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Methylnickel Compounds with Chelating Anionic Ligands. Crystal and Molecular Structures of Methyl(trimethylphosphine)nickel Oxinate and Oxalate Dimer

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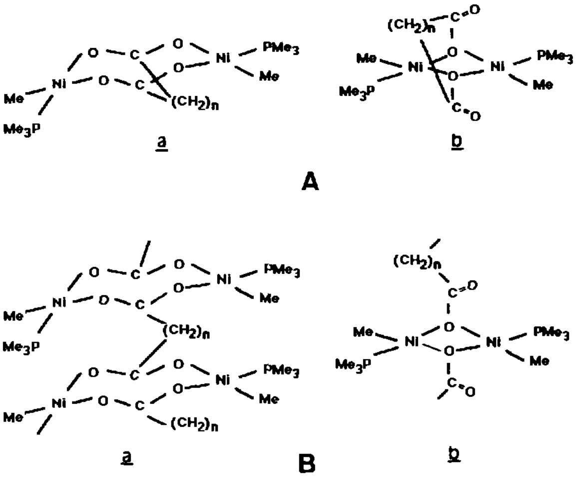
Abstract

Several new methyl–nickel(II) compounds NiMeX(PMe_3) [X = 8-hydroxyquinolate, **1**; X = 1/2[$O_2C(CH_2)_nCO_2$), **2**: $n = 0$; **3**: $n = 1$; **4**: $n = 2$; **5**: $n = 3$; **6**: $n = 4$] were prepared by reacting [$NiMe(PMe_3)(OMe)]_2$ and the corresponding acid. Compound **1** crystallizes in the space group $P\bar{1}$ with $a = 8.868(1)$, $b = 9.303(2)$, $c = 8.452(1)$ Å, $\alpha = 94.29(1)°$, $\beta = 105.85(1)°$, $\gamma = 82.63(1)°$, $V = 671.8(1)$ Å^3, $Z = 2$. Final discrepancy indices are $R = 0.0291$ and $R_w = 0.0303$ for 2255 independent data ($I > 3\sigma(I)$). The coordination geometry around nickel is square planar. The Ni–P and Ni–C distances of 2.125(1) and 1.917(2) Å are on the shortest range of the usually observed values, while the Ni–O and Ni–N values of 1.923(2) and 1.953(2) Å are on the upper one. The oxygen atom of the oxinate ligand is *trans* to the methyl group. Compound **2** crystallizes in the space group $P2_1/n$ with $a = 9.266(1)$, $b = 11.113(2)$, $c = 8.169(2)$ Å, $\beta = 93.46(2)°$, $V = 839.5$ Å^3, $Z = 4$. The final R values are $R = 0.0325$ and $R_w = 0.0334$ for 1221 independent data ($I > 3\sigma(I)$). The molecule shows two nickel atoms bridged by the oxalato group acting as a bidentate ligand to both metals (Ni–O1 = 1.990(3) and Ni–O2 = 1.961(3) Å). The dimer possesses a crystallographic center of symmetry, which is located in the middle of the oxalato C–C bond. The geometry about each metal is square planar, the coordination sphere being completed by the methyl and trimethylphosphine ligands. Compounds **3–6** have been characterized by IR spectroscopy, together with compounds **4a–6a** obtained by reaction with PMe_3 in excess.

Introduction

Methylnickel compounds with non-chelating ligands adopt a *trans*-square planar arrangement of donor centres providing easy pathways for ligand exchange. The 16 electron complexes Ni(Me)X($PMe_3)_2$, while thermally stable in an inert medium, undergo with additional quantities of trimethylphosphine a series of transformations depending on the anionic ligand X. Methylnickel halides [1] (X = Cl, Br, I) may add up to four of the small trimethylphosphines giving the methyltetrakis(trimethylphosphine)nickel cation [2] with an enhanced reactivity of the nickel to carbon σ bond [3, 4] whereas substitution of halide by bridge forming ligands such as NR_2, OR or F favours dimerization with concomitant loss of phosphine [5, 6].



Scheme 1.

It was thus of interest to study the reaction of chelating mono- and dianionic ligands such as $\overset{\frown}{N\,O}^-$ (diacetyldioxinate or 8-hydroxyquinolate) and $^-\overset{\frown}{O\,O}^-$ (dicarboxylates) on methylnickel complexes. A fascinating range of possible molecular structures can be envisaged for the dicarboxylate complexes (Scheme 1) and it is difficult to predict which one will be adopted [1].

We would like to report here the molecular and X-ray structures of the two new Ni–methyl com-

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plexes: NiCH$_3$X(PMe$_3$) (X = 8-hydroxyquinolate, **1**; X = oxalate, **2**), which have been obtained by replacing methoxide as bridging ligand in the methyl nickel alkoxide dimer. Extension of this reaction to the anions of dicarboxylic acids HOOC–(CH$_2$)$_n$–COOH has been studied and different species have been isolated following the value of *n*.

As a point of particular interest, the oxalate compound (*n* = 0) was observed by X-ray diffraction as a possible product of reductive dimerization of carbon dioxide.

Experimental

General Procedures and Materials

All air-sensitive and volatile material was handled by standard vacuum techniques and kept under nitrogen. Microanalyses were carried out by Malissa & Reuter, Microanalytical Laboratory, D-5250 Engelskirchen. Melting points (m.p.) and decomposition temperatures were obtained from sealed capillaries under nitrogen and are uncorrected.

Trimethylphosphine [25] was prepared from triphenylphosphite and methyl-magnesium chloride. Other chemicals (Merck-Schuchardt) were used as purchased.

