| | | | |
|---|---|---|---|
| C(9) | 0.3140 (4) | 0.1925 (8) | 0.2759 (3) | 3.2 (3) |
| C(10) | 0.3723 (4) | 0.110 (1) | 0.2540 (4) | 4.2 (3) |
| C(11) | 0.3695 (4) | 0.0064 (9) | 0.2030 (4) | 4.0 (3) |
| C(12) | 0.3051 (4) | −0.0118 (9) | 0.1712 (3) | 3.7 (3) |
| C(13) | 0.2459 (4) | 0.0654 (9) | 0.1923 (4) | 3.9 (3) |
| C(14) | 0.2505 (4) | 0.1673 (9) | 0.2451 (3) | 3.7 (3) |
| C(15) | 0.2474 (5) | −0.126 (1) | 0.0801 (4) | 6.3 (4) |

Table 2. *Selected geometric parameters* ($\text{\AA}$, °)

| | | | |
|---|---|---|---|
| Te—Cl(1) | 2.521 (4) | Te—Cl(2) | 2.485 (2) |
| Te—C(1) | 2.073 (7) | Te—C(9) | 2.110 (7) |
| C(2)—Cl(3) | 1.722 (8) | O—C(12) | 1.368 (9) |
| O—C(15) | 1.41 (1) | C(1)—C(2) | 1.34 (1) |
| C(2)—C(3) | 1.48 (1) | C(3)—C(4) | 1.39 (1) |
| C(3)—C(8) | 1.38 (1) | C(4)—C(5) | 1.39 (1) |
| C(5)—C(6) | 1.35 (1) | C(6)—C(7) | 1.37 (2) |
| C(7)—C(8) | 1.38 (1) | C(9)—C(10) | 1.38 (1) |
| C(9)—C(14) | 1.38 (1) | C(10)—C(11) | 1.36 (1) |
| C(11)—C(12) | 1.40 (1) | C(12)—C(13) | 1.37 (1) |
| C(13)—C(14) | 1.38 (1) | | |
| Cl(1)—Te—Cl(2) | 177.65 (8) | C(3)—C(4)—C(5) | 119.5 (7) |
| Cl(1)—Te—C(1) | 87.1 (2) | C(4)—C(5)—C(6) | 120.2 (8) |
| Cl(1)—Te—C(9) | 90.6 (2) | C(5)—C(6)—C(7) | 120.8 (9) |
| Cl(2)—Te—C(1) | 90.8 (2) | C(6)—C(7)—C(8) | 119.9 (9) |
| Cl(2)—Te—C(9) | 90.6 (2) | C(3)—C(8)—C(7) | 120.0 (8) |
| C(1)—Te—C(9) | 95.0 (3) | C(10)—C(9)—C(14) | 118.6 (7) |
| C(12)—O—C(15) | 117.3 (6) | C(9)—C(10)—C(11) | 122.4 (7) |
| Cl(3)—C(2)—C(1) | 116.5 (6) | C(10)—C(11)—C(12) | 117.7 (7) |
| Cl(3)—C(2)—C(3) | 117.6 (6) | O—C(12)—C(11) | 113.4 (7) |
| C(1)—C(2)—C(3) | 125.7 (7) | O—C(12)—C(13) | 125.0 (7) |
| C(2)—C(3)—C(4) | 119.5 (7) | C(11)—C(12)—C(13) | 121.5 (7) |
| C(2)—C(3)—C(8) | 120.8 (7) | C(12)—C(13)—C(14) | 119.1 (7) |
| C(4)—C(3)—C(8) | 119.6 (7) | C(9)—C(14)—C(13) | 120.6 (7) |

Data were corrected for Lp effects. The structure was solved by direct methods. H atoms were included as fixed contributors at positions found in a difference synthesis and refined with one overall isotropic temperature factor which converged to $0.079\,(7)\,\text{\AA}^2$. The refinement was by full-matrix least-squares methods.

Programs used: *SHELXS*86 (Sheldrick, 1985), *SHELX*76 (Sheldrick, 1976) and *ORTEP* (Johnson, 1965).

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# Bis[bis(3,5-dimethyl-1-pyrazolyl)phosphinato]copper(II), [Cu{O₂P(N₂C₃HMe₂)₂}₂]

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## Abstract

The title compound, [Cu(C₁₀H₁₄N₄O₂P)₂], consists of pairs of bis(dimethylpyrazolyl)phosphinato groups coordinated to copper(II) atoms sitting on inversion centers. The compound has Cu—N bond distances of 2.009 (4) and 2.010 (4) $\text{\AA}$ and an N—Cu—N angle of 89.27 (13)°. The phosphinato O atoms weakly coordinate the copper ions with bond distances of 2.490 (3) $\text{\AA}$.

