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The reaction of the P_2N_2 Schiff base ligand en=P_2 with MI_2 salts and the reaction of the tetraiodine adduct of en=P_2 with unactivated coarse grain metal powders: a comparative study (en=P_2=*N,N'*-bis[(*o*-diphenylphosphino)benzylidene]ethylenediamine; M=Mn, Co and Ni)

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Abstract

The reaction of the N_2P_2 donor set Schiff base ligand en=P_2 with metal salts MI_2 (M=Mn, Co and Ni) produces compounds of stoichiometry M(en=P_2)I_2. Single crystal X-ray diffraction studies have shown the nickel complex to be five-coordinate [Ni(en=P_2)I]I and to have a square pyramidal structure. This complex appears to exist in a spin-crossover state, $\mu_{eff}=2.35$ μ_B. The analogous cobalt complex has been shown by X-ray powder diffraction to be isostructural with the nickel complex, but is low spin, $\mu_{eff}=2.40$ μ_B. Reaction of en=P_2 with two equivalents of diiodine in dry diethyl ether produces an adduct of stoichiometry (en=P_2)I_4. Solution $^{31}P\{H\}$ NMR studies in $CDCl_3$ indicate one phosphorous environment, $\delta=53.4$ ppm. Addition of two further equivalents of diiodine to this compound in $CDCl_3$ results in no change in the ^{31}P chemical shift, implying that (en=P_2)I_4 exists as the ionic $[(en{=}P_2)I_2]^{2+}2I^-$ in $CDCl_3$ solution. The solid state Raman spectrum of (en=P_2)I_4 shows a strong band at 154 cm^{-1} which is assigned to ν(P–I). Another band is observed at 111 cm^{-1}, which has been tentatively assigned to ν(I–I) indicating that the compound may exist as a molecular charge transfer adduct in the solid state. This tetraiodophosphorous adduct reacts with Mn, Co and Ni coarse grain metal powders to form compounds of stoichiometry M(en=P_2)I_4. The cobalt and nickel complexes have been shown to be isostructural by X-ray powder diffraction methods. Bands in the UV–Vis spectrum at ~293 nm and at 364 nm indicate the presence of the I_3^- ion, which we believe indicates that these compounds adopt a five coordinate geometry analogous to the [M(en=P_2)I]I compounds of [M(en=P_2)I]I_3. This is further supported by the room temperature magnetic moment of [Co(en=P_2)I]I_3 of 3.8 μ_B consistent with a high spin five-coordinate cobalt(II) centre which is in complete contrast to that observed for [Co(en=P_2)I]I. This further highlights the ability of dihalogen adducts of tertiary phosphines to react with coarse grain unactivated metal powders to generate products not attainable by conventional means.

Keywords: Crystal structures; Nickel complexes; Schiff base complexes; Manganese complexes; Cobalt complexes

1. Introduction

Dihalogen adducts of tertiary phosphines have received considerable attention, both for their intrinsic interest, since they represent ubiquitous reagents in chemistry [1], and for their use in organic syntheses [2]. Recent work has demonstrated that three distinct structural motifs are available for such adducts, viz. the molecular trigonal bipyramidal structure [3], the ionic [R_3PX]X which predominates in solution [4], and the very recently established molecular four coordinate 'spoke' charge transfer adduct R_3P–X–X [5].

A range of R_3PX_2 (R=alkyl, aryl; X=Br, I) have been shown to act as powerful oxidising agents capable, for example, of reacting with completely unactivated coarse grain metal powders to give a wide variety of tertiary phosphine complexes of transition [6] and main group metals [7], viz. known metal complexes, novel isomers of known complexes [8], complexes of metals in mixed oxidation states [9], one-step oxidations from

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the crude metal powder to nickel(III) [10] and the formation of, for example, complexes such as $Co(SbPh_3)_2I_3$ [11], a hard cobalt(III) ion coordinated by five extremely soft donor atoms in contravention of the SHAB principle.

