Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HH1018). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Butler, I. R., Cullen, W. R., Kim, T. J., Rettig, S. J. & Trotter, J. (1985). *Organometallics*, **4**, 972–980.

Hor, T. S. A. & Phang, L. T. (1989). *J. Organomet. Chem.* **373**, 319–323.

Hor, T. S. A., Phang, L. T., Liu, L. K. & Wen, Y. S. (1990). *J. Organomet. Chem.* **397**, 29–41.

Sheldrick, G. M. (1990). *SHELXTL-PC*. Version 2.4. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

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Chloro[*o*-(diphenylphosphino)benzaldehyde]-{*N*-[*o*-(diphenylphosphino)benzylidene]ethylamine}(tetrachloro-*o*-catecholato)iridium(III)

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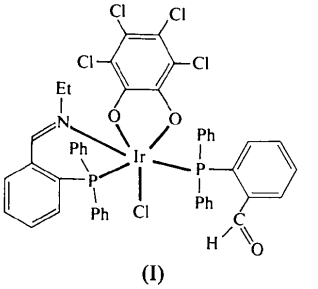
Abstract

The title structure, chloro{2-(diphenylphosphino)-benzaldehyde-*P*}[*N*-{2-(diphenylphosphino)benzylidene}ethylamine-*N*,*P*](3,4,5,6-tetrachloro-1,2-benzenediolato-*O*,*O*′)iridium butanol hemisolvate, [IrCl($C_6Cl_4O_2$)($C_{19}H_{15}OP$)($C_{21}H_{20}NP$)].0.5$C_4H_{10}O$, consists of two independent molecules in the asymmetric unit with an Ir^{III} metal atom pseudo octahedrally coordinated by the following donors: two catecholate O atoms, one Cl^- anion, two phosphine groups and one imino group.

Comment

In the course of our studies on transition metal complexes with *o*-quinoid ligands (Bianchini, Masi, Mealli, Meli, Martini, Laschi & Zanello, 1987; Barbaro, Bianchini, Linn, Mealli, Meli, Laschi & Zanello, 1992; Bianchini, Frediani, Laschi, Meli, Vizza & Zanello, 1990), we have found that the square-planar complex [(NPet)$_2$Ir]Cl (Barbaro, Bianchini, Laschie, Midollini, Moneti, Scapacci & Zanello, 1994) [NPet = {*o*-(diphenylphosphino)-benzylidene}ethylamino] reacts in acetone with a stoichiometric amount of tetrachloro-*o*-quinone (TClQ) to give the title compound [(NPet)(C_6H_4-PPh_2CHO)IrCl(TClCat)], (I) (TclCat = tetrachloro-*o*-catecholato). The product has been characterized by spectroscopic techniques and by an X-ray crystal structure determination.



(I)

The reaction of [(NPet)$_2$Ir]$^+$ with TClQ is not well understood since several products are generally obtained. However, a complex is selectively produced when the reaction mixture is exposed to air. In this case, [(NPet)($C_6H_4PPh_2CHO$)IrCl(TCl-Cat)] forms as a result of the oxidative addition of TClQ to iridium, followed by hydrolysis of one imino group to a formyl group (March, 1985).

A perspective view of one of the two molecules in the asymmetric unit is shown in Fig. 1. The compound has a distorted octahedral structure with the metal center coordinated by the N and P donor

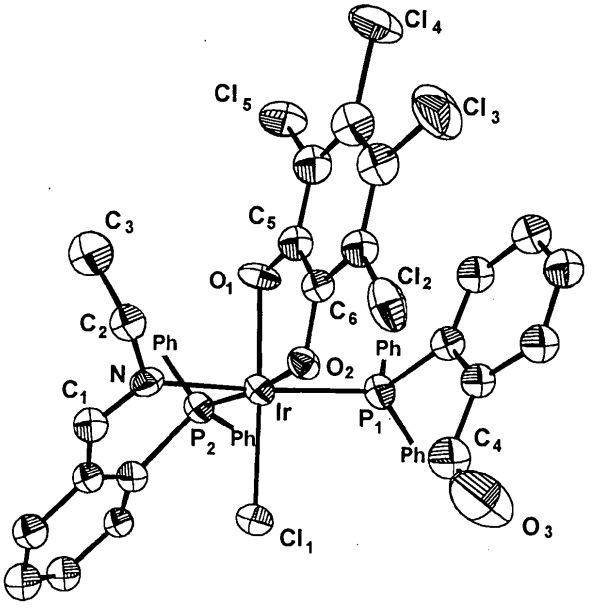


Fig. 1. *ORTEP* drawing of one of the molecules of the title complex showing the labeling scheme. The phenyl substituents on the P atoms are abbreviated for clarity.