## Comment

The title compound, (I), was obtained as a hydrolysis product in a study of the ligation behavior of tris(3,5-dimethyl-1-pyrazolyl)phosphine oxide.



(I)
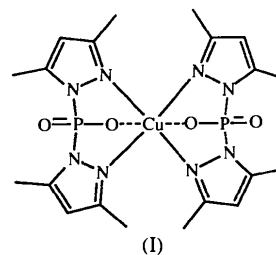
The ready conversion of the phosphine oxide to the phosphinato ion has been noted before: the ligation of tris(3,5-dimethyl-1-pyrazolyl)phosphine oxide with an

allyl molybdenum–carbonyl complex also resulted in hydrolysis with the elimination of a pyrazole group (Joshi, Kale, Sathe, Sarkar, Tavale & Suresh, 1991), similar to the *in situ* hydrolysis of a pyrazolyl gallate ligand (Breakell, Rettig & Trotter, 1979).
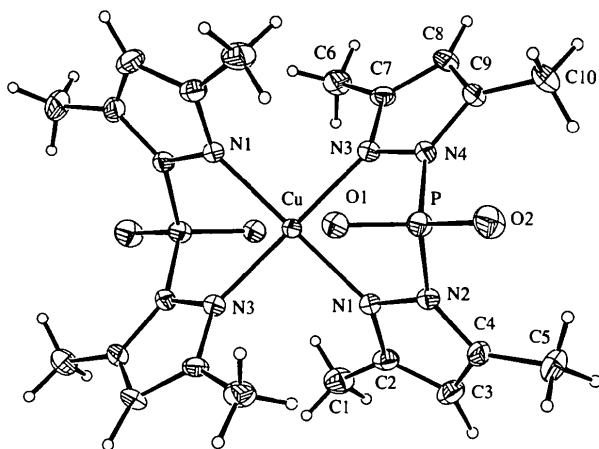


Fig. 1. An *ORTEPII* (Johnson, 1976) drawing of the molecule, with 30% ellipsoids, showing the numbering scheme. H atoms have been omitted for clarity.

## Experimental

The title compound was obtained from the reaction of tris(3,5-dimethyl-1-pyrazolyl)phosphine oxide with copper(II) perchlorate hexahydrate in methylene chloride. Crystals were grown from a mixture of methylene chloride and hexane.

### Crystal data

$[Cu(C_{10}H_{14}N_4O_2P)_2]$
$M_r = 569.98$
Monoclinic
$P2_1/n$
$a = 7.939 (6)$ Å
$b = 17.82 (2)$ Å
$c = 8.734 (9)$ Å
$\beta = 94.51 (8)°$
$V = 1232 (2)$ Å$^3$
$Z = 2$
$D_x = 1.537$ Mg m$^{-3}$

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 21 reflections
$\theta = 8.00-9.50°$
$\mu = 1.06$ mm$^{-1}$
$T = 293$ K
Block
$0.40 \times 0.38 \times 0.24$ mm
Blue

### Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: empirical *via* $\psi$ scans (3 reflections)
$T_{min} = 0.92$, $T_{max} = 1.00$
1858 measured reflections
1721 independent reflections

1304 observed reflections
$[I > 3\sigma(I)]$
$R_{int} = 0.019$
$\theta_{max} = 22.94°$
$h = -8 \rightarrow 8$
$k = 0 \rightarrow 19$
$l = 0 \rightarrow 9$
3 standard reflections
frequency: 60 min
intensity decay: 1.1%

### Refinement

Refinement on $F$
$R = 0.033$
$wR = 0.053$
$S = 0.94$
1304 reflections
160 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F) + 0.0025F^2]$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.61$ e Å$^{-3}$
$\Delta\rho_{min} = -0.30$ e Å$^{-3}$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å$^2$)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

