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Synthesis and characterization of bulky salen-type complexes of Co, Cu, Fe, Mn and Ni with amphiphilic solubility properties

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Several new bulky salen-type Schiff base ligands and their complexes with first-row transition metals Co, Cu, Fe, Mn and Ni have been synthesized and characterized. The ligands contain *tert*-butyl and methyl(triphenylphosphonium chloride) substituents in aromatic rings providing flexible solubility properties. Crystal structures of some of the complexes were determined.

Introduction

Development of biomimetic applications is presently one of the most important topics in chemistry. Additionally, the concept of "green chemistry" is becoming increasingly important in synthetic as well as in industrial chemistry.[1] This idea is often accomplished by using catalytic variations of reactions.

Salen-type complexes have been known since 1933[2] and they constitute a standard system in coordination chemistry. In salens, the ligand backbone and the coordinated metal ion can be easily varied which make these catalysts especially useful in catalytic studies.

The investigation of salen complexes has been very active during the last decade, especially following the discovery of salen-catalyzed enantioselective epoxidation of olefins by the groups of Jacobsen[3] and Katsuki.[4] Numerous salen-type complexes have been synthesized and investigated in relation to a wide variety of reactions.[5] However, the drawback of most of the complexes has been in their limited solubility in aqueous solutions. To overcome this limitation, we have now synthesized a series of complexes with broad solubility properties by introducing both lipophilic and ionic methyl(triphenylphosphonium chloride) substituents in the ligands.

The introduction of bulky groups in ligands also influences the overall catalytic properties of the complexes. Although studies concerning the steric effects of the complexes in epoxidation of alkenes have been extensive, this aspect has been investigated quite rarely in relation to other types of reactions.[6] Increased steric hindrance about the metal center of the complex affects its reactivity, but the effects are not always straightforward. In some cases sterically hindered complexes have been shown to react faster in catalytic reactions compared to less bulky ones.[7]

In this study we have synthesized salen-type Schiff base ligands and their first-row transition metal complexes containing phosphonium substituents on the ligands. Syntheses of salen complexes containing phosphine groups in the ligands have been published earlier,[8] but, to our knowledge, this is the first time that phosphonium substituted salen-type complexes are reported.

Results and discussion

The synthesis of ligands *N*,*N′*-bis{3-*tert*-butyl-5-[(triphenylphosphonium)methyl]salicylidene}-1,2-ethanediamine chloride **V** and *N*,*N′*-bis{3-*tert*-butyl-5-[(triphenylphosphonium)methyl]salicylidene}-1,2-cyclohexanediamine chloride **VI** was performed following standard procedures. Two equivalents of aldehyde **IV**[9] (prepared from 2-*tert*-butylphenol **I** by formylation with paraformaldehyde with subsequent chloromethylation and reaction with PPh_3) was condensed with one equivalent of ethylenediamine or (*R*,*R*)-1,2-diaminocyclohexane in absolute ethanol (Scheme 1). The ligands were obtained in good yields. Because of the high solubility of these compounds in ethanol, they could not be crystallized or precipitated directly from the reaction mixture. However, crystallization from CH_2Cl_2–EtOAc by slow evaporation of the solvent yielded the desired ligands in high yields and purities.

Distinct differences were observed in the ^{1}H NMR spectra of the ligands **V** and **VI** in $CDCl_3$ particularly in the signals of the benzylic methylene protons. For ligand **VI** the signals of these protons were detected as two triplet-like doublets of doublets with coupling constants of J(HH) = −14.3 Hz and J(PH) = 14.3 Hz at δ 4.79 and 5.46. This pattern results from the diastereotopic character of the benzylic protons induced by the chiral diamine bridge.[10] On the other hand, the spectrum of ligand **V** showed only a doublet with J(PH) = 12.2 Hz at δ 5.21 for the benzylic protons. Also the aromatic protons at 4- and 6-positions in the ligands were shifted; in ligand **VI** the chemical shifts were at δ 6.80 and 6.67, whereas in the ligand **V** they were at δ 7.17 and 6.58. $^{13}C\{^1H, ^{31}P\}$ triple resonance experiments were performed to identify the phosphorus–carbon couplings. These revealed that all the aromatic and benzylic carbon atoms were coupled to the phosphorus atom giving doublets with J(PC) ranging from 2.9 Hz to 85.5 Hz. The various solvate molecules retained in the solid ligands were readily identified from NMR spectra. In ES-TOF mass spectra, low intensity ions corresponding to $[M - Cl]^+$ were seen for both ligands **V** and **VI**, while the base peaks of the spectra corresponded to the doubly charged $[M - 2Cl]^{2+}$.

