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Spectroscopic and Structural Investigation of Nickel(II) and Nickel(III) Compounds Stabilized by Identical P,O Ligands

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Introduction

The chemistry of low-valent Ni(0,I,II) compounds with tertiary phosphine ligands is quite rich owing to their importance in the field of homogeneous catalysis.[1] In contrast, Ni(III) compounds with phosphine ligands are less common, presumably due to the general lack of compatibility of soft ligands with higher oxidation state 3d metals. A considerable body of research involving Ni(III) coordination chemistry centers around the biological importance of such compounds with sulfur and sulfur/nitrogen ligands as models for the active sites of Ni enzymes.[2] Ligands with dual hard/soft properties such as P,O ligands with the ability to stabilize metals in a variety of oxidation states also form interesting compounds with Ni(III).

In spite of the wealth of literature regarding the structures and spectroscopic properties of related Ni(II)/Ni(III) compounds, the isolation and structural determination of pairs of Ni(II) and Ni(III) compounds possessing an *identical* ligand set is relatively rare. Notable exceptions are Ni compounds that contain rigid (N, O) or (N, S) ligand sets.[3-7] Structural details of these pairs offer insight into the role of ligand environment and d electron count in dictating the chemistry at the Ni center. Herein we report the syntheses, structures, and properties of $\mathrm{Ni^{II}}$(TMPP-*O*)$_2$ (**1**) and its oxidation product [$\mathrm{Ni^{III}}$(TMPP-*O*)$_2$][BF_4] (**2**) where TMPP-*O* is the monodemethylated form of tris(2,4,6-trimethoxyphenyl)phosphine (TMPP). The choice of the TMPP ligand is based on the presence of six *o*-methoxy groups that increase the ligand cone angle and offer additional binding sites for the metal, both of which aid in the kinetic stability of the products. Ether functionalized ligands are of special interest because weak metal–ether interactions have been correlated with increased reactivity at the metal center,[8,9] for example in the selectivity enhancement in the Ni(II)-catalyzed oligomerization of ethene.[1]

Table 1. Summary of Crystallographic Data for **1**·2$(CH_3)_2CO$ and **2**·2$(CH_3)_2CO$

	1·2$(CH_3)_2CO$	**2**·2$(CH_3)_2CO$
formula	$NiP_2O_{20}C_{58}H_{72}$	$NiP_2O_{20}C_{58}H_{72}BF_4$
fw	1209.84	1296.65
space group	$P\bar{1}$	$P\bar{1}$
a, Å	12.218(4)	12.448(4)
b, Å	12.829(3)	14.554(6)
c, Å	11.940(4)	18.470(6)
α, deg	114.84(2)	73.33(3)
β, deg	114.85(2)	82.21(3)
γ, deg	93.71(3)	71.16(3)
V, Å³	1473(1)	3031(4)
Z	1	2
d_{calc}, g/cm³	1.363	1.421
μ, cm⁻¹	4.54	4.55
temp, °C	−90 ± 1	−85 ± 1
R^a	0.062	0.069
$R_w{}^b$	0.108	0.068

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$.

Table 2. Atomic Positional Parameters and Equivalent Isotropic Displacement Parameters (Å²) and their Estimated Standard Deviations for Ni(TMPP-*O*)$_2$·2$(CH_3)_2CO$

