Inorganica Chimica Acta, 10 (1974) 197–202

Bidentate Group VB Chelates. Part VI. Four- and Five-Coordinate Nickel(II) Complexes of Bisdiphenylphosphinomethane[1]

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Received January 31, 1974

Bisdiphenylphosphinomethane, dpm, forms diamagnetic square-pyramidal [Ni(dpm)$_2$X]Y (X = Cl, Br, I, NCS, NO$_2$; Y = ClO$_4$, BPh$_4$) in which the ligand chelates to the metal. The [Ni(dpm)$_2$(NCS)$_2$] complex is square-planar and contains mono-dentate dpm ligands, while [Ni(dpm)$_2$*(CN)*]*CN is square-planar and contains one bidentate dpm and one monodentate dpm ligand. There is evidence that in solution [Ni(dpm)$_2$I]$^+$ becomes four-coordinate. The recent suggestion that [Ni(dpm)(NCS)$_2$]$_2$ is pentacoordinate has led us to re-examine the available spectroscopic evidence and suggest an alternative structure to this complex. The structures of the complexes are discussed in the light of their visible and infrared spectra.*

Introduction

There have been a number of studies of nickel(II) complexes of ditertiary phosphines. Isslieb and Hohlfeld[2] prepared [Ni{(C$_6$H$_{11}$)$_2$P(CH$_2$)$_n$P(C$_6$H$_{11}$)$_2$}Br$_2$] (n = 3,4,5); Chatt and Hart[3] synthesised [Ni(dpe)Cl$_2$] (dpe = 1,2-bisdiphenylphosphinoethane) and [Ni{*o*-C$_6$H$_4$[P(C$_2$H$_5$)$_2$]}X$_2$] (X = Cl, Br, I); and Wymore and Bailar[4] reported [Ni(dpe)X$_2$], [Ni(dpe)$_2$](ClO$_4$)$_2$, and Ni(dpe)Br$_3$. Van Hecke and Horrocks[5] have published a fairly thorough study of the Ni(II) and Ni(III) complexes Ni{(C$_6$H$_5$)$_2$P(CH$_2$)$_n$P(C$_6$H$_5$)$_2$}$_m$X$_2$ (m = 1, n = 2,3, x = Cl, Br, I; m = 2, n = 1,2, X = Cl, Br, I) and Ni{(C$_6$H$_5$)$_2$P(CH$_2$)$_n$P(C$_6$H$_5$)$_2$}Br$_3$ (n = 2,3). The [Ni(dpp)X$_2$] (dpp = 1,3-bisdiphenylphosphinopropane) complexes exhibit a square-planar (diamagnetic) $\rightleftharpoons$ tetrahedral (paramagnetic) equilibrium in solution in contrast to the corresponding diphosphine (dpe), where the phosphorus atoms are linked by only a two-carbon chelate chain, which remain diamagnetic in solution.

We have previously investigated nickel(II) complexes formed with *cis*-1,2-bisdiphenylphosphinoethylene (vpp) and in this study also it seemed that the chelate chain was an important factor in determining compound structure and stoichiometry.[6] Both planar [Ni(vpp)X$_2$] (X = Cl, Br, I, NCS) and square-pyramidal [Ni(vpp)$_2$X]$^+$ (X = Cl, Br, I) complexes were isolated, whereas it has been found impossible to form pentacoordinate complexes between nickel(II) halides and dpe.[6,7] This was attributed to the differing steric requirements of vpp and dpe.[6]