The syntheses of the transition metal complexes were also performed following the standard method of refluxing the ligand and a slight excess of the desired metal acetate in ethanol (for iron complexes $FeCl_2{\cdot}4H_2O$ was used). The solvent was evaporated and the residue was dissolved in CH_2Cl_2–EtOAc. The complexes were obtained in good yields and high purity by slow evaporation of the solvent mixture at atmospheric pressure. Fe^{2+} and Mn^{2+} ions were oxidized readily to Fe^{3+} and Mn^{3+} during the synthesis while the other metal ions remained in the oxidation state +2. Oxidation of iron and manganese

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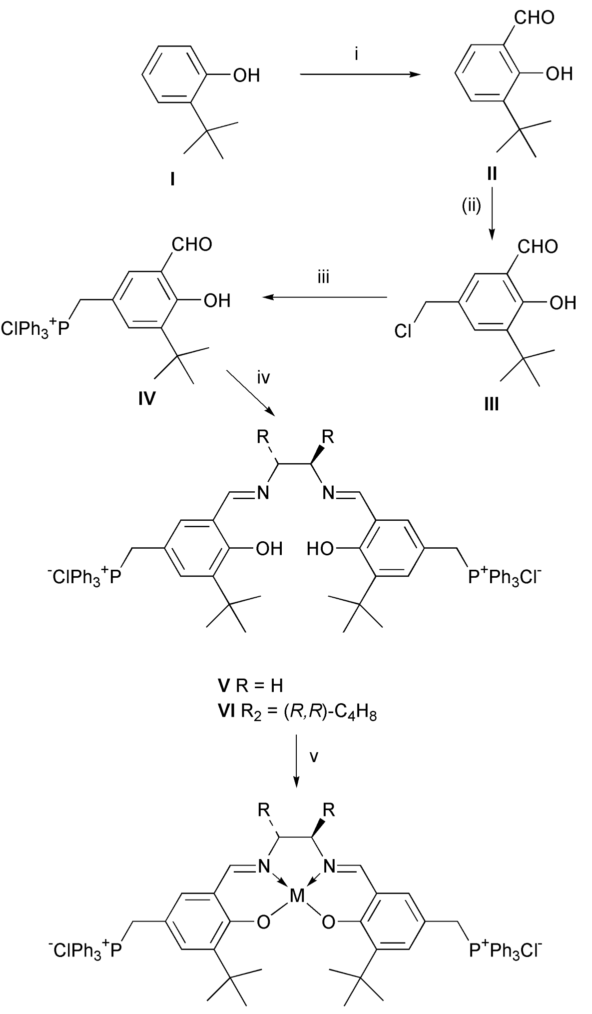

1 R = H, M = Co
2 R = H, M = Cu
3 R = H, M = FeCl
4 R = H, M = Mn(OAc)
5 R = H, M = Ni
6 R$_2$ = (*R*,*R*)-C$_4$H$_8$, M = Co
7 R$_2$ = (*R*,*R*)-C$_4$H$_8$, M = Cu
8 R$_2$ = (*R*,*R*)-C$_4$H$_8$, M = FeCl
9 R$_2$ = (*R*,*R*)-C$_4$H$_8$, M = Mn(OAc)
10 R$_2$ = (*R*,*R*)-C$_4$H$_8$, M = Ni

Scheme 1 Reagents and conditions: i 2,6-lutidine, SnCl$_4$, (CH$_2$O)$_n$, toluene, 100 °C, 8 h; ii (CH$_2$O)$_n$, conc. HCl, 40 °C, 3 d; iii PPh$_3$, benzene, 3 h, 80 °C; iv ethylenediamine or (*R*,*R*)-1,2-cyclohexanediamine, EtOH, 78 °C, 2 or 5 h; v M(OAc)$_2$ or MCl$_2$, EtOH, 78 °C, 2–3 h.

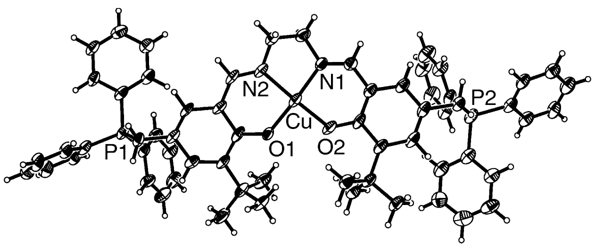

Fig. 1 Crystal structure of the complex cation of **2**. Chloride anions and solvate molecules are omitted for clarity.

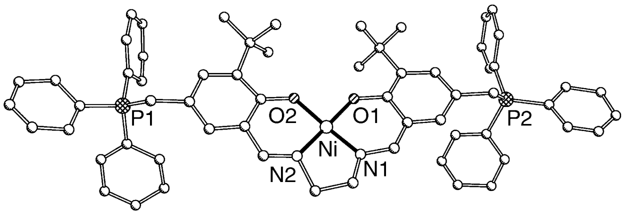

Fig. 2 Crystal structure of the complex cation of **5**. Hydrogen atoms, chloride anions and solvate molecules are omitted for clarity.

ions during complexation is expected, since most Fe- and Mn-complexes of salen-type ligands are obtained in oxidation state +3 when the synthesis is carried out in atmospheric conditions. The oxidation of Co^{2+} and especially Cu^{2+} and Ni^{2+}, on the other hand, usually requires a stronger oxidant than dioxygen.[11]