Infrared spectra were recorded on a Perkin-Elmer, Type 397, spectrophotometer; ^{1}H NMR spectra were obtained on a Varian EM 360 (60 MHz) and Bruker WM 300 (300 MHz), where ^{13}C (75.5 MHz) and ^{31}P (121.5 MHz) NMR spectra were also recorded.

Preparations

Methyl(trimethylphosphine)nickel(8-hydroxyquinolate) (1)

850 mg [NiCH$_3$(OCH$_3$)(PMe$_3$)]$_2$ [5] (2.35 mmol) and 680 mg 8-hydroxyquinoline (4.7 mmol) in 50 ml ether are reacted at 20 °C for 2 h. The red solution is filtered through a sintered disc and cooled to −70 °C to give 1050 mg dark red crystals (80% yield), m.p. 102 °C, insoluble in pentane, soluble in ether (*ca.* 100 mg in 10 ml) and toluene (>250 mg in 10 ml).

Anal. Calc. for C$_{13}$H$_{18}$NNiOP (294.0): C, 53.11; H, 6.17; N, 4.76. Found: C, 53.09; H, 6.24; N, 4.81%.

^{1}H NMR (300 MHz, toluene-d$_8$, 213 K, Me$_4$Si external reference, δ0): δ(NiCH_3) −0.38 (d, 3H, 3J(PH) 5.8 Hz), d(PCH_3) 0.92 (d, 9H, 2J(PH) 10.0 Hz), δ(CH) 7.51 (m, br). ^{13}C{^{1}H} NMR (75.5 MHz, toluene-d$_8$, 213 K, Me$_4$Si external reference, δ0): δ(Ni*C*H$_3$) −13.1 (d, ^2J(PC) 38.4 Hz), δ(P*C*H$_3$) 12.57 (d, ^1J(PC) 28.5 Hz), δ(C$_{ar}$) 108.9–168.8 (9s). ^{31}P{^{1}H} NMR (121.5 MHz, toluene-d8, 293 K, H$_3$PO$_4$ external reference, δ0): δ(P) −5.59(s).

Bis[methyl(trimethylphosphine)nickel] oxalate (2)

1020 mg [NiCH$_3$(OCH$_3$)(PMe$_3$)]$_2$ (2.82 mmol) and 360 mg oxalic acid dihydrate (2.82 mmol) in 50 ml THF are reacted at 20 °C for 2 h. The volatiles are removed *in vacuo* and the residue is crystallized from 50 ml toluene (60 °C) to give 940 mg of dark brown needles, m.p. 112 °C (decomp.), insoluble in pentane or ether, slightly soluble in acetone or toluene (*ca.* 50 mg in 10 ml), soluble in THF (>500 mg in 10 ml). *Anal.* Calc. for C$_{10}$H$_{24}$Ni$_2$O$_4$P$_2$ (387.7): C, 30.98; H, 6.24. Found: C, 31.45; H, 6.29%. ^{1}H NMR (60 MHz, acetone-d$_6$, 308 K, Me$_4$Si external reference, δ0): δ(NiCH_3) −0.77 (s, 3H), δ(PCH_3) 1.29 (d, 9H, ^2J(PH) 10.4 Hz).

Precipitation of 3 with malonic acid and of 4 with succinic acid

770 mg [NiCH$_3$(OCH$_3$)(PMe$_3$)]$_2$ (2.13 mmol) in 50 ml THF are reacted with 222 mg of malonic acid (2.13 mmol) or 242 mg of succinic acid (2.13 mmol), respectively, at 20 °C for 1 h. The orange–brown precipitate is isolated by decantation, washed with two 10 ml portions of THF, and dried *in vacuo*. Yields are virtually quantitative. **3**: m.p. 100 °C (decomp.). *Anal.* Calc. for C$_{11}$H$_{26}$Ni$_2$O$_4$P$_2$ (401.7): C, 32.89; H, 6.52. Found: C, 33.17; H, 6.67%. **4**: m.p. 103 °C (decomp.). *Anal.* Calc. for C$_{12}$H$_{28}$Ni$_2$O$_4$P$_2$ (415.8): C, 34.67; H, 6.79. Found: C, 33.98; H, 7.01%.

Bis[methyl(trimethylphosphine)nickel] pentanedicarboxylate(1,5) (5)

250 mg [NiCH$_3$(OCH$_3$)(PMe$_3$)]$_2$ (0.69 mmol) and 90 mg glutaric acid (0.68 mmol) in 50 ml THF are reacted at 20 °C for 1 h. Addition of 50 ml pentane gives 250 mg of light brown precipitate (84%), m.p. 91 °C (decomp.), soluble in THF or toluene. *Anal.* Calc. for C$_{13}$H$_{30}$Ni$_2$O$_4$P$_2$ (429.8): C, 36.34; H, 7.04. Found: C, 35.20; H, 7.00%. ^{1}H NMR (300 MHz, benzene-d$_6$, 298 K, Me$_4$Si external reference, δ0): **5** *trans* (32%): δ(NiCH_3) −0.28 (d, 3H, ^3J(PH) 6.3 Hz), δ(PCH_3) 0.81 (d, 9H, ^2J(PH) 10.0 Hz), δ(CH_2) 2.28 (t, 4H, ^3J(HH) 7.0 Hz), δ(CH_2) 1.81 (quintet, 2H, ^3J(HH) 7.0 Hz); **5** *cis* (68%): δ(NiCH_3) −0.26 (d, 3H, ^3J(PH) 6.5 Hz), δ(PCH_3) 0.79 (d, 9H, ^2J(PH) 9.7 Hz), δ(CH_2) 1.90 (tt, 2H, ^3J(HH) 7.0 Hz, ^2J(HH) 7.5 Hz), δ(CH_2) 2.18 (tt, 2H, ^3J(HH) 7.0 Hz, ^2J(HH) 7.5), δ(CH_2) 2.36 (tt, 2H, ^3J(HH) 7.0, ^2J(HH) 7.5 Hz).

