intense band at 14,000–20,000 cm^{-1}.[21] Thus if low-spin five-coordinated Ni(II) existed in **6**, similar bands at lower frequencies are expected, due to the lower ligand field by the O and N ligands. Such bands are not apparent in the spectra, and structure **5** seems more probable.

The amorphous nature of the solid complexes, as indicated by their X-ray diffraction patterns, implies that structure **5** may only be the statistical preference. Either **5** does not arise sufficiently often to give rise to a regular arrangement in a crystalline state or perhaps the shape of **5** differs from one molecule to the next (*e.g.*, due to the flexible alkyl chain), thereby leading to disorder.

The properties of the adducts NiL·2py suggest that they have a trans-octahedral monomeric structure while, for $n = 4$, the complex NiL·H$_2$O appears to have a square-pyramidal structure with the water molecule in the apical position.

In all cases the ligands L act as quadridentates about individual nickel atoms, with intermolecular associations *via* Ni–O bonds a possibility for $n = 5$–12 complexes. This fact suggests that similar quadridentate liganding may also occur in the analogous salicylaldimine complexes, in preference to the bridged bidentate structure **2**, postulated for the NiSal complexes with $n = 5$–12[11] and previously for the analogous zinc complexes.[22] We could then explain the apparently anomalous behavior of CuSal with $n = 6$, which would previously have been considered an infinite polymer,

(21) G. S. Benner, W. E. Hatfield, and D. W. Meek, *Inorg. Chem.*, **3**, 1544 (1964).

(22) B. Kirson and H. Sechter, *Bull. Soc. Chim. Fr.*, 2743 (1965).

but which forms a crystalline derivative with copper chloride,[23] **7**. This derivative closely resembles a series

7
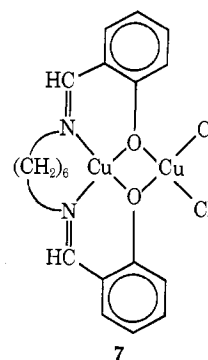
of binuclear complexes containing tetradentate Sal ligands but does not fit into a series of copper chloride derivatives of bidentate salicylaldimine complexes.[24] Similarly, mass spectral data on the cobalt(II) complexes with salicylaldimines **7** ($n = 3$–6) suggested that these complexes, though insoluble in common solvents, were monomeric with the Schiff bases acting as quadridentates.[25]

(23) S. J. Gruber, C. M. Harris, and E. Sinn, *J. Inorg. Nucl. Chem.*, **30**, 1805 (1968).

(24) C. M. Harris and E. Sinn, *ibid.*, **30**, 2723 (1968).

(25) M. Harihan and F. L. Urbach, *Inorg. Chem.*, **8**, 556 (1969); J. Manassen, *ibid.*, **9**, 996 (1970).

Four- and Five-Coordinate Complexes of Nickel(II) with Diethylphosphine

BY P. RIGO* AND M. BRESSAN

Diethylphosphine forms four-coordinate diamagnetic [Ni(HP(C$_2$H$_5$)$_2$)$_3$X]$^+$ complexes (X = Cl, Br, I, NCS), as well as the diamagnetic five-coordinate Ni(HP(C$_2$H$_5$)$_2$)$_3$X$_2$ (X = Br, I) and [Ni(HP(C$_2$H$_5$)$_2$)$_4$X]$^+$ (X = Cl, Br, I, NCS) complexes. The compounds have been characterized by conductivity, magnetic measurements, and electronic spectra. The stability of the five-coordinate complexes in solution has been found to depend markedly on the type of solvent and on the presence of free ligands. Moreover, spectral data show that the previously reported six-coordinate Ni(HP(C$_2$H$_5$)$_2$)$_4$X$_2$ can better be formulated in the solid state as the five-coordinate ionic compounds [Ni(HP(C$_2$H$_5$)$_2$)$_4$X]X.

Introduction

Numerous investigations carried out on the reaction of nickel(II) salts with tertiary phosphines have shown that the stereochemistry of the complexes is strongly dependent upon the type of the anionic ligand, as well as on the nature of the organic substituents at the phosphorus atom of the phosphine. Four- and five-coordinate complexes have been obtained, which contain one, two, three, and four molecules of phosphine.[1–5]

(1) G. Booth, *Advan. Inorg. Chem. Radiochem.*, **6**, 1 (1964), and references therein.