The metal complexes **1**–**10** are soluble in water and most common organic solvents and appeared to be quite stable in water in the pH range 3–10.[12] NMR spectra of the nickel complexes **5** and **10** were well resolved although the ^{1}H signals were slightly broadened. As expected, signals of phenolic hydroxyls were absent and the positions of the signals of the imine protons were shifted upfield (δ 8.14 and 7.97 in ligands **V** and **VI** *vs.* δ 7.36 and 7.40 in complexes **5** and **10**) indicating complexation.[13] ^{13}C{^{1}H, ^{31}P} experiments showed that for complexes **5** and **10** all the aromatic and benzylic carbon atoms were also coupled to phosphorus as in the corresponding ligands with *J*(PC) values between 1.9 and 84.8 Hz. Imine carbons were shifted upfield (δ 166.97 and 164.89 in ligands **V** and **VI** *vs.* δ 162.60 and 158.71 in complexes **5** and **10**). The ability to acquire well resolved NMR spectra revealed that the nickel complexes **5** and **10** are diamagnetic and accordingly have a square-planar coordination around Ni^{2+}.[13]

The complexes and ligands could not be characterized using EI-mass spectrometry because they were not volatile and thus ES-TOF mass spectrometry was chosen as a characterization method. Positive-ion ES-TOF mass spectra revealed ions corresponding to [M − Cl]$^{+}$ for all complexes except for **4**, **6** and **9**. Complex **6** gave an ion [M + H]$^{+}$ but manganese complexes **4** and **9** ions corresponding to [M − 67]$^{+}$ were seen. At present we have no explanation for the origin of these [M − 67]$^{+}$ ions. Characteristic peaks originating from the doubly charged [M − 2Cl]$^{2+}$ were detected in all cases except for complexes **4** and **9**.

However, for these latter compounds ions corresponding to [M − Cl − OAc]$^{2+}$ and [M − 2Cl − OAc]$^{3+}$ were found, giving further evidence for the oxidation state +3 of Mn. Thus the MS spectra could be used to determine the oxidation states of the central metal. In most cases the doubly charged ions corresponded to the base peak of the mass spectrum. In all cases the ion clusters had the expected isotopic distributions including, when appropriate, the peaks corresponding to molecules containing ^{37}Cl.

Single crystals suitable for the X-ray structure determination of these complexes proved to be fairly difficult to obtain. However, copper complex **2** was crystallized from acetonitrile–diisopropyl ether by slow evaporation at 28 °C. The quality of the data was limited because of disorder in the crystal structure. Even so, X-ray analysis for **2** showed that the complex is not planar (unlike many salen complexes[14]) but is twisted about the ethylenediamine bridge leading to distorted square planar coordination around the copper atom (Fig. 1). This may be the reason for the unusual catalytic activity of copper complexes **2** and **7** compared to their unsubstituted analogs.[15]

Crystals of the nickel complex **5** suitable for partial crystal structure measurement grew inside an NMR tube on standing at room temperature. Unfortunately the quality of the data was poor so that it was not possible to obtain precise bond lengths or angles but the structure could be determined and refined isotropically (Fig. 2). Chiral iron complex **8** crystallized from CH$_2$Cl$_2$–acetone by slow evaporation, but the crystals were too small for the structure determination. However, the corresponding complex cation with PF$_6$$^{-}$ counter anions yielded crystals suitable for structural determination. In this complex the iron atom shows square-pyramidal coordination with chloride ion at the apical position.[16] This suggests that iron complexes **3** and **8** also have square-pyramidal coordination geometry with strongly coordinated chloride ligands at apical positions. Also the structure of the complex **7**·6CDCl$_3$ has been solved and in this case the complex cation crystallizes in two different conformations.[17] In both, the coordination geometry around the copper ions is slightly distorted square-planar. A preliminary X-ray structure of the PF$_6^-$ analog of the manganese complex **4** with two apically coordinating imidazole ligands[15] indicated that the complex cation has the structure shown in Scheme 1.

In conclusion, we have synthesized and characterized several new amphiphilic salen-type transition metal complexes. The crystal structure of the complex **2**·2C$_2$H$_3$N·1.5C$_6$H$_{14}$O and a partial crystal structure of **5**·6CDCl$_3$ were determined. The former complex shows a distorted square planar coordination around the copper ion while for the latter, only a general connectivity could be determined. All the complexes and ligands existed as solvates in the solid state as indicated by elemental analyses, NMR spectra and crystal structure analyses.