atoms of the NPet ligand, by the phosphine group of the *o*-(diphenylphosphino)benzaldehyde, by the bidentate-*O*,*O* tetrachlorocatecholate ligand and, finally, by a Cl atom. The latter is *trans* to one O atom of the quinoid ligand, while the two P atoms are *cis* to each other. In spite of minor structural differences, the trends are similar in the two independent molecules. The Ir—O distances are in the expected range for Ir^{III}–catecholate complexes (Barbaro *et al.*, 1992). The Ir—O linkage *trans* to the Ir—P linkage is significantly longer than that *trans* to the Ir—Cl linkage [2.09 (1) *versus* 2.06 (1) Å and 2.11 (1) *versus* 2.04 (2) Å, in the two molecules, respectively]. A similar stronger *trans* influence of the P donor atom toward the catecholate O atom was observed in the structure of $[Ir(NO)(PPh_3)(O_2C_6Br_4)]$ (Shorthill, Buchanan, Pierpont, Ghedini & Dolcetti, 1980), where the linkage *trans* to the P atom is more elongated than that *trans* to the N atom [2.01 (1) *versus* 1.90 (1) Å, respectively]. In this complex, which involves Ir^{I}, all the Ir—O and Ir—P distances are significantly shorter than the present Ir^{III}—O and Ir^{III}—P separations.

Experimental

To a solution of NPet (0.32 g, 1 mmol) in acetone (10 ml, degassed with N_2), solid $[Ir(cyclooctene)_2Cl]_2$ (0.22 g, 0.25 mmol) was added at room temperature to give a red–brown solution of $[(NPet)_2Ir]Cl$. On addition of solid TClQ (0.12 g, 0.5 mmol), the colour of the solution immediately turned light orange. ^{n}BuOH (10 ml) was then added. Crystals were obtained from this solution on slow evaporation of the solvents in air (yield 68%). Selective spectroscopic data: IR (Nujol mulls): 1624 and 1584 cm^{-1} ν(C=N), 1693 cm^{-1} ν(C=O). ^{1}H NMR (DMSO-d_6, 296 K, 200.133 MHz, relative to Me_4Si): $\delta(CH_3)$ 1.08 (*t*, 3H), $\delta(CH_2)$ 3.48 (*q*, 2H), *J*(HH) 7.0 Hz; δ(N=CH) 8.85 (*d*, 1H), *J*(HP) 13.4 Hz; δ(CHO) 10.23 (*s*, 1H). ^{13}C NMR (DMSO-d_6, 296 K, 50.330 MHz, relative to Me_4Si): δ(CHO) 291.99, δ(N=CH) 35.02. ^{31}P NMR (DMSO-d_6, 296 K, 81.015 MHz, relative to 85% H_3PO_4): *AB* spin system, $\delta(P_A)$ −25.18, $\delta(P_B)$ −38.15, *J*(PP) 13.1 Hz.

Crystal data

$[IrCl(C_6Cl_4O_2)(C_{19}H_{15}OP)(C_{21}H_{20}NP)].0.5C_4H_{10}O$
M_r = 1118.27
Triclinic
$P\bar{1}$
a = 18.888 (4) Å
b = 19.495 (5) Å
c = 17.110 (4) Å
α = 64.87 (2)°
β = 69.28 (2)°
γ = 65.86 (2)°
V = 5079.9 (5) Å^3
Z = 4
D_x = 1.04 Mg m^{-3}
D_m = 1.03 Mg m^{-3}
Cu $K\alpha$ radiation
λ = 1.54180 Å
Cell parameters from 25 reflections
θ = 6–11.5°
μ = 8.230 mm^{-1}
T = 294 K
Needle
0.45 × 0.075 × 0.05 mm
Orange