atom	*x*	*y*	*z*	*B*(eq)^a
Ni(1)	0	1/2	1/2	1.96(5)
P(1)	0.1692(2)	0.6601(2)	0.6289(2)	1.96(7)
O(1)	0.1001(7)	0.8962(5)	0.6678(6)	3.8(2)
O(2)	0.175(1)	1.0540(6)	1.1359(8)	6.5(3)
O(3)	0.2484(6)	0.6748(5)	0.9024(6)	2.8(2)
O(4)	0.2039(6)	0.4493(5)	0.4616(6)	3.9(2)
O(5)	0.6464(7)	0.5209(7)	0.7642(8)	5.1(3)
O(6)	0.4398(5)	0.8124(5)	0.8885(6)	2.7(2)
O(7)	0.3329(6)	0.8534(5)	0.6272(6)	3.3(2)
O(8)	0.0554(6)	0.7534(6)	0.1538(6)	3.9(2)
O(9)	−0.0467(6)	0.5348(5)	0.3533(6)	2.7(2)
C(1)	0.1762(7)	0.7847(7)	0.7853(8)	1.9(2)
C(2)	0.1391(8)	0.8874(7)	0.7877(8)	2.2(3)
C(3)	0.1399(9)	0.9736(8)	0.904(1)	3.0(3)
C(4)	0.176(1)	0.9608(8)	1.023(1)	3.3(3)
C(5)	0.2124(8)	0.8619(8)	1.0272(9)	2.8(3)
C(6)	0.2125(8)	0.7741(7)	0.9051(9)	2.2(3)
C(7)	0.106(1)	1.0093(9)	0.679(1)	4.0(4)
C(8)	0.201(2)	1.040(1)	1.256(1)	8.0(7)
C(9)	0.278(1)	0.657(1)	1.021(1)	4.1(4)
C(10)	0.3215(8)	0.6280(7)	0.6780(8)	1.9(3)
C(11)	0.3184(9)	0.5160(8)	0.5811(9)	2.7(3)
C(12)	0.424(1)	0.4755(8)	0.602(1)	3.2(3)
C(13)	0.536(1)	0.5496(9)	0.726(1)	3.3(3)
C(14)	0.5443(9)	0.6645(8)	0.824(1)	3.4(3)
C(15)	0.4372(8)	0.7017(8)	0.7996(9)	2.5(3)
C(16)	0.190(1)	0.342(1)	0.348(1)	5.1(4)
C(17)	0.646(1)	0.404(1)	0.672(1)	5.2(4)
C(18)	0.551(1)	0.8820(9)	1.023(1)	4.2(3)
C(19)	0.1436(8)	0.6986(7)	0.4925(8)	2.1(3)
C(20)	0.2258(8)	0.7880(7)	0.4995(9)	2.3(3)
C(21)	0.1920(9)	0.8050(8)	0.386(1)	2.8(3)
C(22)	0.0776(9)	0.7290(8)	0.2594(9)	2.8(3)
C(23)	0.0009(9)	0.6383(8)	0.2466(8)	2.7(3)
C(24)	0.0319(8)	0.6213(7)	0.3649(8)	2.0(3)
C(25)	0.428(1)	0.930(1)	0.635(1)	4.8(4)
C(26)	−0.054(1)	0.686(1)	0.023(1)	5.7(4)

[a] The equivalent isotropic temperature factor [Fischer and Tillmans *Acta Crystallogr.* **1988**, *C44*, 775–776] is defined as follows: $B(eq) = 8\pi^2/3\ (\sum_{i=1}^{3}\sum_{j=1}^{3} U_{ij}a_i^*\ a_j^*\ \vec{a}_i\cdot\vec{a}_j)$.

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Table 3. Atomic Positional Parameters and Equivalent Isotropic Displacement Parameters (Å^2) and Their Estimated Standard Deviations for $[Ni(TMPP\text{-}O)_2][BF_4]\cdot 2(CH_3)_2CO$

