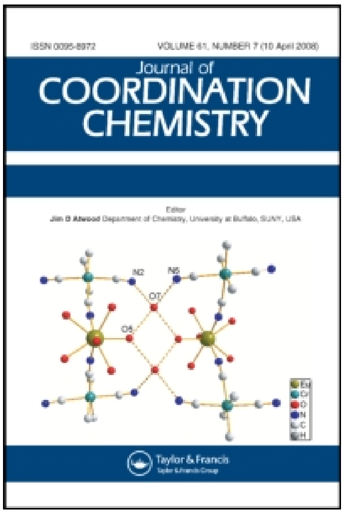

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SYNTHESIS AND CRYSTAL STRUCTURE OF Δ, L-TRIS-METHYLENEBIS-[DIPHENYLPHOSPHINE OXIDE]NICKEL(II) DIPERCHLORATE METHANOL SOLVATE

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SYNTHESIS AND CRYSTAL STRUCTURE OF Δ, L-TRIS-METHYLENEBIS[DIPHENYLPHOSPHINE OXIDE]NICKEL(II) DIPERCHLORATE METHANOL SOLVATE

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Δ,L-*Tris*-methylene*bis*[diphenylphosphine oxide]nickel(II) diperchlorate methanol solvate, Δ, $[Ni(bppom)_3](ClO_4)_2 \cdot MeOH$, was synthesized and its structure determined by single crystal X-ray diffraction at room temperature, and refined to a final $R = 0.099$ The structure consists of *quasi*-octahedral, tetragonally distorted, $[Ni(bppom)_3]^{2+}$ cations and perchlorate anions. One methanol molecule of crystallization per formula unit is present. The average Ni-O equatorial and axial distances are 2.075 Å and 2.185 Å respectively.

KEYWORDS: crystal structure, nickel complex, methylene*bis*(diphenylphosphine oxide), chiral complex

INTRODUCTION

Tetradentate and linear ligands with NSSN skeletons (where the sulphur atoms belong to thioether groups and nitrogen atoms to heterocycles such as pyridine,[1] imidazole,[2] *etc.*) interact with divalent transition metal salts of general formula $MX_2 \cdot nH_2O$ (M = Co, Ni or Cu, X = Cl, Br, I, NO_3 or ClO_4, n = 6) to form cationic complexes of stoichiometry $[M(L)(H_2O)_2]^{2+}$[3] or $[M(L)(H_2O)X]^{+}$[4] and neutral complexes $[M(L)X_2]$[5] (L = tetradentate ligand) in which the central metal ion is octahedrally coordinated by the tetradentate ligand through the two sulphur atoms in the *cis* equatorial positions and the two nitrogen atoms in the *trans* axial positions. One or two water molecules or one or two oxygen atoms from the anions invariably occupy the other two *cis* equatorial positions. These complexes are good starting compounds to carry out replacement reactions in which they react with monodentate[6] or bidentate ligands and also with bichelating tetradentate ligands such as oxalate or oxamide[7] to give dinuclear species which may have unusual magnetic properties.

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A well-known way of synthesising dinuclear complexes of transition metals involves using bidentate diphosphine ligands, particularly *bis*(diphenylphosphine)methane (dppm).[8–12] For this reason, this ligand was selected for the substitution reaction mentioned above and also because it contains two phosphorus donor atoms which are of similar size to the sulphur atoms, so that the probable geometry around each metal atom should be tetragonally-distorted octahedral with consequent alteration in ligand field properties due to the presence of different donor atoms. Diaqua[1,8-bis(2-pyridyl)-3,6-dithiaoctane-*N,N′,S,S′*]nickel(II) diperchlorate, $[Ni(bpdto)(H_2O)_2](ClO_4)_2$, the structure of which is known,[13,14] was selected as the starting complex. However, reaction with the diphosphine ligand was found to give the complex $[Ni(dppom)_3](ClO_4)_2$, in which the phosphine ligand has been oxidised to methylene*bis*(diphenylphosphine oxide), dppom.