Data collection

Philips PW1100 diffractometer
ω–2θ scans
Absorption correction: empirical (*DIFABS*; Walker & Stuart, 1983)
T_{min} = 0.958, T_{max} = 1.035
10 358 measured reflections
10 358 independent reflections
6760 observed reflections [$I \geq 3\sigma(I)$]
θ_{max} = 55°
$h = -16 \rightarrow 17$
$k = -17 \rightarrow 17$
$l = 0 \rightarrow 16$
3 standard reflections monitored every 120 reflections
intensity variation: none

Refinement

Refinement on F
R = 0.063
wR = 0.067
S = 2.46
6760 reflections
493 parameters
$w = 1/\sigma^2(F_o)$
$(\Delta/\sigma)_{max}$ = 0.6
$\Delta\rho_{max}$ = 0.97 e Å^{-3}
$\Delta\rho_{min}$ = −0.98 e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV) for non-H atoms and Stewart, Davidson & Simpson (1965) for H atoms

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

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

	x	y	z	U_{iso}/U_{eq}
Molecule *A*				
Ir	0.0854 (1)	0.8315 (1)	0.7003 (1)	0.051 (1)
P1	0.0538 (3)	0.7565 (3)	0.8506 (3)	0.061 (7)
P2	0.1121 (3)	0.7401 (3)	0.6366 (3)	0.054 (6)
N1	0.1177 (7)	0.9055 (8)	0.5663 (9)	0.054 (18)
O1	0.2004 (6)	0.8006 (7)	0.7106 (8)	0.069 (17)
O2	0.0725 (6)	0.9246 (6)	0.7395 (7)	0.052 (14)
O3	−0.1163 (13)	0.9661 (14)	0.9133 (16)	0.188 (48)
Cl1	−0.0466 (3)	0.8911 (3)	0.6807 (3)	0.063 (6)
Cl2	0.0664 (4)	1.0436 (3)	0.8094 (3)	0.087 (8)
Cl3	0.2183 (5)	1.0013 (5)	0.8741 (4)	0.131 (14)
Cl4	0.3646 (4)	0.8534 (5)	0.8449 (5)	0.139 (14)
Cl5	0.3537 (3)	0.7496 (4)	0.7536 (4)	0.110 (10)
C1	0.0971 (10)	0.9133 (10)	0.4988 (12)	0.064 (5)
C2	0.1640 (11)	0.9592 (11)	0.5474 (12)	0.069 (5)
C3	0.2511 (13)	0.9225 (14)	0.5114 (16)	0.101 (7)
C4	−0.0615 (13)	0.9126 (13)	0.8936 (14)	0.087 (6)
C5	0.2041 (7)	0.8474 (6)	0.7479 (8)	0.063 (5)
C6	0.1395 (7)	0.9131 (6)	0.7605 (8)	0.054 (4)
C7	0.1444 (7)	0.9611 (6)	0.7987 (8)	0.065 (5)
C8	0.2140 (7)	0.9434 (6)	0.8243 (8)	0.081 (6)
C9	0.2786 (7)	0.8777 (6)	0.8117 (8)	0.091 (6)
C10	0.2737 (7)	0.8297 (6)	0.7735 (8)	0.079 (6)
C11	−0.0445 (7)	0.7438 (8)	0.9092 (8)	0.061 (5)
C21	−0.0586 (7)	0.7163 (8)	1.0014 (8)	0.078 (6)
C31	−0.1296 (7)	0.6996 (8)	1.0515 (8)	0.093 (7)
C41	−0.1865 (7)	0.7104 (8)	1.0095 (8)	0.104 (7)
C51	−0.1723 (7)	0.7380 (8)	0.9173 (8)	0.091 (6)
C61	−0.1013 (7)	0.7547 (8)	0.8672 (8)	0.081 (6)
C12	0.0654 (10)	0.8002 (10)	0.9207 (11)	0.062 (5)
C22	0.1278 (11)	0.7647 (11)	0.9620 (12)	0.073 (5)
C32	0.1362 (12)	0.7989 (12)	1.0160 (13)	0.079 (6)
C42	0.0783 (11)	0.8645 (11)	1.0304 (13)	0.075 (6)
C52	0.0127 (11)	0.8990 (11)	0.9943 (12)	0.070 (5)
C62	0.0064 (10)	0.8684 (10)	0.9369 (11)	0.059 (5)
C13	0.1197 (6)	0.6532 (8)	0.8791 (9)	0.068 (5)
C23	0.0874 (6)	0.5903 (8)	0.9262 (9)	0.085 (6)
C33	0.1374 (6)	0.5121 (8)	0.9489 (9)	0.096 (7)
C43	0.2197 (6)	0.4967 (8)	0.9244 (9)	0.101 (7)
C53	0.2520 (6)	0.5596 (8)	0.8773 (9)	0.101 (7)
C63	0.2020 (6)	0.6378 (8)	0.8546 (9)	0.077 (6)

