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Diphosphine complexes of nickel: analogies in molecular structures and variety in crystalline arrangement

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Abstract

This work comprised the preparation of six complexes of Ni(II) and their study by spectroscopy and X-ray diffraction. These complexes are: [Ni(dppe)Cl_2]CH_2Cl_2 (**I**), [Ni(dppen)Cl_2] (**II**), [Ni(dppm)Br_2]CH_2Cl_2 (**III**), [Ni(dppe)$(NCS)_2$] (**IV**), [Ni(dppen)I_2] (**V**), [Ni(dppp)Cl_2]CH_2Cl_2 (**VI**), where dppe = 1,2-bis(diphenylphosphine)ethane, dppen = *cis*-1,2-bis(diphenylphosphine)ethene, dppm = bis(diphenylphosphine)methane, dppp = 1,3-bis(diphenylphosphine)propane. The structures of complexes **III**–**VI** are unknown in the literature. Although the molecular structures of the six complexes present many similarities, their crystalline arrangements vary considerably. This is a feature not presented hitherto in previous work involving complexes of this type. In addition, a systematic spectroscopic study was undertaken on all six complexes.

Keywords: Diphosphine complexes; Nickel complexes; Molecular structures; Crystal packing

1. Introduction

Many authors have investigated the modes of coordination of nickel (II) with diphosphines, as well as the structures and the spectroscopic properties of the resulting complexes [1–7]. These systems are quite attractive in view of their importance in terms of explaining a series of important features of coordination compounds, namely π-bonding, lability and *trans* influence of ligands, geometry, as well as for their importance as precursors in catalytic reactions [4]. Although several complexes have been described in the literature, next to nothing has been written comparing molecular and crystalline structures.

Whereas the former can be similar in various compounds, their crystalline arrangements differ to a great extent. Insofar as most complexes of this kind have been prepared from $NiCl_2$, we decided to investigate the complexation of a series of diphosphines of different organic chains with several Ni salts, namely $NiCl_2$, $NiBr_2$, NiI_2 and $Ni(NCS)_2$.

2. Experimental

All the reactions were carried out under argon in Schlenk glassware and the solvents were dried by standard techniques. Commercial Ni halides and diphosphines were used throughout, and $Ni(NCS)_2$ was obtained in the laboratory from $NiCl_2$ and KNCS. The complexes were prepared according to the following scheme:

$$NiX_2 + \text{diphosphine} \xrightarrow[\text{Ar, 1 h, 50 °C}]{\text{1:1 } CH_2Cl_2-MeOH} [\text{Ni(diphosphine)}X_2]$$

Replacement of $NiCl_2$ by $(Et_4N)_2[NiCl_4]$ in the reaction with dppe, and of the solvent by $MeNO_2$, followed by recrystallisation from CH_2Cl_2, led to a mixture of (I) and its unsolvated analogue, previously reported as forms A (the latter) and B (I), respectively [8]. All complexes were initially obtained as powders in approximately 70% yield. Upon recrystallisation in

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CH_2Cl_2 they produced copious crops of crystals suitable for X-ray work. C, H elemental analysis of the six complexes were consistent with the proposed formulations, which are: $[Ni(dppe)Cl_2]CH_2Cl_2$ (**I**), $[Ni(dppen)Cl_2]$ (**II**), $[Ni(dppm)Br_2]CH_2Cl_2$ (**III**), $[Ni(dppe)(NCS)_2]$ (**IV**), $[Ni(dppen)I_2]$ (**V**), $[Ni(dppp)Cl_2]CH_2Cl_2$ (**VI**). They all decomposed without melting above 140 °C.

FTIR spectra were obtained with an IR760 Nicolet-Magna spectrophotometer, using CsI and polyethylene pellets in the ranges 4000–200 and 600–50 cm^{-1}, respectively. Electronic spectra were recorded from a Varian CARY 1E instrument, using 10^{-4} mol l^{-1} solutions in CH_2Cl_2. Both solid state MAS $^{31}P\{^1H\}$ and solution $^{31}P\{^1H\}$ NMR spectra were obtained from a DRX300 MHz Bruker instrument. Spectroscopic data are given in Table 1.

