Synthesis and Structural Characterisation of Group 10 Homo- and Hetero-Dimetallic Sulfur-Bridged Complexes of the [Ni(ema)(μ-*S*,*S*′)M(diphos)] (M = Ni, Pd, Pt) Type

Samantha E. Duff,[a] J. Elaine Barclay,[a] Sian C. Davies,[a] Peter B. Hitchcock,[b] and David J. Evans*[a]

Keywords: Nickel / Palladium / Platinum / Heterometallic complexes

The series of group 10 homo- and hetero-dimetallic sulfur-bridged complexes [Ni(ema)(μ-*S*,*S*′)M(diphos)], [M = nickel, palladium or platinum; diphos = 1,3-bis(diphenylphosphanyl)-propane or 1,2-bis(diphenylphosphanyl)ethane], have been synthesised. Their properties and the crystal structures of five of the series are described. The dinickel complexes are good structural analogues of the dinickel subunit of the nickel-containing enzyme acetyl-CoA synthase.

Introduction

The nickel enzyme acetyl-CoA synthase catalyses the synthesis of acetyl-CoA. The reaction parallels the industrially important Reppe process for the synthesis of acetic acid, both apparently involving metal–carbonyl, methyl–metal and acyl–metal intermediates.[1] Protein crystallography[2–4] shows at the active site, the A cluster, an Fe_4S_4 cluster bridged through cysteinylthiolate sulfur to a proximal nickel that is then linked to a distal nickel(II) atom in an N_2S_2 coordination environment, Figure 1. The *cis*-planar N_2S_2 coordination is from a deprotonated Cys–Gly–Cys sequence of the protein. Following publication of the crystal structures there has been a renewed vigour in the preparation of dinuclear group 10 complexes as mimics for the dinickel sub-site of the A cluster.[5–10] Herein we report the synthesis and properties of the series of complexes [Ni(ema)(μ-*S*,*S*′)M(diphos)], where M is nickel, palladium or platinum, H_4ema is *N*,*N*′-ethylenebis(2-mercaptoacetamide) and where diphos is 1,3-bis(diphenylphosphanyl)propane (dppp) or 1,2-bis(diphenylphosphanyl)ethane (dppe).

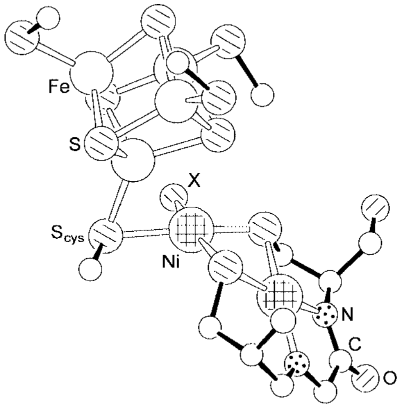

Figure 1. The active site, A cluster, of acetyl-CoA synthase.

Results and Discussion

Synthesis and Spectroscopy

Previously, we have demonstrated that the homonuclear complexes [Ni(ema)(μ-*S*,*S*′)Ni(dppp)] (**1**) and [Ni(ema)(μ-*S*,*S*′)Ni(dppe)] (**2**) can be readily prepared from the reaction of equimolar amounts of $[NEt_4]_2$[Ni(ema)] and $[NiCl_2$(diphos)] in acetonitrile solution.[5] Here, a similar methodology has been applied to isolate, from the appropriate $[MCl_2$(diphos)], the heteronuclear dimetallic complexes [Ni(ema)(μ-*S*,*S*′)M(diphos)], M = Pd, diphos = dppp (**3**) or dppe (**4**); M = Pt, diphos = dppp (**5**) or dppe (**6**), in good yield, Equation (1).

$$[NEt_4]_2[Ni(ema)] + [MCl_2(diphos)] \rightarrow [Ni(ema)(\mu\text{-}S,S')M(diphos)] + 2[NEt_4]Cl \qquad (1)$$

All complexes have been characterised by EI-MS and the structures of **1**[5] and **3**–**6** have been confirmed by X-ray crystallography. Satisfactory elemental analyses (C, H, N) are obtained for all compounds except **3**, which, for reasons unknown, gave consistently poor results. However, spectroscopic parameters and the mass spectrum of this compound are fully consistent with the crystal structure.