Although the reported coordination chemistry of dppom is not very extensive, a number of complexes of this ligand with main group[15] and transition[16] metals have been synthesized and characterized. The cation $[Ni(dppom)_3]^{2+}$ has been synthesized by heating (260–270°C) $[NiX_2(dppm)]$ in the presence of air.[17] However, structural analysis by X-ray diffraction has only been reported for dppom[18] itself and the complexes $[SnPh_2(dppom)(NO_3)_2]$,[19] $[SnBu^n{}_2Cl_2(dppom)]$,[20] $(AlCl_3)_2(dppom)$[21] and $[Cu(dppom)_3][Cu_2Cl_6]$,[22] as well as some derivatives of alkali metals.[15a,23] In this paper, the reaction of $[Ni(bpdto)(H_2O)_2](ClO_4)_2$ with dppm at room temperature to produce the new chiral compound *tris*-methylene*bis*(diphenylphosphine oxide)nickel(II) diperchlorate methanol solvate, is described.

EXPERIMENTAL

Synthesis

Initially, we intended to obtain the cation $[Ni(bpdto)(dppm)]^{2+}$ as a perchlorate by the reaction of $[Ni(bpdto)(H_2)_2](ClO_4)_2$[14] with dppm. However, the product obtained in every case was the *tris*-chelate $[Ni(dppom)_3](ClO_4)_2$.

A solution of bpdto (0.37 g, 1.2 mmol) in 20 cm^3 of hot methanol was added, slowly with stirring, to a solution of $Ni(ClO_4)_2 \cdot 6H_2O$ (0.44 g, 1.2 mmol). The reaction mixture was cooled to room temperature and left stirring continuously for ten days. To this, dppm (0.5 g, 1.2 mmol) was added and stirring was continued for a further 15 days. The solid formed was then filtered, washed with small portions of methanol and air dried.

Crystal structure determination

Suitable crystals for X-ray diffraction were obtained by the slow evaporation and cooling of a methanolic solution of the filtered compound. Crystal data are shown in Table 1. Intensity data for a prismatic crystal with dimensions 0.20 × 0.25 × 0.40 mm were measured at room-temperature, 293 K, on an Enraf-Nonius CAD4 diffractometer with graphite monochromatised Mo*Kα* radiation, $\lambda = 0.71073$ Å. The $\omega/2\theta$ scan technique was employed to measure the intensities for 9594 reflections up to a maximum Bragg angle of 28°. Cell parameters were refined by a least-squares procedure on setting angles of 25 reflections ($7.8 \leq \theta \leq 12.0°$).[24] No decomposition of the crystal occurred during data collection. Corrections were

Table 1 Crystal data for $[Ni(dppom)_3](ClO_4)_2 \cdot MeOH$.

Molecular formula	$C_{76}H_{70}Cl_2NiO_{15}P_6$
Formula mass	1538.86
Crystal system	Triclinic
Space group	$P\bar{1}$
a(Å)	15.856(2)
b(Å)	17.964(1)
c(Å)	14.515(1)
α(°)	111.07(1)
β(°)	101.05(1)
γ(°)	93.73(1)
V(Å^3)	3745.8(6)
Z	2
D_x (g cm^{-1})	2.729
F(000)	3192

applied for Lorenz and polarization effects and for absorption (μ = 1.037 mm^{-1}).[25] A total of 9594 reflections were collected, of which 8204 were unique (R_{int} = 0.023), and of these 4924 satisfied the $I \geq 3.0\sigma(I)$ criterion of observability and were used in the subsequent analysis.

The structure was solved by direct-methods[26] and refined by a full-matrix least-squares procedures based on F.[24] Ni and all O-P-C-P-O atoms were refined with anisotropic displacement parameters, the remaining isotropically. Hydrogen atoms were constrained to idealized positions (C-H = 0.95 Å) and included in structure factor calculations with fixed isotropic B values (B_{eq} = 5.0 Å^2), but not refined. The weighting scheme of the form, $w = 1/\sigma^2(F)$ was introduced and the refinement proceeded smoothly to convergence with a maximum Δ/σ of 0.001 when R = 0.099, R_w = 0.102 and GOF = 4.163 (Goodness-of-Fit) for 482 variables. Correction for extinction was made in the last cycle of refinement.[27] Secondary extinction coefficient was refined to $g = 3.036 \times 10^{-8}$ $\{F_c = F_c/[1 + g(F_c)^2Lp]\}$. Analysis of variance showed no special features and the maximum and minimum residual electron density peaks in the final difference map were + 1.40 and − 1.02 eÅ^{-3}, respectively. Impossibility of refinement with anisotropic displacement factors for all non-hydrogen atoms, slight disorder in the atoms of some phenyl groups, and considerable disorder in the atoms of the perchlorate anions and the atoms of the methanol crystallization molecule may cause the high R value.

