Molecules of the title compound are stacked perpendicular to the *b* axis with 3·40 Å separation between dmp residues. Viewed down this axis, the 2,9-dimethyl groups in alternate layers adopt a *trans* configuration. In the isostructural tetraaquabis(1,10-phenanthroline)-strontium(II) perchlorate 1,10-phenanthroline adduct and the barium(II) complex (Smith, O'Reilly, Kennard & White, 1977), the separation is similar (3·53, 3·52 Å respectively) but the 1,10-phenanthroline residues have the *cis* relationship.

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### References

Atwood, J. L., Roger, R. D., Kutal, C. & Gratsch, P. A. (1977). *J. Chem Soc. Chem. Commun.* pp. 593–594.
Bailey, N. A., Bird, P. H. & Wallbridge, M. G. H. (1966). *Chem. Commun.* pp. 286–287.
Bernstein, E. R., Hamilton, W. C., Keiderling, T. A., LaPlaca, S. J., Lippard, S. J. & Mayerle, J. J. (1972). *Inorg. Chem.* **11**, 3009–3016.
Bird, P. H. & Churchill, M. R. (1967). *Chem. Commun.* p. 403.
Dapporto, P., Midollini, S., Orlandini, A. & Sacconi, L. (1976). *Inorg. Chem.* **15**, 2768–2778.
Dessy, G. & Fares, V. (1979). *Cryst. Struct. Commun.* **8**, 507–510.
Green, B. E., Hawkins, C. J., James, B. D. & Payne, R. (1980). In preparation.
Hall, S. R., Kepert, D. L., Raston, C. L. & White, A. H. (1977). *Aust. J. Chem.* **30**, 1955–1963.
Hämäläinen, R., Ahlgren, M., Turpeinen, U. & Raikas, T. (1979). *Cryst. Struct. Commun.* **8**, 75–80.
Johnson, P. L., Cohen, S. A., Marks, T. J. & Williams, J. M. (1978). *J. Am. Chem. Soc.* **100**, 2709–2716.
Lippard, S. J. & Melmed, K. M. (1967). *Inorg. Chem.* **6**, 2223–2228.
Nakajima, M., Moriyama, H., Kobayashi, A., Saito, T. & Sasaki, Y. (1975). *J. Chem. Soc. Chem. Commun.* pp. 80–81.
Sheldrick, G. M. (1976). *SHELX* 76. Program for crystal structure determination. Univ. of Cambridge, England.
Smith, G., O'Reilly, E. J., Kennard, C. H. L. & White, A. H. (1977). *J. Chem. Soc. Dalton Trans.* pp. 1184–1190.

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# Dichlorobis(triphenylphosphine oxide)zinc(II)

By J. P. Rose and R. A. Lalancette

*Department of Chemistry, Rutgers University, Newark, New Jersey* 07102, *USA*

and J. A. Potenza and H. J. Schugar

*Department of Chemistry, Rutgers University, New Brunswick, New Jersey* 08903, *USA*

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**Abstract.** $[Zn\{(C_6H_5)_3PO\}_2Cl_2]$, $C_{36}H_{30}Cl_2O_2P_2Zn$, orthorhombic, *Fdd*2, $a = 20\cdot728$ (3), $b = 33\cdot042$ (7), $c = 9\cdot769$ (2) Å, $Z = 8$, $D_o = 1\cdot38$ (1), $D_c = 1\cdot38$ Mg m$^{-3}$. The structure contains $[Zn\{(C_6H_5)_3PO\}_2Cl_2]$ molecules with point symmetry 2. Each Zn atom is ligated by two Cl and two O atoms having an approximately tetrahedral arrangement as indicated by the Cl—Zn—Cl′/O—Zn—O′ dihedral angle [87·7 (2)°]. Bond angles within the coordination polyhedron are: O—Zn—O′, 96·8 (3); Cl—Zn—O, 112·0 (2); Cl—Zn—O′, 109·0 (2); and Cl—Zn—Cl′, 116·4 (1)°. The Zn—Cl and Zn—O distances are 2·204 (2) and 1·984 (5) Å, respectively.