C14	0.0874 (6)	0.6473 (6)	0.6971 (8)	0.059 (5)
C24	0.0074 (6)	0.6525 (6)	0.7333 (8)	0.067 (5)
C34	−0.0149 (6)	0.5833 (6)	0.7807 (8)	0.089 (6)
C44	0.0430 (6)	0.5090 (6)	0.7918 (8)	0.100 (7)
C54	0.1230 (6)	0.5039 (6)	0.7556 (8)	0.096 (7)
C64	0.1452 (6)	0.5730 (6)	0.7083 (8)	0.068 (5)
C15	0.2165 (9)	0.7083 (9)	0.5816 (9)	0.060 (5)
C25	0.2352 (9)	0.7105 (9)	0.4942 (9)	0.102 (7)
C35	0.3142 (9)	0.6819 (9)	0.4527 (9)	0.155 (12)
C45	0.3745 (9)	0.6510 (9)	0.4986 (9)	0.132 (10)
C55	0.3558 (9)	0.6488 (9)	0.5860 (9)	0.115 (8)
C65	0.2768 (9)	0.6774 (9)	0.6275 (9)	0.087 (6)
C16	0.0602 (10)	0.7864 (10)	0.5467 (11)	0.058 (5)
C26	0.0599 (10)	0.8641 (10)	0.4920 (11)	0.054 (4)
C36	0.0225 (11)	0.9014 (11)	0.4193 (12)	0.070 (5)
C46	−0.0151 (12)	0.8608 (12)	0.4042 (13)	0.078 (6)
C56	−0.0097 (11)	0.7836 (11)	0.4536 (12)	0.072 (5)
C66	0.0275 (10)	0.7451 (10)	0.5274 (11)	0.057 (4)
Molecule *B*				
Ir	0.2269 (1)	0.3882 (1)	0.4300 (1)	0.058 (1)
P1	0.3176 (3)	0.2955 (3)	0.3605 (3)	0.060 (6)
P2	0.2347 (3)	0.3074 (3)	0.5723 (3)	0.061 (6)
N1	0.1508 (9)	0.4769 (8)	0.4858 (10)	0.075 (21)
O1	0.3181 (7)	0.4310 (7)	0.4027 (8)	0.070 (18)
O2	0.2148 (7)	0.4714 (7)	0.3030 (8)	0.077 (18)
O3	0.2150 (10)	0.3826 (12)	0.1344 (10)	0.132 (32)
Cl1	0.1084 (3)	0.3672 (3)	0.4427 (3)	0.074 (7)
Cl2	0.2169 (4)	0.5811 (4)	0.1200 (4)	0.126 (10)
Cl3	0.3529 (4)	0.6608 (5)	0.0430 (5)	0.163 (12)
Cl4	0.4702 (5)	0.6175 (5)	0.1602 (6)	0.177 (16)
Cl5	0.4498 (4)	0.4945 (4)	0.3537 (5)	0.129 (13)
C1	0.0957 (13)	0.4692 (13)	0.5613 (15)	0.088 (6)
C2	0.1385 (16)	0.5678 (15)	0.4255 (18)	0.117 (8)
C3	0.1849 (19)	0.5834 (19)	0.4529 (21)	0.145 (11)
C4	0.2423 (14)	0.3765 (13)	0.1931 (16)	0.090 (6)
C5	0.3244 (7)	0.4871 (8)	0.3207 (9)	0.078 (6)
C6	0.2722 (7)	0.5056 (8)	0.2688 (9)	0.078 (6)
C7	0.2804 (7)	0.5593 (8)	0.1830 (9)	0.095 (7)
C8	0.3408 (7)	0.5946 (8)	0.1488 (9)	0.109 (8)
C9	0.3930 (7)	0.5762 (8)	0.2007 (9)	0.106 (7)
C10	0.3848 (7)	0.5225 (8)	0.2866 (9)	0.097 (7)
C17	0.2891 (7)	0.2266 (8)	0.3388 (8)	0.074 (5)