Atomic scattering factors and anomalous dispersion corrections for all atoms were taken from *International Tables for X-ray Crystallography*.[28] Fractional atomic coordinates are listed in Table 2 and a *SCHAKAL* drawing[29] of the cation $[Ni(dppom)_3]^{2+}$ with the atom labelling scheme is shown in Figure 1.

RESULTS AND DISCUSSION

The title compound is formed in the reaction of $[Ni(bpdto)(OH_2)_2](ClO_4)_2$ with dppm at room temperature. Unexpectedly, it was found that the ligand $Ph_2P\text{-}CH_2\text{-}PPh_2$ was oxidised and coordinated as dppom. A similar reaction occurred at temperatures around 250°C,[27] and also at room temperature, during the reaction of $[TcNCl_2(Me_2PhP)_3]$ with disulphur dichloride to produce $[Tc(NS)Cl_3(Me_2PhP)$

Table 2 Fractional positional parameters for the atoms in [Ni(dppom)$_3$](ClO$_4$)$_2$·MeOH with e.s.d.s in parentheses; for numbering see Fig. 1.

Atom	*x/a*	*y/b*	*z/c*	$B_{eq}{}^a$
Complex cation				
Ni	0.8007(1)	0.2976(1)	0.5892(2)	5.87(7)
P(11)	0.7245(2)	0.3172(2)	0.7904(3)	3.3(1)
P(12)	0.6304(4)	0.3826(2)	0.6396(3)	2.9(1)
P(21)	0.9881(2)	0.4160(2)	0.6792(3)	3.1(1)
P(22)	0.9889(2)	0.2423(2)	0.6606(3)	3.1(1)
P(31)	0.7364(2)	0.2457(2)	0.3405(3)	3.3(1)
P(32)	0.6537(2)	0.1421(2)	0.4352(3)	2.9(1)
O(11)	0.7984(5)	0.3128(4)	0.7456(6)	2.1(3)
O(12)	0.7011(5)	0.3653(4)	0.5829(7)	3.6(3)
O(21)	0.8910(4)	0.4024(4)	0.6444(7)	3.5(3)
O(22)	0.8990(5)	0.2291(4)	0.5972(7)	3.4(3)
O(31)	0.8001(5)	0.2818(5)	0.4329(6)	2.1(3)
O(32)	0.7093(5)	0.1940(4)	0.5376(7)	3.1(3)
C(1)	0.6224(7)	0.3195(6)	0.712(1)	3.0(4)
C(2)	1.0241(7)	0.3484(6)	0.741(1)	3.0(4)
C(3)	0.6377(7)	0.1959(7)	0.353(1)	3.2(4)
C(11)	0.7439(7)	0.4073(7)	0.901(1)	3.5(3)
C(12)	0.8203(8)	0.4583(7)	0.925(1)	4.3(3)
C(13)	0.8333(9)	0.5335(8)	1.002(1)	5.4(4)
C(14)	0.7734(9)	0.5565(8)	1.058(1)	4.9(3)
C(15)	0.6980(9)	0.5054(8)	1.038(1)	5.5(4)
C(16)	0.6834(9)	0.4303(8)	0.960(1)	4.8(3)
C(21)	0.7054(8)	0.2323(7)	0.826(1)	4.2(3)
C(22)	0.627(1)	0.213(1)	0.846(1)	7.1(4)
C(23)	0.614(1)	0.145(1)	0.870(2)	8.3(5)
C(24)	0.681(1)	0.103(1)	0.878(2)	8.8(6)
C(25)	0.755(1)	0.118(1)	0.857(2)	8.3(5)
C(26)	0.768(1)	0.1870(9)	0.830(1)	6.5(4)
C(31)	0.5263(7)	0.3613(7)	0.553(1)	3.5(3)
C(32)	0.4566(9)	0.3118(8)	0.550(1)	4.9(3)
C(33)	0.383(1)	0.2903(9)	0.469(1)	6.6(4)
C(34)	0.379(1)	0.3207(9)	0.400(1)	6.0(4)
C(35)	0.447(1)	0.371(1)	0.40191)	7.3(5)
C(36)	0.5221(9)	0.3919(8)	0.479(1)	5.6(4)
C(41)	0.6496(7)	0.4862(6)	0.725(1)	3.2(2)
C(42)	0.7196(8)	0.5359(7)	0.725(1)	4.2(3)
C(43)	0.7372(9)	0.6155(8)	0.793(1)	5.2(3)
C(44)	0.6877(9)	0.6449(8)	0.861(1)	5.1(3)
C(45)	0.6188(9)	0.5973(8)	0.864(1)	5.6(4)
C(46)	0.5973(8)	0.5157(8)	0.793(1)	4.7(3)
C(51)	1.0243(7)	0.5162(6)	0.772(1)	5.6(4)
C(52)	1.1110(8)	0.5524(8)	0.801(1)	4.7(3)
C(53)	1.1334(9)	0.6307(8)	0.873(1)	5.4(4)
C(54)	1.073(1)	0.6728(9)	0.912(1)	5.9(4)
C(55)	0.988(1)	0.6379(9)	0.885(1)	6.1(4)
C(56)	0.9637(9)	0.5585(8)	0.815(1)	4.7(3)
C(61)	1.0409(8)	0.4009(7)	0.577(1)	3.9(3)
C(62)	0.9914(9)	0.3969(8)	0.483(1)	5.1(3)
C(63)	1.030(1)	0.380(1)	0.401(1)	7.1(4)
C(64)	1.111(1)	0.369(1)	0.408(2)	8.0(5)
C(65)	1.162(1)	0.372(1)	0.494(1)	7.1(5)
C(66)	1.128(1)	0.3883(8)	0.585(1)	5.8(4)
C(71)	0.9976(8)	0.1890(7)	0.744(1)	4.0(3)