Bis[methyl(trimethylphosphine)nickel] hexanedicarboxylate(1,6) (6)

250 mg [NiCH$_3$(OCH$_3$)(PMe$_3$)]$_2$ (0.69 mmol) and 100 mg adipic acid (0.68 mmol) in 50 ml THF are reacted at 20 °C for 1 h. The solution is filtered through a sintered disc, concentrated to *ca.* 10 ml, and diluted with 50 ml pentane. The dark yellow solid is isolated by decantation, washed with pentane

TABLE I. Crystal Data and Details of Data Collection and Structure Refinement for $C_{13}H_{18}NiNOP$

Formula	$C_{13}H_{18}NiNOP$
Formula weight	293.95
Crystal system	triclinic
Space group	$P\bar{1}$
a (Å)	8.868(1)
b (Å)	9.303(2)
c (Å)	8.452(1)
α (°)	94.29(1)
β (°)	105.85(1)
γ (°)	82.63(1)
V (Å^3)	671.8(1)
Z	2
D_{calc} (g/cm^3)	1.45
μ (Mo Kα) (cm^{-1})	14.72
Temperature (°C)	20 ± 2
Scan method	$\theta/2\theta$
Data collection range (2θ) (°)	$1 < 2\theta < 27$
Take off angle (°)	5.0
No. reflections measured	2757
No. unique data with $(I) > 3\sigma(I)$	2255
No. parameters refined	226
R[a]	0.0291
R_w[b]	0.0303

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

and dried *in vacuo*. Yield: 300 mg (98%), m.p. 106 °C (decomp.). *Anal.* Calc. for $C_{14}H_{32}Ni_2O_4P_4$ (443.8): C, 37.89; H, 7.27. Found: C, 39.01; H, 7.01%. ^{1}H NMR (300 MHz, benzene-d$_6$, 298 K, Me$_4$Si external reference, δ0): δ(NiCH_3) -0.30 (d, 3H, ^3J(PH) 6.6 Hz), δ(PCH_3) 0.81 (d, 9H, ^2J(PH) 10.7 Hz), δ(CH_2) 1.56 (m, 4H), δ(CH_2) 2.13 (m, 4H).

Bis[methylbis(trimethylphosphine)nickel] dicarboxylates (4a), (5a), (6a)

300 mg portions of **4**, **5** or **6** respectively are dissolved in 50 ml THF containing 1 ml trimethylphosphine (excess). After 1 h at 20 °C the volatiles are removed and the yellow residue is carefully dried *in vacuo* for 20 min at 20 °C. Yields are virtually quantitative based on Ni but there is some loss of trimethylphosphine.

4a: (3.2 PMe$_3$) yellow crystals, m.p. 168 °C (decomp.). *Anal.* Calc. for $C_{15.6}H_{38.8}Ni_2O_4P_{3.2}$ (507.0): C, 36.95; H, 7.71. Found: C, 37.20; H, 7.49%. ^{1}H NMR (300 MHz, benzene-d$_6$, 298 K, Me$_4$Si external reference δ0): δ(NiCH_3) -0.76 (s, 6H), δ(PCH_3) 1.07 (m, 29H), δ(CH_2) 2.91 (m, 4H).

5a: (3.5 PMe$_3$) yellow crystals, m.p. 142 °C (decomp.). *Anal.* Calc. for $C_{17.5}H_{43.5}Ni_2O_4P_{3.5}$ (543.9): C, 38.65; H, 8.06. Found: C, 38.64; H, 8.23%. ^{1}H NMR (300 MHz, benzene-d$_6$, 298 K, Me$_4$Si external reference, δ0): δ(NiCH_3) -0.95 (s, 6H), δ(PCH_3) 0.95 (m, 32H), δ(CH_2) 2.21 (quintet, 2H, ^3J(HH) 7.0 Hz), δ(CH_2) 2.42 (t, 4H, ^3J(HH) 7.0 Hz).

TABLE II. Fractional Atomic Coordinates and Isotropic or Equivalent Temperature Factors (Å ×100) of **1**[a]