The molecular and crystal structures of the six complexes were investigated using an automated CAD4 diffractometer, with a graphite monochromator and Mo Kα radiation $\lambda = 0.71073$ Å. The structures were solved by SIR-92 [9] and the refinements were carried out using SHELXL-97 [10]. All non-H atoms were anisotropically refined. Tables 2 and 3 give the pertinent data. Table 4 gives a summary of the most important bond distances and bond angles.

3. Results and discussion

All six complexes have the diphosphines chelated to the Ni atom, which also has, in addition, two halides or pseudo halides. Table 1 shows the spectroscopic data for the complexes. The halide complexes present NiX and NiP IR absorption bands in accordance with previous work for similar complexes [11]. Complex **IV**, $[Ni(dppe)(NCS)_2]$, shows IR absorptions in the ranges expected for N-bonded species [12], with an increase in ν_{CS}, as compared to KNCS, and a lowering in δ_{NCS}. The six complexes show a characteristic electronic transition in the visible region, as well as strong CT bands in the UV [13], as listed in Table 1. Table 1 also shows the $^{31}P\{^1H\}$ NMR chemical shifts in $CDCl_3$ solution as well as in the solid state for all the complexes and the free diphosphines. The spectrum of **I** in the solid state gave only one, somewhat broad absorption at δ 60.7, which in solution was shifted to δ 57.7. Previous results had shown $[Ni(dppe)Cl_2]CH_2Cl_2$ to absorb at δ 61.9 and 60.0 in the solid state, whereas in $CDCl_3$ it absorbed at δ 58.2 [8]. Interestingly, a sample of the complex obtained from the reaction of $(Et_4N)_2[NiCl_4]$ and dppe produced in the solid state NMR. absorptions at δ 60.9, 55.0 and 53.0, respectively. The latter two values correspond to the chemical shifts assigned to the unsolvated form,

Table 1
FTIR, electronic spectroscopy and $^{31}P\{^1H\}$ NMR data for the compounds under study

Compound	Selected IR absorptions (cm^{-1})					Electronic absorptions[a]		$^{31}P\{^1H\}$ NMR, δ (ppm)	
	ν_{CN}	ν_{CS}	δ_{NCS}	ν_{NiP}	ν_{NiX}	λ (nm)	ε, ($l\ mol^{-1}\ cm^{-1}$)	Solid state	$CDCl_3$ solution
$[Ni(dppe)Cl_2]CH_2Cl_2$ (**I**)				390	337	475	(1112)	60.7	57.7
					314	336	(13 896)		
						240	(13 042)		
$[Ni(dppen)]Cl_2$ (**II**)					337	464	(2398)	69.4	64.7
					314	279	(30 481)		
						232	(43 857)		
$[Ni(dppm)Br_2]CH_2Cl_2$ (**III**)					284	493	(1811)	−34.0	−22.5
					275	271	(16 037)		
						230	(29 170)		
$[Ni(dppe)(NCS)_2]$ (**IV**)	2091	842	462		330	436	(723)	65.9	60.3
	2092	822	454		304	257	(31 950)		
						234	(36 930)		
$[Ni(dppen)I_2]$ (**V**)				355		522	(4030)	87.4	87.3
				280		287	(42 170)		
						239	(45 600)		
$[Ni(dppp)Cl_2]CH_2Cl_2$ (**VI**)				365	347	464	(671)	4.8	35.2
					322	287	(13 992)		
						229	(19 705)		
dppe								−12.6	−12.1
dppen								−31.6	−22.7
dppm								−25.5	−21.8
dppp								−21.9	−16.6
KNCS[b]	2053	748	486						
			471						

[a] In CH_2Cl_2.

[b] Ref. [12].