Experimental

^{1}H and ^{13}C NMR spectra were recorded on a Varian Gemini 2000 operating at 200.0 and 50.0 MHz, respectively. ^{13}C{^{1}H, ^{31}P} triple resonance experiments were conducted using a Bruker AMX 400 spectrometer at the Finnish Institute for Verification of the Chemical Weapons Convention (VERIFIN), operating at 400.1 and 100.6 MHz, respectively. CDCl$_3$ was used as solvent and the residual solvent signals (δ 7.27 and 77.1 ppm, respectively) as references. The mass spectra were recorded using a PerSeptive Biosystems Mariner Biospectrometry Workstation ES-TOF spectrometer operating in positive-ion mode in Me$_2$CO–MeOH (9 : 1) solutions ($c = 1.0 \times 10^{-3}$ mol dm^{-3}, spray tip potential 3804 V, nozzle potential 100 V, skimmer potential 10 V, nozzle temperature 140 °C, push pulse potential 734 V, pull pulse potential 235 V, acceleration potential 4000 V, reflector potential 1550 V, detector voltage 2100 V). Elemental analyses were conducted at University of Helsinki, Department of Pharmacy, using a CE-Instruments Eager EA 1110. FTIR spectra were recorded from neat samples pressed against a diamond window using a Perkin-Elmer Spectrum One spectrometer. UV–VIS spectra were recorded using a Varian Cary 5E UV-Vis-NIR spectrophotometer ($c = 2.5 \times 10^{-5}$ mol dm^{-3}). Melting points were measured using an Electrothermal melting point apparatus in open capillaries. Solvents used were analytical or HPLC grade. Compound **IV** was prepared according to the published procedure with slight modification.[9] Ethylenediamine was distilled from sodium before use. Other starting materials were of commercial quality (purity >98%) and used as purchased.

Preparation of ligands and complexes

V·0.2CH$_2$Cl$_2$·EtOAc·EtOH·2H$_2$O. Aldehyde **IV**[9] (2.00 g, 4.09 mmol) was dissolved in absolute ethanol (20 ml). The mixture was heated to boiling and ethylenediamine (138 µl, 2.05 mmol) added. The resulting bright yellow solution was refluxed for 2 h, the solvent evaporated and the residue dissolved in CH$_2$Cl$_2$ (8 ml). Ethyl acetate (6 ml) was added and the resulting solution was allowed to evaporate slowly at room temperature. After 3 days the solid product was filtered off and washed with ethyl acetate and diethyl ether yielding **V** as a yellow powder (2.04 g, 1.72 mmol, 84%), mp 202–204 °C (decomp., from CH$_2$Cl$_2$–EtOAc) (Found: C, 68.67; H, 6.49; N, 2.65. C$_{62}$H$_{64}$Cl$_2$N$_2$O$_2$P$_2$·0.2CH$_2$Cl$_2$·EtOAc·EtOH·2H$_2$O requires C, 68.88; H, 6.98; N, 2.36%); λ_{max}/nm (MeOH) 326 (ε/dm^3 mol^{-1} cm^{-1} 9500), 299 (infl), 267 (infl), 261 (40400), 251 (infl); ν/cm^{-1} 3365 (H$_2$O + EtOH), 1726 (EtOAc), 1629 (C=N); δ_H(CDCl$_3$) 1.06 (18 H, s, Bu^t), 1.13 (3 H, t, *J*(HH) = 7.0 Hz, EtOH), 1.19 (3 H, t, *J*(HH) = 7.0 Hz, EtOAc), 1.97 (3 H, s, EtOAc), 2.31 (4 H, br s, H$_2$O), 3.61 (2 H, q, *J*(HH) = 7.0 Hz, EtOH), 3.72 (4 H, s, CH$_2$N), 4.05 (2 H, q, *J*(HH) = 7.0 Hz, EtOAc), 5.21 (4 H, d, *J*(PH) = 12.2 Hz, CH$_2$P), 5.24 (0.4 H, s, CH$_2$Cl$_2$), 6.58 (2 H, m, Ar), 7.17 (2 H, m, Ar), 7.56–7.69 (30 H, m, Ph), 8.14 (2 H, s, CH=N), 13.97 (2 H, s, OH); δ_C(CDCl$_3$) 14.26 (EtOAc), 18.52 (EtOH), 21.08 (EtOAc), 29.14, 30.35 (d, *J*(PC) = 46.3 Hz), 34.74, 58.45 (EtOH), 58.87 (CH$_2$Cl$_2$), 59.12, 60.44 (EtOAc), 115.44 (d, *J*(PC) = 8.0 Hz), 118.25 (d, *J*(PC) = 85.5 Hz), 118.88 (d, *J*(PC) = 3.0 Hz), 130.25 (d, *J*(PC) = 13.1 Hz), 132.38 (d, *J*(PC) = 4.0 Hz), 133.42 (d, *J*(PC) = 6.0 Hz), 134.53 (d, *J*(PC) = 9.1 Hz), 134.95 (d, *J*(PC) = 3.0 Hz), 138.04 (d, *J*(PC) = 3.0 Hz), 160.89 (d, *J*(PC) = 3.0 Hz), 166.97, 171.23 (EtOAc); *m*/*z* 965 [C$_{62}$H$_{64}$Cl$_2$N$_2$O$_2$P$_2$ − Cl]$^+$ (10), 465 [C$_{62}$H$_{64}$Cl$_2$N$_2$O$_2$P$_2$ − 2Cl]$^{2+}$ (100%).

