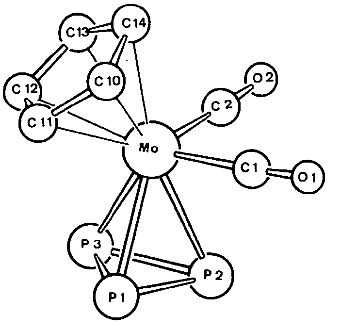

Fig. 1. Molecular structure of (2) (molecule *A*), showing the numbering scheme (H atoms omitted).

equilateral triangle with mean P—P bond lengths of 2·127 (molecule *A*) and 2·134 Å (molecule *B*). These values are in good agreement with that of $[(\text{triphos})M(\eta^3\text{-P}_3)]$,* P—P 2·141 (2) Å, $M = \text{Co}$; 2·152 (2) Å, $M = \text{Rh}$; 2·159 (4) Å, $M = \text{Ir}$, as well as with that of $[(\text{np}_3)\text{Co}(\eta^3\text{-P}_3)]$, P—P 2·135 (6) Å (Di Vaira & Sacconi, 1982). Shorter P—P bond lengths are found for the $P_2$ complexes $[\text{Cp}_2\text{Mo}_2(\text{CO})_4(\mu\text{-}\eta^2\text{-P}_2)]$ (1), P—P 2·079 (2) Å (Scherer, Sitzmann & Wolmershauser, 1984) and $[\text{Co}_2(\text{CO})_5(\text{PPh}_3)(\mu\text{-}\eta^2\text{-P}_2)]$, P—P 2·019 (9) Å (Campana, Vizi-Orosz, Pályi, Markó & Dahl, 1979). With respect to the $P_2$ complex (1) (mean value P—Mo 2·508 Å) the mean P—Mo bond distance for (2) is longer (molecule *A* 2·538 Å, molecule *B* 2·535 Å).

In contrast to molecule *B*, molecule *A* has almost $C_s$ symmetry (Fig. 2). For (2) the $C_5H_5$(cent.)—Mo—$P_3$(cent.) angle of 134·9 (6)° (molecule *A*) and 134·0 (5)° (molecule *B*) differs only slightly from that of $(\eta^5\text{-C}_5\text{Me}_5)\text{Mo}(\text{CO})_2(\eta^3\text{-As}_3)$ with a value of 136 (2)° (Bernal, Brunner, Meier, Pfisterer, Wachter & Ziegler, 1984). A striking difference is found between the bond angles $C_5H_5$(cent.)—Mo—C(1,2) (mean value of molecules *A* and *B* 115·3°) and $P_3$(cent.)—Mo—C(1,2) (mean value of molecules *A* and *B* 96·5°) of the $P_3$ complex compared with those of the $As_3$ complex [$C_5Me_5$(cent.)—Mo—C(1) 96·4 (4)°, $As_3$(cent.)—Mo—C(1) 113·5 (2)°] (Bernal *et al.*, 1984).

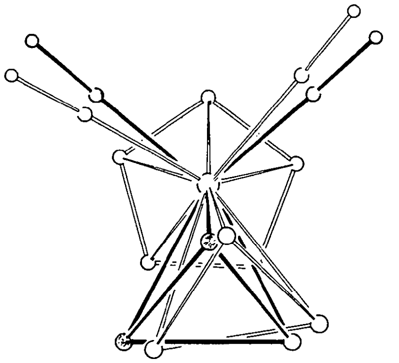

Fig. 2. Projection of molecules *A* (full bonds) and *B* on to the $C_5H_5$(Cp) plane.

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* Abbreviations: triphos = 1,1,1-tris(diphenylphosphinomethyl)-ethane; $\text{np}_3$ = tris(2-diphenylphosphinoethyl)amine; Cp = cyclopentadienyl.

