 (6)	C(10)-C(11)-C(12)	108·4 (5)
N(1)-C(3)-C(2)	110·6 (6)	N(3)—C(12)-C(11)	108·7 (6)
N(1)-C(3)-C(20)	120·0 (6)	N(3)—C(12)-C(22)	121·9 (6)
C(2)-C(3)-C(20)	129·4 (7)	C(11)-C(12)-C(22)	129·4 (6)
N(2)-C(4)-C(5)	121·3 (6)	N(4)—C(13)-C(14)	118·3 (6)
N(2)-C(4)-C(9)	117·6 (6)	N(4)—C(13)-C(18)	119·0 (5)
C(5)-C(4)-C(9)	121·1 (7)	C(14)-C(13)-C(18)	122·7 (5)
C(4)-C(5)-C(6)	119·3 (7)	C(13)-C(14)-C(15)	117·6 (7)
C(5)-C(6)-C(7)	120·7 (7)	C(14)-C(15)-C(16)	120·0 (6)
C(6)-C(7)-C(8)	119·0 (8)	C(15)-C(16)-C(17)	120·8 (5)
C(7)-C(8)-C(9)	120·8 (8)	C(16)-C(17)-C(18)	119·3 (7)
C(4)-C(9)-C(8)	119·0 (7)	C(13)-C(18)-C(17)	119·1 (6)
Zn——O(1)-C(1)	130·5 (3)	Zn——O(2)-C(10)	121·8 (3)
(iii) Involving hydrogen atoms			
C(2)—H(1)	1·07 Å	C(11)-H(7)	0·98 Å
C(5)—H(2)	1·02	C(14)-H(8)	1·01
C(6)—H(3)	1·01	C(15)-H(9)	1·05
C(7)—H(4)	1·03	C(16)-H(10)	1·05
C(8)—H(5)	1·02	C(17)-H(11)	1·03
C(9)—H(6)	1·03	C(18)-H(12)	1·04
C(19)-H(13)	0·85	C(21)-H(19)	0·88
C(19)-H(14)	0·90	C(21)-H(20)	1·01
C(19)-H(15)	0·92	C(21)-H(21)	0·94
C(20)-H(16)	0·97	C(22)-H(22)	0·97
C(20)-H(17)	0·84	C(22)-H(23)	1·03
C(20)-H(18)	0·93	C(22)-H(24)	0·94
C(1)—C(2)—H(1)	126°	C(10)-C(11)-H(7)	130°
C(3)—C(2)—H(1)	125	C(12)-C(11)-H(7)	121
C(4)—C(5)—H(2)	119	C(13)-C(14)-H(8)	120
C(6)—C(5)—H(2)	121	C(15)-C(14)-H(8)	123
C(5)—C(6)—H(3)	119	C(14)-C(15)-H(9)	119
C(7)—C(6)—H(3)	120	C(16)-C(15)-H(9)	121
C(6)—C(7)—H(4)	121	C(15)-C(16)-H(10)	120
C(8)—C(7)—H(4)	120	C(17)-C(16)-H(10)	120
C(7)—C(8)—H(5)	119	C(16)-C(17)-H(11)	121
C(9)—C(8)—H(5)	120	C(18)-C(17)-H(11)	120
C(8)—C(9)—H(6)	121	C(17)-C(18)-H(12)	119
C(4)—C(9)—H(6)	120	C(13)-C(18)-H(12)	122
N(1)—C(19)-H(13)	124	N(3)—C(21)-H(19)	113
N(1)—C(19)-H(14)	93	N(3)—C(21)-H(20)	105
N(1)—C(19)-H(15)	101	N(3)—C(21)-H(21)	115
H(13)-C(19)-H(14)	113	H(19)-C(21)-H(20)	101
H(13)-C(19)-H(15)	120	H(19)-C(21)-H(21)	120
H(14)-C(19)-H(15)	102	H(20)-C(21)-H(21)	98
C(3)—C(20)-H(16)	115	C(12)-C(22)-H(22)	118
C(3)—C(20)-H(17)	120	C(12)-C(22)-H(23)	107
C(3)—C(20)-H(18)	92	C(12)-C(22)-H(24)	111
H(16)-C(20)-H(17)	123	H(22)-C(22)-H(23)	120
H(16)-C(20)-H(18)	99	H(22)-C(22)-H(24)	106
H(17)-C(20)-H(18)	93	H(23)-C(22)-H(24)	93