VI·0.5CH$_2$Cl$_2$·EtOAc·2EtOH. Aldehyde **IV** (2.00 g, 4.09 mmol) was dissolved in absolute ethanol (20 ml). The mixture was heated to boiling and (*R*,*R*)-1,2-diaminocyclohexane (234 mg, 2.05 mmol) was added. The resulting bright yellow solution was refluxed for 5 h. The solvent was evaporated and the residue was dissolved in CH$_2$Cl$_2$ (10 ml). Ethyl acetate (10 ml) was added and the resulting solution was allowed to evaporate slowly at room temperature. After 2 days the solid product was filtered off and washed with ethyl acetate and diethyl ether to yield **VI** as yellow crystals (1.91 g, 1.49 mmol, 73%), mp 203–207 °C (decomp., from CH$_2$Cl$_2$–EtOAc) (Found: C, 69.32; H, 6.90; N, 2.21. C$_{66}$H$_{70}$Cl$_2$N$_2$O$_2$P$_2$·0.5CH$_2$Cl$_2$·EtOAc·2EtOH requires C, 69.97; H, 7.17; N, 2.19%); λ_{max}/nm (MeOH) 329 (ε/dm^3 mol^{-1} cm^{-1} 8100), 300 (infl), 260 (sh), 256 (34700), 252 (infl); ν/cm^{-1} 3301, (H$_2$O), 1717 (EtOAc), 1628 (C=N); δ_H(CDCl$_3$) 1.07 (18 H, s, Bu^t), 1.17 (6 H, t, *J*(HH) = 7.0 Hz, EtOH), 1.22 (3 H, t, *J*(HH) = 7.0 Hz, EtOAc), 1.37 (2 H, m, cyclohexyl), 1.58 (2 H, m, cyclohexyl), 1.78 (2 H, m, cyclohexyl), 1.86 (2 H, m, cyclohexyl), 2.00 (1.5 H, s, EtOAc), 3.21 (2 H, m, CHN), 3.65 (4 H, q, *J*(HH) = 7.0 Hz, EtOH), 4.08 (2 H, q, *J*(HH) = 7.0 Hz, EtOAc), 4.79 (2 H, dd, *J*(HH) = −14.3 Hz, *J*(PH) = 14.3 Hz), 5.21 (1H, s, CH$_2$Cl$_2$), 5.46 (2 H, dd, *J*(HH) = −14.3 Hz, *J*(PH) = 14.3 Hz), 6.67 (2 H, m, Ar), 6.80 (2H, m, Ar), 7.50–7.73 (30 H, m, Ph), 7.97 (2 H, s, CH=N), 13.99 (2 H, s, OH); δ_C(CDCl$_3$) 14.11 (EtOAc), 18.42 (EtOH), 20.94 (EtOAc), 23.93, 29.05, 30.26 (d, *J*(PC) = 46.4 Hz), 32.65, 34.61, 56.22 (CH$_2$Cl$_2$), 58.07 (EtOH), 60.28 (EtOAc), 71.37, 115.22 (d, *J*(PC) = 8.6 Hz), 117.84 (d, *J*(PC) = 85.2 Hz), 118.60 (d, *J*(PC) = 2.9 Hz), 130.13 (d, *J*(PC) = 12.4 Hz), 132.30 (d, *J*(PC) = 4.6 Hz), 132.58 (d, *J*(PC) = 5.9 Hz), 134.24 (d, *J*(PC) = 9.7 Hz), 134.93 (d, *J*(PC) = 3.0 Hz), 137.89 (d, *J*(PC) = 3.1 Hz), 160.70 (d, *J*(PC) = 3.2 Hz), 164.89, 171.02 (EtOAc); *m*/*z* 1019 [C$_{66}$H$_{70}$Cl$_2$N$_2$O$_2$P$_2$ − Cl]$^+$ (8), 492 [C$_{66}$H$_{70}$Cl$_2$N$_2$O$_2$P$_2$ − 2Cl]$^{2+}$ (100%).

1·CH$_2$Cl$_2$·2H$_2$O. Ligand **V** (238 mg, 0.200 mmol) was dissolved in absolute ethanol (4 ml). The resulting solution was heated to boiling and Co(OAc)$_2$·4H$_2$O (50 mg, 0.201 mmol) was added. The yellow solution turned to dark brown immediately and was refluxed for 2 h. The solvent was evaporated and the residue dissolved in CH$_2$Cl$_2$ (2 ml) and ethyl acetate (1 ml) added. The filtered solution was allowed to evaporate slowly at room temperature. The precipitated solid was filtered off and washed with ethyl acetate and diethyl ether. Recrystallization from CH$_2$Cl$_2$–ethyl acetate yielded **1** as a brown powder (189 mg, 0.160 mmol, 80%), mp 151–155 °C (decomp., from CH$_2$Cl$_2$–EtOAc) (Found: C, 64.04; H, 5.83; N, 2.50. C$_{62}$H$_{62}$Cl$_2$CoN$_2$O$_2$P$_2$·CH$_2$Cl$_2$·2H$_2$O requires C, 64.13; H, 5.81; N, 2.37%); λ_{max}/nm (MeOH) 401 (sh), 326 (ε/dm^3 mol^{-1} cm^{-1} 32800), 301 (infl), 266 (68100), 246 (infl), 226 (75400), 218 (infl); ν/cm^{-1} 3428 (H$_2$O), 1641 (C=N); *m*/*z* 1022 [C$_{62}$H$_{62}$Cl$_2$CoN$_2$O$_2$P$_2$ − Cl]$^+$ (2), 493 [C$_{62}$H$_{62}$Cl$_2$CoN$_2$O$_2$P$_2$ − 2Cl]$^{2+}$ (61).