atom	*x*	*y*	*z*	*B*(eq)[a]
Ni(1)	0.3762(1)	0.13449(8)	0.85516(6)	1.53(8)
P(1)	0.4031(2)	0.0866(2)	0.7485(1)	1.6(2)
P(2)	0.3626(2)	0.2968(2)	0.8108(1)	1.6(2)
O(1)	0.1975(5)	0.1538(5)	0.8418(3)	2.6(5)
O(2)	–0.0728(5)	0.1472(5)	0.6810(3)	2.9(5)
O(3)	0.3246(5)	0.0381(4)	0.6259(3)	2.4(5)
O(4)	0.3903(5)	–0.0044(4)	0.9024(3)	2.0(4)
O(5)	0.5653(5)	–0.3474(4)	0.9013(3)	2.2(4)
O(6)	0.5496(4)	–0.0886(4)	0.6744(3)	2.0(4)
O(7)	0.3148(4)	0.2436(4)	0.6041(3)	2.0(4)
O(8)	0.6812(5)	0.2154(4)	0.4733(3)	2.7(5)
O(9)	0.6476(5)	0.0430(4)	0.7301(3)	2.1(4)
O(10)	0.5525(5)	0.1212(5)	0.8717(3)	2.4(5)
O(11)	0.8010(5)	0.2876(5)	0.9108(4)	3.4(5)
O(12)	0.4440(5)	0.4701(4)	0.7918(3)	2.7(5)
O(13)	0.1965(5)	0.5106(4)	0.8215(3)	2.9(5)
O(14)	0.1251(5)	0.4068(5)	1.0867(3)	3.2(5)
O(15)	0.3373(4)	0.1680(4)	0.9505(3)	1.8(4)
O(16)	0.5123(5)	0.3582(4)	0.6727(3)	2.3(4)
O(17)	0.2180(5)	0.5709(5)	0.5107(3)	3.4(5)
O(18)	0.1367(5)	0.3705(4)	0.7578(3)	2.3(5)
C(1)	0.2596(7)	0.1033(6)	0.7295(4)	1.9(7)
C(2)	0.1692(7)	0.1386(6)	0.7787(4)	1.8(6)
C(3)	0.0572(7)	0.1544(6)	0.7646(5)	2.2(7)
C(4)	0.0334(7)	0.1333(6)	0.7007(5)	2.1(7)
C(5)	0.1219(7)	0.0927(6)	0.6521(5)	2.2(7)
C(6)	0.2315(7)	0.0801(6)	0.6669(5)	1.7(6)
C(7)	0.4655(6)	–0.0456(6)	0.7862(4)	1.5(6)
C(8)	0.4419(7)	–0.0740(6)	0.8646(4)	1.6(6)
C(9)	0.4717(7)	–0.1754(6)	0.9048(4)	1.6(6)
C(10)	0.5276(7)	–0.2468(6)	0.8671(4)	1.5(6)
C(11)	0.5547(6)	–0.2219(6)	0.7888(4)	1.6(6)
C(12)	0.5241(7)	–0.1222(6)	0.7496(4)	1.7(6)
C(13)	0.4809(7)	0.1370(6)	0.6657(4)	1.3(6)
C(14)	0.4292(7)	0.2058(6)	0.5998(4)	1.7(7)
C(15)	0.4924(8)	0.2330(6)	0.5334(4)	2.1(7)
C(16)	0.6093(7)	0.1935(6)	0.5342(5)	2.1(7)
C(17)	0.6634(7)	0.1287(6)	0.5981(5)	2.1(7)
C(18)	0.6003(7)	0.1025(6)	0.6629(4)	1.8(7)
C(19)	0.5001(7)	0.2974(7)	0.8312(4)	1.9(7)
C(20)	0.5799(7)	0.2061(6)	0.8657(4)	1.8(6)
C(21)	0.6799(7)	0.2047(6)	0.8937(5)	2.1(7)
C(22)	0.7003(7)	0.2950(7)	0.8834(4)	2.0(7)
C(23)	0.6262(7)	0.3858(6)	0.8489(5)	2.2(7)
C(24)	0.5251(7)	0.3848(7)	0.8242(4)	2.1(7)
C(25)	0.2704(7)	0.3398(6)	0.8853(4)	1.8(6)
C(26)	0.2067(7)	0.4384(6)	0.8894(5)	2.1(7)
C(27)	0.1598(7)	0.4586(6)	0.9558(5)	2.2(7)
C(28)	0.1745(7)	0.3792(7)	1.0218(5)	2.3(7)
C(29)	0.2336(7)	0.2824(6)	1.0210(4)	1.9(7)
C(30)	0.2824(6)	0.2607(6)	0.9524(4)	1.6(6)
C(31)	0.3223(6)	0.3719(6)	0.7179(4)	1.4(6)
C(32)	0.3988(7)	0.3995(6)	0.6597(5)	2.1(7)
C(33)	0.3624(7)	0.4675(6)	0.5907(5)	2.0(7)
C(34)	0.2457(8)	0.5046(6)	0.5802(4)	2.1(7)
C(35)	0.1669(7)	0.4739(6)	0.6347(4)	1.8(6)
C(36)	0.2072(7)	0.4076(6)	0.7020(4)	1.7(6)
C(37)	0.1167(8)	0.1587(8)	0.9036(5)	4(1)
C(38)	–0.1664(8)	0.1877(7)	0.7287(5)	3.1(8)
C(39)	0.3090(8)	–0.0078(7)	0.5702(5)	3.2(8)
C(40)	0.5377(7)	–0.3788(6)	0.9807(5)	2.4(7)
C(41)	0.6168(8)	–0.1631(7)	0.6355(5)	3.3(8)
C(42)	0.2538(8)	0.2895(7)	0.5355(5)	2.7(7)
C(43)	0.6319(8)	0.2852(7)	0.4053(5)	3.4(8)
C(44)	0.7562(8)	–0.0279(7)	0.7259(5)	3.3(8)
C(45)	0.6265(8)	0.0243(6)	0.9145(5)	2.8(7)
C(46)	0.8158(8)	0.3801(8)	0.9171(6)	4(1)
C(47)	0.4619(8)	0.5648(6)	0.7820(5)	3.0(8)
C(48)	0.1578(8)	0.6128(7)	0.8253(6)	3.8(8)
C(49)	0.1479(7)	0.3337(7)	1.1566(5)	3.2(8)
C(50)	0.5929(7)	0.3949(7)	0.6195(5)	2.8(7)
C(51)	0.1030(8)	0.6034(8)	0.4891(5)	4.1(9)
C(52)	0.0185(8)	0.4125(9)	0.7499(6)	5(1)