---

[a] Department of Biological Chemistry, John Innes Centre, Norwich Research Park, Colney, Norwich, NR4 7UH, UK
E-mail: dave.evans@bbsrc.ac.uk
[b] Department of Chemistry, University of Sussex, Falmer, Brighton, BN1 9QJ, UK

DOI: 10.1002/ejic.200500678

In the solid, complexes **1**–**6** exhibit an infra-red amido-carbonyl stretch in the range 1566–1578 cm^{-1}. The ^{31}P{H} NMR chemical shifts for solutions in methanol and in dimethyl sulfoxide are consistent with diphosphane chelate ligation and, as expected, depend on the chelate ring size; the chemical shifts observed for five-membered (dppe) chelate rings (ca. 49 to 62 ppm) are larger than those for six-membered (dppp) rings (ca. –5 to 1 ppm).[11] The single resonance observed in each case confirms the equivalence of the phosphorus atoms in solution at ambient temperature. The values for **2** are comparable to those of the related complexes [Ni(L)(μ-*S*,*S*′)Ni(dppe)](PF$_6$)$_2$ {L = *N*,*N*′-diethyl-3,7-diazanonane-1,9-dithiolate(2–)} (CD$_2$Cl$_2$, 61.1 ppm)[6] and [Ni(CGC)(μ-*S*,*S*′)Ni(dppe)] (CGC = cys–gly–cys) (CD$_3$CN, 56.7 and 57.5 ppm).[8]

In the solid state the nickel complexes are coloured green, palladium blue-black and platinum red. The electronic absorption spectra of solutions of **1**–**6** exhibit several absorbance peaks as expected, and their parameters are collected in Table 1. The colour in solution is dependent on solvent, Table 2. The nickel and palladium complexes show a dramatic colour difference on changing solvent from acetonitrile to methanol. This is a consequence of the ability of such square-planar complexes to coordinate extra (solvent) ligands in solution to establish an equilibrium between four-, five- and six-coordinate species.[12] However, the NMR in methanol does not support the presence of a six-coordinate, paramagnetic species.

Table 2. Colour of solutions of complexes **1**–**6** in acetonitrile and methanol.

Complex		MeCN	MeOH
[Ni(ema)Ni(dppp)]	(**1**)	emerald green	midnight blue
[Ni(ema)Ni(dppe)]	(**2**)	emerald green	indigo
[Ni(ema)Pd(dppp)]	(**3**)	royal blue	deep red
[Ni(ema)Pd(dppe)]	(**4**)	violet	burgundy
[Ni(ema)Pt(dppp)]	(**5**)	cerise	pink
[Ni(ema)Pt(dppe)]	(**6**)	peach	orange

The cyclic voltammogram of **1** in dichloromethane shows a reversible one electron process at $E_{1/2}$ = –0.42 V (vs. SCE) assigned to a Ni^{II}/Ni^{I} couple of the NiP$_2$S$_2$ moiety, a similar process at $E_{1/2}$ = –0.47 V (vs. SCE) has been reported for [Ni(L)(μ-*S*,*S*′)Ni(dppe)](PF$_6$)$_2$.[6] A second feature at E_{pc} = –1.39 V (vs. SCE) may be assigned to an irreversible reduction Ni^{I}/Ni^{0} at NiP$_2$S$_2$ or an irreversible Ni^{II}/Ni^{I} couple at the other nickel site. The cyclic voltammetry of the complexes **2**–**6** has not been investigated.

It has been observed that 1,10-phenanthroline will chelate and extract the proximal nickel from the acetyl-CoA synthase A cluster.[13] The effect has been observed also in a synthetic analogue, [Ni(PhPepS)(μ-*S*,*S*′)Ni(dppe)] {PhPepSH$_4$ = *N*,*N*′-phenyl(*o*-mercaptobenzamide)}, of the dinickel subsite of the A cluster where it is proposed that the nickel is removed from the NiP$_2$S$_2$ unit.[9] The same reaction occurs with complexes **1** and **2**, in dichloromethane solvent, using a ten-fold excess of 1,10-phenanthroline.

Table 1. Electronic absorption spectrum parameters for complexes **1**–**6** in acetonitrile and methanol solution.