2·4H$_2$O. Prepared as for complex **1** using Cu(OAc)$_2$·H$_2$O instead of Co(OAc)$_2$·4H$_2$O. Gray–purple solid, yield 83%, mp 161–164 °C (decomp., from CH$_2$Cl$_2$–EtOAc) (Found: C, 65.70;

H, 6.33; N, 2.46. $C_{62}H_{62}Cl_2CuN_2O_2P_2\cdot 4H_2O$ requires C, 65.57; H, 6.21; N, 2.47%); λ_{max}/nm (MeOH) 569 (ε/dm^3 mol^{-1} cm^{-1} 600), 339 (infl), 370 (11600), 273 (45100), 248 (sh), 227 (82600), 219 (infl); ν/cm^{-1} 3364 (H_2O), 1625 (C=N); *m*/*z* 1027 [$C_{62}H_{62}Cl_2CuN_2O_2P_2 - Cl$]$^+$ (5), 495 [$C_{62}H_{62}Cl_2CuN_2O_2P_2 - 2Cl$]$^{2+}$ (100%).

$3\cdot CH_2Cl_2\cdot 2H_2O$. Prepared as for complex **1** using $FeCl_2\cdot 4H_2O$ as the metal source. Dark red powder, yield 75%, mp 208–210 °C (from CH_2Cl_2–EtOAc) (Found: C, 62.64; H, 5.73; N, 2.32. $C_{62}H_{62}Cl_3FeN_2O_2P_2\cdot CH_2Cl_2\cdot 2H_2O$ requires C, 62.42; H, 5.65; N, 2.31%); λ_{max}/nm (MeOH) 527 (ε/dm^3 mol^{-1} cm^{-1} 4500), 325 (15400), 315 (sh), 290 (infl), 266 (sh), 225 (75900), 218 (infl); ν/cm^{-1} 3382 (H_2O), 1612 (C=N); *m*/*z* 1054 [$C_{62}H_{62}Cl_3FeN_2O_2P_2 - Cl$]$^+$ (1), 509 [$C_{62}H_{62}Cl_3FeN_2O_2P_2 - 2Cl$]$^{2+}$ (100%).

$4\cdot CH_2Cl_2\cdot H_2O$. Prepared as for complex **1** using $Mn(OAc)_2\cdot 4H_2O$ as the metal source. Brown powder, yield 78%, mp 145–147 °C (from CH_2Cl_2–EtOAc) (Found: C, 64.27; H, 5.93; N, 2.66. $C_{64}H_{65}Cl_2MnN_2O_4P_2\cdot CH_2Cl_2\cdot H_2O$ requires C, 64.15; H, 5.71; N, 2.30%); λ_{max}/nm (MeOH) 418 (sh), 288 (sh), 254 (ε/dm^3 mol^{-1} cm^{-1} 60100), 250 (infl), 227 (92100), 218 (infl); ν/cm^{-1} 3378 (H_2O), 1624 (C=N), 1420 (OAc^-); *m*/*z* 1045 [$C_{64}H_{65}Cl_2MnN_2O_4P_2 - 67$]$^+$ (33), 509 [$C_{64}H_{65}Cl_2MnN_2O_4P_2 - Cl - OAc$]$^{2+}$ (36), 327 [$C_{64}H_{65}Cl_2MnN_2O_4P_2 - 2Cl - OAc$]$^{3+}$ (3%).

$5\cdot 2H_2O$. Prepared as for complex **1** using $Ni(OAc)_2\cdot 4H_2O$ as the metal source. Orange–brown powder, yield 87%, mp 222–230 °C (decomp., from CH_2Cl_2–EtOAc) (Found: C, 67.25; H, 6.22; N, 2.55. $C_{62}H_{62}Cl_2N_2NiO_2P_2\cdot 2H_2O$ requires C, 68.02; H, 6.08; N, 2.56%); λ_{max}/nm (MeOH) 416 (ε/dm^3 mol^{-1} cm^{-1} 4300), 376 (infl), 351 (sh), 319 (10200), 268 (47200), 242 (infl), 225 (47700), 219 (infl); ν/cm^{-1} 3352 (H_2O), 1618 (C=N); δ_H($CDCl_3$) 1.06 (18 H, s), 1.67 (4 H, br s, H_2O), 3.26 (4 H, s), 5.20 (4 H, d, *J*(PH) = 13.6 Hz), 6.57 (2 H, m), 7.15 (2 H, m), 7.36 (2 H, s), 7.67–7.76 (30 H, m); δ_C($CDCl_3$) 29.26, 30.05 (d, *J*(PC) = 46.3 Hz), 35.32, 58.41, 111.18 (d, *J*(PC) = 8.6 Hz), 118.18 (d, *J*(PC) = 84.8 Hz), 121.20 (d, *J*(PC) = 2.1 Hz), 130.12 (d, *J*(PC) = 12.3 Hz), 132.96 (d, *J*(PC) = 3.4 Hz), 134.44 (d, *J*(PC) = 9.6 Hz), 134.66 (d, *J*(PC) = 7.6 Hz), 134.77 (d, *J*(PC) = 2.3 Hz), 140.64 (d, *J*(PC) = 2.2 Hz), 162.60, 163.48 (d, *J*(PC) = 1.9 Hz); *m*/*z* 1021 [$C_{62}H_{62}Cl_2N_2NiO_2P_2 - Cl$]$^+$ (9), 493 [$C_{62}H_{62}Cl_2N_2NiO_2P_2 - 2Cl$]$^{2+}$ (100%).