We have now become interested in the chelating properties of the diphosphine bisdiphenylphosphinomethane, dpm. A metal chelate of dpm involves a rather unstable four-membered ring, with $\widehat{\mathrm{P{-}M{-}P}} \leqslant 90°$. Early work with dpm indicated that the ligand generally acted as a monodentate donor in Ni(dpm)$_2$X$_2$ (X = Cl, Br, I) complexes,[5,7] and this was attributed to the strained nature of the four-membered ring which would result upon chelation. It has been considered that chelation does occur in [Ni(CO)$_2$(dpm)][8] and [Ni(dpm)$_2$],[9] and Chatt, *et al.*[10] chelated dpm to palladium and platinum in the zerovalent state. In order to reduce competition between the unchelated phosphorus and anionic donors towards nickel, Foglemen and Jonassen[11] used poorly coordinating anions such as nitrate, perchlorate, and tetrafluoroborate and obtained the planar [Ni(dpm)$_2$]Y$_2$ (Y = NO$_3$, ClO$_4$, BF$_4$).

Recently, Ercolani, Quagliano, and Vallarino[12] have reported their thorough investigation of the interaction of nickel(II) salts with dpm, which includes the monomeric planar [Ni(dpm)X$_2$] (X = Cl, Br, I) which contain chelated dpm. Our results parallel theirs and will not be dealt with further here. We do, however, differ from these workers in our interpretation of the [Ni(dpm)$_2$(NCS)$_2$]$_2$ complex.

Experimental

Reagents

Nitromethane was washed with 5% aqueous sulphuric acid and 5% aqueous sodium bicarbonate, and fractionated, the fraction boiling at 101 °C being collected. Reagent grade tetrahydrofuran was dried over sodium wire for 2 days, and refluxed over calcium hydride for 24 hr and then fractionated (b.pt. 65 °C).

Synthesis of Bisdiphenylphosphinomethane

The white crystalline solid was prepared according to the method of Hewertson and Watson.[13] The crude product was recrystallised from methanol (m.pt. 121 °C).

Preparation of the Complexes

Only typical preparations are quoted:

$[Ni(dpm)_2X]BPh_4$ ($X = Cl, NO_2$)

A solution of the nickel(II) salt (1.32 mmol) in ethanol (20 ml) was added dropwise to a solution of dpm (1.01 g, 2.64 mmol) in dichloromethane (20 ml). A solution of $NaBPh_4$ (0.45 g, 1.32 mmol) in ethanol (20 ml) was added slowly to the mixture to give an immediate dark-red precipitate. The solution was reduced to almost half-volume by gentle warming. It was then cooled, filtered, and the crude product was recrystallised from dichloromethane/ethanol. Yields ~70%.

$[Ni(dpm)_2X]ClO_4$ ($X = Br, I, NCS$)

A solution of "$NiXClO_4$" was prepared by the method of DuBois and Meek.[14] A mixture of $Ni(H_2O)_6(NO_3)_2$ (0.5 mmol) and the sodium salt of the desired univalent anion (1.0 mmol) in ethanol (30 ml) was filtered to remove $NaNO_3$, and $Ni(H_2O)_6(ClO_4)_2$ (0.5 mmol) was added to the filtrate. The resulting solution was heated to reflux (CARE! *Perchlorate*), and dpm (0.76 g, 2.0 mmol) in dichloromethane (20 ml) was added. The dichloromethane was boiled off and the resulting solution was refluxed for an additional half-hour. Upon cooling crystals were deposited. The products were recrystallised from dichloromethane/ethanol. Yields ~70%.

$[Ni(dpm)_2(NCS)_2]$

Nickel thiocyanate (0.174 g, 1.0 mmol) in ethanol solution (20 ml) was slowly added to an acetone solution (20 ml) of dpm (0.76 g, 2.0 mmol). An orange solution was formed which deposited orange crystals after reduction in volume and cooling. After filtering the product was recrystallised from dichloromethane/ethanol. Yield 80%. Attempts to prepare $[Ni(dpm)(NCS)_2]$, both in ethanol or n-butanol, were unsuccessful; the $Ni(dpm)_2(NCS)_2$ complex always being isolated.