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# Structure of Bis(formamide)formatozinc(II) Formate

By Suzanne Fortier

*Department of Chemistry, Queen's University, Kingston, Canada K7L 3N6*

and Katherine A. M. Creber

*Department of Chemistry and Chemical Engineering, Royal Military College of Canada, Kingston, Canada K7L 2W3*

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**Abstract.** $[\text{Zn}(\text{CHO}_2)(\text{CH}_3\text{NO})_2]\text{CHO}_2$, $M_r = 245{\cdot}49$, orthorhombic, $Pnn2$, $a = 11{\cdot}617$ (10), $b = 8{\cdot}717$ (3), $c = 8{\cdot}289$ (2) Å, $V = 839{\cdot}4$ Å$^3$, $Z = 4$, $D_x = 1{\cdot}942$ Mg m$^{-3}$, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71073$ Å, $\mu = 3{\cdot}00$ mm$^{-1}$, $F(000) = 496$, $T = 292$ K, final $R = 0{\cdot}036$ for 1914 observed reflections. Bis(formamide)formato-

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zinc(II) formate crystallizes as a three-dimensional network of Zn–ligand chains. The unusual coordination of formamide through both its N and O atoms simultaneously to two different Zn atoms was observed. Zn is thus six-coordinated, in a pseudo-octahedral environment, to two pairs of bridging formamide groups and two bridging formate groups.

**Introduction.** Zn complexes are well known to crystallize in chains, particularly with O-donor ligands (Roesky, Thomas, Bats & Fuess, 1983; Howell & Wyeth, 1978). Although both N-bonded and O-bonded formamide complexes have been characterized (Balahura & Jordan, 1970), few complexes with bridging formamide ligands have been reported to this date. In the title Zn polymeric structure, bidentate formamide groups, acting as metal–metal bridges, have been found.

**Experimental.** The title compound was prepared by refluxing $ZnCl_2$ (1·0 g) and formic acid (1·0 ml) together in formamide (15 ml) for 30 min. The solution was then left undisturbed for one week as crystals suitable for X-ray investigation formed. Analysis: calcd for $C_4H_8N_2O_6Zn$: C, 19·6; H, 3·3; N, 11·4; O, 39·1%. Found (Canadian Microanalytical Service, Vancouver): C, 19·5; H, 3·2; N, 11·5; O, 39·3%. Pale-pink crystals, specimen 0·20 × 0·40 × 0·40 mm. Enraf–Nonius CAD-4 diffractometer, Zr-filtered Mo $K\alpha$; cell parameters from least squares applied to 25 reflections with $10{\cdot}4 \le \theta \le 20{\cdot}4°$, 3598 unique reflections, 1914 considered observed at $3\sigma(I)$ level, $\theta \le 45°$, $\theta$–$2\theta$ scans, $h\,0\rightarrow22$, $k\,0\rightarrow17$, $l\,0\rightarrow16$. Three standard reflections monitored after every 7200 s of exposure, max. variation in intensity −1%. Lp correction, empirical absorption correction (North, Phillips & Mathews, 1968), min. transmission/max. transmission 0·63. Precession photographs showed space group to be either *Pnn*2 or *Pnnm*, noncentrosymmetric space group initially selected on basis of intensity statistics. Structure solved by direct methods using *MULTAN*80 (Main *et al.*, 1980). Positions of H atoms bonded to C found in difference Fourier maps. Full-matrix least-squares refinement minimizing $\sum w||F_o|-|F_c||^2$, where $w = 4F^2/[\sigma^2(F^2) + (0{\cdot}06F^2)^2]$, with anisotropic temperature factors for non-H atoms. H atoms with isotropic temperature factors equal in magnitude to 1·2 × that of parent atoms included in calculations but not refined. Scattering factors of Cromer & Waber (1974); anomalous-dispersion coefficients from Cromer (1974). Correction for isotropic secondary-extinction effect included in refinement, $g = 1{\cdot}597 \times 10^{-6}$. Final $R = 0{\cdot}036$, $wR = 0{\cdot}052$, $S = 1{\cdot}292$ for all observed reflections, max. final $\Delta/\sigma$ 0·28, max. and min. final $\Delta\rho$ excursions 0·677, in vicinities of formamides, and $-1{\cdot}034$ e Å$^{-3}$, in vicinity of Zn.