Complex	MeCN		MeOH	
	λ [nm]	ε [dm^{3}mol^{-1} cm^{-1}]	λ [nm]	ε [dm^{3}mol^{-1} cm^{-1}]
[Ni(ema)Ni(dppp)] (**1**)	630	1230	586	2550
	468	250	447	1500
	280	22590	320	12710
	–	–	256	28930
	–	–	222	52760
[Ni(ema)Ni(dppe)] (**2**)	623	1040	575	1170
	472	860	459	890
	282	14480	308	8490
			287	9510
			242	13420
[Ni(ema)Pd(dppp)] (**3**)	581	1540	545	1710
	449	2570	438	1760
	319 sh	3860	325 sh	7960
	278 sh	20220	263 sh	21140
	225 sh	44260	221 sh	40470
[Ni(ema)Pd(dppe)] (**4**)	581	1130	546	820
	443	750	445	980
	274	11480	–	–
	224	27770	229	14510
[Ni(ema)Pt(dppp)] (**5**)	535	2910	522	590
	411	5780	395	1890
	365	6740	351	2830
	319	3057	–	–
	227	97080	225	43550
[Ni(ema)Pt(dppe)] (**6**)	533	430	518	340
	414	2290	405	1380
	382	2080	361	2150
	323	2850	–	–
	244	60760	226	24540

There is, however, under similar conditions, no reaction of 1,10-phenanthroline with the heterometallic complexes **3**–**6**, with $[NEt_4]_2[Ni(ema)]$ or with the trinickel complex $[NEt_4]_2$-[Ni{Ni(ema)(μ-*S*,*S*′)}$_2$],[5] which provides further confirmation that the phosphine-ligated nickel is lost and that the nickel atom associated with the Ni(ema) moiety is not chelated by 1,10-phenanthroline.

Structures

The crystal structure of **1**·Et_2O[5] (Figure 2) shows that each nickel ligand sphere is slightly distorted square planar, with nickel(1) ligated by the two phosphorus atoms from the dppp ligand and the two sulfur atoms of the ema ligand and the other nickel, (2), ligated by the two nitrogen and two sulfur atoms of the ema ligand. The dppp-ligated nickel atom may be considered to lie within the S_2P_2 mean plane [displaced 0.0035(5) Å from the plane towards the ema-ligated Ni], which is essentially flat [deviations from the mean planes lie in the range –0.0238(9) to 0.0241(9) Å, where the negative sign indicates opposite side of the mean plane]; the most distorted angle about this nickel is 80.93(3)°. This is similar in the other two dppp-ligated metal complexes, with the metal atoms lying within 0.020(2) Å of the S_2P_2 mean planes, which in turn have atoms lying in the ranges –0.017(3) to 0.017(4) and –0.010(2) to 0.010(2) Å from the mean planes in **3** and **5**, respectively. This is, however, different to the arrangement in the dppe-ligated complexes. In these, the S_2P_2 planes are twisted with atoms lying in the ranges –0.2134(13) to 0.2109(13) Å and –0.2556(13) to 0.2590(13) Å in the two independent molecules in **4** and –0.1925(3) to 0.1949(13) in **6**. The metal atoms lie 0.1075(6) and 0.0712(6) Å from the mean planes in **4** and 0.0591(6) in **6**. The ema-chelated nickel atom lies 0.1534(6) Å from the N_2S_2 plane [displaced in the direction away from Ni(1)] with an angle of 169.52(8)° for a N–Ni–S angle being the most distorted. This distortion is similar in all the complexes. The dihedral (hinge) angle at the bridging sulfur atoms in **1** is 111.22°. The Ni–S bond lengths within the chelate ring (2.12 Å) are slightly shorter and the bridge distances (2.28 Å) slightly longer than those observed (2.14–2.19 Å and 2.19–2.24 Å, respectively) for other synthetic sulfur-bridged dinickel complexes such as [Ni(L)(μ-*S*,*S*′)-Ni(dppe)]$(PF_6)_2$.[6] Other angles and bond lengths about the nickel atoms and the Ni···Ni distance [2.6897(5) Å] are similar to those reported for related "Ni(μ-S)$_2$NiN_2" structures.[7]

The Ni(ema) group of the complex forms a curved "wall" around two of the phenyl groups of the dppp ligand, which are orientated "edge-on" to the Ni(ema) group. Within each PPh group, the normals to the second phenyl rings are orientated at 111.3 and 102.6°, respectively, to those of the first two. The complex molecules are arranged with the Ni(ema) groups forming approximate (due to the curved nature of the ema ligands) planes parallel to the crystallographic *bc* plane; viewed along the crystallographic *b* direction, the molecules are arranged in pairs with the Ni(dppp) groups in alternating *ab* planes lying on opposite sides of the Ni(ema) planes (Figure 3). This packing arrangement is identical to that in **3** and **5**, while the Ni–ema planes are also found in **4** and **6**. There is a difference in the packing in **6**, however, as the Pt–dppe groups are not "staggered" along the crystallographic *a* vector as they are in the other four arrangements.