$[Ni(dpm)(NCS)_2]_2$

When $[Ni(dpm)_2(NCS)_2]$ was dissolved in dichloromethane overnight a bright brick-red solid was precipitated slowly. After filtration, washing with dichloromethane and ethanol, the solid was dried *in vacuo*. Further evaporation of the dichloromethane solution yielded more of this product.

$[Ni(dpm)_2(CN)]CN$

To an ethanolic solution (20 ml) of $Ni(H_2O)_4(CN)_2$ (0.18 g, 1.0 mmol) two drops of distilled water were added, and this mixture then added to a solution of dpm (0.76 g, 2.0 mmol) in acetone (20 ml). The mixture was refluxed for 12 hr and upon cooling a yellow powder was deposited The product was filtered and recrystallised from dichloromethanol/ethanol. Yield 77%.

Physical Measurements

Conductivities were measured on a Cambridge Instruments Ltd. conductivity bridge. Infrared spectra were measured as mulls in Nujol or hexachlorobutadiene on a Perkin–Elmer 621 spectrophotometer, and electronic spectra on a Unicam SP700 spectrophotometer or on a Beckman DK2A spectrophotometer (solid reflectance, using MgO as dilutant). Magnetic susceptibilities were measured by the Gouy method.

Results and Discussion

When a mixture of NiX_2 ($X = Br$, I, NCS) and $Ni(ClO_4)_2 \cdot 6H_2O$ is reacted with dpm (Ni:ligand ratio 1:2) in ethanol a deeply coloured solution forms

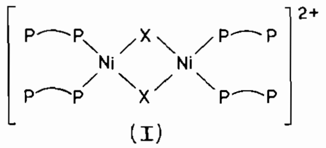
TABLE I. Analytical Data and Physical Properties of the Nickel(II) Complexes.

Compound	Colour	Dec. Pt.	Λ_M[a] (cm^2/ohm mol)	% Carbon[b]	% Hydrogen[b]
$[Ni(dpm)_2Cl]BPh_4$[c]	Dark red	133	70	74.8 (75.2)	5.6 (5.4)
$[Ni(dpm)_2Br]ClO_4$	Purple-red	158	108	60.0 (59.7)	4.4 (4.4)
$[Ni(dpm)_2I]ClO_4$	Deep purple	205	107	55.7 (56.9)	5.0 (4.1)
$[Ni(dpm)_2(NCS)]ClO_4$	Red	163	103	60.7 (60.8)	4.5 (4.4)
$[Ni(dpm)_2(NO_2)]BPh_4$	Red	125	62	75.3 (74.6)	5.6 (5.3)
$[Ni(dpm)_2(NCS)_2]$	Orange	159	51	66.0 (66.1)	4.5 (4.6)
$[Ni(dpm)(NCS)_2]_2$	Brick-red	295		57.9 (57.8)	4.2 (4.0)
$[Ni(dpm)_2(CN)]CN$	Yellow	210	83	69.6 (71.0)	4.8 (5.0)

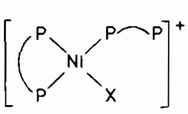
[a] Measured in nitromethane (1×10^{-3} *M*). [b] Calculated percentages in parentheses. [c] All complexes were found to be effectively diamagnetic.

from which the $[Ni(dpm)_2X]ClO_4$ complexes can be isolated. The uncoordinated perchlorate can be easily distinguished in the infrared spectrum as an intense broad, unsplit band at *ca.* 1100 cm^{-1}.[15] The chloro complex could not be formed by this reaction, however, only $[Ni(dpm)_2](ClO_4)_2$ being isolated as a yellow solid. Thus, the chloro, and also the nitrito, complexes were prepared as their tetraphenylborate salts. All the $[Ni(dpm)_2X]^+$ complexes are highly coloured, diamagnetic crystalline solids (Table I).