[a] The equivalent isotropic temperature factor [Fischer and Tillmanns *Acta Crystallogr.* **1988**, *C44*, 775–776] is defined as follows: $B(\mathrm{eq}) = 8\pi^2/3\,(\sum_{i=1}^{3}\sum_{j=1}^{3} U_{ij}\, a_i^*\, a_j^*\, \vec{a}_i\cdot\vec{a}_j)$.

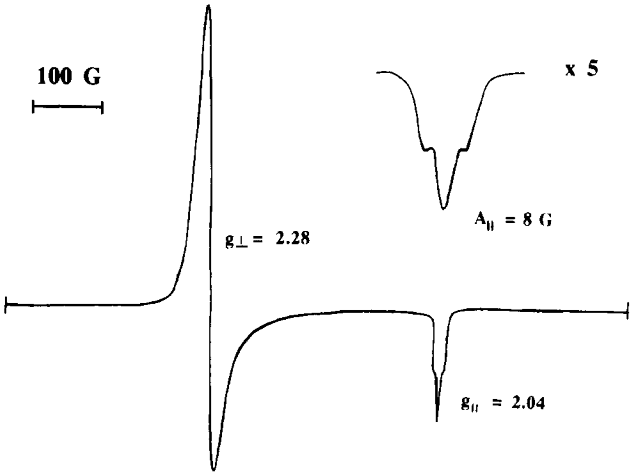

Figure 1. EPR spectrum of **2** at 98 K in $MeTHF/CH_2Cl_2$ (2:1).

Table 4. Selected Bond Distances (Å) and Bond Angles (deg) for $\mathbf{1}\cdot 2(CH_3)_2CO$

Bond Distances			
Ni(1)–P(1)	2.232(3)	P(1)–C(1)	1.841(8)
Ni(1)–O(9)	1.856(5)	P(1)–C(10)	1.834(8)
P(1)–C(19)	1.807(8)		
Bond Angles			
P(1)–Ni(1)–O(9)	87.6(2)	Ni(1)–P(1)–C(1)	115.8(3)
P(1)–Ni(1)–O(9′)	92.4(2)	Ni(1)–P(1)–C(10)	115.4(3)
Ni(1)–P(1)–C(19)	97.7(3)		

Table 5. Selected Bond Distances (Å) and Bond Angles (deg) for $\mathbf{2}\cdot(CH_3)_2CO$

Bond Distances			
Ni(1)–P(1)	2.222(3)	Ni(1)–O(4)	1.918(5)
Ni(1)–P(2)	2.224(3)	Ni(1)–O(10)	2.196(6)
Ni(1)–O(1)	2.189(1)	Ni(1)–O(15)	1.918(5)
Bond Angles			
P(1)–Ni(1)–P(2)	101.2(1)	P(2)–Ni(1)–O(15)	83.5(2)
P(1)–Ni(1)–O(4)	83.9(2)	P(2)–Ni(1)–O(4)	174.7(2)
P(1)–Ni(1)–O(15)	172.5(2)	O(1)–Ni(1)–O(10)	177.0(2)
O(4)–Ni(1)–O(15)	91.6(2)		