Table 2 — *Continued*

Atom	x/a	y/b	z/c	$B_{eq}{}^a$
C(72)	0.948(1)	0.1149(9)	0.708(1)	6.6(4)
C(73)	0.954(1)	0.069(1)	0.775(2)	7.7(5)
C(74)	1.008(1)	0.099(1)	0.863(2)	7.6(5)
C(75)	1.060(1)	0.171(1)	0.900(2)	7.7(5)
C(76)	1.054(1)	0.2164(9)	0.837(1)	6.0(4)
C(81)	1.0634(7)	0.2084(6)	0.582(1)	3.2(2)
C(82)	1.0328(8)	0.1821(7)	0.480(1)	4.0(3)
C(83)	1.089(1)	0.1554(9)	0.413(1)	5.9(4)
C(84)	1.1754(9)	0.1558(9)	0.457(1)	4.9(3)
C(85)	1.2055(9)	0.1811(8)	0.560(1)	4.9(3)
C(86)	1.1503(8)	0.2083(7)	0.623(1)	4.3(3)
C(91)	0.6999(8)	0.3221(7)	0.296(1)	4.0(3)
C(92)	0.661(1)	0.3010(9)	0.195(1)	6.3(4)
C(93)	0.626(1)	0.361(1)	0.162(2)	7.7(5)
C(94)	0.633(1)	0.435(1)	0.230(1)	7.0(4)
C(95)	0.672(1)	0.4584(9)	0.328(1)	6.3(4)
C(96)	0.707(1)	0.3994(9)	0.361(1)	6.0(4)
C(101)	0.7819(8)	0.1780(7)	0.247(1)	3.9(3)
C(102)	0.7367(9)	0.1076(8)	0.169(1)	5.6(4)
C(103)	0.781(1)	0.058(1)	0.101(1)	7.0(4)
C(104)	0.863(1)	0.080(1)	0.109(1)	7.1(4)
C(105)	0.909(1)	0.1480(9)	0.181(1)	6.8(4)
C(106)	0.8688(9)	0.1968(8)	0.252(1)	5.4(4)
C(111)	0.7009(7)	0.0560(7)	0.373(1)	3.6(3)
C(112)	0.7893(9)	0.0601(8)	0.404(1)	5.1(3)
C(113)	0.829(1)	-0.0061(1)	0.347(1)	7.0(4)
C(114)	0.779(1)	-0.069(1)	0.269(1)	7.2(5)
C(115)	0.694(1)	-0.0741(9)	0.242(1)	6.5(4)
C(116)	0.6520(9)	-0.0108(8)	0.293(1)	5.0(3)
C(121)	0.5474(7)	0.1111(6)	0.450(1)	3.2(2)
C(122)	0.5409(8)	0.1106(7)	0.543(1)	3.8(3)
C(123)	0.4605(8)	0.0920(8)	0.560(1)	4.6(3)
C(124)	0.3897(9)	0.0708(8)	0.479(1)	4.8(3)
C(125)	0.3921(9)	0.0687(8)	0.386(1)	5.3(3)
C(126)	0.4738(9)	0.0897(8)	0.368(1)	4.8(3)
Perchlorate anions				
Cl(1)	0.5986(3)	0.6917(3)	0.1805(4)	6.9(1)
O(1)	0.5775(7)	0.7586(6)	0.2638(9)	7.3(3)
O(2)	0.538(1)	0.627(1)	0.138(1)	15.7(6)
O(3)	0.673(1)	0.7104(9)	0.154(1)	12.0(5)
O(4)	0.646(1)	0.655(1)	0.241(2)	18.8(8)
Cl(2)	0.1838(3)	0.1335(3)	0.1602(4)	7.1(1)
O(5)	0.165(1)	0.208(1)	0.216(1)	15.4(6)
O(6)	0.109(1)	0.076(1)	0.126(1)	14.5(6)
O(7)	0.213(1)	0.140(1)	0.076(1)	15.2(6)
O(8)	0.245(2)	0.108(1)	0.209(2)	23.0(9)
Methanol solvent				
O(10)	0.430(2)	0.107(2)	0.118(2)	25.0(9)
C(10)	0.436(2)	0.164(2)	0.065(3)	20.0(9)

