**Correspondence to:**
Professor W. Henderson,
Department of Chemistry,
University of Waikato,
Private Bag 3105,
Hamilton,
New Zealand
e-mail w.henderson@waikato.ac.nz
FAX 0064-7-838-4219

# Synthesis and characterisation of nickel(II) maltolate complexes containing ancillary bisphosphine ligands

KAMAL ALBLAWI, WILLIAM HENDERSON* and BRIAN K. NICHOLSON

*Department of Chemistry, University of Waikato, Private Bag 3105, Hamilton, New Zealand*

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**ABSTRACT**

Cationic nickel(II) complexes containing chelating O,O'-donor maltolate or ethyl maltolate ligands in conjunction with bidentate bisphosphine ligands $Ph_2P(CH_2)_nPPh_2$ were prepared by a one-pot reaction starting from nickel(II) acetate, the bisphosphine, maltol (or ethyl maltol) and trimethylamine base, and isolated as their tetraphenylborate salts. An X-ray structure determination of the complex $[Ni(maltolate)(Ph_2PCH_2CH_2PPh_2)]BPh_4$ shows that the maltolate ligand binds asymmetrically to the (slightly distorted) square-planar nickel(II) centre. The simplicity of the synthetic method was extended to the synthesis of the known platinum(II) maltolate complex $[Pt(maltolate)(PPh_3)_2]BPh_4$ which was obtained in high purity.

*Keywords:* Nickel complexes; Maltol complexes; Phosphine ligands; X-ray crystal structure

## 1. Introduction

Maltol (3-hydroxy-2-methyl-4-pyrone) **1a** is a naturally-occurring, non-toxic substance, approved for use as a food additive, and together with its analogue ethyl maltol (3-hydroxy-2-ethyl-4-pyrone) **1b** has been used to form a wide range of coordination complexes. The ligands bind as bidentate chelating ligands through the keto group and the deprotonated OH, forming a five-membered chelate ring system. The coordination chemistry of such hydroxypyranone ligands and related derivatives has been the subject of a recent comprehensive review.[**1**] Maltolate complexes have attracted particular interest for their medicinal potential; for example aluminium tris(maltolate) has been used to investigate aluminium transport to the brain,[**2**] the corresponding complex of gallium shows promise in cancer chemotherapy,[**3**,**4**,**5**] and bis(ethylmaltolato)oxovanadium(IV) has undergone clinical trials for diabetes treatment.[**6**,**7**,**8**]

In the area of group 10 chemistry, relatively few maltolato complexes are known. For example, the octahedral nickel(II) complex [Ni(maltolato)$_2$($H_2O$)$_2$] **2** has been known for some time,[**9**,**10**,**11**] and in a recent report [**12**] was prepared by reaction of nickel(II) acetate with maltol in the presence of NaOH base, the complex being characterised by an X-ray diffraction study. The stabilities of complexes of divalent metal ions (including $Ni^{2+}$) with maltol had been previously studied.[**13**] In this paper we describe the synthesis of some new nickel(II) complexes containing maltolate and ethyl maltolate ligands with ancillary bis(phosphine) ligands dppe [1,2-bis(diphenylphosphino)ethane] or dppp [1,3-bis(diphenylphosphino)propane]. Related cationic palladium(II) and platinum(II) complexes of maltolate with ancillary nitrogen-donor [**14**,**15**,**16**,**17**] or $PPh_3$ ligands [**18**] are known.

## 2. Results and discussion

A selection of mixed-ligand complexes **3a**-**3d** containing either maltolate or ethylmaltolate and either dppe or dppp were prepared by a one-pot reaction of nickel(II) acetate with the diphosphine and maltol or ethylmaltol in the presence of trimethylamine base. The resulting cationic products were isolated in moderate to good yield by the addition of excess $NaBPh_4$, yielding yellow-orange to orange products which give good microanalytical data. The complexes are slightly soluble in methanol, but soluble in dichloromethane and chloroform.