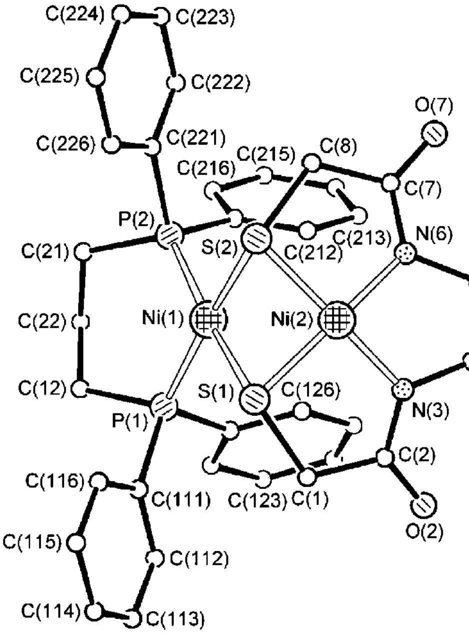

Figure 2. A view of [Ni(ema)(μ-*S*,*S*′)Ni(dppp)] (**1**) showing atom numbering scheme, hydrogen atoms omitted for clarity.

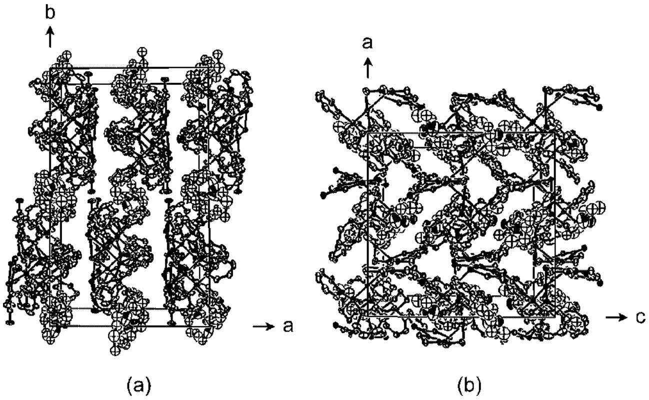

Figure 3. Packing arrangements of [Ni(ema)(μ-*S*,*S*′)Ni(dppp)] (**1**) as viewed along (a) the crystallographic *c* axis and (b) the *b* axis.

The [Ni(ema)(μ-*S*,*S*′)M(diphos)] molecules in complexes **3**, **4**, **5** and **6** have structures similar to complex **1**. In **4** there are two independent molecules within the asymmetric unit. Representative structures of the heterometallic complexes **3** and **4** are shown in Figure 4 and Figure 5, respectively. A comparison of selected bond lengths and angles are given in Table 3. On substitution of nickel(1) by palladium, there is no significant change in the average Ni–N bond length and only a very slight lengthening of the average Ni–S bond length within the Ni(ema); replacement of palladium by

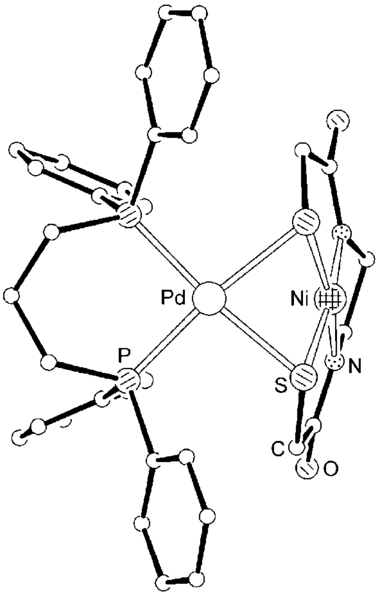

Figure 4. A molecule of [Ni(ema)(μ-*S*,*S*′)Pd(dppp)] (**3**), hydrogen atoms omitted for clarity.