(2) P. Rigo, C. Pecile, and A. Turco, *Inorg. Chem.*, **6**, 1636 (1967).

(3) P. Rigo, G. Guastalla, and A. Turco, *ibid.*, **8**, 375 (1969).

(4) K. A. Jensen and O. Dahl, *Acta Chem. Scand.*, **22**, 1044 (1968).

(5) D. W. Allen, F. G. Mann, and I. T. Millar, *J. Chem. Soc. A*, 1101 (1969).

By contrast, relatively few complexes of nickel(II) with secondary phosphine have been characterized. Dicyclohexylphosphine forms the four-coordinate complexes Ni(HP(C$_6$H$_{11}$)$_2$)$_2$X$_2$ (X = Cl, Br).[6] The reaction of diphenylphosphine with nickel(II) halides in nonionizing solvents yields *trans*-[Ni(HP(C$_6$H$_5$)$_2$)$_2$I$_2$] and five-coordinate Ni(HP(C$_6$H$_5$)$_2$)$_3$X$_2$ (X = Cl, Br, I).[7] With diethylphosphine only the six-coordinate complexes Ni[HP(C$_2$H$_5$)$_2$]$_4$X$_2$ (X = Cl, Br) have been reported.[6]

As part of a study of the properties, spectra, and stereochemistry of complexes of nickel(II) with sec-

(6) K. Issleib and G. Doell, *Z. Anorg. Allg. Chem.*, **305**, 1 (1960).

(7) R. G. Hayter, *Inorg. Chem.*, **2**, 932 (1963).

TABLE I

PROPERTIES AND ANALYTICAL DATA OF THE NICKEL(II) COMPLEXES[a]

Compound	Color	Mp,[b] °C	C Calcd	C Found	H Calcd	H Found	Ni Calcd	Ni Found	Other Calcd	Other Found
Ni(DEP)₄I₂	Red	93–95	28.27	28.55	6.78	6.59	8.53	8.72	37.52	37.70 (I)
Ni(DEP)₃Br₂	Dark red	81–83	29.79	29.49	6.72	6.80	12.20	12.01	32.51	32.70 (Br)
Ni(DEP)₃I₂	Violet	92–93	24.57	24.73	5.68	5.70	9.73	10.07	43.43	43.55 (I)
[Ni(DEP)₃Cl]B(C₆H₅)₄	Yellow	116–118	63.28	63.24	7.83	7.81	8.59	8.58	5.22	5.18 (Cl)
[Ni(DEP)₃Br]B(C₆H₅)₄	Yellow	128–133	59.84	59.38	7.41	7.34	8.03	8.06	11.11	10.97 (Br)
[Ni(DEP)₃I]B(C₆H₅)₄	Yellow	123–126	55.91	55.78	7.03	6.89	7.60	7.57	16.42	16.37 (I)
[Ni(DEP)₃(NCS)]B(C₆H₅)₄	Yellow	110–112	63.17	62.92	7.57	7.56	8.29	8.31	2.02	1.98 (N)
[Ni(DEP)₄Cl]B(C₆H₅)₄	Red	79–81	61.82	62.09	8.37	8.34	7.56	7.58	4.43	4.58 (Cl)
[Ni(DEP)₄Br]B(C₆H₅)₄	Red	90–91	58.70	58.71	7.88	7.88	7.13	7.17	9.72	9.76 (Br)
[Ni(DEP)₄I]B(C₆H₅)₄	Red	110–114	55.95	55.52	7.62	7.45	6.85	6.78	14.85	14.66 (I)
[Ni(DEP)₄(NCS)]B(C₆H₅)₄	Red	86–91	62.00	61.83	7.90	8.09	7.31	7.37	1.58	1.75 (N)

[a] All of these complexes are diamagnetic. [b] Uncorrected, determined in closed tube under nitrogen.

ondary phosphines, we have reinvestigated the reaction of nickel(II) salts with diethylphosphine (DEP).

We report here the preparation of four- and five-coordinate complexes [Ni(DEP)₃X]B(C₆H₅)₄, [Ni(DEP)₄X]B(C₆H₅)₄ (X = Cl, Br, I, NCS), and Ni(DEP)₃X₂ (X = Br, I).

Experimental Section

Apparatus.—All preparative work and handling of compounds were carried out under an atmosphere of dry nitrogen. Electronic spectra were obtained with an Optica CF4NI spectrophotometer. Reflection spectra were recorded using solid compounds and MgCO₃ as inert diluent. Molecular weights were measured cryoscopically in benzene. Molar conductivities were determined in dichloroethane at 25°. Magnetic susceptibilities were measured by the standard Gouy method at room temperature and were corrected for the diamagnetism of the ligands.