Table 2
Crystal data and structure refinement for **I**, **II** and **III**

Complex	**I**	**II**	**III**
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$C2$	$P2_1/n$
Unit cell			
a (Å)	12.258(1)	15.524(3)	10.762(1)
b (Å)	15.403(3)	8.005(1)	20.468(1)
c (Å)	15.299(2)	12.455(1)	12.597(1)
β (°)	104.804(8)	124.628(9)	93.86(1)
V (Å^3)	2792.7(6)	1273.6(3)	2768.5(4)
Z, D_{calc} (Mg m^{-3})	4/1.458	2/1.372	4/1.650
μ (mm^{-1})	1.207	1.108	3.910
Crystal size (mm)	0.40 × 0.35 × 0.20	0.38 × 0.23 × 0.20	0.23 × 0.40 × 0.57
Theta range for data collection	2.32/27.4	3.0/30.0	2.4/28.1
Temperature (K)	293(2)	293(2)	293(2)
Index ranges	$-15 \le h \le 15$	$-21 \le h \le 17$	$0 \le h \le 14$
	$0 \le k \le 19$	$-11 \le k \le 0$	$0 \le k \le 27$
	$0 \le l \le 19$	$0 \le l \le 17$	$-16 \le l \le 16$
Reflections collected	6581	2061	7038
Reflections unique	6344	1980	6692
Reflections $I > 2\sigma(I)$	3322	1620	3180
R_{int}	0.055	0.018	0.055
Refined parameters	304	141	298
Goodness-of-fit	1.008	1.055	1.059
R $[I > 2\sigma(I)]$	$R_1 = 0.053$	$R_1 = 0.038$	$R_1 = 0.055$
	$wR_2 = 0.123$	$wR_2 = 0.095$	$wR_2 = 0.146$
R (all data)	$R_1 = 0.160$	$R_1 = 0.058$	$R_1 = 0.179$
	$wR_2 = 0.155$	$wR_2 = 0.105$	$wR_2 = 0.178$
$\Delta\rho$ (e A^{-3})	0.086/−0.713	0.584/−0.406	0.556/−0.594

Table 3
Crystal data and structure refinement for **IV**, **V** and **VI**

Complex	**IV**	**V**	**VI**
Crystal system	trigonal	monoclinic	orthorhombic
Space group	$P3_121$	$P2_1/n$	$Pnma$
Unit cell			
a (Å)	8.662(2)	8.7624(8)	12.238(1)
b (Å)		14.630(1)	15.239(1)
c (Å)	31.800(2)	20.278(1)	15.620(2)
β (°)		92.895(9)	
V (Å^3)	2066.30(7)	2596.2(1)	2913.1(5)
Z, D_{calc} (Mg m^{-3})	3/1382	4/1.814	4/1.430
μ (mm^{-1})	0.992	3.26	1.159
Crystal size (mm)	0.25 × 0.25 × 0.30	0.075 × 0.125 × 0.50	0.20 × 0.35 × 0.50
Theta range for data collection	2.7/29.4	2.5/30.0	2.5/26.3
Temperature (K)	273(2)	293(2)	293(2)
Index ranges	$0 \le h \le 10$	$-12 \le h \le 0$	$-14 \le h \le 15$
	$0 \le k \le 10$	$-21 \le k \le 0$	$-18 \le k \le 18$
	$-43 \le l \le 43$	$-28 \le l \le 28$	$-19 \le l \le 18$
Reflections collected	2520	8000	5483
Reflections unique	2237	7552	3073
Reflections $I > 2\sigma(I)$	1235	4948	2160
R_{int}	0.098	0.025	0.076
Refined parameters	159	281	164
Goodness-of-fit	1.026	1.012	1.012
R $[I > 2\sigma(I)]$	$R_1 = 0.046$	$R_1 = 0.034$	$R_1 = 0.038$
	$wR_2 = 0.103$	$wR_2 = 0.075$	$wR_2 = 0.103$
R (all data)	$R_1 = 0.121$	$R_1 = 0.085$	$R_1 = 0.062$
	$wR_2 = 0.124$	$wR_2 = 0.087$	$wR_2 = 0.110$
$\Delta\rho$ (e A^{-3})	0.362/−0.220	1.223/−0.794	0.485/−0.675