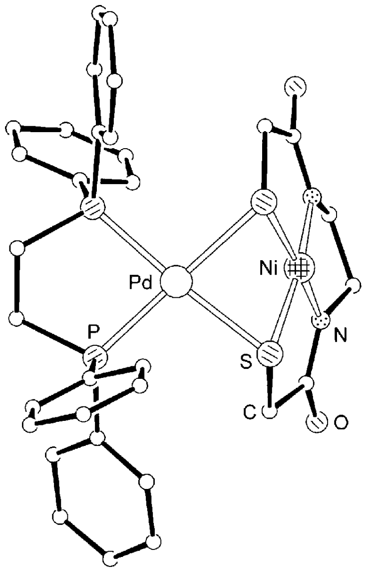

Figure 5. Molecular structure of [Ni(ema)(μ-*S*,*S*′)Pd(dppe)] (**4**), hydrogen atoms omitted for clarity.

platinum leads to no further increase in bond length. Within the NiP_2S_2 fragment there is again an elongation of the M–P and M–S bond lengths on substitution of nickel(1) by palladium (0.08 and 0.13 Å, respectively) but no further change when palladium is replaced by platinum. On changing from dppp to dppe chelation, independent of metal, there is a decrease in the M–P–C(alkane) angle from ca. 116° to ca. 108° that helps maintain the square-planar environment. The dihedral (hinge) angle at the bridging sulfur atoms is similar in all complexes, ranging from 111–117°. The nickel to metal distance increases from 2.6897(8) Å in **1** to 2.780(2) Å in **3**, which is similar to the distance in the heterometallic complexes **4** and **5** and slightly shorter than that in **6** [2.8653(5) Å]. The longer platinum–nickel distance is consistent with the larger hinge angle in the latter complex.

Conclusions

The series of six group 10 homo- and hetero-dimetallic sulfur-bridged complexes of the [Ni(ema)(μ-*S*,*S*′)-M(diphos)] (M = Ni, Pd, Pt; diphos = dppp, dppe) type have been prepared and characterised; five by X-ray crystallography. The geometric parameters about the metal atoms for complex **1** and **3**–**6** resemble those reported for the dinickel subunit of the A-cluster of acetyl-CoA synthase: in complex **1** the nickel(1) and nickel(2) atoms mimic the A cluster distal nickel and proximal nickel, respectively.

Experimental Section

General: All manipulations were performed under dinitrogen, unless otherwise stated, using either Schlenk or vacuum-line techniques. Solvents were dried with appropriate drying agents and distilled under dinitrogen prior to use. $[NiCl_2(dppp)]$ was purchased from Aldrich and $[Pd(1,5\text{-cylcooctadiene})Cl_2]$, $[Pt(1,5\text{-cylcooctadiene})Cl_2]$ and $[PdCl_2(dppe)]$ were purchased from Alfa Aeser. $[NEt_4]_2$-[Ni(ema)],[14] $[PtCl_2(dppp)]$, $[PtCl_2(dppe)]$ and $[PdCl_2(dppp)]$ were obtained by adaptation of published procedures.[15] [Ni(ema)(μ-*S*,*S*′)Ni(dppp)] (**1**) and [Ni(ema)(μ-*S*,*S*′)Ni(dppe)] (**2**) were prepared as we recently reported.[5] IR spectra were recorded with a Shimadzu FTIR-8000 spectrophotometer and UV/Vis spectra with a Perkin–Elmer Lambda 25. ^{31}P NMR were obtained with a Jeol Lambda 400 spectrometer. Electrospray ionisation mass spectra, in methanol solution, were measured with a Deca XP_{plus} ion trap mass spectrometer from Thermo Finnigan. Elemental analyses were by Medac Ltd, Egham, Surrey, UK.

Table 3. Comparison of selected bond lengths [Å], metal–metal separation [Å] and hinge angle [°] in complexes **1** and **3**–**6**.