Materials.—Diethylphosphine was prepared by reduction of tetraethyldiphosphine disulfide with lithium aluminium hydride, following the method of Issleib, *et al.*[8]

[Ni(DEP)₃X]B(C₆H₅)₄ (X = Cl, Br, I, NCS).—Nickel nitrate hexahydrate (1 mmol), sodium tetraphenylboron (1 mmol), and sodium halide or thiocyanate (1 mmol) were mixed in 25 ml of anhydrous ethanol and sodium nitrate was filtered off. Diethylphosphine (3 mmol) in 10 ml of anhydrous ethanol was added. The yellow crystals obtained were collected and washed with ethanol and *n*-hexane. All the complexes were recrystallized from methylene chloride–ethanol.

[Ni(DEP)₃X]B(C₆H₅)₄ (X = Cl, Br, I, NCS).—Stoichiometric amounts (1 mmol) of nickel nitrate hexahydrate, sodium tetraphenylboron, and NaX were mixed in 25 ml of anhydrous ethanol and sodium nitrate was filtered off. Diethylphosphine (5 mmol) in 10 ml of ethanol was added. The red precipitates obtained were recrystallized from methylene chloride–ethanol, in the presence of small amounts of phosphine.

Ni(DEP)₃Br₂.—Ni(DEP)₄Br₂ dissolved in boiling petroleum (bp 70–120°) to give deep red solutions. On cooling, dark red crystals were obtained, which were recrystallized from petroleum.

Ni(DEP)₃I₂.—[Ni(DEP)₃I]B(C₆H₅)₄ (1 mmol) and [N(C₄H₉)₄]I (1 mmol) dissolved in 10 ml of dichloromethane. After evaporation to dryness the residue was treated with ethyl ether and dark crystals were obtained by adding *n*-hexane to the solution. The complex was recrystallized from ethyl ether–*n*-hexane. Repeated recrystallizations are necessary to obtain the pure diamagnetic compound.

Ni(DEP)₄X₂ (X = Cl, Br, I) were prepared following the method of Issleib,[8] by reaction of the ligand with the appropriate nickel salt.

Results and Discussion

The physical properties and analytical data of the nickel(II) compounds are listed in Tables I and II. The band maxima with their extinction coefficients of the electronic spectra are listed in Table III. Infrared spectra of all of the complexes show a weak band

(8) K. Issleib and A. Tzschach, *Chem. Ber.,* **92,** 704 (1959).

TABLE II

MOLAR CONDUCTANCE ON 1,2-DICHLOROETHANE SOLUTION AT 25°[a]

Compound	ΛM, cm² ohm⁻¹ mol⁻¹	Compound	ΛM, cm² ohm⁻¹ mol⁻¹
Ni(DEP)₄Cl₂	0.22	Ni(DEP)₄I₂	2.1
Ni(DEP)₄Cl₂ + DEP[b]	28.2	Ni(DEP)₄I₂ + DEP[b]	20.5
[Ni(DEP)₃Cl]B(C₆H₅)₄	15.2	Ni(DEP)₃I₂	1.3
[Ni(DEP)₄Cl]B(C₆H₅)₄	31.0	Ni(DEP)₃I₂ + DEP[b]	25.2
Ni(DEP)₄Br₂	2.7	[Ni(DEP)₃I]B(C₆H₅)₄	27.7
Ni(DEP)₄Br₂ + DEP[b]	15.9	[Ni(DEP)₄I]B(C₆H₅)₄	25.4
Ni(DEP)₃Br₂	1.5	[Ni(DEP)₃(NCS)]B(C₆H₅)₄	22.8
Ni(DEP)₃Br₂ + DEP[b]	26.3	[Ni(DEP)₄(NCS)]B(C₆H₅)₄	24.1
[Ni(DEP)₃Br]B(C₆H₅)₄	26.5	DEP[b]	0.004
[Ni(DEP)₄Br]B(C₆N₅)₄	28.1		

[a] For approximately 10⁻³ M solutions. [b] Approximately 10⁻¹ M.