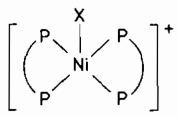
The conductivity values of these complexes are in the range expected for 1 : 1 electrolytes in nitromethane, and it is noticeable that the values of the complexes with the more mobile perchlorate anion are greater than the tetraphenylborate salts. There are three possible formulations for these complexes: (i) dimeric four-coordinate planar complexes containing monodentate phosphine ligands and bridging X^- groups (Structure I); (ii) four-coordinate planar species involving one bidentate and one monodentate phosphine ligand (Structure II); (iii) pentacoordinate involving two bidentate phosphine ligands (Structure III).



(I)



(II)



(III)

The electronic spectra are most helpful in assigning structures to the $[Ni(dpm)_2X]^+$ complexes. We observed no colour changes on dissolving these complexes in dichloromethane save for the iodo complex which formed a yellow solution. Apart from the iodo complex, therefore, the structure of the complexes in the solid state and in dichloromethane solution would appear to be similar, as evidenced by the close similarity of the visible absorptions of the $[Ni(dpm)_2X]^+$ complexes in both states (Table II, Fig. 1). The $[Ni(dpm)_2X]^+$ ($X = Cl$, Br) spectra bear a remarkable resemblance to the $[Ni(vpp)_2X]^+$ spectra,[6] and the latter have been assigned a square-pyramidal structure, and so on this basis the chloro and bromo complexes may be assigned a similar structure. The band which absorbs *ca.* 20,000 cm^{-1} is thus assigned to the transition of d-orbital character $d_{z^2} \rightarrow d_{x^2-y^2}$. In many of the complexes a band *ca.* 29,000 cm^{-1} can be distinguished which may be assigned to nickel–phosphorus charge-transfer. This band appears to be sensitive to the coordination of the anionic ligands as both its energy and intensity change with change of X^-.

TABLE II. Electronic Spectra of the Nickel(II) Complexes.

Compound	E_{max} Solution[a] kK(εmax)	E_{max}Solid[b] kK
$[Ni(dpm)_2Cl]BPh_4$	20.8 (2,640)	20.7
	29.0 (15,180)	28.7sh
	34.6 (26,470)	
	36.8 (29,130)	
$[Ni(dpm)_2Br]ClO_4$	20.2 (2,480)	20.4
	31.0 (16,810)	28.5sh
	36.4 (14,080)	
$[Ni(dpm)_2I]ClO_4$	18.85 (2,470)	17.9
	29.6 (20,040)	28.5
	32.2 (22,540)	
	37.6 (19,440)	
$[Ni(dpm)_2(NCS)]ClO_4$	20.7 (2,004)	20.6
	32.0 (24,800)	
$[Ni(dpm)_2(NO_2)]BPh_4$	20.3 (1,890)	20.4
	34.6 (28,990)	
	36.4 (28,900)	
$[Ni(dpm)_2(NCS)_2]$	22.0 (2,840)	21.2
	25.0 (2,740)	25.3
$[Ni(dpm)(NCS)_2]_2$	22.7 (2,400)	19.0
	24.4sh	24.3

[a] In dichloromethane. [b] Solid reflectance.

The shift in the frequency of almost 1,000 cm^{-1} of the visible absorption of $[Ni(dpm)_2I]ClO_4$ to higher energy upon dissolution in dichloromethane (17.9 kK to 18.85 kK) suggests that the pentacoordinate square pyramidal solid (III; X = I) has become square planar (I; X = I) in solution. In fact the solution band is at a similar energy to that reported by Van Hecke and Horrocks[8] for their square planar $[Ni(dpm)_2I_2]$ complex (18.7 kK).