However, in contrast to the investigations of the synthesis and subsequent use of the dihalogen adducts of monotertiary phosphines, analogous investigations of ditertiary phosphines are almost non-existent. Some adducts have been reported, but no attempt was made to characterise these species [12]. Furthermore, no dihalogen adducts of mixed-donor chelating ligands have been synthesised, despite the wide use of these ligands in coordination chemistry, especially in their ability to stabilise metal ions in a wide variety of geometries and oxidation states [13].

We felt that by taking a known N_2P_2 donor ligand, and then reacting diiodine with this, a reagent capable of opening a new area of coordination chemistry might be generated. We chose the diiminophosphine ligand *N*,*N*′-bis[(*o*-diphenylphosphino)benzylidene]ethylenediamine, $en{=}P_2$, which is itself known to form complexes of nickel, copper and silver [14]. From spectroscopic and X-ray crystallographic data it appears that this is a most versatile ligand, being capable of acting as a tetradentate species in tetrahedral, square planar or square pyramidal complexes, but can also act as a tridentate ligand either in the PNP or PNN donor mode. Hence the combination of the $en{=}P_2$ ligand, with its variety of donor modes, and the potential of further investigating the reactivity of the tetraiodine adduct, $(en{=}P_2)I_4$, was of interest.

2. Results and discussion

This paper presents three phenomena: (i) the isolation and characterisation of the tetraiodine adduct of $en{=}P_2$, i.e. $(en{=}P_2)I_4$; (ii) the reaction of the native ligand $en{=}P_2$ with the iodide salts of divalent manganese, cobalt and nickel; (iii) the reaction of $(en{=}P_2)I_4$ with coarse grain metallic manganese, cobalt and nickel. Clearly, a comparison of the products of the reactions of systems (ii) and (iii) is of interest.

2.1. Synthesis of $(en{=}P_2)I_4$

The diiminophosphine, $en{=}P_2$, was prepared as previously reported [14] and reacted with diiodine in diethyl ether in a 1:2 ratio to produce a mustard coloured solid of stoichiometry $(en{=}P_2)I_4$. The $^{31}P\{H\}$ NMR spectrum of $(en{=}P_2)I_4$ in $CDCl_3$ solution consists of a single band at 53.4 ppm. The addition of two further equivalents of diodine to $(en{=}P_2)I_4$ resulted in the formation of the ionic adduct $[(en{=}P_2)I_2]^{2+}2I_3^-$. The ^{31}P chemical shift exhibited by this compound in $CDCl_3$ is identical to that of $(en{=}P_2)I_4$ in $CDCl_3$, thus implying that $(en{=}P_2)I_4$ exists as the ionic $[(en{=}P_2)I_4]^{2+}2I^-$ in $CDCl_3$ solution.

The solid state Raman spectrum of $(en{=}P_2)I_4$ exhibits a strong band at 154 cm^{-1} which is assigned to ν(P–I). Another strong band is also observed at 111 cm^{-1}, which may be tentatively assigned to ν(I–I), implying that this compound may exist as a molecular charge transfer adduct in the solid state. Without X-ray crystallographic or solid state ^{31}P NMR data, it is difficult, however, to assign a particular solid state structure to $(en{=}P_2)I_4$ on the basis of Raman data alone.