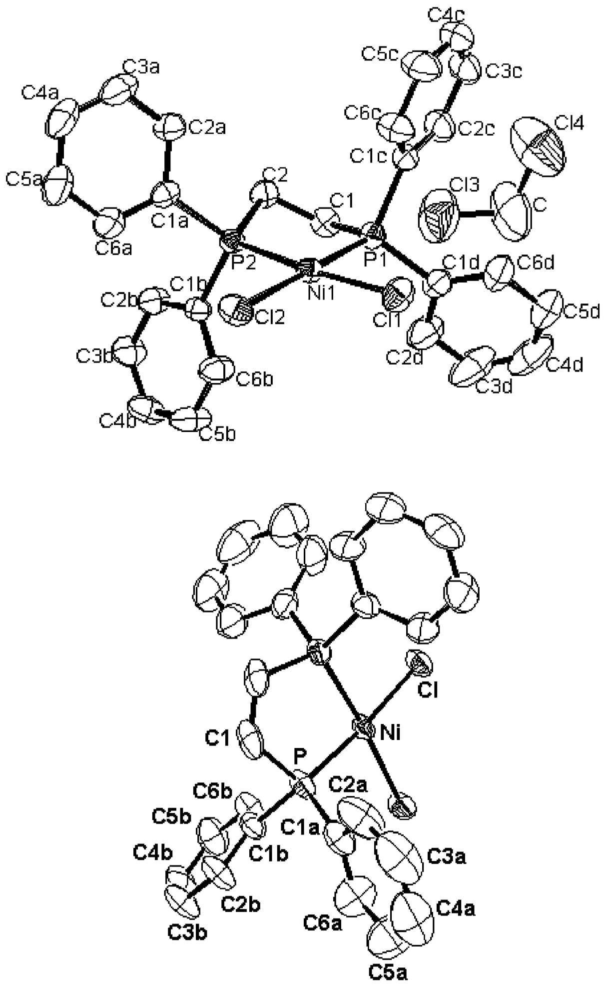


Fig. 1. Molecular structures of complexes **I** (top) and **II** (bottom).

namely [Ni(dppe)Cl_2] [8]. Table 1 shows that when one goes from the free ligands to the complexes the chemical shifts undergo a notable increase. Complexation deshields the phosphorus atoms considerably, due to a shift in the electron cloud to the region between phosphorus and the metal. It is interesting to note that the phosphorus nuclei in complex **VI** show a lesser chemical shift variation compared to the free ligand than the situation prevailing in the other complexes. This is likely to be related to the decreased strain and less π backbonding present in this complex, as the discussion of the molecular structures will show. The dppm complex, **III**, on the other hand, is the only one in which a decrease in δ was observed in solution as well as in the solid state on going from the free ligand to the complex. Our NMR data follow a trend similar to what has been observed in diphosphine organo-platinum complexes, in which the ring formed by the metal and the diphosphine greatly affects the phosphorus chemical shift values: [Me_2Pt(dppm)], δ -40.0; [Me_2Pt(dppe)], δ 54.5; [Me_2Pt(dppp)], δ 3.3 [14].

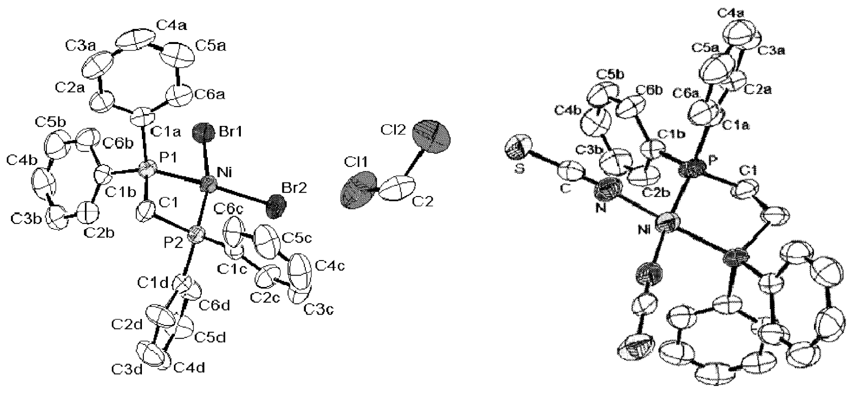
By far the most interesting results are those dealing with the structural data, given by the X-ray diffraction. Table 4 gives the most important bond lengths and bond angles of the complexes, and Figs. 1 and 2 show the molecular structures of complexes **I**–**VI**. The structures of complexes **I** [7,8,15] and **II** [7] are known and will be given here for comparison. All other structures are being reported for the first time.