Complex		Ni(2)–S	Ni(2)–N	M–P	M–S	M–Ni	Hinge angle
[Ni(ema)Ni(dppp)]	(**1**)	2.1224(5)	1.8298(76)	2.1892(2)	2.2812(2)	2.6897(5)	111.22
[Ni(ema)Pd(dppp)]	(**3**)	2.1465(20)	1.8338(64)	2.2712(3)	2.4092(18)	2.7803(14)	110.37
[Ni(ema)Pd(dppe)]	(**4**)[a]	2.1556(35)	1.8400(19)	2.2651(44)	2.4064(48)	2.7927(129)	112.16
[Ni(ema)Pt(dppp)]	(**5**)	2.1560(24)	1.8377(21)	2.2624(20)	2.4098(8)	2.7950(7)	110.78
[Ni(ema)Pt(dppe)]	(**6**)	2.1597(92)	1.8398(41)	2.2578(65)	2.4084(93)	2.8653(5)	117.22

[a] Average values from the two independent molecules within the asymmetric unit.

Preparations

[Ni(ema)(μ-*S*,*S*′)Pd(dppp)] (3): A slurry of [PdCl$_2$(dppp)] (0.146 g, 2.49×10^{-4} mol) in MeCN (20 mL) was added to a stirred solution of [NEt$_4$]$_2$[Ni(ema)] (0.130 g, 2.49×10^{-4} mol) in MeCN (10 mL). The resultant black solution was stirred at room temp. for 12 h, then diethyl ether (10 mL) was added dropwise. Within 4 h blue-black crystals were formed and collected by filtration (0.12 g, 62%). IR (KBr): $\tilde{\nu}_{max}$ = (CO) 1578 cm^{-1}. ^{31}P NMR (162 MHz. CD$_3$OD; ref. H$_3$PO$_4$): δ = –5.11 (s) ppm, ([D$_6$]DMSO): δ = 5.22 (s) ppm. MS: *m*/*z* = 783 (100) [M$^+$ + H$^+$].

[Ni(ema)(μ-*S*,*S*′)Pd(dppe)] (4): To a slurry of [PdCl$_2$(dppe)] (0.300 g, 5.22×10^{-4} mol) in MeCN (10 mL) was added solid [NEt$_4$]$_2$[Ni(ema)] (0.273 g, 5.22×10^{-4} mol) and additional MeCN (5 mL). The resultant black solution was stirred at room temp. for 30 min, then diethyl ether (5 mL) was added dropwise. A brown solid (0.25 g, 63%) was collected by filtration. $C_{32}H_{32}N_2NiO_2P_2PdS_2$ (767.80): calcd. C 50.1, H 4.2, N 3.7; found C 50.0, H 4.2, N 3.7. IR (KBr): $\tilde{\nu}_{max}$ = (CO) 1567 . ^{31}P NMR (162 MHz. CD$_3$OD; ref. H$_3$PO$_4$): δ = 62.64 (s) ppm, ([D$_6$]DMSO): δ = 61.96 (s) ppm. MS: *m*/*z* = 769 (100) [M$^+$ + H$^+$]. Recrystallisation from a methanol/diethyl ether mixture gave blue-black crystals of **4**·1½MeOH (0.22 g, 52%).

[Ni(ema)(μ-*S*,*S*′)Pt(dppp)] (5): To a white slurry of [PtCl$_2$(dppp)] (0.330 g, 4.87×10^{-4} mol) in MeCN (20 mL) was added a solution of [NEt$_4$]$_2$[Ni(ema)] (0.255 g, 4.87×10^{-4} mol) in MeCN (10 mL). The solution was stirred for a further 10 min before the volume was decreased in vacuo to 15 mL. Diethyl ether was layered onto the solution and a red product precipitated overnight which was collected by filtration (0.29 g, 68%). $C_{33}H_{34}N_2NiO_2P_2PtS_2$ (870.48): calcd. C 45.5, H 3.9, N 3.2; found C 46.0, H 4.4, N 3.2. IR (KBr): $\tilde{\nu}_{max}$ = (CO) 1578 cm^{-1}. ^{31}P NMR (162 MHz. CD$_3$OD; ref. H$_3$PO$_4$): δ = –3.70 (s) ppm; ([D$_6$]DMSO): δ = –2.87 (s) ppm. MS: *m*/*z* =871 (100) [M$^+$ + H$^+$]. Recrystallisation from dichloromethane gave crystals of **5**·2CH$_2$Cl$_2$.