$^aB_{eq}$ is defined as $4/3[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + \ldots]$

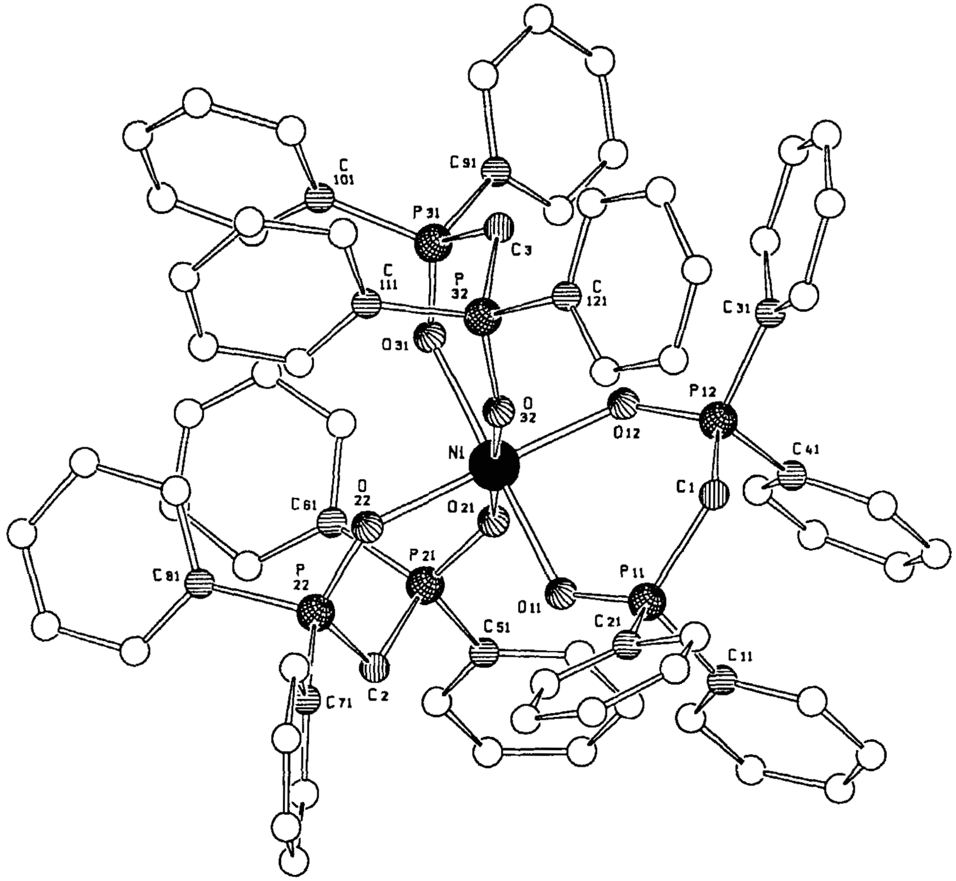

Figure 1 Perspective view of $[Ni(dppom)_3]^{2+}$ showing the atom numbering scheme.