obtainable as Supplementary Publication No. SUP. 30002,* and copies are available from the authors on request. Their agreement is satisfactory and there is no indication of secondary extinction or other uncorrected effects.

The atomic scattering factors used are those of Cromer & Mann (1968) for Zn, O, N and C and those of Stewart, Davidson & Simpson (1965) for H.

All the calculations were performed on the Olivetti

---

[*] This information has been deposited with the National Lending Library, England, as Supplementary Publication No. SUP 30002. Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 4. Zn–Cl *and* Zn–O *distances in some tetrahedral and octahedral* Zn*complexes*

	Zn–Cl	Zn–O tetrahedral	Zn–O octahedral	Literature
Tetramethylammonium tetrachlorozincate	2·244 (4) Å 2·246 (3) 2·253 (4)			Wiesner, Srivastava, Kennard, Di Vaira & Lingafelter (1967)
Di-imidazolezinc dichloride	2·258 (3) 2·239 (3)			Lundberg (1966)
Bis(semicarbazide)zinc chloride	2·594 (4)		2·06 (1) Å	Nardelli, Fava, Boldrini & Giraldi (1965)
Mono(thiosemicarbazide)zinc chloride	2·247 (9) 2·238 (10)			Cavalca, Nardelli & Branchi (1960)
Bis(thiourea)zinc chloride	2·32			Kunchur & Truter (1958)
Bis(biuret)zinc chloride	2·529 (3)			Nardelli, Fava & Giraldi (1963)
Bis(thiourea)zinc acetate		1·973 (6) Å 1·954 (8)		Cavalca, Fava, Andreetti & Domiano (1967)
Tris(thiourea)zinc sulphate		1·975 (9)		Andreetti, Cavalca & Musatti (1968)
Hydrozincite		1·95(average)	2·10(average)	Ghose (1964)
Catena-di-μ-hydrazine-zinc diacetate			2·147 (5)	Ferrari, Braibanti, Bigliardi & Lanfredi (1965)
Zinc ammonium sulphate hexahydrate			2·129 (12) 2·117 (12) 2·075 (12)	Montgomery & Lingafelter (1964)
Bis(*N*-nicotinato)tetra-aquozinc			2·117 (7)	Biagini Cingi, Domiano, Guastini, Musatti & Nardelli (1971)
Dichlorobis(antipyrine)zine	2·249 (2) 2·242 (4)	1·997 (4) 2·019 (6)		Present paper

Elea 6001/S computer of the Centro di Calcolo Elettronico dell'Università di Parma, using the programs of Nardelli, Musatti, Domiano & Andreetti (1964, 1965).

Discussion

The structure of the complex is shown in the clinographic projection of Fig. 1 and bond distances and angles are quoted in Table 3. The structure consists of discrete complex molecules each formed by a zinc atom tetrahedrally surrounded by two oxygen atoms from the antipyrine molecules and two chlorine ions. The Zn–Cl distances agree quite well with the values found in other compounds as shown in Table 5 and the same can be said for the Zn–O distances which correspond well to the values observed in other tetrahedral zinc complexes (see Table 4). It is worth while observing that these distances are slightly but significantly shorter than those found in octahedral complexes ($\Delta/\sigma = 5{\cdot}03$ for the values given in Table 4).

The conformation of antipyrine is similar in the two molecules and the values for the corresponding distances are not significantly different [$(\Delta/\sigma)_{\max} = 1{\cdot}7$]; these values agree well with those found in hexa(antipyrine)metal complexes as shown in Table 5.