Atom	x/a	y/b	z/c	U_{eq}
Ni	0.30909(6)	0.82488(6)	0.11078(7)	3.78(3)
P(1)	0.1675(1)	0.9103(1)	0.2680(1)	4.12(6)
C(11)	0.1557(7)	1.1026(5)	0.3241(8)	6.3(3)
H(111)	0.102(6)	1.154(5)	0.233(6)	7(2)
H(112)	0.092(6)	1.118(5)	0.395(6)	8(2)
H(113)	0.258(7)	1.137(6)	0.364(6)	9(2)
C(12)	0.2295(8)	0.8230(7)	0.4617(7)	6.6(4)
H(121)	0.335(7)	0.839(6)	0.511(6)	9(2)
H(122)	0.171(6)	0.862(6)	0.525(6)	9(2)
H(123)	0.211(7)	0.724(7)	0.441(7)	11(2)
C(13)	−0.0380(6)	0.8808(7)	0.1927(7)	6.4(3)
H(131)	−0.092(5)	0.901(5)	0.270(6)	7(1)
H(132)	−0.085(7)	0.936(6)	0.104(7)	10(2)
H(133)	−0.046(7)	0.770(7)	0.169(7)	11(2)
N	0.4375(4)	0.7273(4)	−0.0270(4)	4.3(2)
O	0.1437(3)	0.7213(3)	−0.0257(3)	4.7(2)
C(1)	0.4759(6)	0.9262(6)	0.2463(7)	5.6(3)
H(1)C1	0.508(5)	0.990(5)	0.185(6)	7(2)
H(2)C1	0.564(6)	0.850(5)	0.287(6)	8(2)
H(3)C1	0.471(6)	0.974(6)	0.345(7)	9(2)
C(20)	0.1942(5)	0.6338(4)	−0.1334(5)	4.4(2)
C(21)	0.1045(6)	0.5397(5)	−0.2406(6)	5.7(3)
HC(21)	0.008(5)	0.532(5)	−0.234(5)	7(1)
C(22)	0.1695(7)	0.4489(5)	−0.3505(6)	6.1(3)
HC(22)	0.102(5)	0.388(4)	−0.425(5)	6(1)
C(23)	0.3216(7)	0.4491(5)	−0.3548(5)	6.3(3)
HC(23)	0.363(5)	0.383(5)	−0.434(5)	8(1)
C(24)	0.4187(5)	0.5411(4)	−0.2471(5)	5.0(3)
C(25)	0.5786(7)	0.5491(6)	−0.2340(7)	6.9(3)
HC(25)	0.626(6)	0.491(6)	−0.302(6)	9(2)
C(26)	0.6611(7)	0.6405(6)	−0.1242(7)	7.1(4)
HC(26)	0.765(5)	0.649(4)	−0.108(5)	5(1)
C(27)	0.5867(5)	0.7303(5)	−0.0217(6)	5.5(3)
HC(27)	0.648(5)	0.799(4)	0.057(5)	5(1)
C(28)	0.3531(5)	0.6340(4)	−0.1372(5)	4.0(2)

[a] e.s.d.s given in parentheses.

6a: (3 PMe$_3$) yellow crystals, m.p. 109 °C (decomp.). *Anal.* Calc. for $C_{17}H_{41}Ni_2O_4P_3$ (519.9): C, 39.27; H, 7.94. Found: C, 30.29; H, 7.82%. ^{1}H NMR (300 MHz, benzene-d$_6$, 298 K, Me$_4$Si external reference, δ0): δ(NiCH_3) -0.84 (s, 6H), δ(PCH_3) 0.99 (m, 27H), δ(CH_2) 1.60 (m, 4H), δ(CH_2) 2.22 (m, 4H).

X-ray Data Collection and Reduction: Complex 1

The selected crystal, which belongs to the triclinic system, was sealed in a Lindemann glass capillary and mounted on an Enraf-Nonius CAD 4 diffractometer. Matrix transformation and least-squares fit of settings angles of 25 reflections led to the cell constants given in Table I. Data reduction was performed [7]. Intensity standards showed a linear decrease of about 4%. Empirical absorption corrections were made [7]. All non-zero reflections (2255) were used in subsequent calculations.

TABLE III. Crystal Data and Details of Data Collection and Structure Refinement for $C_{10}H_{24}Ni_2O_4P_2$

Formula	$C_{10}H_{24}Ni_2O_4P_2$
Formula weight	387.69
Crystal system	monoclinic
Space group	$P2_1/n$
a (Å)	9.266(1)
b (Å)	11.113(2)
c (Å)	8.169(2)
β (°)	93.36(2)
V (Å^3)	839.5(2)
Z	4
D_{calc} (g/cm^3)	1.53
μ(Mo Kα) (cm^{-1})	23.34
Temperature (°C)	20 ± 2
Scan method	$\theta/2\theta$
Data collection range (2θ) (°)	$1 < 2\theta < 30$
Take off angle (°)	4.4
No. reflections measured	2700
No. unique data with $(I) > 3\sigma(I)$	1221
No. parameters refined	82
R^a	0.0325
R_w^b	0.0334

$^aR = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $^bR_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$.

Structure Solution and Refinement: Complex 1

The structure was solved by the heavy-atom method. The position of Ni atom was revealed from a Patterson map. Least-squares refinement was performed when all the non-hydrogen atoms were located. Hydrogen atoms were refined isotropically. All other atoms were refined anisotropically. The last refinement cycle led to $R = 0.029$ and $R_w = 0.030$. Final atomic coordinates are given in Table II.

X-ray Data Collection and Reduction: Complex 2

The selected crystal, which belongs to the monoclinic system, was sealed in a Lindemann glass capillary and mounted on an Enraf-Nonius CAD 4 diffractometer. Matrix transformation and least-squares fit of the settings angles of 25 reflections led to the cell constants given in Table III. Data reduction was performed [7]. Intensity standards showed a linear decrease of about 5%. Empirical absorption corrections were made. All non-zero reflections (1221) were used in subsequent calculations.

Structure Solution and Refinement: Complex 2

The structure was solved by the heavy-atom method. The position of Ni atom was revealed from a Patterson map. Least-squares refinement was performed when all the non-hydrogen atoms were located. Hydrogen atoms were calculated (C–H = 0.97 Å) and given an isotropic temperature factor, $U_H = 0.08$ Å^2, kept fixed. All other atoms were refined anisotropically. The last refinement cycle led to $R = 0.032$ and $R_w = 0.033$. Final atomic coordinates are given in Table IV.

