

intramolecular distances between non-H atoms shows that the crystal is stabilized by van der Waals interactions only; shortest distance is C(47)—C(54) ( $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$ ) = 3.511 (15) Å.

Comparison of the title compound with [Rh-(norbornadiene)-{(+)binap}](ClO<sub>4</sub>) (Toriumi, Ito, Takaya, Souchi & Noyori, 1982) reveals considerable differences in the orientation of the phenyl groups and in the conformation of the seven-membered chelate ring. Table 3 compares some torsion angles for both compounds. The main difference is the orientation of phenyl group *E*. The torsion angles Rh—P(2)—C(51)—C(52) are 124.5 (8) and 54.8 (5)°, respectively. Since the orientation of the phenyl groups provides the chiral environment at the olefin coordination site this difference has effects on the optical yields when the ligands binap and dimep are used as catalysts for asymmetric synthesis (Frejd, 1986).

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## On the Structure of Zn(C<sub>4</sub>H<sub>8</sub>N<sub>2</sub>O<sub>6</sub>)

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**Abstract.** The crystal structure of this compound, originally formulated as bis(formamide)formatozinc(II) formate, was described in space group *Pnn2* and refined to  $R = 0.036$ ,  $S = 1.292$ . It is correctly described in *Pnna* [orthorhombic;  $a = 8.717$  (3),  $b = 11.617$  (10),  $c = 8.289$  (2) Å,  $Z = 4$ ]. Refinement in *Pnna*, to  $R = 0.032$  and  $S = 1.12$ , shows that the compound contains formamidine rather than formamide, the correct formulation being formamidinium tris(formato)zinc(II), [HC(NH<sub>2</sub>)<sub>2</sub>]<sup>+</sup>[Zn(HCO<sub>2</sub>)<sub>3</sub>]<sup>-</sup>. The Zn<sup>II</sup> atom is surrounded by six O atoms in approximately octahedral coordination, with Zn—O distances from 2.066 (1) to 2.115 (1) Å. The formamidinium ion forms H bonds to the formate groups, with N...O distances of 2.866 (3) and 2.941 (3) Å.

**Introduction.** Recently, Fortier & Creber (1985; FC) reported on the preparation and crystal structure of a

compound they thought to be [Zn(CHO<sub>2</sub>)-(CH<sub>3</sub>NO)<sub>2</sub>]<sup>+</sup>.CHO<sub>2</sub><sup>-</sup> — bis(formamide)formatozinc(II) formate. The structure was described in space group *Pnn2* and refined to an  $R$  of 0.036 for 1914 reflections. Upon reinterpreting FC's data, I find that the structure is properly described in space group *Pnna* and that the correct formulation of the compound is [Zn(CHO<sub>2</sub>)<sub>3</sub>]<sup>-</sup>. [CH(NH<sub>2</sub>)<sub>2</sub>]<sup>+</sup> — formamidinium tris(formato)zinc(II).

**Experimental.** The starting model in *Pnna* was obtained by transforming the coordinates in Table 1 of FC to  $x' = y + 0.25$ ,  $y' = x$ ,  $z' = z + 0.25$  and, where necessary, averaging equivalent atoms. The  $F_o$  and  $\sigma(F)$  values for 1914 reflections 'observed at  $3\sigma(I)$  level' were obtained from SUP 42448. Included in these 1914 reflections was only one, 110, which violates the extinction condition for the *a*-glide plane of *Pnna*; it had, at 2.5 e<sup>-</sup>, the smallest  $F_o$  value in the entire table. Refinement was by full-matrix minimization of

\* Contribution No. 7403.

$\sum w(F_o^2 - F_c^2)^2$ , with weights  $w$  equal to  $[4F_o^2\sigma^2(F) + (0.06F_o^2)^2]^{-1}$  [corresponding to the function used by FC for their minimization of  $\sum w(F_o - F_c)^2$ ].

In the *Pnna* model, the two groups presumed by FC to be formamides would have to be disordered, since their O(1) becomes equivalent to N(2) and O(2) to N(1). During the initial *Pnna* refinements the sites of these atoms were assigned composition parameters  $c$  (= amount of N in the site;  $1 - c$  = amount of O) of 0.5. These parameters immediately shifted to 0.0 within their e.s.d.'s of about 0.02, indicating that there is no N in these sites; these groups are formates rather than formamides. Where, then is the N, shown to be present by the chemical analysis (FC)? A difference map calculated in the plane of the non-coordinating formate groups C(5)–O(5) and C(6)–O(6) (FC) quickly provided the answer: the 'O' atoms in these two groups (which are symmetry-equivalent in *Pnna*) lay in regions of negative density and had as neighbors two well-resolved peaks, 0.5–0.6 e Å<sup>-3</sup> in height, where one would expect to find the amino H atoms of a formamidinium ion HC(NH<sub>2</sub>)<sub>2</sub><sup>+</sup>. Subsequent refinement of the composition parameter of the N site and of the *B* parameters of the H atoms confirmed that this group is indeed formamidinium, with the full complement of H atoms and no O atoms.

