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Some Nickel(II) Complexes of Tertiary Phosphines Containing o-Carborane as Backbone

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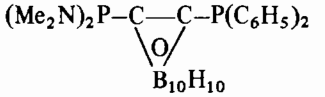
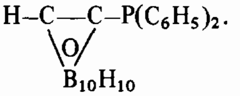
Complexes of the type NiX_2L *and* $NiX_2L'_2$ *(L = 1-bis(dimethylamino)phosphino, 2-diphenylphosphino-o-carborane; L′ = 1-diphenylphosphino-o-carborane and X = Cl, Br, I, SCN) have been prepared and characterized by IR, Raman, and electronic spectroscopies and magnetic measurements.*

The electronic and magnetic measurements indicate a square planar structure both in solution and solid state. The vibrational spectra show that the $NiX_2L'_2$ *complexes possess a* trans *structure and that in the thiocyanate complex the NCS group is N-bonded. The* NiX_2L *species have the expected* cis *square planar structure.*

For the NiX_2L *(X = Cl, Br) complexes the formation constants have also been determined. The study allows us to infer that the main equilibrium can be represented by* $NiX_2 + L \rightleftarrows NiX_2L$ *and that the complex species is the predominant one in acetonitrile solution.*

Introduction

Perhaps the best known ditertiary phosphine is the 1,2-bis(diphenylphosphino)ethane (dpe) whose complexation properties have been extensively studied [1, 2]. Other common backbones are -CH=CH-, -NR-, -$(CH_2)_n$-, -$(CH_2)_n$–O- and aromatic ring systems. *Ortho*-carborane ($B_{10}C_2H_{12}$) is a particularly interesting backbone because of its electron-withdrawing power, extensive formal delocalization and large size [3]. Several diphosphines with this backbone and their complexes have been reported [3–8]. The electron-withdrawing power of the *o*-carborane moiety seems to favor the π-backbonding in the metal–phosphorus bond. As pointed out previously [3, 4] a number of symmetrical and unsymmetrical ditertiary phosphines can be prepared. The rather large size of this backbone would allow us to test the trend that bulky substituents on phosphorus favor a tetrahedral over a square-planar geometry for Ni(II) complexes, as found by Venanzi [9].

In this work we have prepared and spectroscopically characterized a series of complexes of the type NiX_2L and $NiX_2L'_2$ where X is Cl, Br, I or NCS and L is  $(Me_2N)_2P{-}\underset{B_{10}H_{10}}{C{-}C}{-}P(C_6H_5)_2$ and L′ is  $H{-}\underset{B_{10}H_{10}}{C{-}C}{-}P(C_6H_5)_2$. We have also determined the stability constant of the $NiCl_2L$ and $NiBr_2L$ species in an attempt to learn about the solution chemistry of these species.

Experimental

Preparative

The L and L′ ligands were prepared as described previously [3, 4, 10].

The complex compounds were prepared by a general method. An ethanolic solution of the nickel(II) halide was mixed with the stoichiometric amount of the ligand dissolved in CH_2Cl_2. The red solution obtained was stirred for two hours and the solvent pumped off. The iodide derivative was also made by this method, but the nickel(II) iodide was prepared *in situ* from NaI and nickel(II) nitrate in ethanol. The undesired sodium nitrate was easily removed by filtering. The analytical data and conductivity and magnetic susceptibility measurements are given in Table I.

Physical Measurement

Conductivity measurements were carried out at 20 °C in acetonitrile (approx. m*M* concentration) using a WTW conductimeter. The electronic spectra were run in either a Beckman DBGT and DU8 and Zeiss DMR22 Spectrophotometers using acetonitrile or ethanol or as nujol mulls. The magnetic susceptibility measurements were obtained by the Faraday method in a Cahn/Ventron RM2 electrobalance using a *ca.* 8 KGauss magnetic field. The IR and Raman spectra were recorded as described elsewhere [11].

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TABLE I. Analytical, Conductivity and Magnetic Data for the NiX_2L and $NiX_2L'_2$ Complexes[a] ($L = B_{10}H_{32}C_{18}P_2N_2$; $L' = B_{10}H_{21}C_{14}$).

Compound	C%	H%	N%	Ni%	A_M20	χ_M^{Corr}, ×10^6
$NiCl_2L$	37.5(37.7)	5.6(6.1)	9.6(9.7)	9.9(10.1)	78	10
$NiBr_2L$	32.2(32.4)	4.8(4.9)	9.4(9.7)	8.6(8.7)	85	62
NiI_2L	27.4(28.4)	4.0(4.2)	3.5(3.6)	7.6(7.7)	86	12
$Ni(NCS)_2L$	36.7(38.6)	5.2(6.3)	8.6(9.0)	9.2(9.4)	47	89
$NiCl_2L'_2$	41.8(41.7)	3.9(4.1)	–	7.0(7.2)	78	40
$NiBr_2L'_2$	36.2(37.6)	5.1(4.7)	–	6.1(6.5)	83	35
$Ni(NCS)_2L'_2$	44.5(44.0)	5.3(5.3)	–	6.5(6.9)	34	57

[a]Calculated values are given in parentheses.