TABLE IV. Fractional Atomic Coordinates of 2^a

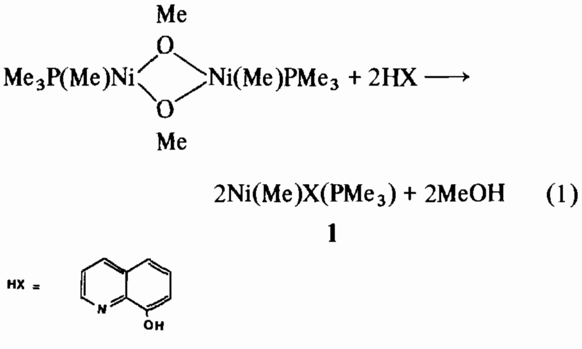
Atom	x/a	y/b	z/c
Ni(1)	0.25221(6)	0.09950(5)	0.03786(7)
P(1)	0.1276(1)	0.2311(1)	−0.0927(2)
C(11)	0.2186(7)	0.3742(5)	−0.0819(8)
C(12)	0.1069(6)	0.1979(5)	−0.3086(6)
C(13)	−0.0534(6)	0.2669(6)	−0.0413(7)
C(1)	0.1168(5)	0.0941(6)	0.2032(6)
O(1)	0.4040(3)	0.1020(3)	−0.1245(4)
C(2)	0.5074(5)	0.0349(4)	−0.0799(5)
O(2)	0.3797(3)	−0.0177(3)	0.1532(4)

^{a}e.s.d.s given in parentheses.

Results and Discussion

Syntheses

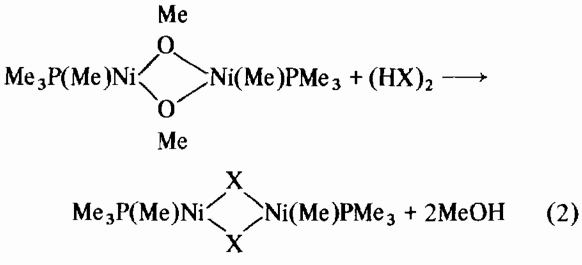
As a convenient high yield starting material, methyl(trimethylphosphine)nickel methoxide [5] reacts with two equivalents of acid according to eqns. (1) and (2) to form mononuclear, dinuclear or polymeric material depending on the anion.



$$[Me_3P(Me)Ni(\mu\text{-}OMe)_2Ni(Me)PMe_3] + 2HX \longrightarrow 2Ni(Me)X(PMe_3) + 2MeOH \quad (1)$$

1

HX =



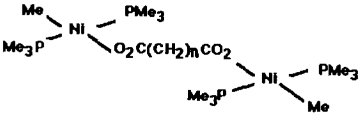
$$[Me_3P(Me)Ni(\mu\text{-}OMe)_2Ni(Me)PMe_3] + (HX)_2 \longrightarrow [Me_3P(Me)Ni(\mu\text{-}X)_2Ni(Me)PMe_3] + 2MeOH \quad (2)$$

$(HX)_2 = HOOC(CH_2)_nCOOH$

n	0	1	2	3	4
	2	**3**	**4**	**5**	**6**

Methylnickel complexes of lower molecular weight **1**, **5**, **6** are soluble in pentane or ether, while coordination polymers 3 and 4 require *ca.* 200 cm^3 THF for 10 mg. The oxalate 2 is readily dissolved in THF and moderately in toluene or acetone (*ca.* 50 mg in 10 cm^3). At first glance, large crystals may appear to be stable in air for hours, but under the microscope their surface looks altered and all compounds 1–6 are immediately decomposed upon dissolution under air.

In case of coordination polymers, 3 and 4, microcrystalline solids were obtained after careful washing and were characterized by elemental analyses and infrared spectra. By reaction with trimethylphosphine, these compounds could be degraded according to eqn. (3) to give dinuclear complexes **C** (Scheme 2) with bridging dicarboxylate ligands. Only 1 and 2 with their stable chelate rings failed to take up additional phosphine ligands.



C

Scheme 2.

Complexes 4–6 react with excess PMe$_3$, according to eqn. (3), involving a degradation of coordination polymers and oligomers that readily gives soluble complexes **4a**–**6a**. Crystalline material is easily obtained but is difficult to keep unaltered. Elementary analyses are consistent with losses of up to one equivalent of phosphine per nickel atom ('Experimental').

$$\underset{\textbf{4–6}}{2/x[\mathrm{Ni(Me)PMe_3)OOC(CH_2)}_{n/x}]x} + 2\mathrm{PMe_3} \longrightarrow \underset{\textbf{4a–6a}}{[\mathrm{Ni(Me)(PMe_3)_2OOC(CH_2)}_{n/x}]_2} \qquad (3)$$

4a–**6a** form yellow crystals (from THF/pentane) that give off some phosphine ligand at 20 °C *in vacuo* and are slowly decomposed in air. Solubilities of **3a**–**6a** in ether solvents are better than those of their parent compounds 3–6.

Infrared Spectra

Infrared spectra obtained from suspensions (nujol mulls) or solids (KBr discs) of 1–6 and **4a**–**6a** contain the bands of coordinated trimethylphosphine with normal relative intensities in their usual positions. In 1, oxinate ligands display bands that coincide with those of nickel bis(8-hydroxyquinolate) to within 5 cm^{-1}. Spectra of methylnickel dicarboxylates contain very strong bands of OCO vibrations that indicate the mode of coordination by their difference of frequencies ν_{as}(OCO)–ν_s(OCO) [8].