C27	0.2151 (7)	0.2137 (8)	0.3784 (8)	0.076 (6)
C37	0.1957 (7)	0.1623 (8)	0.3581 (8)	0.099 (7)
C47	0.2501 (7)	0.1239 (8)	0.2982 (8)	0.110 (8)
C57	0.3241 (7)	0.1368 (8)	0.2586 (8)	0.117 (8)
C67	0.3435 (7)	0.1882 (8)	0.2789 (8)	0.108 (8)
C18	0.3661 (11)	0.3465 (10)	0.2470 (12)	0.066 (5)
C28	0.3258 (12)	0.3749 (12)	0.1781 (14)	0.082 (6)
C38	0.3621 (13)	0.4133 (12)	0.0897 (14)	0.087 (6)
C48	0.4355 (14)	0.4158 (14)	0.0756 (16)	0.103 (7)
C58	0.4772 (14)	0.3854 (13)	0.1401 (15)	0.094 (7)
C68	0.4404 (12)	0.3489 (12)	0.2285 (14)	0.085 (6)
C19	0.4033 (8)	0.2329 (8)	0.4119 (9)	0.067 (5)
C29	0.4368 (8)	0.1526 (8)	0.4193 (9)	0.088 (6)
C39	0.5027 (8)	0.1063 (8)	0.4574 (9)	0.116 (8)
C49	0.5352 (8)	0.1404 (8)	0.4879 (9)	0.113 (8)
C59	0.5017 (8)	0.2208 (8)	0.4804 (9)	0.103 (7)
C69	0.4358 (8)	0.2670 (8)	0.4424 (9)	0.085 (6)
C110	0.2830 (9)	0.3296 (8)	0.6303 (8)	0.074 (5)
C210	0.3189 (9)	0.3898 (8)	0.5874 (8)	0.096 (7)
C310	0.3548 (9)	0.4061 (8)	0.6334 (8)	0.120 (9)
C410	0.3548 (9)	0.3621 (8)	0.7224 (8)	0.126 (9)
C510	0.3189 (9)	0.3018 (8)	0.7654 (8)	0.118 (8)
C610	0.2830 (9)	0.2856 (8)	0.7194 (8)	0.090 (6)
C111	0.2702 (7)	0.2010 (8)	0.5966 (9)	0.067 (5)
C211	0.3379 (7)	0.1516 (8)	0.6307 (9)	0.079 (6)
C311	0.3613 (7)	0.0698 (8)	0.6477 (9)	0.104 (7)
C411	0.3170 (7)	0.0373 (8)	0.6306 (9)	0.100 (7)
C511	0.2493 (7)	0.0868 (8)	0.5966 (9)	0.107 (7)
C611	0.2259 (7)	0.1686 (8)	0.5796 (9)	0.082 (6)
C112	0.1350 (10)	0.3234 (10)	0.6418 (11)	0.063 (5)
C212	0.0817 (10)	0.3994 (10)	0.6264 (11)	0.059 (5)
C312	0.0072 (13)	0.4130 (14)	0.6864 (15)	0.095 (7)
C412	−0.0147 (14)	0.3498 (14)	0.7562 (15)	0.099 (7)
C512	0.0368 (13)	0.2749 (14)	0.7712 (15)	0.093 (7)
C612	0.1162 (13)	0.2599 (13)	0.7123 (14)	0.088 (6)
C21*S*†	0.408 (5)	0.253 (5)	−0.011 (5)	0.17 (3)
C22*S*	0.478 (5)	0.199 (6)	0.014 (5)	0.19 (3)
C23*S*	0.511 (7)	0.119 (7)	0.028 (7)	0.26 (5)
C24*S*	0.596 (7)	−0.003 (7)	0.060 (7)	0.27 (5)
C25*S*	0.676 (6)	−0.080 (6)	0.045 (7)	0.24 (4)