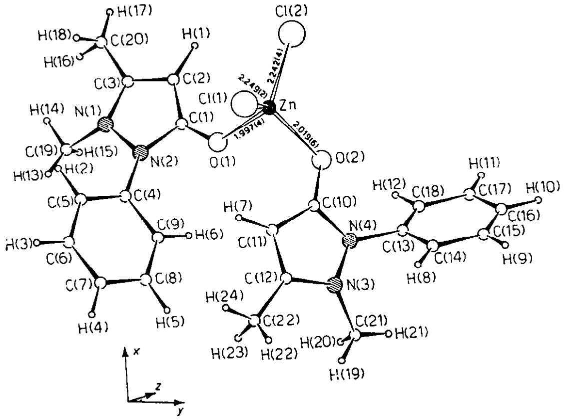


Fig. 1. Clinographic projection of the structure.

The benzene and pyrazolone rings in both molecules can be considered planar, the maximum calculated shift from the least-squares planes being 0·03 Å for pyrazolone and 0·01 Å for benzene. In both molecules benzene is rotated with respect to pyrazolone by 49·9° and 73·6° respectively; of these angles the first is smaller and the second larger than the corresponding ones (68·6°, 62·3°, 62·5°) found in the isostructural series of the perchlorates of hexa(antipyrine)–Pb, –Mg, –Ca (Vijayan & Viswamitra, 1966, 1967, 1968). This rotation indicates that there is no conjugation through the C–N bond between the benzene and pyrazolone rings, in agreement with the values found for the distances C(4)–N(2) and C(13)–N(4) [1·43 (1), 1·44 (1) Å] which are not far from the theoretical value (1·47 Å) for a C(sp^2)–N(sp^3) single bond.

Bond distances indicate that in both pyrazolone rings (see Table 3) there is some π-delocalization; π-bond character is most evident in the ketonic groups C(1)–O(1) and C(10)–O(2), and least evident in N(1)–N(2) and (N3)–N(4). This lack of complete resonance explains the lack of coplanarity observed for the bonds surrounding each nitrogen atom: C(19) and C(21) are out of the respective pyrazolone planes by 0·46 and 0·55 Å and C(4) and C(13) are out of the same planes by 0·27 and 0·39 Å. No contacts which can be considered as hydrogen bonds are observed, so packing is due only to the van der Waals interactions of which those less than 3·6 Å are as follows:

Cl(1)–C(19$^{\text{i}}$)	3·54 (1) Å	i	$\bar{x}$	$\frac{1}{2}+y$	$\frac{1}{2}-z$
N(1)–C(14$^{\text{ii}}$)	3·40 (1)	ii	$\bar{x}$	$\frac{1}{2}-y$	$\frac{1}{2}-z$
C(3)–C(14$^{\text{ii}}$)	3·48 (1)	iii	$\bar{x}-1$	$y-\frac{1}{2}$	$\frac{1}{2}-z$
C(1)–C(15$^{\text{ii}}$)	3·58 (1)				
C(8)–C(15$^{\text{iii}}$)	3·57 (2)				

Table 5. *Corresponding distances of antipyrine molecule in some metal-complexes*