**Introduction.** The spectroscopic properties of approximately tetrahedral $Cu^{II}$ complexes are of considerable current interest. A coordination polyhedron of this type was reported for the $[Cu\{(C_6H_5)_3PO\}_2Cl_2]$ analogue of the title complex (Bertrand & Kalyanaraman, 1971). The neat $Cu^{II}$ complex displayed electronic spectral and EPR features appropriate for a flattened tetrahedral $Cu^{II}Cl_2O_2$ chromophore having point symmetry 2 (Bertini, Gatteschi & Martini, 1973). The title complex has been used as a host lattice for EPR studies of $Mn^{II}$ and $Cu^{II}$ ions (Vivien & Gibson, 1975). On the basis of these EPR studies and space-group analyses, the structures

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of the title complex and $[Cu\{(C_6H_5)_3PO\}_2Cl_2]$ were thought to be identical (Vivien & Gibson, 1975). However, some structural differences may be expected due to the electronic differences between $d^{10}$ and $d^9$ species. We chose to characterize the title complex structurally so that the geometrical parameters of these $ZnO_2Cl_2$ and $CuO_2Cl_2$ polyhedra could be compared.

Colorless elongated prisms were obtained by slowly cooling a warm solution of $ZnCl_2$ and the ligand (1 : 2) in a mixture of absolute ethanol and cyclohexane (2 : 1). A single crystal of dimensions 0·2 × 0·2 × 0·3 mm, mounted on a glass fiber, was used. Weissenberg and precession photographs revealed an orthorhombic lattice and showed systematic absences for $hkl$, $h + k$, $h + l$, and $k + l = 2n + 1$; $0kl$, $k + l = 4n + 1$; and $h0l$, $h + l = 4n + 1$, indicating space group $Fdd2$. Unit-cell parameters were determined at 296 ± 1 K from a least-squares analysis of the $\theta$, $\chi$ and $\varphi$ values of 15 reflections which were carefully centered on a Syntex $P2_1$ diffractometer using graphite-monochromated Mo $K\alpha$ radiation ($\lambda$ = 0·71069 Å). Assuming eight molecules per cell, the observed (flotation in $CCl_4$–hexane) and calculated densities agreed well. Data were collected at 296 ± 1 K using the Syntex $P2_1$ automated diffractometer ($\theta$–$2\theta$ scan) and graphite-monochromated Mo $K\alpha$ radiation. 1202 reflections ($4 < 2\theta < 50°$) having $F^2 > 3\sigma(F^2)$ were considered observed, corrected for Lp and absorption effects ($\mu$ = 1·045 mm$^{-1}$ for Mo $K\alpha$ radiation), and used in the refinement. Three standard reflections, measured at 47-reflection intervals, remained constant to ±3% throughout the data-collection period.

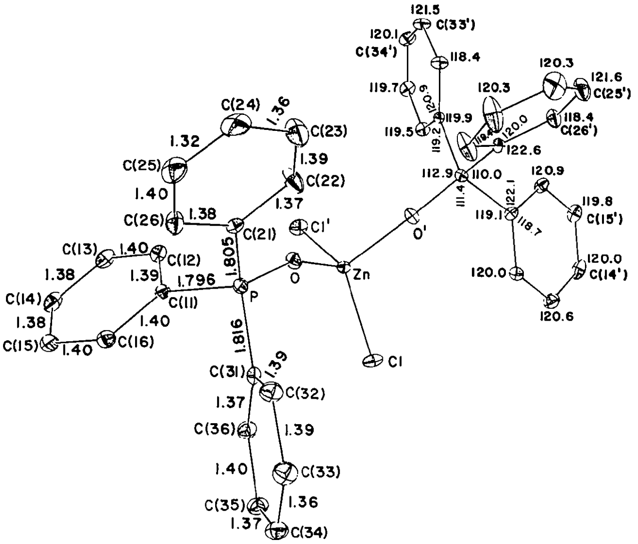

Fig. 1. View of the title complex showing the atom-numbering scheme and selected bond distances (Å) and angles (°). Additional angles not shown are: P–C(21)–C(22), 117·4; O–P–C(21), 108·8; C(21)–P–C(31), 107·8; C(31)–P–C(11), 105·9°. Average e.s.d.'s are as follows: P–C, 0·007; C–C, 0·01 Å; O–P–C, 0·3; C–P–C, 0·3; P–C–C, 0·5; C–C–C, 0·8°.

The structure was solved by direct methods and refined by full-matrix least-squares techniques using programs described previously (Fawcett, Ushay, Rose, Lalancette, Potenza & Schugar, 1979). An $E$ map, calculated using 300 phases from the starting set having the highest combined figure of merit, revealed the positions of the Zn, P, Cl and O atoms; the remaining non-hydrogen atoms were located on a subsequent difference Fourier map. Neutral-atom scattering factors, obtained from *International Tables for X-ray Crystallography* (1974), were used in the refinement; anomalous-dispersion corrections were applied to Zn, Cl and P.