The $[Ni(dpm)_2X]^+$ ($X = NCS$, NO_2) may be assigned similar square pyramidal complexes both in the solid state and in solution. The infrared spectrum of the isothiocyanato complex exhibits a ν(CN) absorption at 2085 cm^{-1}, and the position and broadness of this band indicates Ni–NCS coordination.[16] Similarly, bands at 1340, 1140, and 840 cm^{-1}, which are absent in the infrared spectrum of dpm, indicate that the NO_2^- is coordinated as nitrito, Ni–ONO, in $Ni(dpm)_2(NO_2)BPh_4$.[17]

Attempts to prepare $[Ni(dpm)(NCS)_2]$ and $[Ni(dpm)(CN)_2]$ directly were not successful, the only complexes which could be isolated were the orange $[Ni(dpm)_2(NCS)_2]$ and the yellow $[Ni(dpm)_2(CN)]CN$. No ligand field transitions could be observed in the electronic spectrum of the cyano complex, presumably charge-transfer bands obscure them. Two strong infrared absorptions at 2120 cm^{-1} and 2080 cm^{-1} in the mull spectrum of $[Ni(dpm)_2(CN)]CN$ indicate the presence of both coordinated and uncoordinated cyanide.[16] Moreover, the conductivity of this complex in nitromethane is typical of a 1 : 1 electrolyte (Table I).

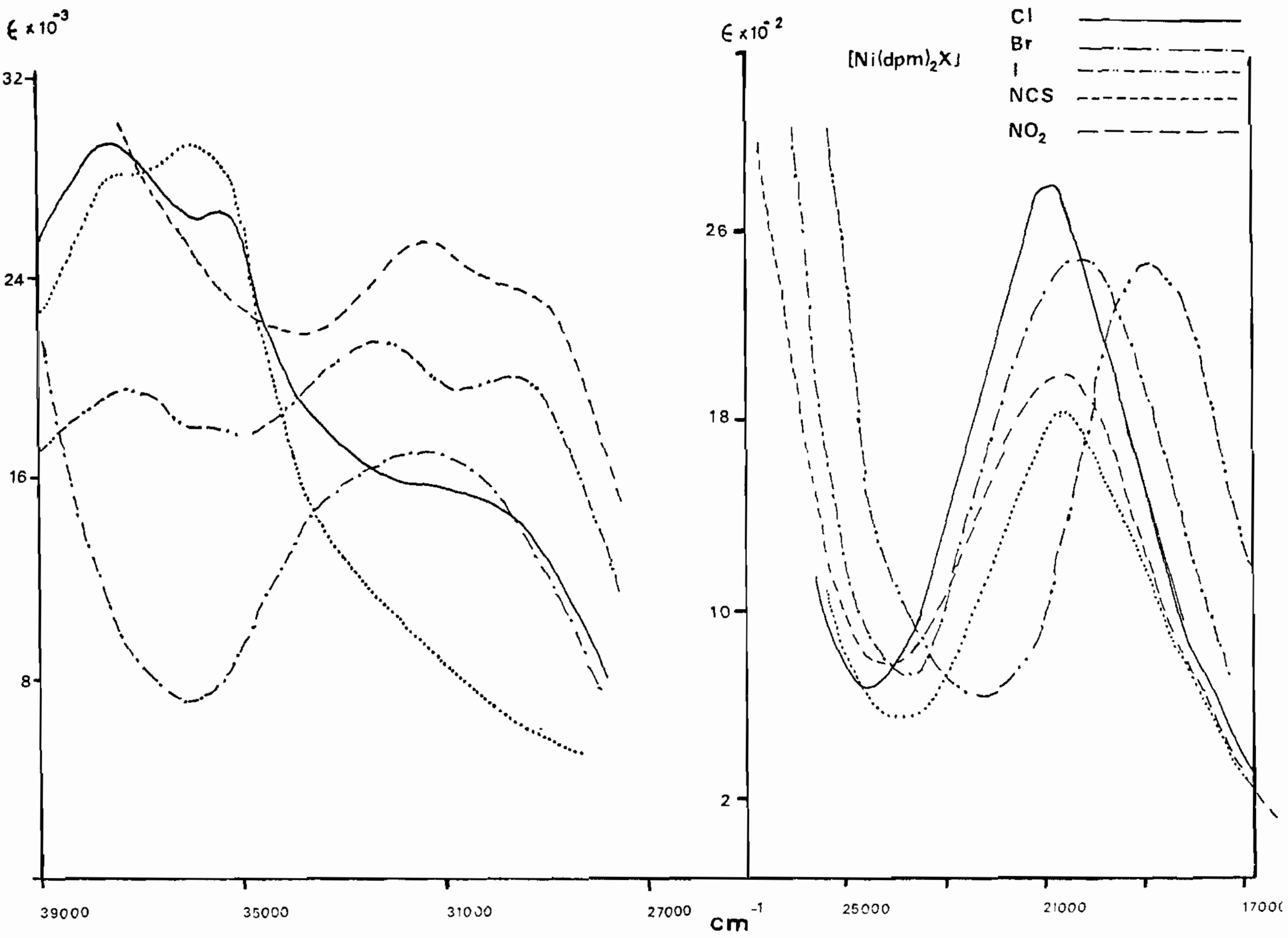
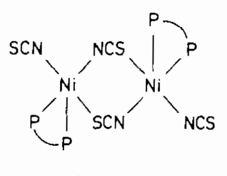