TABLE V. C–O Stretching Frequencies and Coordination Modes of Methylnickel Dicarboxylato Complexes

Compound	ν_1(CO)	ν_2(CO)	$\Delta\nu$	Coordination mode
2	1635vs	1339s	296	(OCCO)$_2$ tetradentate
3^a	1600vs	1366vs	234	unidentate
4	1588vs	1430vs	158	OCO-bridging
5	1580vs 1572vs	1425s 1418s	155	OCO-bridging
6	1587vs	1441vs 1430vs	152	OCO-bridging
4a	1582vs	1371vs	211	unidentate
5a	1598vs 1589vs	1375vs	219	unidentate
6a	1600vs	1380vs	220	unidentate

^{a}3a was obtained as oil. No satisfactory elemental analyses were obtained for 3a. No further data could be used for a thorough characterization.

Doubly bridging tetradentate oxalate has the strongest absorption in the spectrum of 2. Because of its high symmetry (D_{2h} for Ni$_2$C$_2$O$_4$) it exhibits only two ν(CO) that appear at 1635 and 1339 cm^{-1} close to the free ion value (1625 and 1317 cm^{-1} in sodium oxalate [9]) in accordance with cobalt(III) complexes containing tetradentate oxalate ligands [10].

Dicarboxylate ligands at either end may act as unidentate, bidentate or bridging units. Table V gives assignments and the likely coordination modes as derived from the differences between ν(C=O)(ν_1) and ν(C–O)(ν_2) of an asymmetric or between ν_{as}(COO)(ν_1) and ν_s(COO)(ν_2) of a symmetric carboxylate group [8].

From the ν(CO) data (Table V), a bridging mode of carboxylato ligands Ni(OCO)$_2$Ni for compounds 4–6 is indicated by a difference $152 < \Delta\nu < 158$ cm^{-1} that has been also found in dimeric methyl(trimethylphosphine)nickel acetate [5]. Cleavage of eight-membered rings **Aa** or **Ba** (Scheme 1) in 4–6 gives (CH$_2$)$_n$-connected nickel units (16 electrons) with monodentate carboxylato ligands of the form **C** corresponding to methylbis(trimethylphosphine)nickel acetate [5]. A rather high value $\Delta\nu = 234$ cm^{-1} for 3 indicating unidentate carboxylate ions suggests that the polymer contains four-membered Ni$_2$O$_2$ rings and may be described by **Bb**. A NiONi-bridging oxygen atom is expected to accentuate the difference of C=O and C–O bonds and thereby give a particularly large $\Delta\nu$.

NMR Spectra

Methyl(trimethylphosphine)nickel units of 2 are *trans* to each other and coplanar (see Fig. 3). Accordingly, only one NiC*H*$_3$ singlet and one NiPC*H*$_3$ doublet are observed indicating exchange of phosphine ligands at 308 K [1]. While no NMR data

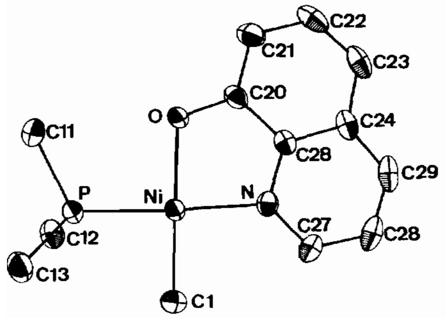


Fig. 1. Perspective view of NiMe(PMe$_3$)(C$_9$H$_6$NO) (1).

were obtained from insoluble **3** and **4**, there is good evidence for *cis* and *trans* isomers of **5** (*cis*/*trans* = 68/32) in benzene solution (see 'Experimental'). In particular, the ^{1}H NMR signals of (CH$_2$)$_3$ bridges of **5** show a symmetric (*trans*: A$_4$B$_2$) and an asymmetric (*cis*: A$_2$B$_2$C$_2$) pattern, the latter being reduced to A$_4$B$_2$ in **5a**.

Crystal Structure of 1

A view of the molecule is shown in Fig. 1 and the bond length and bond angle values are presented in Table VI.

The structure consists of discrete molecules containing nickel in square planar surroundings of atoms C1, P, N and O. The best least-squares planes through these five atoms (plane 1) and through the hydroxyquinolate atoms (plane 2) are given in Table VII. The presence of a dihedral angle of 6.65° between these two planes does not indicate a serious deviation of the molecule from an overall planarity that extends like a layer throughout the crystal. The packing as indicated in Fig. 2 shows sheets of molecules that are separated from each other by 3.6 Å.

Bonding characteristic of Ni(II) systems containing chelating and non-chelating ligands has been well established for square planar Ni(II) complexes [11–19]. Ni–ligand distances are shorter than in tetrahedral or octahedral complexes and Ni–N values in the range 1.85–1.95 Å and Ni–O distances in the range 1.80–1.90 Å are usual. The hydroxyquinolate ion has been used as ligand with various metals. Large variations in M–O (1.92–2.30 Å) and M–N (1.98–2.50 Å) distances have been observed following the metal and its coordination number [20]. Generally, M–O distances are larger than M–N distances as expected from single bond radii values [21].