Experimental Section

Preparation of $Ni^{II}(TMPP\text{-}O)_2$ (1). A mixture of $[Ni(NCCH_3)_6][BF_4]_2$[10] and TMPP in a molar ratio of 1:4 in THF was stirred under argon for 12 h at room temperature and filtered to remove a white solid identified as $[CH_3\text{-}TMPP][BF_4]$. Recrystallization of the filtrate residue from THF and diethyl ether gave the orange-brown compound $Ni^{II}(TMPP\text{-}O)_2$ (**1**) in 51% yield. ^1H NMR data for **1** (δ, acetone-d_6, –80 °C): –OMe, 2.98 (s, 6H), 3.24 (s, 6H), 3.29 (s, 6H), 3.40 (s, 6H), 3.49 (s, 6H), 3.68 (s, 6H), 3.73 (s, 6H), 4.10 (s, 6H); meta-H, 5.21 (br, s, 2H), 5.27 (br, s, 2H), 5.47 (br, s, 2H), 5.78 (br, s, 2H), 5.87 (br, s, 2H), 6.33 (br, s, 2H). Anal. Calcd for **1**, $NiP_2O_{18}C_{52}H_{60}$: C, 57.11; H, 5.53. Found: C, 56.92; H, 5.68. Cyclic voltammetry: $(E_{1/2})_{ox} = -0.07$ V *vs* Ag/AgCl.

Preparation of $[Ni^{III}(TMPP\text{-}O)_2][BF_4]$ (2). $Ni^{II}(TMPP\text{-}O)_2$ was treated with 1 equiv of $[Cp_2Fe][BF_4]$ in acetone at room temperature for 1 h, after which time the solvent was removed under vacuum. The crude product was washed with diethyl ether to remove Cp_2Fe. The dark green compound $[Ni^{III}(TMPP\text{-}O)_2][BF_4]$ (**2**) was obtained in 71% yield. Anal. Calcd for **2**, $NiP_2O_{18}C_{52}H_{60}BF_4$: C, 52.91; H, 5.12. Found, C, 52.54; H, 5.20.

X-ray Crystallography. Single crystals of compounds **1** and **2** were obtained as acetone solvates from acetone solutions of the compounds that had been carefully layered with hexanes. Geometric and intensity data were collected on a Rigaku AFC6S diffractometer for **1** and a Nicolet P3/F upgraded to a Siemens P3/V for **2**; both are equipped with graphite-monochromated Mo Kα (λ_α = 0.710 69 Å) radiation. Data were corrected