[Ni(ema)(μ-*S*,*S*′)Pt(dppe)] (6): Compound **6** was prepared similarly to **5** in 69% yield from [PtCl$_2$(dppe)]. $C_{32}H_{32}N_2NiO_2P_2PtS_2$ (856.46): calcd. C 44.9, H 3.8, N 3.3; found C 43.9, H 4.0, N 3.3. IR (KBr): $\tilde{\nu}_{max}$ = (CO) 1566 cm^{-1}. ^{31}P NMR (162 MHz. CD$_3$OD; ref. H$_3$PO$_4$): δ = 49.01 (s) ppm; ([D$_6$]DMSO): δ = 48.92 (s) ppm. MS: *m*/*z* =857 (100) [M$^+$ + H$^+$].

Crystal Data

[Ni(ema)(μ-*S*,*S*′)Ni(dppp)]·Et$_2$O (1·Et$_2$O): $C_{33}H_{34}N_2Ni_2O_2P_2S_2$, $C_4H_{10}O$, M = 808.2; orthorhombic, space group *Pcab* (equiv. to *Pbca*, no. 61), a = 16.557(3), b = 16.799(8), c = 26.931(5) Å, V = 7491(4) Å^3, Z = 8, $D_{calcd.}$ = 1.433 mg/m^3; data collection method: CAD4 scintillation counter, ω scans at T = 150(2) K, λ = 0.71073 Å, θ_{max} = 28.0°; 9000 unique reflections used, 5793 with $I > 2\sigma_I$, F(000) = 3376, μ = 1.240 mm^{-1}, R_1/wR_2 [$I > 2\sigma(I)$] = 0.039/0.078, R_1/wR_2 (all data) = 0.073/0.094, goodness-of-fit on F^2 = 1.040.

[Ni(ema)(μ-*S*,*S*′)Pd(dppp)]·Et$_2$O (3·Et$_2$O): $C_{33}H_{34}N_2NiO_2P_2PdS_2$, $C_4H_{10}O$, M = 855.9; orthorhombic, space group *Pbca*, a = 16.7601(8), b = 27.0435(14), c = 16.9278(5) Å, V = 7672.6(6) Å^3, Z = 8, $D_{calcd.}$ = 1.482 mg/m^3; data collection method: 95mm CCD camera on κ-goniostat, CCD rotation images, thick slices, scans at T = 173(2) K, λ = 0.71073 Å, θ_{max} = 24.12°; 6067 unique reflections used, 3610 with $I > 2\sigma(I)$, F(000) = 3520, μ = 1.189 mm^{-1}, R_1/wR_2 [$I > 2\sigma(I)$] = 0.084/0.128, R_1/wR_2 (all data) = 0.158/0.149, goodness-of-fit on F^2 = 1.128.

[Ni(ema)(μ-*S*,*S*′)Pd(dppe)]·1.5MeOH (4·1.5MeOH): $C_{32}H_{32}N_2NiO_2P_2PdS_2\cdot1.5(CH_4O)$ M = 815.8; triclinic, space group $P\bar{1}$, a = 11.8017(3), b = 16.9502(4), c = 19.2990(4) Å, α = 65.591(1), β = 72.565(1), γ = 81.065(1), V = 3351.81(14) Å^3, Z = 4, D_c = 1.617 mg/m^3; data collection method: 95 mm CCD camera on κ-goniostat, CCD rotation images, thick slices, scans at T = 173(2) K, λ = 0.71073 Å, θ_{max} = 25.02°; 11766 unique reflections used, 9510 with $I > 2\sigma_I$, F(000) = 1668, μ = 1.358 mm^{-1}, R_1/wR_2 ($I > 2\sigma_I$) = 0.036/0.077, R_1/wR_2 (all data) = 0.052/0.084, goodness-of-fit on F^2 = 1.016.