2.2. Reaction of $(en{=}P_2)$ with MI_2 salts ($M{=}Mn$, Co, Ni)

The transition metal salts MnI_2, CoI_2 and NiI_2 were reacted with $en{=}P_2$ in an equimolar ratio in acetonitrile under anaerobic and anhydrous conditions. In all cases the stoichiometric product $M(en{=}P_2)I_2$ was formed as brown (M = Co), black (M = Ni) or orange (M = Mn) crystalline materials, see Table 1. All of these products show remarkable stability to air and moisture; particularly surprising is the stability of $Mn(en{=}P_2)I_2$, which is stable on the bench for a period of several days, although decomposition in 'wet' acetonitrile is extremely rapid. This is further highlighted by the results of FAB (FAB = fast atom bombardment); peaks have been assigned using ^{55}Mn, ^{59}Co, ^{58}Ni and ^{127}I, all values stated for the fragments given correspond to the calculated values. All complexes exhibit parent ion peaks corresponding to the fragment $M(en{=}P_2)I^+$ $[Mn(en{=}P_2)I]$-H^+ $m/z=787$, 51%; $[Co(en{=}P_2)I]^+$ $m/z=790$, 93%; $[Ni(en{=}P_2)I]^+$ $m/z=789$, 52%; fragments corresponding to $M(en{=}P_2)$ are observed for cobalt and nickel (Co $m/z=664$, 27%; Ni $m/z=662$, 35%); and a fragment corresponding to $Co_2(en{=}P_2)I_3^+$ is also observed at $m/z=1707$. Structural information can be tentatively deduced from this data. As all of the $M(en{=}P_2)I_2$ complexes show parent ions corresponding to the loss of one iodide ion it may be postulated that this ion is non-coordinated, whilst the second iodide ion is bound to the metal leading to the higher percentage of the $M(en{=}P_2)I^+$ fragment over $M(en{=}P_2)^{2+}$ fragments.

This hypothesis is further supported by X-ray studies on the complexes. Single crystal X-ray diffraction studies of $Ni(en{=}P_2)I_2$, Fig. 1, show it to consist of an axially elongated square pyramidal nickel(II) cation with an axial iodine atom and an I^- counterion; Ni–N = 1.98 Å (av.) and Ni–P = 2.21 Å (av.) bond distances are comparable with those observed in the pnnp complex [Ni(pnnp)Br]Br of 2.00(2) and 2.21(2) Å, respectively, in which axial elongation occurs towards the coordinated iodine atom (pnnp = *N*,*N*-bis-(2-diphenylphosphinoethyl)-*N*-(2-ethylaminomethyl)amine) [15]. Bond lengths

Table 1
Analytical data for the complexes

Compound	Elemental analysis [a]					μ_{eff}	ν(C=N) (cm^{-1})	λ_{max} (nm)
	C	H	N	I	P			
(en=P$_2$)I$_4$	43.9(43.2)	3.1(3.1)	2.5(2.5)	45.9(45.7)			1627 [b]	
[Mn(en=P$_2$)I]	52.3(52.6)	3.5(3.7)	3.4(3.1)	27.7(27.8)		5.91	1620 [c]	
[Co(en=P$_2$)I]I	52.5(52.5)	4.0(3.7)	3.4(3.1)	25.8(27.7)		2.40	1628 [c]	391(253.5)
[Ni(en=P$_2$)I]I	52.1(52.5)	3.4(3.7)	3.0(3.1)	25.9(27.7)		2.35	1628 [c]	421(1036) 490(sh) (625)
[Mn(en=P$_2$)I]I$_3$	41.2(41.2)	3.1(2.9)	2.5(2.4)	43.3(43.5)		6.01		
[Co(en=P$_2$)I]I$_3$	41.4(41.0)	3.1(2.9)	2.5(2.4)	42.0(43.4)		3.80	1626 [b]	764.0 724(247.7) 701.0 661.5
[Ni(en=P$_2$)I]I$_3$	41.5(41.0)	2.7(2.9)	2.5(2.4)		5.1(5.3)			

[a] Theoretical values in parentheses.
[b] Raman.
[c] Infrared.