The important features of this structure are the Ni–C(sp^3) and Ni–P distances, respectively of 1.917(5) and 2.125(1) Å, which both lie on the shortest range of the values observed in square planar Ni(II) complexes and the Ni–N and Ni–O distances of 1.953(3) and 1.924(3) Å which are in the upper range for the Ni–N and Ni–O distances. Such variations in bond lengths may result from the *trans* effect of the methyl and trimethylphosphine ligands. Moreover, choice by the nitrogen atom of the hydroxyquinolate ion of the position *trans* to the phosphorus has for consequence a decrease of the Ni–P bond distance by π back bonding effect. For comparison, observed Ni–P distances are: 2.125(1) Å in **1** compared to 2.141 Å in [NiBr(PN$_3$)]BPh$_4$ (P *trans* to N) [19], 2.213(7) Å in NiBr$_2$(PMe$_3$)$_2$ (P *trans* to P) [22], 2.159 Å in NiMe(acac)(PCy$_3$) (P *trans* to O) [12] and 2.197 Å in Ni(COMe)(Cl)(PMe$_3$)$_2$ (P *trans* to P) [14].

TABLE VI. Important Distances (Å) and Angles (°) of 1

Bond distances			
Ni–P	2.125(1)	Ni–O	1.924(3)
Ni–N	1.953(3)	Ni–C1	1.917(5)
P–C11	1.814(5)	P–C12	1.814(5)
P–C13	1.809(5)	O–C20	1.315(4)
N–C28	1.364(5)	C21–C22	1.406(6)
C23–C24	1.399(6)	C24–C28	1.420(5)
C26–C27	1.402(6)	C20–C28	1.419(5)
C20–C21	1.378(6)	C22–C23	1.359(7)
C24–C25	1.403(7)	C25–C26	1.343(7)
C27–N	1.315(5)		
Bond angles			
N–Ni–P	174.3(1)	O–Ni–N	84.9(1)
O–Ni–P	92.5(1)	C1–Ni–P	88.1(2)
C1–Ni–N	94.4(2)	C1–Ni–O	179.3(2)
Ni–P–C11	119.4(2)	C11–P–C12	104.0(3)
Ni–P–C12	111.7(2)	C12–P–C13	103.4(3)
Ni–P–C13	114.2(2)	C11–P–C13	102.4(3)
Ni–O–C20	111.7(2)	Ni–N–C28	110.1(2)
C28–C20–C21	117.7(4)	C20–C21–C22	120.4(5)
C21–C22–C23	122.0(5)	C22–C23–C24	120.0(4)
C23–C24–C28	118.2(4)	C28–C24–C25	115.6(4)
C25–C26–C27	119.8(5)	C26–C27–N	122.2(5)
Ni–N–C27	131.3(3)	C28–N–C27	118.4(4)
N–C28–C20	115.4(3)	N–C28–C24	123.0(4)
C20–C28–C24	121.6(4)	O–C20–C21	124.6(4)
		O–C20–C28	117.7(3)

TABLE VII. Calculated Best Least-squares Planes in Compound 1

Plane 1: ONiNP1C1

$$-0.0532x + 0.8062y - 0.5892z - 5.3642 = 0$$

Plane 2: hydroxyquinolate anion

$$-0.0054x + 0.7405y - 0.6720z - 5.0803 = 0$$

	Plane 1	Plane 2
O	0.034	−0.016
Ni	0.039	−0.102
N	−0.054	0.019
P1	−0.049	
C1	0.031	

Dihedral angle between plane 1 and 2: 6.65°.

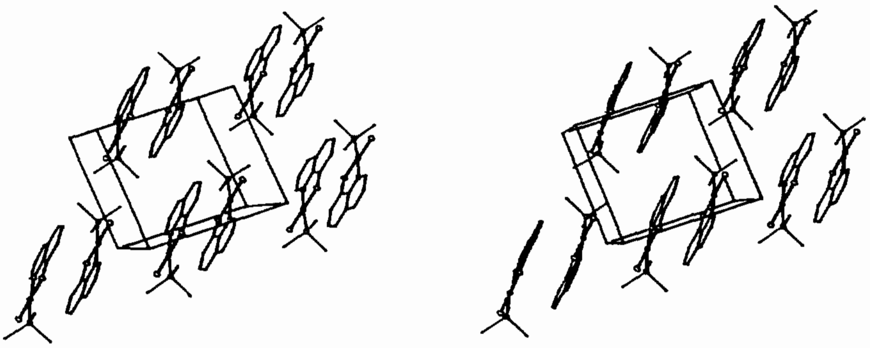


Fig. 2. Stereoscopic view of the packing diagram of structure 1 (atoms are represented by spheres of arbitrary size; hydrogens are omitted for simplicity).

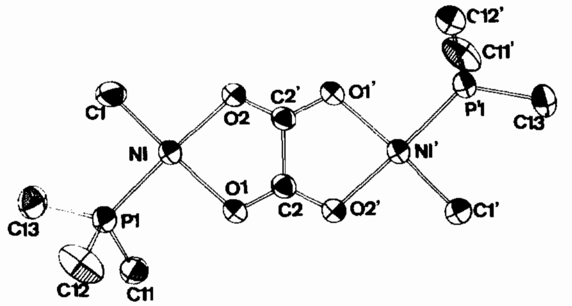


Fig. 3. Ortep drawing of $[NiMe(PMe_3)(CO_2)]_2$ (2).

The distances and angles of the hydroxyquinolate anion are normal and so are those of the trimethylphosphine ligand (Table VI).