Crystals of complex **3a** suitable for an X-ray structure determination were obtained by slow diffusion of diethyl ether into a dichloromethane solution of the complex, and the structure was determined in order to provide comparative data with the known nickel(II) bis-maltolate complex **2**. The molecular structure of the cation is shown in Figure 1 together with the atom numbering scheme, while Table 1 gives selected bond lengths and angles for the core of the cation. The maltolate ligand is disordered over two equivalent overlapping orientations in a 2:1 ratio. The orientation of the minor component is indicated in Figure 1 by the dotted lines; the major effect of this disorder is increased uncertainty in bond parameters of those atoms of the maltolate ligand most remote from the nickel atom, specifically bonds involving the pyranyl oxygen O(3).

The binding of the maltolate ligand in **3a** is somewhat asymmetric; the P(2)-Ni(1)-O(1) bond angle is 96.81(13)°, while P(1)-Ni(1)-O(2) is 90.5(11)°. The Ni-O bond distances are also different, with Ni(1)-O(1) 1.817(3) Å (from the C-O 'single' bond), and 1.995(3) Å (from the C=O 'double' bond). Ni-O bond distances in related cationic β-diketonate complexes of nickel(II) that also contain the dppe ligand, *viz.* $[Ni(CH_3COCHCOCH_3)(dppe)]^+X^-$ [X = $BF_4$, 1.866(2) and 1.869(2) Å; X = $ClO_4$, 1.875(3)

and 1.865(3) Å] [**19**] are similar to the average Ni-O distance in **3a**. However, the Ni-O bond lengths in complex **2** [2.039(1) and 2.052(1) Å] are considerably longer, due to the octahedral coordination geometry of the nickel centre in this complex. The asymmetry in the Ni-O bond lengths of **3a** is not reflected in the Ni-P distances which are very similar to each other [Ni(1)-P(2) 2.1471(8), Ni(1)-P(1) 2.1497(8) Å].

While the C=O bond lengths of complexes **2** and **3a** are the same [complex **2** 1.266(2) Å; complex **3a** C(1)-O(2) 1.265(5) Å], the C(2)-O(1) single bond of **3a** [1.369(6) Å] is longer than the corresponding bond distance of 1.333(2) Å in **2**. The bite angle of the maltolate ligand of **3a** [87.26(16)°] is less acute than for the ligand in complex **2** [82.40(5)°], which reflects the longer Ni-O bond distances in **2**.

A further point of difference between the two structures concerns the conformation of the maltolate ligands. In complex **2** these are planar, but in complex **3a** there is a slight puckering of the nickel-maltolate moiety, as defined by an angle of 9.50° between the O(1)-Ni(1)-O(2) coordination plane, and the plane of the pyranyl ring [defined by atoms C(1), C(2), C(3), C(4), C(5) and O(3)]. There is also a slight distortion from regular square-planar geometry at the nickel centre, with an angle of 9.46° between the O(1)-Ni(1)-O(2) and P(1)-Ni(1)-P(2) planes. The $\tau_4$ parameter [**20**] of the complex is 0.100, which indicates that the distortion from perfect square-planar geometry is relatively small. The other bond parameters of the maltolate ligand of **3a** are similar (given the uncertainty arising from the disorder) to those of **2**.

The ethylmaltolate complex **3c** has been characterised by $^{31}P\{^1H\}$ and $^1H$ NMR spectroscopy. The $^{31}P\{^1H\}$ NMR spectrum shows two doublets at $\delta$ 56.3 and 54.7 ppm, due to the two inequivalent $PPh_2$ groups of the dppe ligand, showing $^2J(PP)$ coupling of 80 Hz. The $^1H$ NMR spectrum of **3c** shows characteristic resonances of the ethyl group in the form

of a quartet at δ 2.69 [$^{3}$J(HH) 7.6], and corresponding triplet at δ 1.12. The dppe $CH_2$ protons appear as a broad multiplet at δ 1.78 and a broad singlet at δ 1.54. The maltolate CH proton adjacent to the C=O group appears as a doublet at δ 6.57 [$^{3}$J(HH) 5.0 Hz], while the other CH proton is superimposed on the multitude of signals from the phenyl rings. The dppp complexes gave broad $^{31}$P NMR spectra, e.g. for the maltolate complex **3b**, which gave two broad peaks at δ 12.7 and 9.9.