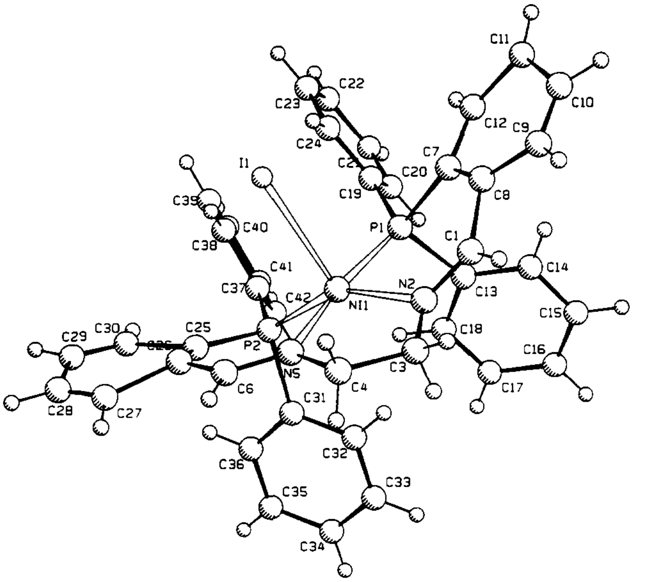

Fig. 1. A Pluto plot of the X-ray crystal structure of the [Ni(en=P$_2$)I]$^+$ cation.

Table 2
Selected bond lengths (Å) and angles (°) for [Ni(en=P$_2$)]I

Ni(1)–N(2)	2.02(5)
Ni(1)–N(5)	1.94(4)
Ni(1)–P(1)	2.20(1)
Ni(1)–P(2)	2.21(1)
Ni(1)–I(1)	2.807(6)
P(1)–Ni(1)–P(2)	98.2(5)
P(1)–Ni(1)–N(2)	86(2)
P(1)–Ni(1)–N(5)	172(1)
P(2)–Ni(1)–N(2)	149(1)
P(2)–Ni(1)–N(5)	86(1)
N(2)–Ni(1)–N(5)	86(2)
N(2)–Ni(1)–I(1)	106(1)
N(5)–Ni(1)–I(1)	90(1)
P(1)–Ni(1)–I(1)	94.9(4)
P(2)–Ni(1)–I(1)	103.5(4)

and angles are given in Table 2. Comparison of the X-ray powder diffraction patterns of M(en=P$_2$)I$_2$ (M=Co, Ni) shows them to be isostructural, Fig. 2; whilst the powder diffraction pattern of Mn(en=P$_2$)I$_2$ differs from those of the nickel and cobalt complexes.

IR data are consistent with the type of coordination observed by X-ray methods, with all metal complexes showing a shift in the imine stretch from the free ligand (ν(C=N)=1634 cm^{-1}) to lower frequency, consistent with M–N coordination (ν(CN)=1620 cm^{-1}, Mn; 1628 cm^{-1}, Co; 1628 cm^{-1}, Ni).

Room temperature magnetic moments of the metal complexes are consistent with the proposed five-coordinate geometries. That of Co(en=P$_2$)I$_2$ is 2.4 μ_B,

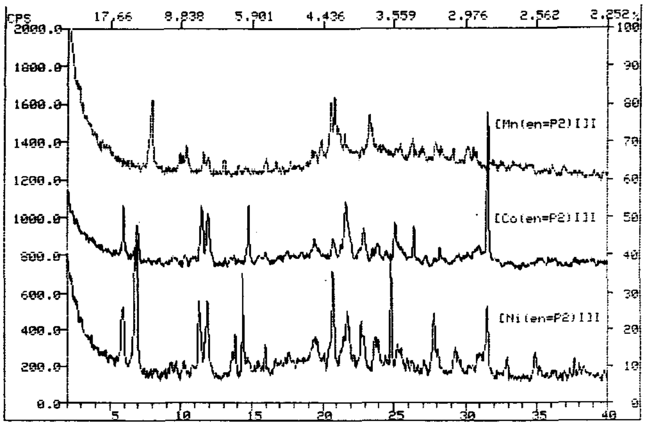

Fig. 2. The X-ray powder diffraction patterns of: (a) [Mn(en=P$_2$)I]I; (b) [Co(en=P$_2$)I]I; (c) [Ni(en=P$_2$)I]I.