Results and Discussion

The magnetic susceptibility measurements clearly show that the compounds are diamagnetic in the solid state. Table II lists the absorption bands of the electronic spectra both in solution and in the solid state. The spectra of the nickel(II) complexes reported here show a band which has been assigned to the $^1A_{1g} \rightarrow {}^1A_{2g}$ electronic transition, in agreement with the data for some Ni(II) square-planar complexes reported in the literature [12].

Generally speaking, for a nickel(II) square-planar species three transitions should be observed; however in most cases only one is detected, the other two being masked by charge-transfer bands or π–π^* transitions of the aromatic rings. The IR spectra of the L and L′ ligands show (see Table II) some few changes upon complexation. In fact, the P–C(phenyl) stretching mode shifts by *ca.* 10 cm^{-1} in the L and L′ complexes. It is worth noting that this vibration is not pure but is coupled with some phenyl ring vibrations. The increase in the frequency of the P–C(phenyl) mode is probably due to a dπ–pπ interaction which produces an increase in the P–C bond order.

In the IR spectrum of L a band at *ca.* 2800 cm^{-1} is observed. This band has been assigned to the symmetric C–H stretching mode of the -$N(CH_3)_2$ group which appears when nitrogen is not coordinated [13] (Table III). Therefore, the presence of such a band is additional evidence that the L ligand is coordinated through the phosphorus atoms and not through the nitrogen. The P–N symmetric stretching mode is at 970 cm^{-1} in the free ligand, whereas in the complexes this mode is detected in the range 975–995 cm^{-1}. This implies that the P–N bond order has also been increased as a result of a rather strong p$\pi \rightarrow$ dπ N → P interaction [3]. The typical carborane cage vibrations are observed in the same region as reported previously [4]. The L′ ligand and its complexes show the expected band at *ca.* 3050 cm^{-1} due to the C–H stretching mode of the cage.

The shifts in the frequencies of the three fundamentals of the thiocyanate ion upon complexation have been widely used to infer the bonding mode of the NCS ligand. The C–S stretching frequency is detected at 690–720 for a thiocyanate complex, whereas for an isothiocyanate this mode is observed at 780–860 cm^{-1}. Unfortunately, this mode can be erroneously assigned because of its low intensity and the appearance of the first overtone of δ(NCS) in the same region. On the other hand, the N–C–S bending mode in an isothiocyanate complex consists of a medium intensity band located at 460–490

TABLE II. Electronic Spectra of the NiX_2 and $NiX_2L'_2$ Complexes.

Compound	ν (solution)[a,b]	ν (nujol)
$NiCl_2L$	21978(2284)	22220
$NiBr_2L$	21053(1776)	20833
NiI_2L	25000(1296)	24039
$Ni(NCS)_2L$	25641(1000)	23720
$NiCl_2L'_2$	20833(875)	21277
$NiBr_2L'_2$	22727(817)	22727
$Ni(NCS)_2L'_2$	23529(1360)	24390

[a]Extinction coefficients are given in parentheses. [b]Solution spectra taken in ethanol or acetonitrile.

TABLE III. Selected IR Bands (cm^{-1}) of the L and L′ Complexes of Ni(II).

Complex	P–Phenyl	C–H(cage)	P–N	C–H(Me_2N)
L	1090s		975s 960s	2800ms
L′	1090s	3050w	–	–
$NiCl_2L$	1095m	–	975br	2800m
$NiBr_2L$	11002	–	985m	2800m
NiI_2L	1100s	–	995m	2830m
$Ni(NCS)_2L$	1100s	–	975s	2800m
$NiCl_2L'_2$	1095s	3050m	–	–
$NiBr_2L'_2$	1095s	3020w	–	–
$Ni(NCS)_2L'_2$	1100s	3050w	–	–

cm^{-1} whereas in the thiocyanate complexes it shows up at 410–440 cm^{-1}. The most commonly band used to infer the bonding mode is, however, the C–N stretching mode. The ν(C–N) frequencies increase in the order $NCS^- \sim M{-}NCS < M{-}SCN < M{-}SCN{-}M$ [14].

In a M–NCS complex this mode has been observed as a strong and broad band near or below 2050 cm^{-1}, whereas in a M–SCN complex the absorption is sharp and near to 2100 cm^{-1}. In a bridging thiocyanate the ν(CN) shows up well at over 2100 cm^{-1}. In the $NiL(NCS)_2$ and $NiL'_2(NCS)$ this vibrational mode appears respectively at 2155 and 2148 cm^{-1} in the solid state, whereas in acetone solution the above bands shift to 2080 and 2095 cm^{-1}. This would imply that the thiocyanate group is bridging two nickel atoms to produce polymeric species, there being interaction between the NCS groups and the bulky ligand in the solid state. In acetone solution these bridges no longer exist and the complexes are better formulated as N-bonded complexes. It is worth noting that frequency shifts when going from the solid state to the solution are a well known effect in isothiocyanates. The thiocyanates do not show such changes [15]. The $NiL'_2(NCS)_2$ can possess either a *cis* or *trans* configuration. The number of ν(CN) can be used to infer the geometry of the $ML_2(NCS)_2$ square planar complexes. In fact, in a *cis* (C_{2v}) configuration two ν(CN) should be observed, whereas only one is to be detected in a *trans* (D_{2h}) symmetry. The appearance of just one ν(CN) in this complex indicates a *trans* (D_{2h}) configuration.