Refinement converged at an *R* of 0.0317 for 1914 reflections and a GOF of 1.12 for 78 parameters (including coordinates and isotropic *B*'s for the H atoms and an isotropic extinction parameter); the corresponding numbers reported by FC were 0.036 and 1.29 for, apparently, 118 parameters (the H atoms were not refined). The maximum  $\Delta/\sigma$  was 0.18 for an H atom, 0.04 otherwise; the largest features on a difference map were 0.6–0.65 e Å<sup>-3</sup>, near the Zn atoms. Final parameters are given in Table 1.\*

**Discussion.** The compound turns out to be [HC(NH<sub>2</sub>)<sub>2</sub>]<sup>+</sup>. [Zn(HCO<sub>2</sub>)<sub>3</sub>]<sup>-</sup> — formamidinium tris(formate)zinc(II). The Zn atom lies on a C<sub>2</sub> axis parallel to *a*, the formamidinium ion C(3), N(4) and one formate group C(2), O(3) lie on (different) C<sub>2</sub> axes parallel to *c*, and the other formate group C(1), O(1), O(2) occupies a general position. The formate ions link Zn atoms together in a three-dimensional network, with each Zn atom surrounded by six O atoms in approximately octahedral coordination; the O–Zn–O angles range from 85.5 (1) to 100.4 (1)° and from 172.5 (1)

Table 1. *Final atomic coordinates* ( $\times 10^5$ , H  $\times 10^3$ ) and *U<sub>eq</sub>* (Å<sup>2</sup>  $\times 10^4$ ) values (*B<sub>iso</sub>* for H), *space group Pnna*

Cell dimensions (FC):  $a = 8.717$  (3),  $b = 11.617$  (10),  $c = 8.289$  (2) Å; secondary extinction:  $g = 4.2$  (3)  $\times 10^{-6}$ .

Cell	dimensions	(FC):	$a = 8.717$ (3),	$b = 11.617$ (10),	$c = 8.289$ (2) Å;	secondary extinction:	$g = 4.2$ (3) $\times 10^{-6}$ .
	<i>M</i> <sup>*</sup>	FC†	<i>x</i>	<i>y</i>	<i>z</i>	<i>U<sub>eq</sub></i> or <i>B<sub>iso</sub></i>	
Zn	4	Zn	23547 (3)	25000	25000	165 (1)	
O(1)		O(1),N(2)	41277 (15)	31678 (12)	10538 (15)	319 (2)	
O(2)		O(2),N(1)	58376 (16)	32346 (11)	-8862 (16)	349 (3)	
O(3)		O(3),O(4)	23734 (13)	40508 (10)	38366 (14)	255 (2)	
N(4)		O(5),O(6)	64938 (31)	6326 (21)	22335 (24)	461 (5)	
C(1)		C(1),C(2)	47011 (20)	28029 (15)	-2233 (19)	245 (3)	
C(2)	4	C(3),C(4)	25000	50000	31394 (25)	230 (4)	
C(3)	4	C(5),C(6)	75000	0	29427 (42)	404 (6)	
H(C1)			425 (3)	213 (2)	-62 (3)	3.1 (5)	
H(C2)	4		250	500	190 (5)	2.6 (8)	
H(C3)	4		750	0	393 (5)	5.5 (13)	
H(N4) <sub>A</sub>			654 (3)	65 (3)	142 (2)	3.6 (6)	
H(N4) <sub>B</sub>			588 (4)	99 (2)	284 (3)	4.4 (6)	

\* Number in cell, if other than 8.

† Corresponding atom(s) in Table 1 of Fortier & Creber (1985).

Table 2. *Bond distances* (Å) and *some angles* (°)

Zn–O(1)	2.104 (1)	C(3)–N(4)	1.286 (4)
Zn–O(2)	2.066 (1)	C(1)–H(C1)	0.94 (2)
Zn–O(3)	2.115 (1)	C(2)–H(C2)	1.03 (4)
C(1)–O(1)	1.245 (2)	C(3)–H(C3)	0.82 (4)
C(1)–O(2)	1.239 (2)	N(4)–H(N4) <sub>A</sub>	0.68 (3)
C(2)–O(3)	1.250 (2)	N(4)–H(N4) <sub>B</sub>	0.84 (3)
O(1)–C(1)–O(2)	124.1 (2)	N(4)–O(1 <sup>b</sup> )	2.866 (3)
O(3)–C(2)–O(3 <sup>b</sup> )	124.9 (2)	N(4)–O(3 <sup>c</sup> )	2.941 (3)
N(4)–C(3)–N(4 <sup>ab</sup> )	125.6 (3)		

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

to 179.1 (1)°. The formamidinium ions are not coordinated to the Zn atoms; rather, they are H-bonded through their N–H groups to adjacent formate groups. Bond distances and some angles are given in Table 2. It is worthy of note that the two O atoms that accept H bonds – O(1) and O(3) – show the longest Zn–O distances.

The compound was formed by refluxing ZnCl<sub>2</sub> and formic acid in formamide, and allowing the solution to stand for one week (FC). The formamidine probably formed during this process; the production of amidines from amides in the presence of a halogenating agent is a well-documented reaction (see, for example, Gautier, Mioque & Farnoux, 1975).

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#### References

\* Lists of observed (from SUP 42448) and calculated structure factors, and anisotropic *U<sub>ij</sub>*'s for the *Pnna* refinement have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 43089 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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