consistent with a low-spin five coordinate cobalt(II) complex, whilst that of $Ni(en{=}P_2)I_2$ is 2.35 μ_β. The values reported for other high-spin square-pyramidal complexes of nickel(II) indicate that a magnetic moment in the range 3.2–3.4 μ_β is expected for this geometry [16]. The observed value of 2.35 μ_β in the complex indicates that there may be a spin-state equilibrium. This effect indicates that the N_2P_2 donor set leads to complexes on the spin-crossover border for nickel, since low-spin complexes have previously been reported for this type of geometry and donor set [17]. Such behaviour has also previously been reported for cobalt [18]. The room temperature magnetic moment of the manganese complex is 5.9 μ_β which is the value expected for a magnetically dilute high-spin d^5 system. As there is no CFSE and no particular stereochemistry is preferred, it is not unreasonable to propose that the complex $Mn(en{=}P_2)I_2$ is isostructural with its cobalt and nickel analogues, and that the differences in the X-ray diffraction powder pattern may be due to the difference in the size of the manganese ion rather than any structural differences.

2.3. *Reaction of $(en{=}P_2)I_4$ with manganese, cobalt and nickel coarse grain unactivated metal powders*

The tetraiodophosphorus compound, $(en{=}P_2)I_4$, was reacted in a 1:1 ratio with the coarse grain metal powders, Mn, Co and Ni, in diethyl ether under strictly anhydrous and anaerobic conditions. The resultant yellow (M = Mn, Co) and orange (M = Ni) solids were found to have the stoichiometry $M(en{=}P_2)I_4$, see Table 1. The compounds from this reaction route are much more sensitive to air and moisture than those produced by the reaction of $en{=}P_2$ with the MX_2 salts. As a result of this sensitivity to air and moisture, we have been unable to observe any meaningful fragments by mass spectral analysis, relating to complexes of the form $M(en{=}P_2)I_4$. However, fragments relating to the oxidised complexes containing the diphosphine dioxide ligand are observed, including the base peak $m/z = 637$, 100% corresponding to $[en{=}P_2O_2]H^+$. Other peaks of interest include $m/z = 695$, 30%, $Co(en{=}P_2O_2)$; 822, 90% $Co(en{=}P_2O_2)I$; $m/z = 821$, 10% $Ni(en{=}P_2O_2)I$; and $m/z = 818$, 10% $Mn(en{=}P_2O_2)I$. The presence of strong bands in the UV–Vis spectrum of each of the complexes at ~293 nm and a slightly weaker band at 364 nm are indicative of the presence of the I_3^- ion [19]. We believe that the observation of the free I_3^- ion in solution together with the observation of coordinated iodide in all mass spectra indicate that these compounds adopt the five coordinate geometry $[M(en{=}P_2)I]I_3$ analogous with the complexes $[M(en{=}P_2)I]I$.

The IR spectra of the $[M(en{=}P_2)I]I_3$ compounds show an absence of any imine band in the range 1600–1630 cm^{-1}. However, the $\nu(C{=}N)$ stretch is observed in the Raman spectrum of $[Co(en{=}P_2)I]I_3$ at 1626 cm^{-1} (cf. 1636 cm^{-1} for the free ligand) indicating the presence of this bond. No Raman data could be obtained for the manganese and nickel complexes due to strong fluorescence bands. X-ray powder diffraction indicates that the samples $[Co(en{=}P_2)I]I_3$ and $[Ni(en{=}P_2)I]I_3$ are isostructural. As with the $[M(en{=}P_2)I]I$ compounds the powder pattern of the manganese complex $[Mn(en{=}P_2)I]I_3$ differs from those of the nickel and cobalt complexes.