[Ni(ema)(μ-*S*,*S*′)Pt(dppp)]·2CH$_2$Cl$_2$ (5·2CH$_2$Cl$_2$): $C_{33}H_{34}N_2NiO_2P_2PtS_2$, CH$_2Cl_2$, M = 1040.33; orthorhombic, space group *Pbca*, a = 16.6045(3), b = 27.3310(5), c = 17.1881(2) Å, V = 7800.3(2) Å^3, Z = 8, D_c = 1.772 mg/m^3; data collection method: 95 mm CCD camera on κ-goniostat, CCD rotation images, thick slices, scans at T = 173(2) K, λ = 0.71073 Å, θ_{max} = 26.01°; 7652 unique reflections used, 5827 with [$I > 2\sigma(I)$], F(000) = 4112, μ = 4.564 mm^{-1}, R_1/wR_2 ($I > 2\sigma_I$) = 0.038/0.083, R_1/wR_2 (all data) = 0.061/0.092, goodness-of-fit on F^2 = 1.045

[Ni(ema)(μ-*S*,*S*′)Pt(dppe)] (6): $C_{32}H_{32}N_2NiO_2P_2PtS_2$, M = 856.46; monoclinic, space group $P2_1/c$, a = 11.0225(4), b = 16.4895(5), c = 17.3899(4) Å, β = 100.920(2), V = 3103.5(2) Å^3, Z = 4, $D_{calcd.}$ = 1.833 mg/m^3; data collection method: 95 mm CCD camera on κ-goniostat, CCD rotation images, thick slices, scans at T = 173(2) K, λ = 0.71073 Å, θ_{max} = 26.02°; 6094 unique reflections used, 5193 with [$I > 2\sigma(I)$], F(000) = 1688, μ = 5.381 mm^{-1}, R_1/wR_2 [$I > 2\sigma(I)$] = 0.027/0.051, R_1/wR_2 (all data) = 0.038/0.054, goodness-of-fit on F^2 = 1.041.

CCDC-258104 (for **1**), -279513 (for **3**), -279514 (for **4**), -279515 (for **5**) and -279516 (for **6**) contain 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.

Acknowledgments

The Biotechnology and Biological Sciences Research Council are thanked for funding and the John Innes Foundation for a postgraduate studentship (S. E. D). Dr Lionel Hill, JIC Metabolite Service is thanked for mass spectrometry.

---

[1] D. J. Evans, *Coord. Chem. Rev.* **2005**, *249*, 1582–1595.
[2] T. I. Doukov, T. M. Iverson, J. Seravalli, S. W. Ragsdale, C. L. Drennan, *Science* **2002**, *298*, 567–572.
[3] C. Darnault, A. Volbeda, E. J. Kim, P. Legrand, X. Vernède, P. A. Lindahl, J. C. Fontecilla-Camps, *Nat. Struct. Mol. Biol.* **2003**, *10*, 271–279.
[4] V. Svetlitchnyi, H. Dobbek, W. Meyer-Klaucke, T. Meins, B. Thiele, P. Römer, R. Huber, O. Meyer, *Proc. Natl. Acad. Sci. U. S. A.* **2004**, *101*, 446–451.
[5] S. E. Duff, J. E. Barclay, S. C. Davies, D. J. Evans, *Inorg. Chem. Commun.* **2005**, *8*, 170–173.
[6] Q. Wang, A. J. Blake, E. S. Davies, E. J. L. McInnes, C. Wilson, M. Schröder, *Chem. Commun.* **2003**, 3012–3013.
[7] P. V. Rao, S. Bhaduri, J. Jiang, R. H. Holm, *Inorg. Chem.* **2004**, *43*, 5833–5849.
[8] R. Krishnan, C. G. Riordan, *J. Am. Chem. Soc.* **2004**, *126*, 4484–4485.
[9] T. C. Harrop, M. M. Olmstead, P. K. Mascharak, *J. Am. Chem. Soc.* **2004**, *126*, 14714–14715.
[10] P. V. Rao, S. Bhaduri, J. Jiang, D. Hong, R. H. Holm, *J. Am. Chem. Soc.* **2005**, *127*, 1933–1945.
[11] P. E. Garrou, *Chem. Rev.* **1981**, *81*, 229–266.
[12] M. Schröder, in: *Encyclopedia of Inorganic Chemistry* (Ed.: R. B. King), John Wiley & Sons, Chichester, England, **1994**, *5*, pp. 2392–2412.

[13] W. Shin, P. A. Lindahl, *J. Am. Chem. Soc.* **1992**, *114*, 9718–9719.
[14] H.-J. Krüger, G. Peng, R. H. Holm, *Inorg. Chem.* **1991**, *30*, 734–742.
[15] J. DePriest, G. Y. Zheng, C. Woods, D. R. Rillema, N. A. Mikirova, M. E. Zandler, *Inorg. Chim. Acta* **1997**, *264*, 287–296.

Received: July 28, 2005