Isotropic refinement led to convergence with $R_F = \sum||F_o| - |F_c||/\sum|F_o| = 0{\cdot}075$ while refinement of both the positional and anisotropic thermal parameters reduced $R_F$ to 0·053. Ideal H atom positions were calculated assuming a C–H distance of 0·95 Å; H

Table 1. *Fractional atomic coordinates*

Estimated standard deviations are given in parentheses. Equivalent isotropic temperature factors $B_{eq}$ (Å$^2$) for the nonhydrogen atoms have been calculated by $B_{eq} = \frac{1}{3}(B_{11}\,a^{*2}a^2 + B_{12}a^*b^*ab\cos\gamma + \ldots)$.

| | $x$ | $y$ | $z$ | $B_{eq}$ |
|---|---|---|---|---|
| Zn | 0 | 0 | 0 | 2·6 |
| Cl | 0·07586 (9) | −0·03079 (7) | 0·1190 (2) | 4·9 |
| P | 0·08365 (8) | 0·07018 (5) | −0·1802 (2) | 2·8 |
| O | 0·0365 (2) | 0·0386 (1) | −0·1348 (5) | 3·7 |
| C(11) | 0·0758 (3) | 0·1157 (2) | −0·0810 (7) | 3·2 |
| C(12) | 0·0177 (3) | 0·1239 (2) | −0·0165 (8) | 3·9 |
| C(13) | 0·0113 (4) | 0·1585 (3) | 0·0645 (9) | 5·4 |
| C(14) | 0·0628 (5) | 0·1845 (2) | 0·0832 (9) | 5·4 |
| C(15) | 0·1205 (4) | 0·1771 (2) | 0·0180 (10) | 5·2 |
| C(16) | 0·1272 (4) | 0·1427 (2) | −0·0636 (9) | 4·5 |
| C(21) | 0·0700 (3) | 0·0810 (2) | −0·3590 (7) | 3·2 |
| C(22) | 0·0356 (6) | 0·0532 (3) | −0·4330 (11) | 7·3 |
| C(23) | 0·0283 (8) | 0·0585 (4) | −0·5730 (12) | 10·0 |
| C(24) | 0·0526 (7) | 0·0921 (4) | −0·6352 (11) | 7·8 |
| C(25) | 0·0845 (6) | 0·1194 (3) | −0·5633 (11) | 6·6 |
| C(26) | 0·0942 (5) | 0·1150 (3) | −0·4221 (10) | 5·1 |
| C(31) | 0·1670 (3) | 0·0542 (2) | −0·1613 (7) | 2·9 |
| C(32) | 0·2036 (4) | 0·0455 (3) | −0·2766 (9) | 4·5 |
| C(33) | 0·2669 (3) | 0·0330 (3) | −0·2584 (11) | 5·0 |
| C(34) | 0·2935 (3) | 0·0301 (3) | −0·1314 (10) | 4·9 |
| C(35) | 0·2573 (4) | 0·0390 (2) | −0·0176 (9) | 4·5 |
| C(36) | 0·1929 (3) | 0·0512 (2) | −0·0329 (8) | 4·0 |
| H[C(12)] | −0·018 | 0·106 | −0·026 | |
| H[C(13)] | −0·029 | 0·164 | 0·106 | |
| H[C(14)] | 0·058 | 0·207 | 0·140 | |
| H[C(15)] | 0·155 | 0·195 | 0·027 | |
| H[C(16)] | 0·167 | 0·137 | −0·106 | |
| H[C(22)] | 0·017 | 0·031 | −0·389 | |
| H[C(23)] | 0·008 | 0·038 | −0·625 | |
| H[C(24)] | 0·047 | 0·096 | −0·730 | |
| H[C(25)] | 0·100 | 0·143 | −0·607 | |
| H[C(26)] | 0·118 | 0·134 | −0·372 | |
| H[C(32)] | 0·186 | 0·049 | −0·366 | |
| H[C(33)] | 0·293 | 0·026 | −0·336 | |
| H[C(34)] | 0·337 | 0·022 | −0·123 | |
| H[C(35)] | 0·276 | 0·037 | 0·069 | |
| H[C(36)] | 0·167 | 0·057 | 0·046 | |

atoms were assigned temperature factors according to $B_H = B_N + 1$ where $N$ is the atom bonded to H. The H atoms were included as fixed contributions to the structure factors and several additional cycles of refinement (unit weights) led to convergence with $R_F = 0{\cdot}033$ and $R_{wF} = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2} = 0{\cdot}036$ for all reflections with $F^2 \geq 3\sigma(F^2)$. For the final cycle, all parameter changes were less than $0{\cdot}05\sigma$, where $\sigma$ is the e.s.d. obtained from the inverse matrix. On a final difference map, the largest positive peak was 0·1 e Å$^{-3}$ indicating that the model chosen gives a good account of the electron density in the unit cell. Final atomic coordinates* are listed in Table 1, while a view of the structure is given in Fig. 1.