The complexes **3a-d** were also characterised by positive-ion ESI MS, with all complexes giving strong $[M]^+$ cations at the expected *m/z* values (refer Experimental section), and with good agreement between observed and calculated isotope patterns. For the dppe complexes **3a** and **3c**, an additional unidentified ion at *m/z* 905 was observed, while for the dppp complexes **3b** and **3d** an additional ion was observed at *m/z* 933. The mass difference (28 *m/z*) suggests two phosphine ligands (differing in total by two $CH_2$ groups), and the isotope pattern suggests the presence of two Ni centres, but we have been unable to provide a sensible assignment for these ions.

Using the same synthetic method, the platinum(II) triphenylphosphine complex **4** was prepared as a white solid in 89% yield starting from *cis*-$[PtCl_2(PPh_3)_2]$. This complex has been previously prepared by the reaction of the dioxygen complex $[Pt(\eta^2\text{-}O_2)(PPh_3)_2]$ with maltol under a nitrogen atmosphere,[**18**] but the product in this case was obtained as a yellow solid, the colour of which may be due to impurities. Although $^{31}$P NMR data for complex **4** were not reported previously, the $^{31}P\{^{1}H\}$ NMR spectrum of **4** revealed a highly pure Pt complex, giving two doublets at δ 9.0 and 5.1 showing coupling to $^{195}$Pt with $^{1}$J(PtP) values of 3908 and 3563 Hz respectively, consistent with $PPh_3$ ligands *trans* to different oxygen-donors of the maltolate ligand. The phosphine at δ 5.1 is assigned as the one *trans* to the deprotonated maltol hydroxyl donor, because related catecholate and dioxolene complexes of

platinum(II) show similar $^{1}J(PtP)$ coupling constants, e.g. [Pt(1,2-$O_2C_6Cl_4$)($PPh_3$)$_2$] (3613 Hz).[**21**] The phosphine at δ 9.0 is accordingly *trans* to the putative C=O donor of the maltolate ligand; its value of $^{1}J(PtP)$ (3908 Hz) is also comparable with values of 3931 and 3932 Hz for the acetone complexes *cis*-[Pt($OCMe_2$)$_2$$L_2$]($ClO_4$)$_2$ (L = $PMePh_2$ or $L_2$ = dppe).[**22**] The positive-ion ESI mass spectrum of **4** shows a single dominant ion at *m/z* 844.245 for the parent cation, together with a minor fragment ion at *m/z* 718 due to the cyclometallated $PPh_3$ species [Pt($C_6H_4PPh_2$)($PPh_3$)]$^{+}$, this being commonly observed in mass spectra of Pt-$PPh_3$ complexes.[**23**]

In conclusion we have synthesised the first examples of nickel(II) complexes containing maltolate and phosphine ligands, including an X-ray structure determination on one complex. The simplicity of our synthetic method, validated in the synthesis of the known platinum(II) derivative [Pt(maltolate)($PPh_3$)$_2$]$BPh_4$ in high yield and purity, suggests it could find use in the synthesis of maltolate complexes of other metals, which is currently under investigation.

## 3. Experimental

Maltol (3-hydroxy-2-methyl-4-pyrone, Aldrich), ethyl maltol (2-ethyl-3-hydroxy-4*H*-pyran-4-one, Aldrich), nickel(II) acetate tetrahydrate (BDH), sodium tetraphenylborate (BDH) and aqueous trimethylamine (BDH, 25-30% w/v), 1,2-bis(diphenylphosphino)ethane (dppe, Aldrich) and 1,3-bis(diphenylphosphino)propane (dppp, Aldrich) were used as supplied. The complex *cis*-[$PtCl_2$($PPh_3$)$_2$] was prepared by reaction of [$PtCl_2$(COD)] [**24**] (COD = cyclo-octa-1,5-diene) with 2 mole equivalents of $PPh_3$ in $CH_2Cl_2$ solution.

ESI mass spectra were recorded on a Bruker MicrOTOF instrument, calibrated using a solution of sodium formate. Samples of isolated products were prepared for analysis by

dissolution in a few drops of dichloromethane followed by dilution with methanol and centrifugation. Ion assignment was based on a comparison of experimental and theoretical [**25**] isotope patterns. NMR spectra were recorded in $CDCl_3$ solution on a Bruker AC300P instrument. Elemental analyses were obtained from the Campbell Microanalytical Laboratory, University of Otago, Dunedin, New Zealand.