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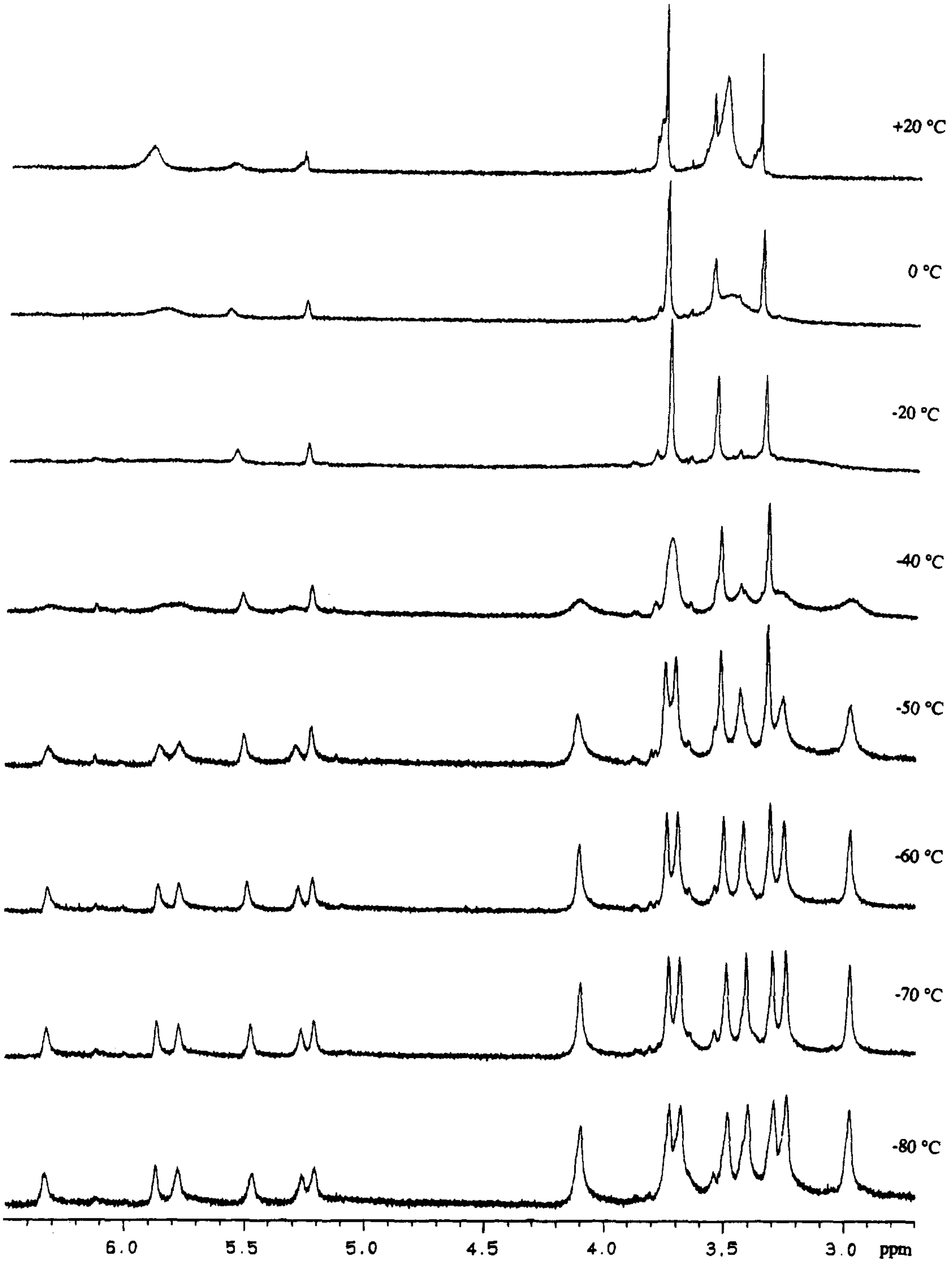

Figure 2. Variable temperature ^{1}H NMR spectra of **1** in acetone-d_6.

for Lorentz and polarization effects. Calculations were performed on a VAXSTATION 4000 computer using programs from the TEXSAN Crystallographic Package of the Molecular Structure Corp.[11] Crystal parameters and basic information pertaining to data collection and structure refinement are summarized in Table 1. Atomic positional parameters for **1**·2(CH$_3$)$_2$CO and **2**·2(CH$_3$)$_2$CO are listed in Tables 2 and 3 and selected bond distances and angles are listed in Tables 4 and 5.

A red-brown platelet of dimensions 0.15 × 0.44 × 0.59 mm^3 of **1**, and a dark green block of dimensions 0.34 × 0.78 × 0.39 mm^3 of **2** were mounted at the tips of glass fibers with the use of epoxy cement at −90 ± 2 and −85 ± 2 °C, respectively. Unit cell parameters were determined by least-squares refinement of 24 reflections in the range $19 \leq 2\theta \leq 30°$ for **1** and 24 reflections in the range $15.4 \leq 2\theta \leq 24.4°$ for **2**. Intensity data were collected over the 2θ range 4–47° by the ω–2θ scan mode for both crystals. Both structures were solved by direct methods using MITHRIL,[12] with subsequent development in the DIRDIF[13] program. An empirical absorption correction was applied to both data sets by using the program DIFABS after all non-hydrogen atoms had refined isotropically to convergence.[14] For **1**, 4605 unique reflections were collected, 2875 of which with $F_o^2 \geq 3\sigma(F_o)^2$ were used for the final full-matrix refinement to give $R = 0.062$ and $R_w = 0.108$ for 367 parameters and a goodness-of-fit of 2.77. For **2**, 9006 unique reflections were collected, 5102 of which with $F_o^2 \geq 3\sigma(F_o)^2$ were used for the final full-matrix

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(11) TEXSAN-TEXRAY Structure Analysis Package, Molecular Structure Corp., 1985.