Calculations performed on a PDP 11/23 computer using *SDP* program system (Enraf–Nonius, 1979) and *ORTEP* by Johnson (1965).

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{4}{3}\textstyle\sum_i\sum_j\beta_{ij}(\mathbf{a}_i.\mathbf{a}_j).$$

| | $x$ | $y$ | $z$ | $B_{eq}$(Å$^2$) |
|---|---|---|---|---|
| Zn | 0·25010 (7) | 0·98543 (3) | 0·000 | 1·330 (3) |
| O(1) | 0·1870 (2) | 0·6647 (3) | 0·3607 (3) | 2·12 (4) |
| O(2) | 0·1765 (2) | 0·3334 (3) | 0·3436 (4) | 2·65 (5) |
| O(3) | 0·4052 (2) | 0·9848 (3) | 0·1373 (3) | 1·94 (4) |
| O(4) | 0·4054 (2) | 0·4909 (3) | 0·3704 (3) | 2·14 (4) |
| O(5) | 0·0623 (5) | 0·4060 (9) | −0·0154 (5) | 7·8 (2) |
| O(6) | 0·4351 (3) | 0·3986 (4) | 0·0341 (3) | 3·16 (5) |
| N(1) | 0·1766 (3) | 0·8343 (3) | 0·1667 (4) | 2·47 (4) |
| N(2) | 0·1793 (3) | 0·1608 (4) | 0·1488 (4) | 2·27 (5) |
| C(1) | 0·2175 (3) | 0·7177 (4) | 0·2333 (4) | 1·66 (4) |
| C(2) | 0·2231 (4) | 0·2220 (5) | 0·2787 (4) | 2·27 (6) |
| C(3) | 0·000 | 0·500 | 0·5567 (4) | 1·20 (5) |
| C(4) | 0·000 | 0·000 | −0·0743 (5) | 2·09 (8) |
| C(5) | 0·500 | 0·000 | 0·5395 (7) | 2·7 (1) |
| C(6) | 0·500 | 0·500 | −0·0518 (6) | 3·7 (2) |

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

| | | | |
|---|---|---|---|
| Zn–O(1) | 2·076 (4) | O(2)–C(2) | 1·234 (9) |
| Zn–O(2) | 2·041 (4) | O(3)–C(3) | 1·295 (5) |
| Zn–O(3) | 2·131 (4) | O(4)–C(4) | 1·193 (4) |
| Zn–O(4) | 2·102 (4) | O(5)–C(5) | 1·184 (9) |
| Zn–N(1) | 2·091 (4) | O(6)–C(6) | 1·363 (5) |
| Zn–N(2) | 2·130 (5) | N(1)–C(1) | 1·250 (7) |
| O(1)–C(1) | 1·206 (7) | N(2)–C(2) | 1·305 (8) |
| O(1)–Zn–O(2) | 89·3 (2) | O(3)–Zn–N(2) | 91·1 (2) |
| O(1)–Zn–O(3) | 90·1 (2) | O(4)–Zn–N(1) | 90·1 (2) |
| O(1)–Zn–O(4) | 90·1 (2) | O(4)–Zn–N(2) | 87·0 (2) |
| O(1)–Zn–N(1) | 170·2 (2) | N(1)–Zn–N(2) | 84·9 (2) |
| O(1)–Zn–N(2) | 85·3 (1) | O(1)–C(1)–N(1) | 125·8 (6) |
| O(2)–Zn–O(3) | 89·1 (2) | O(2)–C(2)–N(2) | 120·6 (6) |
| O(2)–Zn–O(4) | 92·8 (2) | O(3)–C(3)–O(3) | 117·9 (6) |
| O(2)–Zn–N(1) | 100·4 (1) | O(4)–C(4)–O(4) | 134·8 (7) |
| O(2)–Zn–N(2) | 174·6 (2) | O(5)–C(5)–O(5) | 134·9 (9) |
| O(3)–Zn–O(4) | 178·1 (2) | O(6)–C(6)–O(6) | 117·0 (7) |
| O(3)–Zn–N(1) | 89·4 (2) | | |