† The assigned population factor of the atoms of the solvent molecule denoted *S* (all treated as C atoms) is 0.5.

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

	Molecule *A*	Molecule *B*
Ir—P1	2.354 (4)	2.338 (5)
Ir—P2	2.267 (6)	2.289 (4)
Ir—O1	2.06 (1)	2.04 (2)
Ir—O2	2.09 (1)	2.11 (1)
Ir—N1	2.15 (1)	2.09 (2)
Ir—Cl1	2.360 (5)	2.357 (6)
O1—C5	1.35 (2)	1.37 (2)
O2—C6	1.34 (2)	1.33 (2)
O3—C4	1.20 (3)	1.23 (4)
O2—Ir—Cl1	89.6 (4)	88.2 (4)
O1—Ir—Cl1	169.5 (4)	167.5 (4)
O1—Ir—O2	81.4 (5)	81.2 (6)
N1—Ir—Cl1	86.0 (4)	84.2 (6)
N1—Ir—O2	87.1 (5)	89.6 (6)
N1—Ir—O1	88.0 (6)	89.2 (6)
P2—Ir—Cl1	93.1 (2)	92.4 (2)
P2—Ir—O2	170.5 (3)	174.9 (4)
P2—Ir—O1	94.8 (4)	97.6 (4)
P2—Ir—N1	84.0 (4)	85.4 (5)
P1—Ir—Cl1	96.1 (2)	99.1 (2)
P1—Ir—O2	88.6 (3)	87.8 (4)
P1—Ir—O1	89.3 (4)	87.1 (4)
P1—Ir—N1	175.2 (4)	175.7 (5)
P1—Ir—P2	100.2 (2)	97.2 (2)
O1—Ir—O2—C6	−6.8 (2)	2.8 (9)

The structure was solved by Patterson and Fourier methods. Refinement was by full-matrix least-squares methods with anisotropic displacement parameters for Ir, P, N, Cl and O atoms; all the phenyl rings were treated as rigid bodies with D_{6h} symmetry (C—C = 1.39 Å). The H atoms were introduced at calculated positions (C—H = 1.08 Å). Programs used were *SHELX*76 (Sheldrick, 1976) and *ORTEP* (Johnson, 1976) adapted for the Digital DEC 5000/200 workstation.

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: LI1061). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Barbaro, P., Bianchini, C., Laschie, F., Midollini, S., Moneti, S., Scapacci, G. & Zanello, P. (1994). *Inorg. Chem.* **33**, 1622–1630.

Barbaro, P., Bianchini, C., Linn, K., Mealli, C., Meli, A., Laschi, F. & Zanello, P. (1992). *Inorg. Chim. Acta*, **200**, 31–56.

Bianchini, C., Frediani, P., Laschi, F., Meli, A., Vizza, F. & Zanello, P. (1990). *Inorg. Chem.* **29**, 3402–3409.

Bianchini, C., Masi, D., Mealli, C., Meli, A., Martini, G., Laschi, F. & Zanello, P. (1987). *Inorg. Chem.* **26**, 3683–3693.

Johnson, C. K. (1976). *ORTEP*. ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

March, J. (1985). *Advanced Organic Chemistry*, pp. 784–785, and references therein. New York: Wiley Interscience.

Sheldrick, G. M. (1976). *SHELX*76. *Program for Crystal Structure Determination*. Univ. of Cambridge, England.

Shorthill, W. B., Buchanan, R. M., Pierpont, C. G., Ghedini, M. & Dolcetti, G. (1980). *Inorg. Chem.* **19**, 1803–1805.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3181.
Walker, N. & Stuart, D. (1983). *Acta Cryst.* A**39**, 158–166.