Crystal Structure of 2

A view of the molecular structure is shown on Fig. 3. Bond length and bond angle values are presented in Table VIII. The crystal packing shown in Fig. 4 indicates no special features. All Ni–Ni separa-

TABLE VIII. Important Distances (Å) and Angles (°) of 2

Bond distances					
Ni–P	2.112(1)	Ni–C1	1.899(4)		
Ni–O1	1.990(3)	Ni–O2	1.961(3)		
O2–C2	1.251(5)	C2–O1	1.252(5)		
P1–C11	1.799(6)	P1–C12	1.801(5)		
P1–C13	1.798(5)				
Bond angles					
C1–Ni–P1	90.9(2)	P1–Ni–O1	92.3(1)	O1–Ni–C1	176.3(2)
O2–Ni–P1	176.1(1)	O2–Ni–C1	92.4(2)	C11–P1–C13	103.5(3)
C12–P1–C13	103.2(3)	O2–Ni–O1	84.3(1)	Ni–O1–C2	110.9(3)
Ni–P1–C11	110.3(2)	C12–P1–C11	104.6(3)	Ni–P1–C12	112.0(2)
Ni–P1–C13	121.6(2)				

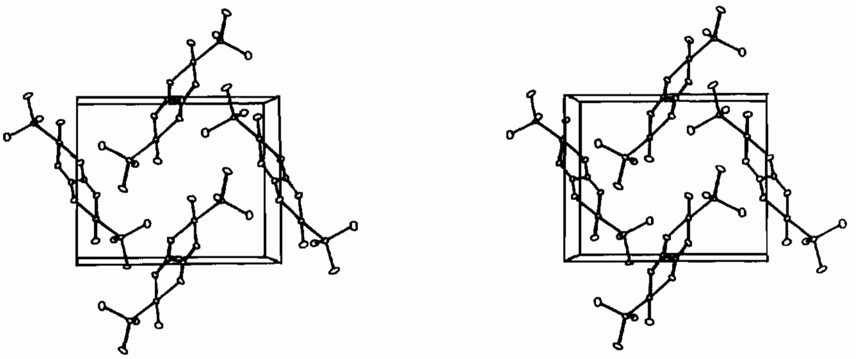


Fig. 4. Stereoscopic view of the packing diagram of structure 2.

TABLE IX. Calculated Best Least-squares Planes in Compound 2

Plane 1: NiO1O2P1C1

$$-0.4560x - 0.7321y - 0.5060z - 2.0484 = 0$$

Plane 2: NiO1O2C2C2′

$$-0.4241x - 0.7487y - 0.5095z - 1.9586 = 0$$

	Plane 1	Plane 2
Ni	0.026	−0.010
O1	−0.003	0.013
O2	−0.010	0.009
P1	−0.009	
C1	−0.004	
C2		−0.010
C2′		−0.002

Dihedral angle between plane 1 and 2: 2.07°.

tions are large enough to exclude direct metal–metal interaction.

The molecule 2 consists of two nickel atoms bridged by the oxalato ligand, the coordination sphere of the nickel atom being completed by the methyl and the trimethylphosphine ligands. The two halves of the dinuclear unit are related by a crystallographic center of symmetry located at the midpoint of the C–C bond. The bridging oxalate ligand is thus tetradentate, utilizing all four of its oxygen atoms to form a five-membered ring at each Ni atom.

The metal coordination geometry is square planar, the nickel atom lying in the plane defined by the O1, O2, C1, P1 atoms (Table IX). A contraction is noted in the O1NiO2 angle of 84.3(1)°, which is related to the oxalate bite and has been observed in other complexes.

The finding of two inequivalent Ni–O distances, 1.961(3) and 1.990(3) Å, is not unexpected, the methyl group having a stronger *trans* influence than the phosphine. Such M–O distance has been reported in the square planar $[Cu(CO_2)L]_2$ complex: Cu–O = 1.977(4) Å [23]. All these values are significantly larger than those observed in **1**. Accordingly, the nickel–carbon and nickel–phosphine distances (1.899(4) and 2.112(1) Å, respectively) are shorter than those observed in **1**.

The metallocycle is again planar. The deviations of the atoms from the least-squares plane fitting the atoms of the metallocycle are reported in Table IX. The distances and angles values are similar to those observed in the oxalate anion, respectively 1.2595(16) and 1.2473(7) Å in $K_2C_2O_4 \cdot H_2O$ [24]. The C–O bond lengths equal to 1.252(5) Å, are shorter than those expected for a single bond emphasising electron delocalisation. The C–C distance of 2 corresponds well with a single bond.

Conclusions

The bridging mode of dicarboxylate dianions with square planar methyl(trimethylphosphine)nickel moieties depends on several factors all related to the best conformation, that arranges two donor centres D at angles DNiD in the range 84–90°, and to the ring size of the metallocycle. A five-membered ring as in **1** is absolutely preferred in the oxalate complex **2** and neither of them can be cleaved with phosphine ligands. In the absence of free phosphine, an eight-membered metallocycle is only slightly preferred over a four-membered Ni_2O_2 ring and no prediction is possible to determine which of the two will be formed in a $(CH_2)_n$ connected methylnickel polymer. Both rings are cleaved by phosphine ligands and all carboxylate functions are utilized as monodentate ligands. Instead of polymeric methylnickel dicarboxylates, the first examples of metalorganic ‘ansa’ molecules are formed as dinuclear exceptions arising from an optimum number of three or four methylene groups that happen to fit the low energy conformation of one dicarboxylate ligand being engaged with both ends in the same eight-membered metallocycle. As part of eight-membered metallocycles, the square planar methylnickel units adopt a mutual *trans* orientation, but may also choose to be *cis* in ‘ansa’ compounds.

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