**Synthesis of [Ni(maltolate)(dppe)]$BPh_4$ 3a**

A mixture of $Ni(OAc)_2.4H_2O$ (200 mg, 0.804 mmol) and dppe (320 mg, 0.804 mmol) in methanol (25 mL) was stirred with gentle warming for 5 min., to give a clear yellow solution. Maltol (220 mg, 1.74 mmol) was added, giving a more orange solution. Aqueous trimethylamine (10 drops) was added, and the mixture warmed to around 60 ˚C, giving an orange solution. After filtration to remove a small quantity of insoluble material, solid $NaBPh_4$ (300 mg, 0.88 mmol) was added to the filtrate, to give a yellow-orange precipitate. After cooling to room temperature, the product was filtered, washed with cold methanol (5 mL), and dried under vacuum to give **3a** (377 mg, 52%). Found: C 74.85; H 5.56; N 0.00. $C_{56}H_{49}BNiO_3P_2$ ($M_r$ 901.01) requires C 74.58; H 5.48; N 0.00%. ESI MS *m/z* 581.145 (calcd. 581.094), [**3a** – $BPh_4$]$^+$. $^{31}P\{^1H\}$ NMR, δ 57.4 [d, $^2J(PP)$ 81], 55.8 [d, $^2J(PP)$ 81]. $^1H$ NMR, δ 7.75-6.80 (m, Ph and CH of maltolate), 6.53 [d, CH of maltolate, $^3J(HH)$ 5], 2.30 (s, $CH_3$ of maltolate), 1.79 (m, br, $CH_2$ of dppe), 1.52 (s, br, $CH_2$ of dppe).

**Synthesis of [Ni(maltolate)(dppp)]$BPh_4$ 3b**

$Ni(OAc)_2.4H_2O$ (200 mg, 0.804 mmol) and dppp (332 mg, 0.806 mmol) in methanol (30 mL) was stirred with gentle warming for 5 min., to give a clear orange solution. Maltol (220 mg, 1.74 mmol) was added, giving a lighter orange solution, followed by 10 drops of aqueous trimethylamine. After briefly warming to 60 ˚C the solution was filtered and $NaBPh_4$

(300 mg, 0.88 mmol) was added to the filtrate, giving an orange precipitate. Water (4 mL) was added to assist precipitation. After cooling to room temperature the solid was filtered, washed with water (2 x 10 mL) and then 1:1 methanol-water (10 mL), and dried under vacuum to give **3b** as an orange solid (463 mg, 63%). Found: C 74.75; H 5.65; N 0.00. $C_{57}H_{51}BNiO_3P_2$ ($M_r$ 915.02) requires C 74.75; H 5.62; N 0.00%. ESI MS *m/z* 595.162 (calcd. 595.110), [**3b** – $BPh_4$]$^+$. $^{31}P\{^1H\}$ NMR, δ 12.7 and 9.9 (br).

**Synthesis of [Ni(Et-maltolate)(dppe)]$BPh_4$ 3c**

Following the procedure for **3a**, $Ni(OAc)_2.4H_2O$ (200 mg, 0.804 mmol) with dppe (320 mg, 0.804 mmol) in methanol (25 mL), with ethyl maltol (250 mg, 1.78 mmol), aqueous trimethylamine (10 drops) and $NaBPh_4$ (300 mg, 0.88 mmol) gave a yellow-orange precipitate. After cooling to room temperature, water (3 mL) was added to assist precipitation. The product was filtered, washed with water (2 x 10 mL), then 1:1 methanol-water (10 mL) and dried under vacuum to give **3c** (531 mg, 72%) as a deep yellow solid. Found: C 74.68; H 5.39; N 0.00. $C_{57}H_{51}BNiO_3P_2$ ($M_r$ 915.02) requires C 74.75; H 5.62; N 0.00%. ESI MS *m/z* 595.163 (calcd. 595.110), [**3c** – $BPh_4$]$^+$. $^{31}P\{^1H\}$ NMR, δ 56.3 [d, $^2J$(PP) 80], 54.7 [d, $^2J$(PP) 80]. $^1H$ NMR, δ 7.73-6.78 (m, Ph and CH of Et-maltolate), 6.57 [CH of Et-maltolate, $^3J$(HH) 5.0 Hz], 2.69 [q, $CH_2$ of Et-maltolate, $^3J$(HH) 7.6], 1.78 (m, br, $CH_2$ of dppe), 1.54 (s, br, $CH_2$ of dppe), 1.12 [t, $CH_3$ of Et-maltolate, $^3J$(HH) 7.5].