		$Zn(antip)_2Cl_2$*		$Pb(antip)_6(ClO_4)_2$†	$Mg(antip)_6(ClO_4)_2$†	$Ca(antip)_6(ClO_4)_2$†
Molecule 1	Molecule 2	Molecule 1	Molecule 2			
C(1)–O(1)	C(10)–O(2)	1·27 (1) Å	1·27 (1) Å	1·28 (2) Å	1·30 (1) Å	1·28 (1) Å
C(1)–C(2)	C(10)–C(11)	1·42 (1)	1·42 (1)	1·40 (3)	1·39 (1)	1·39 (1)
C(2)–C(3)	C(11)–C(12)	1·38 (1)	1·39 (1)	1·39 (3)	1·35 (2)	1·36 (2)
C(3)–N(1)	C(12)–N(3)	1·35 (1)	1·37 (1)	1·35 (3)	1·36 (1)	1·37 (1)
N(1)–N(2)	N(3)–N(4)	1·40 (1)	1·42 (1)	1·36 (3)	1·41 (1)	1·41 (1)
N(2)–C(1)	N(4)–C(10)	1·40 (1)	1·39 (1)	1·39 (2)	1·38 (1)	1·40 (1)
C(3)–C(20)	C(12)–C(22)	1·52 (1)	1·50 (1)	1·53 (4)	1·56 (2)	1·54 (2)
N(1)–C(19)	N(3)–C(21)	1·47 (1)	1·47 (1)	1·48 (3)	1·49 (1)	1·49 (2)
N(2)–C(4)	N(4)–C(13)	1·43 (1)	1·44 (1)	1·41 (2)	1·43 (1)	1·42 (1)
C(4)–C(5)	C(13)–C(14)	1·39 (1)	1·40 (1)	1·42 (3)	1·40 (1)	1·39 (1)
C(5)–C(6)	C(14)–C(15)	1·40 (1)	1·41 (1)	1·42 (3)	1·41 (1)	1·42 (1)
C(6)–C(7)	C(15)–C(16)	1·39 (1)	1·40 (1)	1·36 (3)	1·37 (1)	1·38 (1)
C(7)–C(8)	C(16)–C(17)	1·42 (1)	1·40 (1)	1·37 (4)	1·39 (2)	1·39 (2)
C(8)–C(9)	C(17)–C(18)	1·39 (1)	1·41 (1)	1·41 (3)	1·43 (2)	1·41 (2)
C(9)–C(4)	C(18)–C(13)	1·40 (1)	1·39 (1)	1·40 (2)	1·40 (1)	1·40 (1)

* Present paper.

† Vijayan & Viswamitra (1966, 1967, 1968).

References

ANDREETTI, G. D., CAVALCA, L. & MUSATTI, A. (1968). *Acta Cryst.* B**24**, 683.
BIAGINI CINGI, M., DOMIANO, P., GUASTINI, C., MUSATTI, A. & NARDELLI, M. (1971). *Gazz. Chim. Ital.* **101**, 455.
CAVALCA, L., FAVA, G., ANDREETTI, G. D. & DOMIANO, P. (1967). *Acta Cryst.* **22**, 90.
CAVALCA, L., NARDELLI, M. & BRANCHI, G. (1960). *Acta Cryst.* **13**, 688.
CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A**24**, 321.
CRUICKSHANK, D. W. J. (1949). *Acta Cryst.* **2**, 65.
CRUICKSHANK, D. W. J. (1950). *Acta Cryst.* **3**, 72.
CRUICKSHANK, D. W. J. (1956). *Acta Cryst.* **9**, 754.
FERRARI, A., BRAIBANTI, A., BIGLIARDI, G. & LANFREDI, A. M. (1965). *Acta Cryst.* **19**, 548.
GHOSE, S. (1964). *Acta Cryst.* **17**, 1051.
KUNCHUR, N. R. & TRUTER, M. R. (1958). *J. Chem. Soc.* p. 3478.
LUNDBERG, B. K. S. (1966). *Acta Cryst.* **21**, 901.
MONTGOMERY, H. & LINGAFELTER, E. C. (1964). *Acta Cryst.* **17**, 1295.
NARDELLI, M. & FAVA, G. (1960). *Ric. Sci.* **30**, 898.
NARDELLI, M., FAVA, G., BOLDRINI, P. & GIRALDI BATTISTINI, G. (1965). *Acta Cryst.* **19**, 491.
NARDELLI, M., FAVA, G. & GIRALDI, G. (1963). *Acta Cryst.* **16**, 343.
NARDELLI, M., MUSATTI, A., DOMIANO, P. & ANDREETTI, G. (1964). *Ric. Sci.* **34**, II-A, 711.
NARDELLI, M., MUSATTI, A., DOMIANO, P. & ANDREETTI, G. D. (1965). *Ric. Sci.* **35**, II-A, 469, 477 & 807.
ROLLETT, J. S. & SPARKS, R. A. (1960). *Acta Cryst.* **13**, 273.
STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175.
VIJAYAN, M. & VISWAMITRA, M. A. (1966). *Acta Cryst.* **21**, 522.
VIJAYAN, M. & VISWAMITRA, M. A. (1967). *Acta Cryst.* **23**, 1000.
VIJAYAN, M. & VISWAMITRA, M. A. (1968). *Acta Cryst.* B**24**, 1067.
WIESNER, J. R., SRIVASTAVA, R. C., KENNARD, C. H. L., DI VAIRA, M. & LINGAFELTER, E. C. (1967). *Acta Cryst.* **23**, 565.