All six complexes present an approximately square planar environment around the Ni atom. Complex **VI** is the only one to show P–Ni–P and X–Ni–X angles close to 90°, as expected. The ligand dppp has a longer chain and can be accommodated in the chelate structure without causing any great strain. All other complexes present an X–Ni–X angle considerably greater than 90°, and a P–Ni–P angle below 90°, which in the case of complex **III** is dramatically lowered to only 75.62°. This reflects the considerable strain posed by the four-membered ring which the Ni atom is constrained to form by dppm. The bond distance data also show a marked difference between **VI**, on the one hand, and the other complexes, on the other. If one compares the complexes with the Cl^- ligand, the Ni–Cl distances show only slight variations. Now if we take the Ni–P distances, those found for **VI**, 2.1791 Å, are higher than those for all other complexes. The longer carbon chain in dppp is likely to make this ligand to accept less π backbonding from the Ni atom than the other diphosphines, hence the longer Ni–P distances in **VI**. In complex **IV**, the N–C and C–S distances are quite in accordance with expected values for the N-bonded isothiocyanate ligand, and also in agreement with the results shown by the IR results given in Table 1.

It is quite interesting to look at the crystal arrangements of complexes **I**–**VI**. In spite of a certain regularity in their molecular structures, their packing in the crystalline state varies considerably, and is given in Figs. 3 and 4. These figures show the dppe and dppen complexes, i.e. **I**, **II**, **IV** and **V**, to form layered structures, whereas **III** forms lump-like clusters. The most interesting structure is that of **VI**, in which the layers present tubular arrangements for the phenyl rings.

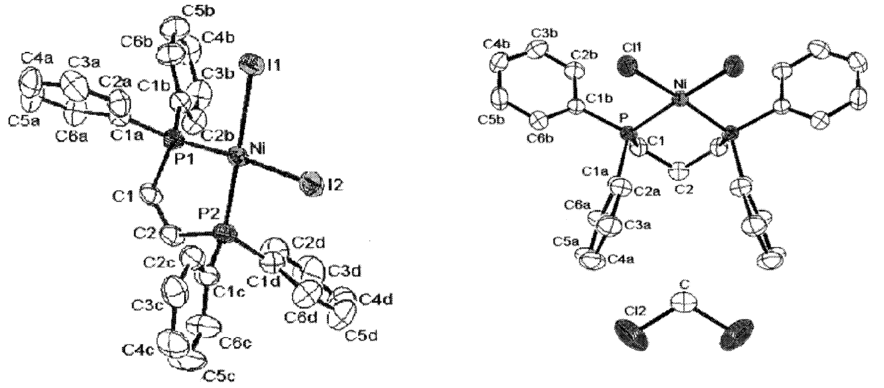
The molecular structure of the monoclinic complex [Ni(dppe)Cl_2], **I**, shows that the dihedral angle between rings **a** and **b** is 70.42°, whereas that between rings **c** and **d** is 63.53°. The presence of a solvent molecule is likely to contribute to this asymmetry, which is absent in the analogous [Ni(dppe)$(NCS)_2$] complex, **IV**. In the latter, the angles between the phenyl rings on each phosphorus is 59.46°. The crystal structure of the two complexes shows this difference markedly. Whereas **I** forms monoclinic crystals, the crystals of **IV** are trigonal.

The two dppen complexes, [Ni(dppen)Cl_2], **II**, and [Ni(dppen)I_2], **V**, are both monoclinic, but whereas **II** presents a higher molecular symmetry, with an angle of 59.46° between both sets of phenyl rings, **V**, possibly



III, [Ni(dppm)Br$_2$]CH$_2$Cl$_2$

IV, [Ni(dppe)(NCS)$_2$]