Acta Cryst. (1994). C**50**, 1417–1419

[*N*,*N*′-Bis(2-hydroxybenzyl)-*N*-methyl-*N*′-(2-pyridylmethyl)-1,3-propanediamine]-oxovanadium(IV) Hemihydrate, [VO(bbmppn)].0.5H_2O

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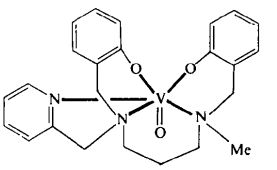
Abstract

The novel title complex, {2,2′-[*N*-methyl-*N*′-(2-pyridylmethyl-κN)-1,3-propanediyldinitrilo-$\kappa^2 N,N'$-methylene]diphenolato-$\kappa^2 O,O'$}oxovanadium(IV) hemihydrate, [VO(bbmppn)], [VO($C_{24}H_{27}N_3O_2$)].0.5H_2O, has been synthesized and its structure determined. The coordination environment around the VO^{2+} group is defined by two phenolate O and two amine N atoms in the equatorial plane, where atoms of the same type occupy *cis* positions with respect to one another. The pyridyl N atom of the pentadentate ligand, in a *trans* position with respect to the terminal oxo group, completes the coordination sphere.

Comment

As a result of the reported binding of vanadium to tyrosinate residues in vanadium-modified transferrin (Harris & Carrano, 1984) and its interaction with the characterized polyphenol tunichrome in the vandocytes of the tunicates (Bruening, Olttz, Furukawa, Nakanishi & Kustin, 1985), vanadium phenolate chemistry is receiving considerable attention from inorganic chemists (Riley, Pecoraro, Carrano, Bonadies & Raymond, 1986; Neves, Ceccato, Erasmus-Buhr, Gehring, Haase, Paulus, Nascimento & Batista, 1993). Here we report the synthesis and crystal structure of a vanadyl(IV) complex containing a new N_3O_2-donor ligand (H_2bbmppn) which contains phenolate and pyridine as pendant arms.



(I)

The V ion lies in a highly distorted octahedral environment with the V centre being displaced above the equatorial plane by 0.245 (1) Å towards the oxo ligand. The V=O distance is short [1.602 (5) Å], indicating the considerable double-bond character typical of vanadyl(IV) complexes (Neves, Walz, Wieghardt, Nuber & Weiss, 1988; Neves *et al.*, 1993). Consequently, the V—N(pyridine) bond *trans* to the V=O group is long [V—N(1) = 2.259 (5) Å], which is characteristic of the strong *trans* influence of the V=O group. The V—O(phenolate) [average 1.916 (5) Å] and V—N(amine) [average 2.209 (6) Å] bond distances in the equatorial plane are identical to those found in the closely related [VO^{IV}(bbpen)] complex [1.923 (2) and 2.208 (3) Å, respectively], where H_2bbpen = *N*,*N*′-bis(2-hydroxybenzyl)-*N*,*N*′-bis(2-pyridylmethyl)ethylenediamine (Neves *et al.*, 1993).

However, despite the similarities between the title structure and [VO(bbpen)], it is worth noting that the V—N bond lengths *trans* to the V=O group are significantly different in the two complexes {2.259 (5) Å in the title structure and 2.307 (2) Å in [VO(bbpen)]}. This fact reflects the smaller displacement (0.245 Å) of the V centre from the N_2O_2 plane in the present complex compared with that (0.345 Å) in [VO(bbpen)]. In the title complex, the six-membered chelate ring formed by the 1,3-propanediamine group, which requires a larger bite angle [N(2)—V—N(3) = 93.2 (2)°], is in the equatorial plane. On the other hand, in the [VO(bbpen)] complex, one of the amine N atoms of the ethylenediamine backbone which forms the more rigid five-membered ring is coordinated *trans* rather than *cis* to the V=O bond. As a consequence, the higher flexibility of the six-membered ring in the title structure allows coordination of the pyridyl arm *trans* to the V=O group. From this information we must conclude that, despite the similarities between the H_2bbmppn and H_2bbpen ligands, it is possible to observe significant structural differences in their corresponding vanadyl(IV) complexes.

Finally, the structure shows two hydrogen bonds involving the O(*W*) water molecule, placed in a special position, as a donor to the O(1) and O(1^i) atoms [symmetry code: (i) $1-x$, y, $\frac{3}{2}-z$], characterized by symmetrical distances of 2.752 Å for O(*W*)···O(1) and O(*W*)···O(1^i), and an O(1)···O(*W*)···O(1^i) angle of 131.3° [H(*W*)—O(*W*)—H(W^i) = 116.1°].