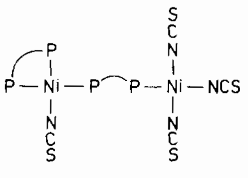
Fig. 1. Electronic Spectra of the Nickel(II)-dpm Complexes.

Thus, this complex may have structures (II) or (III). Turco[19] has observed that pentacoordinate $[Ni(dpe)_2(CN)]^+$ absorbs strongly in the visible region of the spectrum, and as we do not observe any visible absorptions for the $[Ni(dpm)_2(CN)]CN$ complex, then a planar structure of type (II) may be assigned to this complex. On the other hand the infrared spectrum of the isothiocyanato complex exhibits only one ν(CN) absorption at 2070 cm^{-1}, which indicates only one type of Ni–NCS linkage and so this complex can be assigned a *trans* square planar structure. This is the same conclusion as that of Ercolani *et al.*[12] Thus assigning a C_{2v} symmetry to this complex, ligand field theory predicts the possible spin-allowed d–d transitions: $^1A_1 \rightarrow {}^1B_2$, $^1A_1 \rightarrow {}^1A_2$, $^1A_1 \rightarrow {}^1B_1$. The observed absorptions at 22,000 cm^{-1} and 25,000 cm^{-1} can thus be tentatively assigned to the $^1A_1 \rightarrow {}^1B_2$ and $^1A_1 \rightarrow {}^1A_2$ transitions, respectively. The higher-energy transition is presumably swamped by charge-transfer absorptions. In a fresh nitromethane solution of this complex exhibits significant conductance, which indicates that an appreciable amount of coordinated isothiocyanate is becoming ionic, and the conductivity increases slowly with time. Unfortunately it is not possible to tell whether this is straightforward substitution of $MeNO_2$ for NCS^- or whether an uncoordinated phosphine group is coordinating.

When $[Ni(dpm)_2(NCS)_2]$ is dissolved in dichloromethane a brick-red solid, analysing as $Ni(dpm)(NCS)_2$, precipitates after some considerable time. Ercolani, Quagliano, and Vallarino[12] assigned a dimeric pentacoordinate structure (IV). These workers



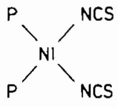
(IV) (ref.12)