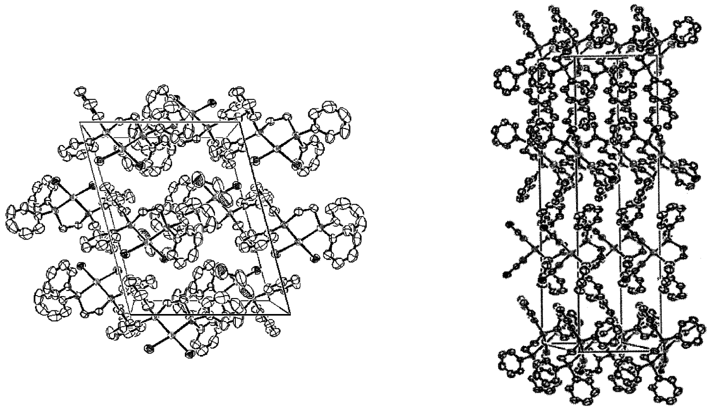
V, [Ni(dppen)I$_2$]

VI,[Ni(dppp)Cl$_2$]CH$_2$Cl$_2$

Fig. 2. Molecular structures of complexes **III**–**VI**.

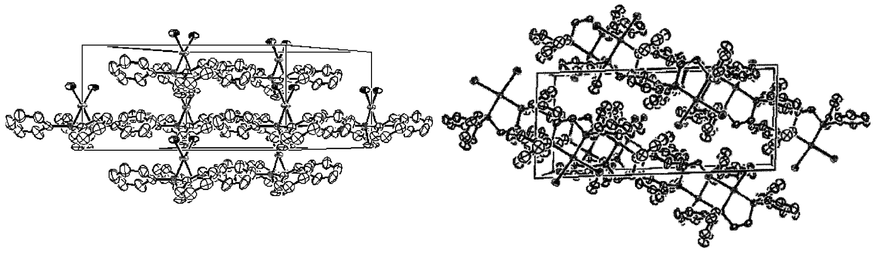
Table 4
Selected bond distances (Å) and angles (°) for complexes **I**–**VI**

	[Ni (dppe)Cl$_2$]CH$_2$Cl$_2$ (**I**)	[Ni(dppen)Cl$_2$] (**II**)	[Ni(dppm)Br$_2$]CH$_2$Cl$_2$ (**III**)	[Ni(dppe)(NCS)$_2$] (**IV**)	[Ni(dppen)I$_2$] (**V**)	[Ni(dppp)Cl$_2$]CH$_2$Cl$_2$ (**VI**)
Bond distances						
Ni–P(1)	2.145(1)	2.144(1)	2.143(2)	2.151(1)	2.1569(9)	2.1791(8)
Ni–P(2)	2.160(1)	2.144(1)	2.152(2)	2.151(1)	2.1632(10)	2.1791(8)
Ni–X(1)	2.208(1)	2.189(1)	2.335(1)	1.880(4)	2.5353(5)	2.1991(9)
Ni–X(2)	2.200(1)	2.189(1)	2.324(1)	1.880(4)	2.5184(5)	2.1991(9)
P(1)–C(1)	1.841(4)	1.799(4)	1.847(8)	1.831(5)	1.808(3)	1.827(3)
P(2)–C(2)	1.826(4)	1.799(4)	1.852(2)	1.831(5)	1.808(4)	1.827(3)
C(1)–C(2)	1.505(6)	1.314(3)	–	1.47(1)	1.320(5)	1.515(4)
N–C	–	–	–	1.149(6)	–	–
C–S	–	–	–	1.609(6)	–	–
Bond angles						
P(1)–Ni–P(2)	86.99(5)	86.71(7)	75.62(8)	86.99(7)	87.81(4)	91.77(4)
P(1)–Ni–X(1)	88.78(5)	86.71(7)	91.90(7)	89.2(1)	89.69(3)	88.705(6)
P(1)–Ni–X(2)	175.11(5)	174.52(5)	169.98(8)	176.1(1)	174.60(3)	175.28(4)
P(2)–Ni–X(1)	175.29(5)	174.52(5)	165.76(7)	176.1(1)	176.76(3)	175.28(4)
P(2)–Ni–X(2)	88.92(5)	87.82(4)	95.59(6)	89.2(1)	88.29(3)	88.705(6)
X(1)–Ni–X(2)	95.41(5)	97.65(6)	97.37(5)	94.6(3)	94.341(16)	90.82(5)
P(1)–C(1)–P(2)	–	–	90.8(3)	–	–	–
C–N–Ni	–	–	–	167.1(5)	–	–
N–C–S	–	–	–	178.2(5)	–	–