$6\cdot 2CH_2Cl_2\cdot H_2O$. Ligand **VI** (376 mg, 0.294 mmol) was dissolved in absolute ethanol (5 ml). The resulting solution was heated to reflux and $Co(OAc)_2\cdot 4H_2O$ (74 mg, 0.297 mmol) was added, the yellow solution turning dark brown immediately. The mixture was refluxed for 3 h. After evaporating the solvent, the residue was dissolved in CH_2Cl_2 (3 ml), and ethyl acetate (3 ml) was added. The filtered solution was allowed to evaporate slowly at room temperature and the precipitated solid was filtered off and washed with ethyl acetate and diethyl ether. Recrystallization from CH_2Cl_2–ethyl acetate yielded **6** as a brown powder (300 mg, 0.231 mmol, 79%), mp 133–136 °C (decomp., from CH_2Cl_2–EtOAc) (Found: C, 62.91; H, 5.89; N, 2.50. $C_{66}H_{68}Cl_2CoN_2O_2P_2\cdot 2CH_2Cl_2\cdot H_2O$ requires C, 62.78; H, 5.73; N, 2.15%); λ_{max}/nm (MeOH) 401 (sh), 328 (ε/dm^3 mol^{-1} cm^{-1} 24500), 302 (infl), 265 (53400), 247 (infl), 226 (71300), 218 (infl); ν/cm^{-1} 3397 (H_2O), 1640 (C=N); *m*/*z* 1112 [$C_{66}H_{68}Cl_2CoN_2O_2P_2 + H$]$^+$ (1), 520 [$C_{66}H_{68}Cl_2CoN_2O_2P_2 - 2Cl$]$^{2+}$ (29%).

$7\cdot 3H_2O$. Prepared as for complex **6** using $Cu(OAc)_2\cdot H_2O$ as the metal source. Gray–purple solid, yield 90%, mp 202–204 °C (from CH_2Cl_2–EtOAc) (Found: C, 67.14; H, 6.66; N, 2.38. $C_{66}H_{68}Cl_2CuN_2O_2P_2\cdot 3H_2O$ requires C, 67.65; H, 6.37; N, 2.39%); λ_{max}/nm (MeOH) 568 (ε/dm^3 mol^{-1} cm^{-1} 500), 371 (9500), 336 (infl), 274 (34500), 248 (51300), 240 (infl), 228 (66200), 220 (infl); ν/cm^{-1} 3347 (H_2O), 1615 (C=N); *m*/*z* 1080 [$C_{66}H_{68}Cl_2CuN_2O_2P_2 - Cl$]$^+$ (4), 522 [$C_{66}H_{68}Cl_2CuN_2O_2P_2 - 2Cl$]$^{2+}$ (100%).

$8\cdot CH_2Cl_2\cdot 2H_2O$. Prepared as for complex **6** using $FeCl_2\cdot 4H_2O$ as the metal source. Dark red powder, yield 90%, mp 202–204 °C (from CH_2Cl_2–EtOAc) (Found: C, 63.52; H, 6.30; N, 2.36. $C_{66}H_{68}Cl_3FeN_2O_2P_2\cdot CH_2Cl_2\cdot 2H_2O$ requires C, 63.55; H, 5.89; N, 2.21%); λ_{max}/nm (MeOH) 527 (ε/dm^3 mol^{-1} cm^{-1} 3900), 329 (14900), 310 (sh), 290 (infl), 266 (sh), 226 (90300), 219 (infl); ν/cm^{-1} 3357 (H_2O), 1610 (C=N); *m*/*z* 1108 [$C_{66}H_{68}Cl_3FeN_2O_2P_2 - Cl$]$^+$ (2), 536 [$C_{66}H_{68}Cl_3FeN_2O_2P_2 - 2Cl$]$^{2+}$ (100%).

$9\cdot CH_2Cl_2\cdot 2H_2O$. Prepared as for complex **6** using $Mn(OAc)_2\cdot 4H_2O$ as the metal source. Brown powder, yield 90%, mp 142–145 °C (from CH_2Cl_2–EtOAc) (Found: C, 64.53; H, 6.12; N, 2.40. $C_{68}H_{71}Cl_2MnN_2O_4P_2\cdot CH_2Cl_2\cdot 2H_2O$ requires C, 64.29; H, 6.02; N, 2.17%); λ_{max}/nm (MeOH) 405 (sh), 290 (sh), 260 (sh), 226 (ε/dm^3 mol^{-1} cm^{-1} 87700), 218 (infl); ν/cm^{-1} 3377 (H_2O), 1623 (C=N), 1437 (OAc^-); *m*/*z* 1099 [$C_{68}H_{71}Cl_2MnN_2O_4P_2 - 67$]$^+$ (11), 536 [$C_{68}H_{71}Cl_2MnN_2O_4P_2 - Cl - OAc$]$^{2+}$ (100), 346 [$C_{68}H_{71}Cl_2MnN_2O_4P_2 - 2Cl - OAc$]$^{3+}$ (9%).