The low-frequency IR and Raman bands can be easily used to infer the symmetry of these species. However, the metal–phosphorus stretching modes are of too low intensities [16, 17] and in most cases we have only been able to observe the metal–halogen stretching modes. Table IV shows the IR and Raman bands in the low-frequency region and their assignments. In a *trans* ML_2X_2 species of D_{2h} symmetry, group theory predicts one M–X (X = halogen) IR active and one Raman active modes. From the data in Table IV it can be inferred that the *trans* configuration assigned to the L′ complexes on the basis of the ν(CN) modes is confirmed. The complexes of the bidentate L ligand possess a C_{2v} symmetry if one considers the MP_2X_2 skeleton. Group theory predicts four metal–ligand vibrations, all IR and Raman actives [18]. Most of the predicted bands for this symmetry have been observed in the L complexes, confirming their *cis*-C_{2v} symmetry. The Ni–P and Ni–X vibrational modes have been assigned by comparison with the corresponding bands of the Ni(dpe)-X_2 and related compounds. The Ni–X stretching bands are in the range of previously reported Ni(II) complexes [17, 18], whereas the ν(Ni–P) show up at higher frequencies than in the dpe complexes. This would imply that the Ni–P bond has been strengthened in our complexes, due to the presence of electronegative substituents (*o*-carborane cage) on the phosphorus atom that will in turn favor a stronger πM–P bonding.

TABLE IV. IR and Raman Spectra in the Low-frequency Region of the NiX_2L and $NiX_2L'_2$ Complexes.

Compound	ν(Ni–X)		ν(Ni–P)	
	IR	Raman	IR	Raman
$NiCl_2L$	315s 294m	318m 285m	410ms 355s	405mw 355w
$NiBr_2L$	310s 272s	n.o. n.o.	385m 360ms	398w 366w
NiI_2L	250s	246s 231s	379s	373vw
$Ni(NCS)_2L$	325s 262s	320mw 258w	385s 363ms	383w 368w
$NiCl_2L'_2$	420s	388s	n.o.	n.o.
$NiBr_2L'_2$	375s	331ms	n.o.	n.o.

[a]n.o. = not observed.

In general, the metal–halogen stretching modes of the *cis*-L complexes show up at lower frequencies than in the *trans*-L′ species. This can be rationalized in terms of the stronger *trans* influence of the phosphine group on the Ni–halogen bond.

Finally, for the $NiCl_2L$ and $NiBr_2L$ complexes we have determined their formation constants in acetonitrile in an attempt to obtain more information about these species in solution. In the determination of the formation constants we have used the method proposed by Rose and Drago [19]:

$$K^{-1} = \frac{A - A_o}{\epsilon'} = C_I - C_L + \frac{C_I C_L}{A - A_o}\,\epsilon' \qquad (1)$$

Eqn. 1 was solved by analytical methods. Thus, for a set of experimental C_I, C_L and $A - A_o$ data, a set of ϵ' is selected to calculate K^{-1}. This procedure is repeated for each set of C_I, C_L and $A - A_o$. The plot of the calculated K^{-1} *vs.* ϵ' yields a family of curves that converge to a very small area, which allows us to estimate the accuracy of the determination. Figure 1 shows the plot of K^{-1} *vs.* ϵ' for the $NiCl_2L$ complex. The calculated K values for the equilibrium

$NiX_2 + L \rightleftharpoons NiX_2L$ X = Cl or Br

are $7 \pm 3 \times 10^4$ and $10 \pm 4 \times 10^4$ for the chloride and bromide, respectively. From Fig. 1 and the calculated values of K, it can be inferred that NiX_2L is the predominant species in solution. Any other species are confidently ruled out.

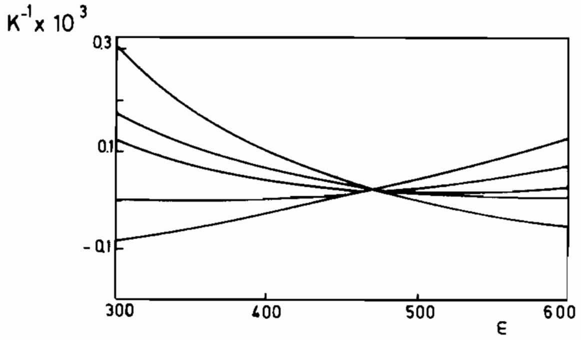

Fig. 1. Plot of K^{-1} *vs.* ϵ' for $NiCl_2L$.

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