(12) MITHRIL: Integrated Direct Methods Computer Program, Gilmore. C. J. *J. Appl. Crystallogr.* **1984**, *17*, 42.

(13) DIRDIF: Direct Methods for Difference Structure, An Automatic Procedure for Phase Extension; Refinement of Difference Structure Factors: Beurskens, R. T. Technical Report, 1984.

(14) DIFABS: Walker, N., Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.

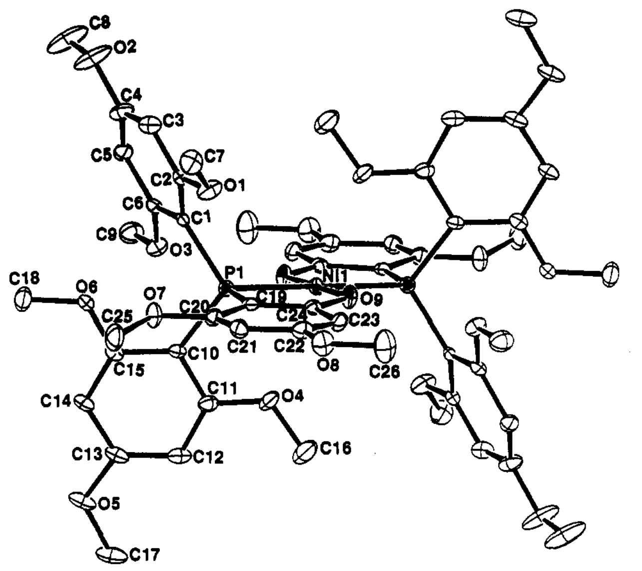

Figure 3. ORTEP drawing of the Ni(II) compound 1, Ni(TMPP-*O*)$_2$, with 25% probability ellipsoids.

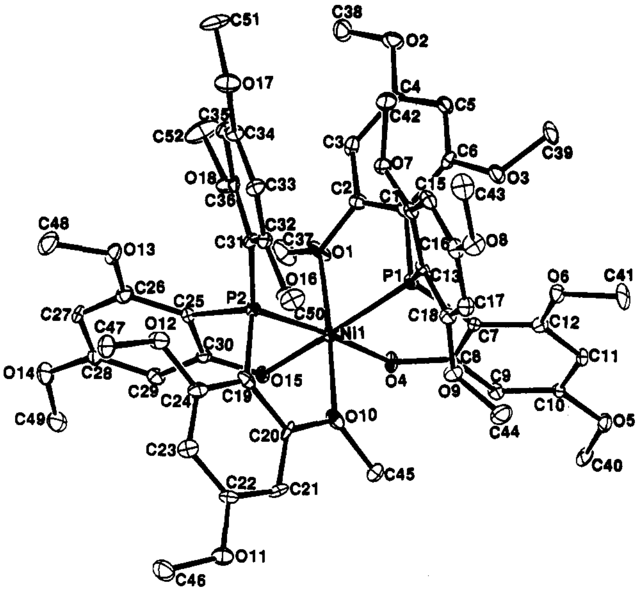

Figure 4. ORTEP drawing of the Ni(III) compound 2$^+$, [Ni(TMPP-*O*)$_2$]$^+$, with 25% probability ellipsoids.

refinement to give $R = 0.069$ and $R_w = 0.068$ for 735 parameters and a goodness-of-fit of 2.60.