$(Me_2PhPO)]$[30] and of $[ReOCl_3(Ph_3P)_2]$ with Me_3SiNCS to form $[Re(NCS)_4 (Ph_3P)(Ph_3PO)]$.[31]

The geometry around the metal ion is *pseudo*-octahedral, similar to that typically found in *tris*-chelate metal complexes with bidentate ligands such as ethylenediamine, oxalate, acetylacetonate, *etc.* The peculiar helicoidal configuration of complexes of this type necessarily confers chiral properties. The important difference in this case is that the three six-membered chelate rings are not flat and have different conformations. While ring **1** adopts a boat conformation, rings **2** and **3** have a conformation lying between chair and twist-boat,[32] although these two have opposite orientations. In Figure 2, the structure corresponding the Δ isomer is illustrated.

Table 3 provides a selection of bond lengths and angles for the Ni(II) coordination polyhedron. All angles are close to ideal, the larger deviations being those for O(11)-Ni-O(22) and O(22)-Ni-O(31), 88.0(4)° and 92.7(4)°, respectively. However, tetragonal distortion can be deduced from an analysis of Ni-O distances. Thus, the values in the range 2.059(8)-2.089(7) Å found for four of the distances are similar

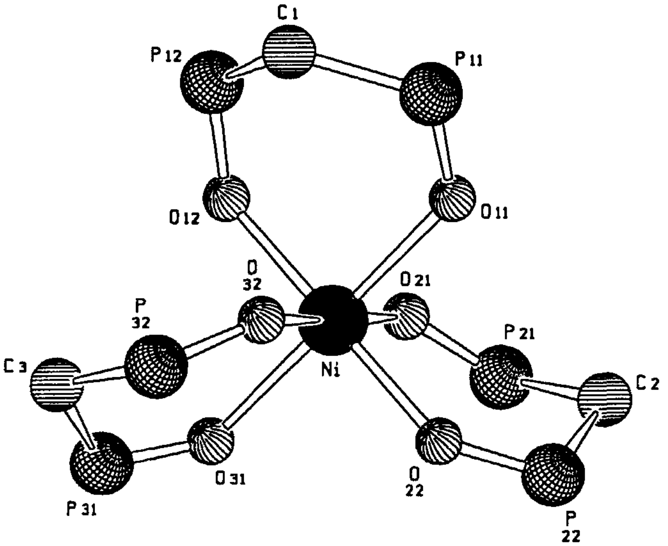

Figure 2 Coordination sphere arrangement of the △ ion in the unit cell.

those found for other nickel-oxygen bonds for which the mean value is 2.05 Å.[33] However, the other two distances, Ni-O(11) and Ni-O(31), are well above the mean value. In $[Cu(dppom)_3]^{2+}$, the other known structure of the tris-chelate with a transition metal,[22] each dppom ligand is coordinated to the copper giving a short Cu-O distance close to the above mean value and a long distance, which is between 0.10 and 0.25 Å above the mean value.

Structural data indicate that each of the three dppom molecules surrounding each phosphorus (Table 4) have similar bond distances and angles to those of dppom [18] and abovementioned complexes.[15a,19–23] However, there are remarkable differences in some of the P-O distances, undoubtedly related to distortions described above. Thus, while in molecule **2** the P-O distances, 1.498(7) Å and 1.493(8) Å, coincide with those normally found for phosphine oxides,[32] in the other two molecules one

Table 3 Coordination bond distances (Å) and angles (°) for $[Ni(dppom)_3](ClO_4)_2 \cdot MeOH$

Distances			
Ni-O(11)	2.194(9)	Ni-O(12)	2.063(8)
Ni-O(21)	2.089(7)	Ni-O(22)	2.059(8)
Ni-O(31)	2.181(9)	Ni-O(32)	2.087(7)
Angles			
O(11)-Ni-O(12)	91.1(4)	O(11)-Ni-O(21)	89.7(4)
O(11)-Ni-O(22)	88.0(4)	O(11)-Ni-O(31)	178.9(3)
O(11)-Ni-O(32)	88.9(3)	O(12)-Ni-O(21)	89.8(3)
O(12)-Ni-O(22)	178.9(4)	O(12)-Ni-O(31)	88.2(4)
O(12)-Ni-O(32)	89.6(3)	O(21)-Ni-O(22)	90.8(3)
O(21)-Ni-O(31)	91.2(4)	O(21)-Ni-O(32)	178.5(5)
O(22)-Ni-O(31)	92.7(4)	O(22)-Ni-O(32)	89.8(3)
O(31)-Ni-O(32)	90.2(3)		

Table 4 Selected bond distances Å and angles (°) for $CH_2(OPPh_2)_2$ ligands.