TABLE III

OPTICAL SPECTRA OF THE NICKEL(II) COMPLEXES IN 1,2-DICHLOROETHANE SOLUTION

Compound	Band max, cm⁻¹ (ε)[a]
[Ni(DEP)₃I]B(C₆H₅)₄	22,750 (860)[d]
[Ni(DEP)₃Br]B(C₆H₅)₄	24,400 (910)[d]
[Ni(DEP)₃Cl]B(C₆H₅)₄	24,650 (950)[d]
[Ni(DEP)₃(NCS)]B(C₆H₅)₄	24,750 (850)[d]
Ni(DEP)₃I₂	14,700 sh (650), 18,000 (1210), 22,500 (1080), 28,600 sh (2750)[d]
Ni(DEP)₃Br₂	21,500 (730), 26,000 (1190)[d]
Ni(DEP)₃Cl₂[b]	22,000 (880), 28,600 (1040)
Ni(DEP)₃(NCS)₂[b]	22,000 sh (1300), 23,800 (1870), 27,400 (2960)
[Ni(DEP)₄I]B(C₆H₅)₄[c]	20,000 (1920)
[Ni(DEP)₄Br]B(C₆H₅)₄[c]	20,400 (1260), 22,750 sh (1110)
[Ni(DEP)₄Cl]B(C₆H₅)₄[c]	21,300 sh (1170), 23,800 (1330)
[Ni(DEP)₄(NCS)]B(C₆H₅)₄[c]	24,400 b (1670)

[a] Molar extinction coefficient in parentheses. [b] Obtained from [Ni(DEP)₃X]⁺ solutions in the presence of excess X⁻. [c] In the presence of excess free DEP. [d] Solid-state spectra are practically identical.

in the 2300-cm⁻¹ region attributable to P–H group of the phosphine.

The Complexes [Ni(DEP)₃X]B(C₆H₅)₄ (X = Cl, Br, I, NCS).—Diethylphosphine forms yellow diamagnetic complexes [Ni(DEP)₃X]B(C₆H₅)₄ when mixed with "NiXB(C₆H₅)₄" in a 3:1 stoichiometric ratio. The conductivity data for 10⁻³ M solutions of these complexes in 1,2-dichloroethane indicate that they are essentially 1:1 electrolytes (Table II). The electronic absorption spectra of 1,2-dichloroethane solutions of all of the complexes are characterized by a band, consistent with a four-coordinate planar structure, in which the energy of the maximum produces the series I < Br < Cl < NCS (Table III). Mull spectra are quite

similar. Thus analyses, optical spectra, conductivity data, and the observed diamagnetism strongly suggest that these compounds are square-planar cationic complexes of nickel(II). Few examples of structures of this type are known for nickel(II) complexes containing monodentate ligands and none with secondary phosphine has yet been reported. Probably the low steric requirements of diethylphosphine are the main factor in determining the stereochemistry of these species.

It is noteworthy that on starting from NiX_2, we have been unsuccessful in attempts to prepare complexes of the type $Ni(DEP)_2X_2$. Moreover, no evidences, even in solution, have been obtained for the formation of these neutral complexes.

The Complexes $[Ni(DEP)_4X]B(C_6H_5)_4$ (X = Cl, Br, I, NCS).—The reaction of the phosphine with "$NiXB(C_6H_5)_4$" in ethanol in a stoichiometric ratio greater than 4:1 yields red compounds which analyze as $[Ni(DEP)_4X]B(C_6H_5)_4$. All the complexes are diamagnetic and 1:1 electrolytes in 1,2-dichloroethane solution (Table II). The reflectance spectra of the complexes are similar to each other and show a broad multicomponent band in the 20,000–25,000-cm^{-1} region (Figure 1). The lowest energy band of $[Ni(DEP)_4$-
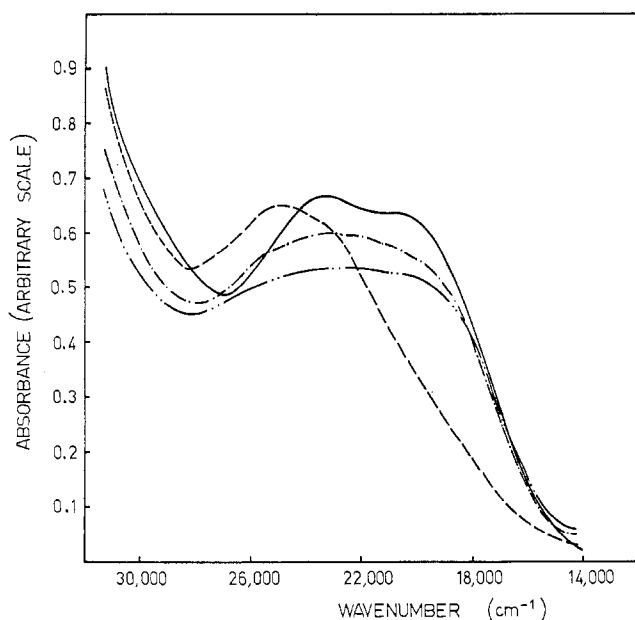