**Synthesis of [Ni(Et-maltolate)(dppp)]$BPh_4$ 3d**

Following the procedure for **3b**, $Ni(OAc)_2.4H_2O$ (200 mg, 0.804 mmol) with dppp (332 mg, 0.806 mmol) in methanol (30 mL), with ethyl maltol (250 mg, 1.78 mmol), aqueous trimethylamine (10 drops) and $NaBPh_4$ (300 mg, 0.88 mmol) gave an orange precipitate. After cooling to room temperature, water (3 mL) was added to assist precipitation. The

product was filtered, washed with water (2 x 10 mL), then 1:1 methanol-water (10 mL) and dried under vacuum to give **3d** (610 mg, 82%) as an orange powder. Found: C 74.96; H 5.86; N 0.00. $C_{58}H_{53}BNiO_3P_2$ ($M_r$ 929.04) requires C 74.92; H 5.75; N 0.00%. ESI MS *m/z* 609.178 (calcd. 609.125), [**3d** – $BPh_4$]$^+$.

**Synthesis of [Pt(maltolate)($PPh_3$)$_2$]$BPh_4$ 4**

To a suspension of *cis*-[$PtCl_2(PPh_3)_2$] (307 mg, 0.389 mmol) in methanol (30 mL) was added maltol (220 mg, 1.74 mmol) and aqueous trimethylamine (2 mL, excess). The mixture was stirred and heated to reflux for 15 minutes, whereupon the Pt complex slowly dissolved giving a clear, very pale yellow solution. After filtration to remove a trace of insoluble matter, solid $NaBPh_4$ (250 mg, 0.73 mmol) was added to the filtrate, giving a slightly off-white precipitate that was filtered, washed with water (10 mL) and then 1:1 methanol-water (10 mL) and dried under vacuum to give **4** (402 mg, 89%). Found: C 68.28; H 4.81; N 0.00. $C_{66}H_{55}BO_3P_2Pt$ ($M_r$ 1163.44) requires C 68.07; H 4.76; N 0.00%. ESI MS *m/z* 844.245 (calcd. 844.171), [**4** – $BPh_4$]$^+$. $^{31}P\{^1H\}$ NMR, δ 9.0 [d, $^1J$(PtP) 3908, $^2J$(PP) 24], 5.1 [d, $^1J$(PtP) 3563, $^2J$(PP) 24]. $^1H$ NMR, δ 7.47-6.70 (m, Ph and CH of maltolate), 6.25 [CH of maltolate, $^3J$(HH) 5.0 Hz], 1.99 (s, Me).

**X-ray structure determination of [Ni(maltolate)(dppe)]$BPh_4$ 1a**

The complex crystallises as red block-like crystals by vapour diffusion of diethyl ether into a dichloromethane solution at room temperature.

X-ray data were collected on a Bruker Apex II CCD diffractometer and were corrected for absorption by a multi-scan method (SADABS).[**26**] The structure was solved and refined with SHELX97.[**27**] The maltolate ligand was disordered over two equivalent, overlapping orientations in a 0.67: 0.33 ratio, and the minor component was refined with

isotropic temperature factors. H atoms were not included for the disordered ligand. Electron density in a general position in the lattice was modelled as two 0.5 Cl atoms from a disordered $CH_2Cl_2$ molecule.

**Crystal data for $C_{56}H_{59}BClNiO_3P_2$**

$M_r$ = 946.94; triclinic; space group P-1; *a* = 9.5013(4) Å; *b* = 14.8195(6) Å; *c* = 16.8470(8) Å; α = 95.959(2)°; β = 99.641(2)°; γ = 95.873(2)°; V = 2308.59(17) $Å^3$; *Z* = 2; T = 89(2) K; λ(Mo-$K_\alpha$) = 0.71073 Å; μ(Mo-$K_\alpha$) = 0.594 $mm^{-1}$; $d_{calc}$ = 1.362 g $cm^{-3}$; 56420 reflections collected; 11087 unique ($R_{int}$ = 0.0533); giving $R_1$ = 0.0546, $wR_2$ = 0.1330 for data with [I>2σ(I)] and $R_1$ = 0.0715, $wR_2$ = 0.1414 for all data. Residual electron density ($e^-$ $Å^{-3}$) max/min: 1.385/-0.959.