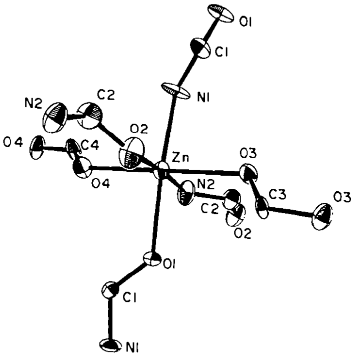

Fig. 1. *ORTEP* diagram (Johnson, 1965) and atom-numbering scheme. Ellipsoids are drawn at the 50% probability level.

**Discussion.** The atomic coordinates and equivalent isotropic temperature factors are given in Table 1.* Bond lengths and angles are given in Table 2. The crystal structure consists of $[Zn(CHO_2)(NH_2CHO)_2]^+$ cations and $[CHO_2]^-$ anions well separated by normal van der Waals distances. The Zn is six-coordinated, in a pseudo-octahedral environment, to two bridging formate groups and two pairs of bridging formamide groups. A perspective view showing the coordination environment of the Zn and the atom-numbering scheme is presented in Fig. 1. In the $[Zn(CHO_2)(NH_2CHO)_2]^+$ three-dimensional cationic polymer, the formate groups link the $Zn^{2+}$ ions by an '*anti–anti*' carboxylate bridge [following the nomenclature of Catterick & Thornton (1977)] to form infinite Zn—O—C—O—Zn chains along the **a** direction of the unit cell. In the *bc* plane of the unit cell, the formamides act as metal–metal bridges, thus forming an infinite two-dimensional network as depicted in Fig. 2. Few complexes with bridging formamide ligands have been reported to this date. Another example can be found in Balahura, Ferguson & Schneider (1975). The minimum Zn···Zn distance is 5·806 Å. The Zn—N and Zn—O distances are in the expected ranges. High-order-data refinement on accurate low-temperature X-ray measurements for the free formamide molecule (Stevens, 1978) yielded C—N and C—O bond lengths of 1·326 and 1·239 Å respectively and a bond angle of 124·9°. In the two independent formamide groups in the present structure, differences from these values are found for C(1)—N(1) and C(1)—O(1), both shorter than the reported values for the free molecule, and for the N(2)—C(2)—O(2) bond angle. Examination of sections through the final difference Fourier map indicates that the large differences found in the formate C—O bond distances are probably due to disordering around the twofold axes.

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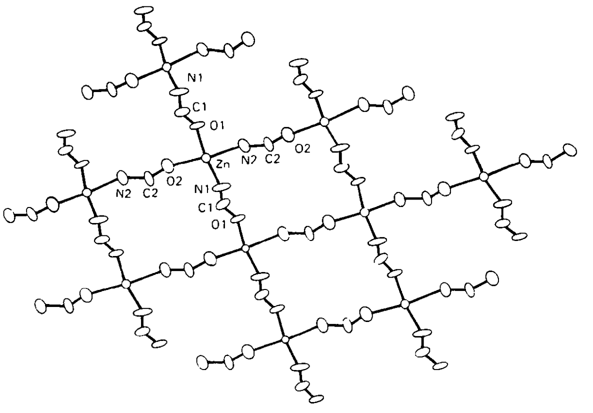

Fig. 2. The *bc* plane of the unit cell showing the coordination of the formamides.

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* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42448 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.