**Discussion.** The structure consists of discrete $[\mathrm{Zn}\{(\mathrm{C_6H_5})_3\mathrm{PO}\}_2\mathrm{Cl_2}]$ molecules with point symmetry 2. Each Zn atom is ligated by two O atoms and two Cl atoms which yield a distorted tetrahedral coordination geometry. Structural parameters required to compare the coordination polyhedra of the title complex and its Cu$^{\mathrm{II}}$ analogue are presented in Table 2; the structural parameters of the single crystallographically unique $(\mathrm{C_6H_5})_3\mathrm{PO}$ ligand (Fig. 1) agree closely with those reported for the Cu$^{\mathrm{II}}$ analogue (Bertrand & Kalyanaraman, 1971).

Table 2. *Selected structural parameters for the title complex and its* Cu$^{\mathrm{II}}$ *analogue*

Cell edges and bond distances are in Å and angles are in deg.

| | *M* = Zn | *M* = Cu |
|---|---|---|
| *a* | 20·728 (3) | 20·839 (4) |
| *b* | 33·042 (7) | 31·961 (4) |
| *c* | 9·769 (2) | 9·886 (2) |
| *M*–Cl | 2·204 (2) | 2·170 (2) |
| *M*–O | 1·984 (5) | 1·958 (4) |
| P–O | 1·496 (5) | 1·492 (4) |
| Cl–*M*–Cl′ | 116·4 (1) | 102·2 (1) |
| O–*M*–O′ | 96·8 (3) | 93·0 (1) |
| Cl–*M*–O | 112·0 (2) | 104·7 (2) |
| Cl–*M*–O′ | 109·0 (2) | 127·5 (2) |
| *M*–O–P | 153·4 (3) | 150·9 (3) |
| Cl–*M*–Cl′/O–*M*–O′ | 87·7 (2) | 71·6 |

In agreement with the prediction based on EPR observations (Vivien & Gibson, 1975), the structures of the Zn$^{\mathrm{II}}$ and Cu$^{\mathrm{II}}$ complexes are quite similar. Both crystallize in the same space group with similar cell dimensions and eight molecules of point symmetry 2. There are, however, small but significant differences between the Zn$^{\mathrm{II}}$ and Cu$^{\mathrm{II}}$ coordination polyhedra.

For the Cu$^{\mathrm{II}}$ complex, the coordination polyhedron has been described as a flattened tetrahedron with the $\mathrm{CuCl_2O_2}$ unit compressed along an axis which bisects the equivalent Cl–Cu–O′ and Cl′–Cu–O angles [127·5 (2)°] and lies approximately along the [010] direction. As a result of this compression, the remaining angles within the Cu$^{\mathrm{II}}$ coordination polyhedron are all smaller than the tetrahedral value. Moreover, the observed Cl–Cu–Cl′/O–Cu–O′ dihedral angle (71·6°) is reduced from the ideal tetrahedral value (90°) towards the ideal value for planar coordination (0°). In contrast, for the Zn$^{\mathrm{II}}$ complex, both the Cl–Zn–O′ angle [109·0 (2)°] and the Cl–Zn–Cl′/O–Zn–O′ dihedral angle [87·7 (2)°] lie close to the ideal values for the tetrahedron, indicating that the Zn$^{\mathrm{II}}$ complex is, to a large extent, free of the flattening noted above. Greater compression of the Cu$^{\mathrm{II}}$ polyhedron approximately along [010] is consistent with the unit-cell dimensions of the two complexes. Compared with the Zn$^{\mathrm{II}}$ complex, the Cu$^{\mathrm{II}}$ analogue shows larger *a* and *c* cell edges and a smaller *b* cell edge.

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## References

Bertini, I., Gatteschi, D. & Martini, G. (1973). *J. Chem. Soc. Dalton Trans.* pp. 1644–1646.

Bertrand, J. A. & Kalyanaraman, A. R. (1971). *Inorg. Chim. Acta*, **5**, 341–345.

Fawcett, T. G., Ushay, M., Rose, J. P., Lalancette, R. A., Potenza, J. A. & Schugar, H. J. (1979). *Inorg. Chem.* **18**, 327–332.

*International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.

Vivien, D. & Gibson, J. F. (1975). *J. Chem. Soc. Faraday Trans.* 2, pp. 1640–1653.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35340 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.