Results and Discussion

Compound 1 was obtained from the reaction of [Ni(NCCH$_3$)$_6$][BF$_4$]$_2$ and 4 equiv of TMPP in ~50% yield. The low yield of 1 is due to the difficulty in separating it from the [CH$_3$-TMPP][BF$_4$] byproduct. The two extra equivalents of TMPP in this reaction act as nucleophiles that attack the electrophilic methyl groups of the coordinated ether–TMPP moieties, leading to a more stable phosphino–phenoxide product. If the reaction is carried out with only 2 equiv of TMPP under the same conditions, only [CH$_3$-TMPP][BF$_4$] and [H-TMPP][BF$_4$] are isolated in large quantities. Reactions involving chlorinated solvents or chloride-containing starting materials produced only salts analogous to [H-TMPP][MCl$_4$] or [H-TMPP]$_2$[M$_2$Cl$_6$] (M = Fe, Co).[15]

Of considerable interest in this work is the discovery that 1 exhibits a facile and reversible oxidation at –0.07 V, the location of which suggested to us that a stable Ni(III) analog should be accessible by chemical methods.[2d] Indeed, chemical oxidation with ferrocenium proceeds smoothly to give a high yield of the d^7 Ni(III) analogue 2. The EPR spectrum is typical of a d^7 system possessing a d$_{z^2}$ ground state with an axial elongation in an octahedral field,[7,16] with *g* values of $g_\perp = 2.28$ and $g_\parallel = 2.04$ and a hyperfine coupling to the phosphorus center ($I = {}^1/_2$) of $A_\parallel = 8$ G (Figure 1). These results are in accord with a participation of the axial ether group in a bonding interaction with the Ni(III) metal center.

A ^{1}H NMR spectrum of 1 at room temperature revealed broad resonances which suggested that a dynamic process was occurring in solution. Variable-temperature ^{1}H NMR of 1 from +20 to –80 °C in acetone-d_6 as shown in Figure 2 confirmed the fluxionality of the ligand. The spectrum at –80 °C contains eight distinct resonances between 2.9 and 4.2 ppm due to the inequivalent *o*- and *p*-methoxy groups and six resonances between 5.2 and 6.4 ppm attributed to the meta protons.

Single crystal X-ray crystallographic studies of [Ni(TMPP-*O*)$_2$]$^{0,+}$ as acetone solvates were performed at low temperature. To our knowledge, these results represent the first example of a structurally characterized Ni(II)/Ni(III) pair supported by an ether–phosphine ligand. ORTEP drawings along with selected bond distances and bond angles for 1 and 2 are given in Figures 3 and 4, respectively. Compound 1 exhibits a square-planar geometry with the Ni(II) center residing on a crystallographic inversion center which relates two *trans* phosphorus and two phenoxide oxygen atoms. Axial interactions involving the nickel center and pendant methoxy groups are longer then the sum of the covalent radii of the two atoms (Ni(1)-O(4) = 2.78 Å). The P(1)–Ni(1)–O(9) and the P(1)–Ni(1)–O(9′) angles are 87.6(2) and 92.4(2)°, respectively, leading to a nearly perfect square planar geometry about the metal center. Compound 2 exhibits a distorted octahedral geometry, with two mutually *cis* phosphorus and two phenoxide oxygen atoms in the equatorial plane and two methoxy oxygen atoms in axial positions. The average Ni–P bond distance in 2 is ~0.01 Å shorter than that in 1. The average Ni–O(phenoxide) bond distance in 2 is 1.918[5] Å, whereas the average Ni–O(ether methoxy) axial interaction is 2.193[6] Å. The axial elongation is consistent with the results of the EPR experiment and with the expected trend for metal–ether distances vs metal–phenoxide bonds. The reported range for Ni–O bonds in the octahedral Ni(II) compound [Ni(*o*-C$_6$H$_4$(OH)-CH=N—NHCSNH$_2$)$_2$]Cl$_2$ is 2.09–2.14 Å.[17] The angles P(2)–Ni(1)–O(15), P(1)–Ni(1)–O(4), O(4)–Ni(1)–O(15), and P(1)–Ni(1)–P(2) range from 83.5(2)° to 101.2(1)° in the distorted equatorial plane. The isomerization of the TMPP-*O* ligand from *trans* to *cis* upon going from the d^8 Ni(II) to the d^7 Ni(III) compound clearly reflects subtle electronic effects and not steric influences.

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Supplementary Material Available: Tables of crystallographic parameters, atomic positional and thermal parameters, bond distances and angles for 1·2(CH$_3$)$_2$CO and 2·2(CH$_3$)$_2$CO (39 pages). Ordering information is given on any current masthead page.

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