(V)

report IR bands at 2085 and 2055 cm^{-1}, ν(CN), and 865 cm^{-1}, ν(CS). Because the solid state electronic spectrum of this insoluble dimeric complex is similar to that of [Ni(dpm)I_2]$_2$, to which Ercolani *et al.* assign a pentacoordinate structure, they assign a similar structure, (IV), to the thiocyanate analogue. The electronic spectra of our sample (Table II) of [Ni (dpm)$(NCS)_2$]$_2$ is almost identical to those reported by Ercolani *et al.*, and the infrared spectrum in Nujol is also very similar (2085, 2062, 865 cm^{-1}). We do not think that structure (IV) is very likely for this complex, as the available data do not fit it. Firstly, it is extremely unlikely that the electronic spectrum of [Ni(dpm)I_2]$_2$ (donor set P_2I_3) will be similar to complex (IV) of similar stereochemistry (donor set P_2SN_2); the spectrochemical effect of N-bonded thiocyanate is much greater than that of iodide.[20] Moreover, the ν(CN) absorption at 2085 cm^{-1} is much too low to be assigned to any species other than a terminal N-bonded thiocyanate group.[16,20]

The insolubility of [Ni(dpm)$(NCS)_2$]$_2$ does, indeed, suggest a dimeric structure. The large separation in energy between the two ν(CN) absorptions also indicates that a monomeric complex, (VI), is unlikely, as isothiocyanate groups in this complex are in identical situations and would be expected to give rise to a small splitting of a single ν(CN) absorption because of their relative *cis* positions. Of the two possible dimeric structures, (V) and (VII), which do not involve bridging –NCS– groups, (V) seems more likely than does (VII). Firstly, it explains why two visible absorption bands of almost equal intensity are exhibited in the solid reflectance spectrum (one due to the NiP_3N^+ chromophore and one due to the $NiPN_3^-$ chromophore), and secondly two ν(CN) absorptions at different energies might be expected to arise from the –NCS groups *trans* to the soft phosphine donors and from –NCS groups *trans* to the hard N-bonded isothiocyanate. The dimeric structure (VII) does not fit the data as well as (V), but a final answer to this question may only be known from X-ray crystallographic studies.



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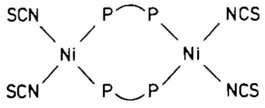

(VII)

The slight solubility of [Ni(dpm)$(NCS)_2$]$_2$ in dichloromethane allowed us to obtain a visible absorption spectrum (Table II). We are in agreement with the conclusions of Ercolani *et al.*[12] that the species in solution is the monomer (VI).

Foglemen and Jonassen[11] observed that an absorption at 778 cm^{-1} in the infrared spectrum of dpm is shifted to higher frequencies in chelated dpm, but is unchanged in complexes where dpm is monodentate. This absorption is in the –CH_2– rocking region, but it has also been assigned to a vibration associated with the P–C–P group.[21] We have observed a similar pattern. In the pentacoordinate complexes [Ni$(dpm)_2$X]$^+$ (X = Cl, Br, I, NCS, NO_2) this frequency is shifted about 20 cm^{-1} to higher energy in the mull spectra. On the other hand the spectrum of the square planar [Ni$(dpm)_2(NCS)_2$] exhibits an unshifted band at 778 cm^{-1}. The assignment of structure (II) to [Ni $(dpm)_2$CN]CN is borne out by infrared measurements; two absorptions at 778 cm^{-1} and 796 cm^{-1} can be clearly identified.

The available evidence from this work and that of Ercolani, Quagliano, and Vallarino[12] indicates that dpm is a versatile ligand. The identification of dpm with monodentate or bridging bidentate behaviour is now seen to be not a good reflection of the bonding abilities of this ligand, and it readily forms stable chelate rings despite the expected strained nature of the four-membered species. However, there is now a lot of evidence that diphosphines frequently promote the formation of pentacoordinate Ni(II) complexes, and it may be suggested that this tendency of nickel to become pentacoordinate is yet another important factor in promoting chelation of the diphosphine in the [Ni$(dpm)_2$X]$^+$ complexes. There also appears to be special factors operating in the cyano complex, but this has been noted in other complexes of diphosphines with Ni$(CN)_2$.[19]

Acknowledgement

K.K.C. is grateful to The British Council for a Fees Award.

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