Acta Cryst. (1972). B**28**, 672

The Crystal Structure of Lidocaine Hydrohexafluoroarsenate

BY A. W. HANSON

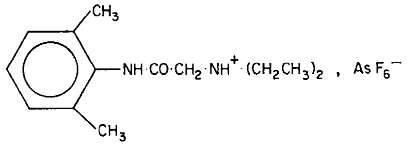
Biochemistry Laboratory, National Research Council of Canada, Ottawa, Canada K1A OR6

(*Received* 15 *June* 1971)

Crystals of lidocaine (2-diethylamino-2′,6′-acetoxylidide) hydrohexafluoroarsenate, $C_{14}H_{23}N_2OAsF_6$ are monoclinic, $C2/c$, with $a=22{\cdot}82$ (1), $b=9{\cdot}19$ (1), $c=18{\cdot}89$ (1) Å, $\beta=120{\cdot}79$ (6)°, $D_m=1{\cdot}58$, $Z=8$, $D_x=1{\cdot}57$. 2582 of a possible 3043 independent reflexions in the range $\sin\theta/\lambda\le 0{\cdot}59$ were observed and measured diffractometrically. The crystal structure was determined by heavy-atom methods and refined by block-diagonal least-squares to a final R index of 0·044. The lidocaine moiety was found to be in the biologically active cationic form, with the amino nitrogen atom protonated. This atom is strongly hydrogen-bonded to the oxygen atom of an adjacent cation. Pairs of such bonds join pairs of cations across centres of symmetry. The amido nitrogen atom is weakly hydrogen-bonded to a fluorine atom of the hexafluoroarsenate anion.

Introduction

It has been suggested that hydrogen bond donation is essential to the action of local anaesthetics (Sax & Pletcher, 1969). The hydrogen-bonding properties of lidocaine (2-diethylamino-2′,6′-acetoxylidide), a widely used local anaesthetic and nerve block, are thus of obvious interest. The infrared spectra of some crystalline salts of lidocaine have been studied by Neville & Regnier (1969), and one of their conclusions is that the hydrohexafluoroarsenate (I) is essentially free of hydrogen bonding. The X-ray analysis to be described is in conflict with this conclusion, demonstrating unequivocally that the amino nitrogen atom is strongly hydrogen bonded to the oxygen atom of a neighbouring cation.



(I)

Experimental

Crystal data: $C_{14}H_{23}N_2OAsF_6$; F.W. 424·3; monoclinic, $a=22{\cdot}82$ (1), $b=9{\cdot}19$ (1), $c=19{\cdot}89$ (1) Å; $\beta=120{\cdot}79$ (6)°; $V=3583$ Å^3; $D_m=1{\cdot}58$, $D_x=1{\cdot}57$ g.cm^{-3}; $Z=8$; $\mu=33{\cdot}6$ cm^{-1}, (Cu $K\alpha$, $\lambda(\alpha_1)=1{\cdot}54051$, $\lambda(\alpha_2)=1{\cdot}54433$ Å, all measurements at 20°C). Space group Cc or $C2/c$, from precession and Weissenberg photographs: $C2/c$ is confirmed by the structure analysis.