Figure 1.—Solid-state electronic spectra of the $[Ni(DEP)_4X]$-$B(C_6H_5)_4$ complexes: —, X = I; ·-·-·, X = Br; ·····-·, X = Cl; ---, X = NCS.

Cl]$^+$ complex ($\sim$21,000 cm^{-1}) occurs at higher energy than the trigonal-bipyramidal complex $[Ni(QP)Cl]^+$ (QP = tris(o-diphenylphosphinophenyl)phosphine) (17,500 cm^{-1})[9] and in the same energy range as that of the square-pyramidal $[Ni(VPP)_2Cl]^+$ (VPP = cis-1,2-bis(diphenylphosphino) ethylene) (20,600 cm^{-1}).[10] All these complexes are $Ni(P)_4Cl^+$ chromophores. However a shift toward higher energies of the ligand field band of the $[Ni(DEP)_4X]^+$ complexes is expected in going from the QP to DEP ligand.[11] Thus a trigonal-

bipyramidal structure, which is also consistent with the strong asymmetric band,[12,13] could not be excluded.

By contrast all the absorption spectra of 10^{-3} M solutions in 1,2-dichloroethane are practically identical with those of the $[Ni(DEP)_3X]^+$ complexes. On addition of excess phosphine the typical band of $[Ni(DEP)_3$-X]$^+$ chromophores disappears and, in the case of X = Cl, Br, or NCS, is replaced by an asymmetric band in the 20,000–25,000-cm^{-1} region (Table III). These spectral patterns are similar to the solid-state spectra of the $[Ni(DEP)_4X]B(C_6H_5)_4$ complexes (Figure 1), indicating that the structures of the complexes in the solid state are essentially identical with those in solution, in the presence of excess phosphine.

This does not seem the case of $[Ni(DEP)_4I]B$-$(C_6H_5)_4$, solid-state and solution spectra of which (even in the presence of excess phosphine) are very different. The solid-state spectrum consists of a composite band with maxima at 23,250 and 20,000 cm^{-1}, whereas solution spectra show a single peak at 20,000 cm^{-1}. Probably a more regular structure of the complex in solution justifies the spectral change.

It is concluded that all the $[Ni(DEP)_4X]^+$ complexes are low spin five-coordinate in the crystals. In 1,2-dichloroethane solutions they are extensively dissociated according to

$$[Ni(DEP)_4X]^+ \rightleftharpoons [Ni(DEP)_3X]^+ + DEP$$

The presence of excess free ligand represses dissociation. As expected the 1,2-dichloroethane solutions of four-coordinate $[Ni(DEP)_3X]B(C_6H_5)_4$ complexes containing phosphine behave similarly.

The Complexes $Ni(DEP)_3X_2$ (X = Cl, Br, I, NCS).—Repeated recrystallization from petroleum ether resulted in the decomposition of $Ni(DEP)_4Br_2$ and the deep red solution obtained deposited red needles, which were identified as $Ni(DEP)_3Br_2$. The analogous compound $Ni(DEP)_3I_2$ can be obtained by reaction of stoichiometric amounts of I^- and $[Ni(DEP)_3I]^+$.

The solid-state electronic spectra (Table III) of the $Ni(DEP)_3X_2$ complexes are similar in shape with those of the corresponding complexes with diphenylphosphine,[7] for which X-ray investigation[14] has ascertained a distorted trigonal-pyramidal structure. The absorption bands of diethylphosphine complexes, however, occur at considerably higher energy, and this suggests a configuration closer to square-pyramidal structure.

Solution spectra have been found markedly dependent upon the nature of solvent. The spectra in ethanol are practically coincident with those of the four-coordinate $[Ni(DEP)_3X]^+$ species according to a dissociation equilibrium

$$Ni(DEP)_3X_2 \rightleftharpoons [Ni(DEP)_3X]^+ + X^-$$

strongly displaced to the right.