I, [Ni(dppe)Cl_2]CH_2Cl_2

IV, [Ni(dppe)$(NCS)_2$]



II, [Ni(dppen)Cl_2]

V, [Ni(dppen)I_2]

Fig. 3. Crystal packing of complexes **I**, **II**, **IV** and **V**.

because of distortion due to the larger iodide ligands, shows angles of 70.14° between rings **a** and **b** and 56.35° between rings **c** and **d**. They also pack quite distinctly in the crystals: while the more symmetric complex **II** shows all the Cl atoms sticking towards the same direction, **V** shows an alternation amongst the Cl atoms.

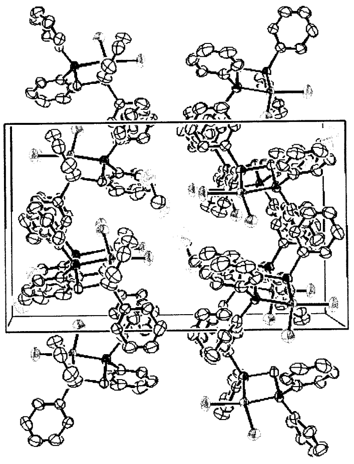
Complexes **III**, [Ni(dppm)Br_2]CH_2Cl_2, and **VI**, [Ni(dppp)Cl_2] CH_2Cl_2, form monoclinic and orthorhombic crystals, respectively. The former shows an asymmetry in the molecular arrangement due to the position of the solvate molecule. As a consequence, the phenyl rings in **III** have angles of 70.14° (rings **a** and **b**) and 56.35° (rings **c** and **d**). Complex **VI**, on the other hand, is very symmetric regarding both the molecular as well as the crystal structure. The position occupied by the CH_2Cl_2 solvate molecule is such that the angles between the two sets of phenyl rings are the same (86.54°).

4. Conclusion

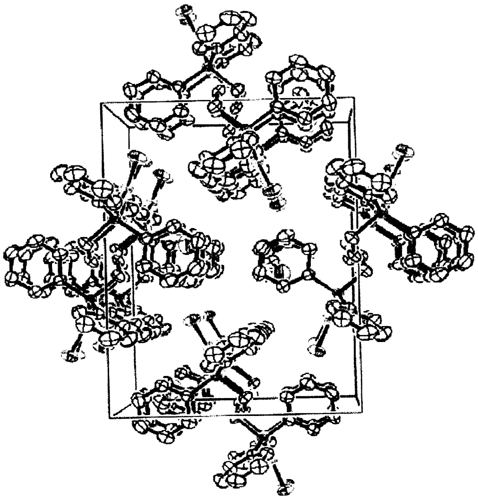
This work showed that homologous Ni(II) diphosphine complexes, in spite of their similarities, differ in several aspects of their molecular geometry, and that differences in their crystalline arrangement are even more marked, possibly leading to quite different properties in the solid state. This was shown especially in complexes **III** and **VI**, for which the solid state arrangements deviate considerably from those of their counterparts (**I**, **II**, **IV** and **V**), as given by the crystallographic data and the solid state ^{31}P NMR results. Therefore caution should be exerted when comparing data obtained for a series of apparently similar complexes. In addition to solution data and molecular structures, a knowledge of the packing of individual molecules, as this study showed, can lead to important differences which may be reflected in the chemistry of the compounds.

5. Supplementary data

Crystallographic data for the complexes have been deposited at the Cambridge Crystallographic Data Centre. The CCDC numbers are 188923 for complex **I**, 188924 for complex **II**, 189328 for complex **III**, 188926 for complex **IV**, 188925 for complex **V** and 189327 for complex **VI**. The copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).



III, [Ni(dppm)Br_2]CH_2Cl_2



VI, [Ni(dppp)Cl_2]CH_2Cl_2

Fig. 4. Crystal packing of complexes **III** and **VI**.

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