We have been unable to measure meaningful magnetic data for the complexes $[Co(en{=}P_2)I]I_3$ and $Ni(en{=}P_2)I]I_3$ due to a trace quantity of unreacted metal powder. However, the product from the reaction of $Co_2(CO)_8$ with $en{=}P_2I_4$ produces a compound shown by X-ray diffraction to be isostructural with that from the metal powder route. The room temperature moment of this compound is 3.8 μ_β consistent with a high-spin five coordinate cobalt(II) structure. It may be possible that the spin state of the cation could be influenced by the anion. If the compounds have the formulation $[M(en{=}P_2)I_3]I$, rather than $[M(en{=}P_2)I]I_3$ it is possible that a different five-coordinate geometry could arise, and hence different magnetic properties. However, we believe that the complexes possess the same five-coordinate geometry $[M(en{=}P_2)I]^+$ as those produced by conventional means. The room temperature magnetic moment of $[Mn(en{=}P_2)I]I_3$ is 6.01 μ_β. This value is slightly higher than would be expected for high-spin magnetically dilute d^5 manganese(II) although this value may also be due to the presence of a trace of unreacted manganese. The failure to obtain meaningful magnetic data for $[Ni(en{=}P_2)I]I_3$ is disappointing, although it is likely that like complex $[Ni(en{=}P_2)I]I$ it lies on the spin cross over border [1].

3. Conclusions

The reaction of $en{=}P_2$ with MI_2 salts (M = Mn, Co, Ni) leads to five-coordinate compounds of the stoichiometry $[M(en{=}P_2)I]I$, which show remarkable stability to air and moisture. The reaction of $en{=}P_2I_4$ with the corresponding unactivated coarse grain metal powders appears to produce compounds isostructural to those produced from the more conventional synthetic

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[1] A referee has suggested that the higher magnetic moment of 3.8 μ_β for $[Co(en{=}P_2)I]I_3$ may be due to phosphine oxide contamination. The weak field N_2O_3 donor set of the diphosphine-dioxide ligand $(en{=}P_2O_2)$ would indeed be expected to give high-spin complexes. However, the complete absence of bands in the infrared spectra that are assignable to $\nu(P{=}O)$ in all complexes, indicates that this is not the case. This indicates that the spin-state change is a direct result of this alternative synthetic route.

route of reacting the ligand with the MI_2 salt. However, these compounds are much more sensitive to air and moisture. Interestingly, the compound $[Co(en{=}P_2)I]I_3$ exists in a high-spin state whilst $[Co(en{=}P_2)I]I$ exists in a low-spin state, highlighting the ability of this alternative synthetic route to generate products not attainable by conventional means.

4. Experimental

All compounds are to varying degrees sensitive to air and moisture. Consequently strictly anaerobic and anhydrous conditions were adhered to during the synthesis of the complexes. Anhydrous MnI_2 was prepared by the thermal dehydration of $MnI_2 \cdot 4H_2O$ (Ross Chemicals) by progressive heating to 120 °C in vacuo over a period of ~7 days. After Karl-Fischer water analysis indicated $<0.03\%$ H_2O the salt was stored under nitrogen. CoI_2 and NiI_2 (STREM) were used as received and stored under nitrogen. en$=P_2$ was prepared as previously reported [14]. Diethyl ether was stored over sodium wire for 1 day and then distilled over CaH_2. Acetonitrile (HPLC grade, Aldrich) was distilled over CaH_2. Solvents were subsequently distilled directly into the pre-dried reaction vessel.

All manipulations were carried out using standard vacuum line and Schlenk techniques inside a Vacuum Atmospheres HE-493 glove box (argon atmosphere of <100 ppm dioxygen). All glassware was heated to 200 °C for ~1 day before being transferred, hot, to the glove box.

4.1. Preparation of $(en{=}P_2)I_4$

en$=P_2$ (0.30 g, 0.50 mmol) was added to a 100 cm^3 rotaflo tube to which dry degassed Et_2O (50 cm^3) has been added. I_2 (0.25 g, 1.00 mmol) was then added resulting in the rapid precipitation of a yellow solid. The solution was stirred at room temperature for 2 days before separation by filtration.

4.2. Preparation of metal complexes $[M(en{=}P_2)I]I$

Analogous preparations were adopted for all metal salts which is typified by that used for manganese. Anhydrous MnI_2 (0.19 g, 0.62 mmol) was added to a 100 cm^3 rotaflo tube to which dry degassed CH_3CN (50 cm^3) and (en$=P_2$) (0.375 g, 0.62 mmol) were then added. The sealed vessel was heated to 60 °C for 48 h with stirring and then allowed to cool slowly, producing a microcrystalline product which was isolated by filtration.