**Supplementary data**

CCDC 802226 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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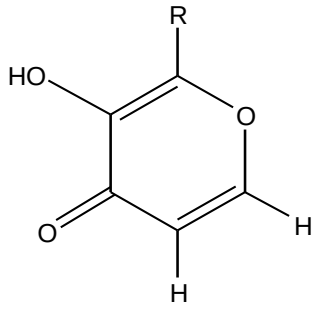
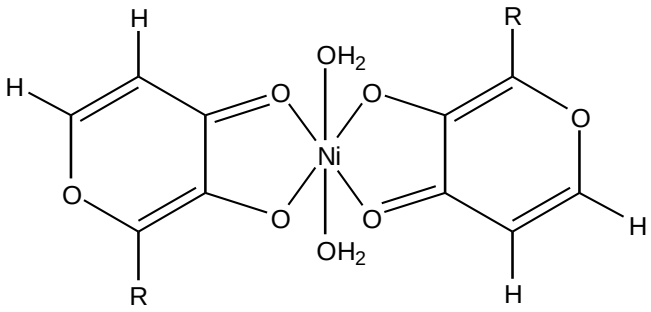
**Table 1** Selected bond lengths (Å) and angles (°) for [Ni(maltolate)(dppe)]$BPh_4$ **1a**

| | | | |
|---|---|---|---|
| Ni(1)-O(1) | 1.817(3) | Ni(1)-O(2) | 1.995(3) |
| Ni(1)-P(2) | 2.1471(8) | Ni(1)-P(1) | 2.1497(8) |
| O(1)-C(2) | 1.369(6) | O(2)-C(1) | 1.265(5) |
| O(3)-C(4) | 1.319(13) | O(3)-C(3) | 1.390(11) |
| C(1)-C(2) | 1.419(7) | C(1)-C(5) | 1.447(7) |
| C(2)-C(3) | 1.368(6) | C(3)-C(6) | 1.470(7) |
| C(4)-C(5) | 1.346(7) | | |

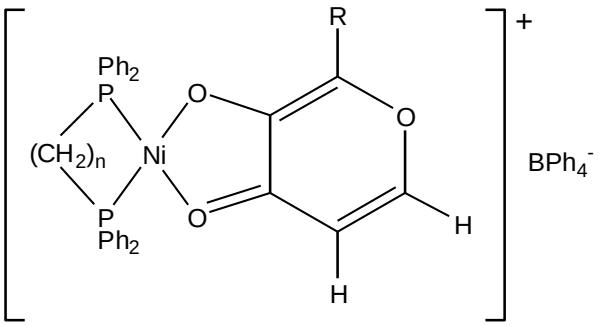
| | | | |
|---|---|---|---|
| O(1)-Ni(1)-O(2) | 87.26(16) | O(1)-Ni(1)-P(2) | 96.81(13) |
| O(2)-Ni(1)-P(1) | 90.51(11) | P(2)-Ni(1)-P(1) | 86.09(3) |
| O(2)-Ni(1)-P(2) | 171.33(9) | O(1)-Ni(1)-P(1) | 174.52(11) |
| C(2)-O(1)-Ni(1) | 109.3(3) | C(1)-O(2)-Ni(1) | 107.7(3) |
| O(2)-C(1)-C(2) | 117.3(4) | O(1)-C(2)-C(1) | 117.4(4) |