Molecule I			
P(11)-O(11)	1.439(9)	P(12)-O(12)	1.489(7)
P(11)-C(1)	1.806(12)	P(12)-C(31)	1.814(15)
P(11)-C(11)	1.784(12)	P(12)-C(31)	1.792(10)
P(11)-C(21)	1.801(17)	P(12)-C(41)	1.793(17)
O(11)-P(11)-C(1)	115.8(7)	O(12)-P(12)-C(1)	112.3(6)
O(11)-P(11)-C(11)	109.1(5)	O(12)-P(12)-C(31)	110.7(6)
O(11)-P(11)-C(21)	116.6(6)	O(12)-P(12)-C(41)	110.1(5)
O(1)-P(11)-C(11)	106.2(6)	C(1)-P(12)-C(31)	105.2(6)
C(1)-P(11)-C(21)	105.4(7)	C(1)-P(12)-C(41)	108.5(7)
P(11)-C(1)-P(12)	114.2(7)	C(31)-P(12)-C(41)	109.8(5)
Molecule II			
P(21)-O(21)	1.498(7)	P(22)-O(22)	1.493(8)
P(21)-C(2)	1.814(15)	P(22)-C(2)	1.822(10)
P(21)-C(51)	1.792(10)	P(22)-C(71)	1.785(18)
P(21)-C(61)	1.793(17)	P(22)-C(81)	1.782(14)
O(21)-P(21)-C(2)	110.9(6)	O(22)-P(22)-C(2)	111.3(5)
O(21)-P(21)-C(51)	110.0(5)	O(22)-P(22)-C(71)	112.8(6)
O(21)-P(21)-C(61)	112.4(7)	O(22)-P(22)-C(81)	110.4(69)
C(2)-P(21)-C(51)	106.3(6)	C(2)-P(22)-C(71)	106.2(7)
C(2)-P(21)-C(61)	107.9(7)	C(2)-P(22)-C(81)	109.1(6)
C(51)-P(21)-C(61)	109.1(6)	C(871)-P(22)-C(81)	106.9(7)
Molecule III			
P(31)-O(31)	1.417(8)	P(32)-O(32)	1.500(9)
P(31)-C(3)	1.820(14)	P(32)-C(3)	1.786(17)
P(31)-C(91)	1.800(16)	P(32)-C(111)	1.779(12)
P(31)-C(101)	1.773(14)	P(32)-C(121)	1.819(13)
O(31)-P(31)-C(3)	113.8(7)	O(32)-P(32)-C(3)	111.5(5)
O(31)-P(31)-C(91)	104.2(6)	O(32)-P(32)-C(111)	112.2(5)
O(31)-P(31)-C(101)	109.7(6)	O(32)-P(32)-C(121)	108.8(6)
C(3)-P(31)-C(91)	104.2(6)	C(3)-P(32)-C(111)	106.6(7)
C(91)-P(31)-C(101)	111.0(6)	C(3)-P(32)-C(121)	107.4(6)
C(91)-P(31)-C(101)	108.1(8)	C(111-P(32)-C(121)	110.2(5)
P(31)-C(3)-P(32)	115.4(7)		

of the distances is normal [P(12)-O(12) = 1.498(7) Å, P(32)-O(32) = 1.500(8) Å] and the other is considerably shorter [P(11)-O(11) = 1.439(9) Å, P(31)-O(31) = 1.417(8) Å], the atoms O(11) and O(31) occupying the axial positions in the nickel(II) coordination gemometry. The disparity between the Ni-O and P-O distances could perhaps be explained by a high level of atom disorder. However, this is not the case here, as of all oxigen atoms, O(11) and O(31), have the lowest equivalent isotropic temperature factors, thus indicating that they are fixed in the structure. At this stage, the question is whether distortion is governed by a steric interactions with Ni(II) or by the π nature of the P-O bonds.

SUPPLEMENTARY MATERIAL

Further information on the structure solution as well as full list of atomic positions, anisotropic displacement factors, interatomic bond lengths and angles and observed and calculated structure factors are available from A.C. upon request.

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