| | x | y | z | $U_{eq}$ |
|---|---|---|---|---|
| Cu | 0 | 1/2 | 0 | 0.0250 (3) |
| P | −0.13461 (15) | 0.37484 (6) | 0.18989 (12) | 0.0316 (6) |
| O1 | 0.0371 (3) | 0.40725 (15) | 0.2132 (3) | 0.0334 (14) |
| O2 | −0.2054 (4) | 0.31488 (17) | 0.2781 (3) | 0.0497 (19) |
| N1 | −0.2136 (4) | 0.51330 (17) | 0.1061 (4) | 0.0284 (17) |
| N2 | −0.2686 (4) | 0.45198 (18) | 0.1860 (4) | 0.0303 (17) |
| N3 | −0.0976 (4) | 0.40630 (18) | −0.0998 (4) | 0.0291 (17) |
| N4 | −0.1575 (4) | 0.35277 (18) | −0.0033 (4) | 0.0302 (17) |
| C1 | −0.3107 (6) | 0.6423 (3) | 0.0493 (6) | 0.048 (3) |
| C2 | −0.3277 (5) | 0.5662 (2) | 0.1194 (5) | 0.034 (2) |
| C3 | −0.4548 (5) | 0.5407 (3) | 0.2065 (5) | 0.043 (3) |
| C4 | −0.4163 (5) | 0.4683 (3) | 0.2465 (5) | 0.039 (2) |
| C5 | −0.5094 (6) | 0.4141 (3) | 0.3407 (6) | 0.056 (3) |
| C6 | −0.0748 (6) | 0.4224 (3) | −0.3761 (5) | 0.045 (3) |
| C7 | −0.1228 (5) | 0.3787 (2) | −0.2416 (4) | 0.033 (2) |
| C8 | −0.1985 (6) | 0.3082 (2) | −0.2364 (5) | 0.040 (2) |
| C9 | −0.2186 (5) | 0.2924 (2) | −0.0858 (5) | 0.035 (2) |
| C10 | −0.2885 (7) | 0.2250 (3) | −0.0119 (6) | 0.051 (3) |

Table 2. *Selected geometric parameters* (Å, °)

| | | | |
|---|---|---|---|
| Cu—O1 | 2.490 (3) | N2—C4 | 1.355 (5) |
| Cu—N1 | 2.009 (4) | N3—N4 | 1.381 (5) |
| Cu—N3 | 2.010 (4) | N3—C7 | 1.333 (5) |
| P—O1 | 1.480 (3) | N4—C9 | 1.362 (5) |
| P—O2 | 1.455 (3) | C2—C3 | 1.387 (6) |
| P—N2 | 1.737 (4) | C3—C4 | 1.365 (7) |
| P—N4 | 1.728 (4) | C7—C8 | 1.395 (6) |
| N1—N2 | 1.386 (5) | C8—C9 | 1.366 (6) |
| N1—C2 | 1.319 (5) | | |
| O1—Cu—N1 | 77.74 (13) | P—N2—C4 | 135.2 (3) |
| O1—Cu—N3 | 77.97 (14) | N1—N2—C4 | 110.1 (3) |
| N1—Cu—N3 | 89.27 (13) | Cu—N3—N4 | 116.7 (2) |
| O1—P—O2 | 127.11 (19) | Cu—N3—C7 | 137.2 (3) |
| O1—P—N2 | 104.46 (18) | N4—N3—C7 | 106.2 (3) |
| O1—P—N4 | 104.38 (17) | P—N4—N3 | 115.0 (2) |
| O2—P—N2 | 109.3 (2) | P—N4—C9 | 134.6 (3) |
| O2—P—N4 | 109.53 (18) | N3—N4—C9 | 110.4 (3) |
| N2—P—N4 | 98.27 (17) | N1—C2—C3 | 110.4 (4) |
| Cu—O1—P | 95.90 (15) | C2—C3—C4 | 107.0 (4) |
| Cu—N1—N2 | 116.8 (2) | N2—C4—C3 | 106.6 (4) |
| Cu—N1—C2 | 137.3 (3) | N3—C7—C8 | 109.6 (4) |
| N2—N1—C2 | 105.9 (3) | C7—C8—C9 | 107.5 (3) |
| P—N2—N1 | 114.7 (3) | N4—C9—C8 | 106.4 (4) |

The data crystal was mounted on a glass fiber with silicone rubber. The intensity scans were $(1.0 + 0.35\tan\theta)°$ with scan speeds in the range 4–16° min$^{-1}$. The total exposure time was 22.3 h. The structure was solved by direct methods. In the final least-squares refinement, the H atoms were constrained to idealized positions (C—H = 0.95 Å) based on the orientations of the methyl groups, which had been determined by difference maps.