4.3. Preparation of metal complexes $[M(en{=}P_2)I]I_3$

Analogous preparations were adopted for all metal powders typified by that used for manganese. Coarse grain unactivated manganese powder (0.018 g, 0.33 mmol) was added to a 100 cm^3 rotaflo tube to which dry degassed Et_2O (50 cm^3) and $(en{=}P_2)I_4$ (0.36 g, 0.33 mmol) were then added. The sealed vessel was stirred for 14 days. The resulting yellow precipitate was collected by filtration.

4.4. Physical measurements

Elemental analyses and FAB mass spectra were performed by the inhouse services at UMIST. $^{31}P\{H\}$ NMR measurements were made on a Brüker AM200 high resolution multiprobe NMR spectrometer. IR spectra were recorded on a Nicolet 5PC FT-IR spectrophotometer. Magnetic moments were measured on an Oxford Instruments Faraday balance with a 4″ electromagnet employing a CI Robal Microbalance and an Oxford Instruments ITC4 temperature controller. X-ray powder diffraction patterns were recorded using a Scintag XRD200 powder diffractometer, using Cu Kα radiation of $\nu = 1.5418$ Å. Electronic spectra were obtained in CH_3CN on Shimadzu UV-2101PC UV–Vis scanning spectrophotometer.

Raman spectra were recorded using a Coherent Innova 90 argon-ion laser and a SPEX1403 0.85 m focal length, double monochromator fitted with a BGCS microscope sampling attachment. Radiation was detected with a Hammamatsu R928 photomultiplier tube, cooled to 30 °C by a Products for Research Inc. T.E. 177 RF-005 cooler housing. The data was processed using a SPEX DM1B data station.

4.5. Single crystal X-ray studies

A suitable crystal was mounted in a Lindeman tube under dry argon. All measurements were performed on a Rigaku AFC6S diffractometer using graphite monochromated Mo Kα radiation. Details of the data collection and structure refinement are presented in Table 3. The structure was solved using SHELX 86 [20] and all other calculations were performed using the TEXSAN [21] suite of computer programs. The material crystallised as very thin plates, which due to their instability had to be handled in a glove box under argon.

After several attempts at placing a single crystal in a Lindeman tube we succeeded in wedging a thin plate in a 0.4 diameter tube. Unfortunately the thinness of the crystal reduced the number of observed reflections and led to absorption problems. This problem was compounded by pseudo-symmetry (the cation is very nearly mirror symmetric with respect to the *ac* plane).

Table 3
Crystal data and details of refinement for $[Ni(en{=}P_2)I]I$

Formula	$C_{40}H_{34}P_2N_2NiI_2$
M	917.18
Crystal system	monoclinic
Space group	$P2_1/c$ (No. 14)
a (Å)	9.449(4)
b (Å)	18.212(6)
c (Å)	25.834(8)
β (°)	95.26(4)
U (Å^3)	4427
Z	4
D_c (g cm^{-3})	1.376
F(000)	1808
μ (cm^{-1})	19.16
Crystal size (mm)	0.40×0.40×0.025
Maximum 2θ (°)	50
Total data measured	8425
No. unique reflections	7855
No. observed reflections ($F_o > 3\sigma(F_o)$)	694
No. parameters	167
P_{min}, P_{max} (e Å^{-3})	−0.56, 0.91
Maximum least-squares	0.1
Weighting scheme parameter g in $w = 1/[\sigma_2(F)+gF_2]$	0.005
Final R	0.091
Final R'	0.109

An absorption correction was applied using the azimuthal scan technique (maximum, minimum transmission 1, 0.79).

5. Supplementary material

Full tables of bond distances and angles, anisotropic thermal parameters, hydrogen atom coordinates, and observed and calculated structure factors are available from the authors on request.

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