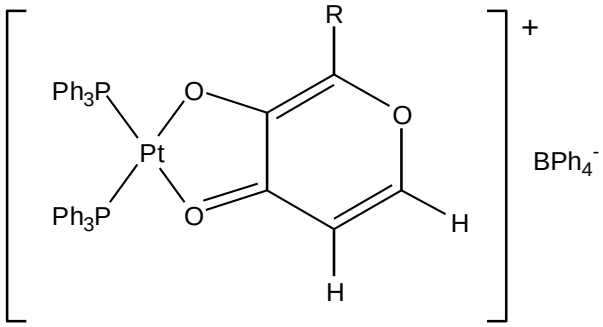

**1a** maltol, R = Me
**1b** ethylmaltol, R = Et




**2**




**3a**, n = 2, R = Me
**3b**, n = 3, R = Me
**3c**, n = 2, R = Et
**3d**, n = 3, R = Me

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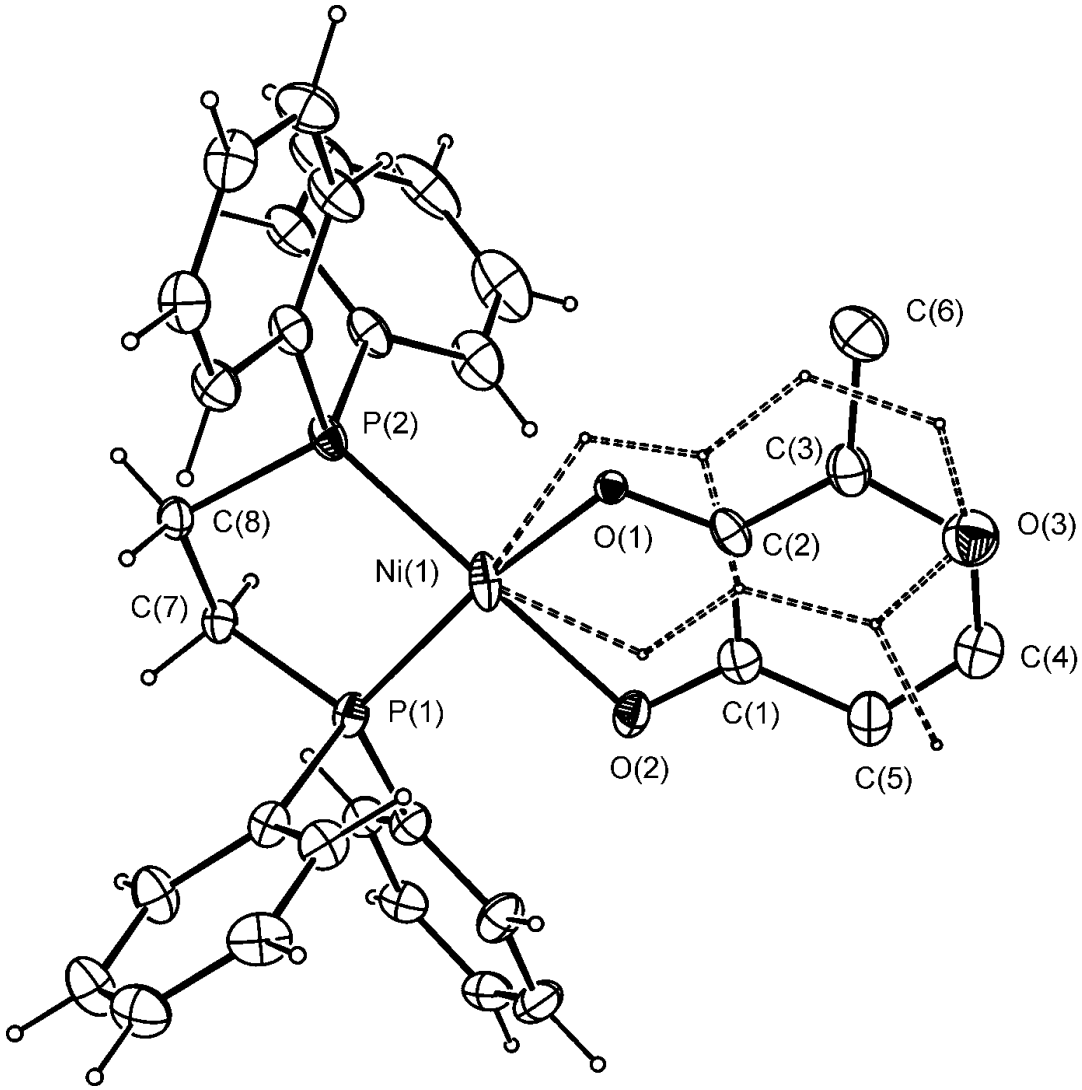


**Figure 1** Structure of the cation of [Ni(maltolate)(dppe)]$BPh_4$ **1a** showing the atom numbering scheme. Thermal ellipsoids are shown at the 50% probability level. The dotted line shows the disordered component of the maltolate ligand.

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