Data collection: *CAD-4-PC* (Enraf–Nonius, 1993). Cell refinement: *CAD-4-PC*. Data reduction: *NRCVAX* (Gabe, Le

Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *NRCVAX*. Program(s) used to refine structure: *NRCVAX*. Molecular graphics: *NRCVAX*. Software used to prepare material for publication: *NRCVAX*.

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# Dipyridiniomethane *trans*-Dichloro-tetrafluoroosmate(IV) Hydrate, *trans*-[(C₅H₅N)₂CH₂][OsF₄Cl₂].H₂O

trans-[(C$_5$H$_5$N)$_2$CH$_2$][OsF$_4$Cl$_2$].H$_2$O

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## Abstract

The X-ray diffraction study of dipyridiniomethane *trans*-dichlorotetrafluoroosmate(IV) hydrate [or *N,N*-methylenedipyridinium dichlorotetrafluoroosmate(IV) hydrate] at room temperature revealed the complete ordering of the complex anions, *i.e.* trans-[OsF$_4$Cl$_2$]$^{2-}$, into *AB*-type salts with the doubly charged dipyridiniomethane cation [(C$_5$H$_5$N)$_2$CH$_2$]$^{2+}$. A water molecule is linked to the F atoms by hydrogen bridges, resulting in the formation of chains. Hydrogen-bridged F atoms show Os—F distances of 1.938 (3) and 1.944 (3) Å compared with non-bridged F atoms of the anion exhibiting Os—F distances of 1.924 (3) and 1.938 (3) Å. The Os—Cl bond lengths are 2.341 (2) and 2.334 (2) Å.

## Comment

Octahedrally coordinated halide complexes of platinum group metals are well studied prototype species that have a variety of applications in spectroscopy. Mixed-ligand complex ions of the type [OsF$_n$Cl$_{6-n}$]$^{2-}$ (*n* = 0–6) have been synthesized systematically by stereospecific substitution reactions in order to examine the effects of altered symmetry on NMR, UV–Vis and vibrational spectra (Preetz, Ruf & Tensfeldt, 1984; Parzich, Peters & Preetz, 1993; Alyoubi, Greenslade, Foster & Preetz, 1990). Unfortunately, single-crystal structure analyses of alkali metal and alkylammonium salts revealed partial or complete statistical arrangement of the mixed halogeno complexes in the anion sublattices (Keller & Homborg, 1976). The bent and doubly charged dipyridiniomethane cation (Brüdgam & Hartl, 1986) provides an *AB*-type lattice of low symmetry in which the complex sublattice is perfectly ordered (Bruhn & Preetz, 1994*a,b*; Bruhn, Drews, Meynhardt & Preetz, 1995). In the course of our work on mixed F/Cl complexes of Os$^{IV}$, we isolated the title compound, (I), by ion-exchange chromatography.



(I)
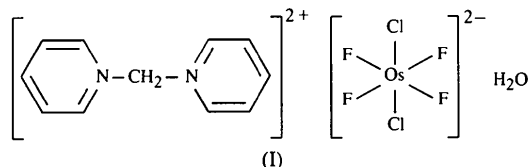
In the triclinic unit cell, two inequivalent Os atoms reside on special positions [Os1 at 0,0,0 and Os2 at $\frac{1}{2},\frac{1}{2},\frac{1}{2}$]. Due to the location of the Os atoms on inversion centers, the F and Cl atoms form linear F—Os—F and Cl—Os—Cl axes, respectively, with Os—F bond lengths Os1—F11 1.924 (3), Os1—F12 1.938 (3), Os2—F21 1.938 (3) and Os2—F22 1.944 (3) Å, and Os—Cl bond distances Os1—Cl1 2.341 (2) and Os2—Cl2 2.334 (2) Å. These axes are almost orthogonal, close to the ideal value of 90° in octahedral complexes, with a maximum deviation of 1.5°. One of the F—Os—F axes is bridged to a water molecule and the bridging H atoms are linked to the complex ions forming chains with F···O distances O···F12 2.897 (7) and O···F22 2.845 (7) Å, and F···O···F angles of 103.5 (2)°. The bridging H atoms are not collinear with F···O, forming angles of 144 (9)° for O—H1···F12 and 161 (13)° for O—H2···F22 (Fig. 1).

In the dipyridiniomethane dication, the normals to the pyridine rings are almost perpendicular, making an angle of 85.9 (2)° with respect to one another. The interplanar angles of the pyridine rings with the plane through atoms C*M*, N1 and N2 are 56.8 (4) and 69.8 (4)°. All the atoms of the cation lie in general positions. The packing in the triclinic unit cell is shown in Fig. 2.