In benzene or 1,2-dichloroethane the spectra show the same band contours and energy maxima as are obtained in the solid state, indicating that no structural rearrangement occurs on dissolving the compounds in these solvents. The complexes are monomeric in freezing benzene and essentially nonelectrolytes in 1,2-

(9) G. Dyer, J. G. Hartley, and L. M. Venanzi, *J. Chem. Soc.*, 1293 (1965).

(10) C. A. McAuleffe and D. W. Meek, *Inorg. Chem.*, **8**, 904 (1969).

(11) For example, the ligand field band of the complex Ni(PC$_2$H$_5$(C$_6$H$_5$)$_2$)$_3$-(CN)$_2$ occurs at 23,000 cm^{-1}, while the corresponding band of Ni(DEP)$_3$-(CN)$_2$ occurs at 25,650 cm^{-1}: P. Rigo and M. Bressan, unpublished results.

(12) G. S. Benner and D. W. Meek, *Inorg. Chem.*, **6**, 1399 (1967), and references therein.

(13) J. R. Preer and H. B. Gray, *J. Amer. Chem. Soc.*, **92**, 7306 (1970), and references therein.

(14) J. A. Bertrand and D. L. Plymale, *Inorg. Chem.*, **5**, 879 (1966).

dichloroethane solution (Table II). When phosphine is added to the 1,2-dichloroethane solutions of Ni(DEP)$_3$X$_2$, the conductance increases quite markedly and values expected for typical 1:1 electrolytes were obtained (Table II). In the same time visible spectra are considerably altered and new bands typical of the ionic five-coordinate [Ni(DEP)$_4$X]$^+$ complexes appear.

The above spectroscopic and conductivity data are in agreement with the equilibrium

$$Ni(DEP)_3X_2 + DEP \rightleftharpoons [Ni(DEP)_4X]^+ + X^-$$
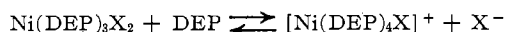
Only the bromo and the iodo complexes have been isolated in the solid state. However, the reaction between [Ni(DEP)$_3$X]$^+$ and X$^-$ in 1,2-dichloroethane solution resulted in the formation of the five-coordinate Ni(DEP)$_3$X$_2$ species, even for X = Cl and NCS.

When X$^-$ is added to the yellow 1,2-dichloroethane solutions of the [Ni(DEP)$_3$X]$^+$ complexes (X = Cl, Br, I, NCS), the color turned to red and a spectrophotometric study with mole ratio method showed that the anionic ligand reacted in the mole ratio 1:1.

In the presence of excess anionic ligand, the spectra of the solution of the bromo and iodo complexes are respectively coincident with those of the compound Ni(DEP)$_3$X$_2$ discussed above. Also in the case of chloro and thiocyanate complexes the solution spectra show two bands, with shapes and λ_{max} in agreement with those of Ni(DEP)$_3$Br$_2$, strongly suggesting that five-coordinate tris-phosphine complexes are the predominant species in these solutions. The bands move to higher energy in the order I < Br < Cl < NCS, according to the spectrochemical series (Table III).

The Complexes Ni(DEP)$_4$X$_2$ (X = Cl, Br, I).—Addition of excess diethylphosphine to absolute ethanolic solutions of nickel(II) halides results in the immediate formation of intensely colored solutions, which deposit red diamagnetic compounds of composition Ni(DEP)$_4$X$_2$.

For the chloro and bromo complexes, previously reported by Issleib, *et al.*,[6] a low-spin six-coordinate structure with halogen atoms in the cis position has been proposed, on the basis of conductivity, dipole moment, and molecular weight measurements. No spectral data have been reported and discussed.

We found that the solid-state visible spectra of all the Ni(DEP)$_4$X$_2$ complexes show a broad band in the 25,000–20,000-cm^{-1} region, which closely resembles that of the [Ni(DEP)$_4$X]$^+$ chromophores (Figures 1 and 2).

Thus, in agreement with spectral evidences, we believe that these compounds in the solid state can be better formulated as ionic [Ni(DEP)$_4$X]X, wherein only one halogen atom is directly bound to the metal.

Solution spectra have been found markedly dependent upon the concentration, the nature of the solvent, and the presence of free phosphine. The predominant species in ethanolic solutions are the square-planar four-coordinate [Ni(DEP)$_3$X]$^+$ complexes. Addition of a phosphine excess produces the five-coordinate [Ni(DEP)$_4$X]$^+$, while addition of X$^-$ (about 100:1 molar ratio) does not appreciably change the spectral pattern.