$10\cdot 2H_2O$. Prepared as complex **6** using $Ni(OAc)_2\cdot 4H_2O$ as the metal source. Orange–brown microcrystalline product, yield 94%, mp 240–243 °C (decomp., from CH_2Cl_2–EtOAc) (Found: C, 68.13; H, 6.41; N, 2.45. $C_{66}H_{68}Cl_2N_2NiO_2P_2\cdot 2H_2O$ requires C, 69.00; H, 6.32; N, 2.44%); λ_{max}/nm (MeOH) 418 (ε/dm^3 mol^{-1} cm^{-1} 5900), 380 (infl), 356 (sh), 317 (13900), 268 (65500), 242 (infl), 225 (67200), 221 (infl); ν/cm^{-1} 3327 (H_2O), 1613 (C=N); δ_H($CDCl_3$) 1.06 (18 H, s), 1.21 (4 H, br s), 1.74 (4 H, br s, H_2O), 2.40 (2 H, br s), 2.89 (2 H, br s), 5.18 (4 H, m,), 6.38 (2 H, s), 7.40 (4 H, s), 7.68–7.77 (30 H, m); δ_C($CDCl_3$) 24.38, 29.20, 29.34, 30.43 (d, *J*(PC) = 43.1 Hz), 35.40, 70.41, 110.64 (d, *J*(PC) = 8.6 Hz), 118.48 (d, *J*(PC) = 84.5 Hz), 121.44 (d, *J*(PC) = 2.3 Hz), 130.26 (d, *J*(PC) = 12.3 Hz), 132.70 (d, *J*(PC) = 2.9 Hz), 134.57 (d, *J*(PC) = 9.5 Hz), 134.84 (d, *J*(PC) = 2.6 Hz), 135.71 (d, *J*(PC) = 6.0 Hz), 140.80 (d, *J*(PC) = 2.5 Hz), 158.71, 163.93 (d, *J*(PC) = 2.2 Hz); *m*/*z* 1075 [$C_{66}H_{68}Cl_2N_2NiO_2P_2 - Cl$]$^+$ (6), 520 [$C_{66}H_{68}Cl_2N_2NiO_2P_2 - 2Cl$]$^{2+}$ (100%).

X-Ray crystallography

General. The unit cell parameters were determined and the data collected on a Rigaku AFC7S diffractometer at −80 °C. The data were corrected for Lorentz-polarization effects but no corrections for absorption were applied. The structures were solved by direct methods using the SHELXS97[18] program and refined by using the SHELXL97 program. Hydrogen atoms, except those belonging to the solvate molecules, were included in calculated positions and treated as riding atoms using SHELXL97[18] default parameters.

Crystal structure determination. **$2\cdot 2C_2H_3N\cdot 1.5C_6H_{14}O$.** *Crystal data.* $C_{75}H_{89}Cl_2CuN_4O_{3.5}P_2$, $M = 1298.88$, triclinic, space group $P\bar{1}$, $a = 14.941(8)$, $b = 19.023(8)$, $c = 13.869(6)$ Å, $\alpha = 95.42(5)$, $\beta = 116.06(5)$, $\gamma = 88.96(5)°$, $V = 3524(3)$ Å^3, $T = 193(2)$ K, $Z = 2$, λ(Mo-Kα) = 0.71073 Å, μ(Mo-Kα) = 0.48 mm^{-1}, $F(000) = 1376$, 8953 unique reflections collected ($2.58 < \theta < 24°$), $R1(I > 2\sigma(I)) = 0.110$, ($wR2 = 0.134$) for 757 parameters. The structure contains acetonitrile and poorly defined, distorted and partially occupied diisopropyl ether solvate molecules.

5·6$CDCl_3$. The structure determination was not of sufficient quality to allow full publication, but the general connectivity was clearly established. Owing to the quality of the data it is not possible to discuss any bond lengths or angles for this structure.

Crystal data for **5**·6$CDCl_3$: $C_{68}H_{62}Cl_{20}D_6NiO_2P_2$, $M = 1780.93$, monoclinic, space group $P2_1/c$, $a = 13.410(8)$,

$b = 13.047(8)$, $c = 45.995(14)$ Å, $\beta = 93.39(4)°$, $V = 8033(7)$ Å^3, $Z = 4$, $R1[I > 2\sigma(I)] = 0.152$ for 526 parameters.

CCDC reference numbers 158146 and 158147.

See http://www.rsc.org/suppdata/dt/b0/b008167l/ for crystallographic data in CIF or other electronic format.

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