The spectral patterns of diluted solutions of Ni(DEP)$_4$X$_2$ in 1,2-dichloroethane ($\sim$5 × 10^{-4} M) are consistent with those of Ni(DEP)$_3$X$_2$. On increasing
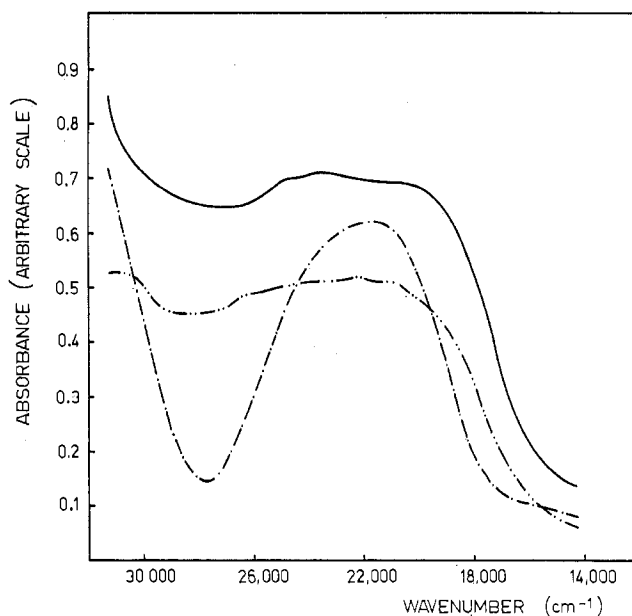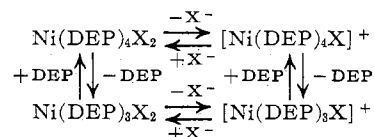

Figure 2.—Solid-state electronic spectra of the Ni(DEP)$_4$X$_2$ complexes: —, X = I; ······, X = Br; -----, X = Cl.

the concentration of the complex, the spectrum typical of Ni(DEP)$_3$X$_2$ is altered, indicating the existence in solution of different species. The formation of ionic species in the more concentrated solutions was ruled out because the conductivity was as negligible as in the diluted solutions. On the other hand the presence of relevant amounts of the compound [Ni(DEP)$_4$X]$^+$ could be excluded also on the basis of the spectral evidences. The simplest interpretation of these data is that the equilibria in concentrated solutions involve also a six-coordinate species Ni(DEP)$_4$X$_2$.

Also in this solvent, addition of diethylphosphine gives the five-coordinate cationic complexes [Ni(DEP)$_4$X]$^+$, as shown by spectra and conductivity evidences.

The combined results presented above provide evidence for the existence of a series of equilibria, strongly dependent on the nature of the solvent, according to the scheme

$$Ni(DEP)_4X_2 \underset{+X^-}{\overset{-X^-}{\rightleftharpoons}} [Ni(DEP)_4X]^+$$
$$+DEP\Big\uparrow\Big\downarrow-DEP \qquad +DEP\Big\uparrow\Big\downarrow-DEP$$
$$Ni(DEP)_3X_2 \underset{+X^-}{\overset{-X^-}{\rightleftharpoons}} [Ni(DEP)_3X]^+$$

Conclusions

The most notable result of this work is the characterization of two series of low-spin five-coordinate complexes with the sets of donor atoms P$_4$X and P$_3$X$_2$ (X = halogen or pseudohalogen).

Whereas complexes of the type NiL$_3$X$_2$ are now fairly common with tertiary and secondary phosphines, [Ni(DEP)$_4$X]$^+$ complexes appear to be one of few examples of five-coordinate cationic complexes of nickel(II) with monodentate ligands.

It is interesting to note that the stability of the five-coordinate Ni(HPR$_2$)$_3$X$_2$ complexes (X = halogen) depends greatly on the nature of the organic substituent attached to the phosphorus atom of the phosphine, the order being HP(C$_6$H$_{11}$)$_2$ < HP(C$_6$H$_5$)$_2$ < HP(C$_2$H$_5$)$_2$.

In fact the tris-diethylphosphine complexes are

much more stable in solution than the corresponding diphenylphosphine complexes,[7] and no evidences of tris-phosphine adducts have been obtained with dicyclohexylphosphine.[15] The same stability order is found in the case of the [Ni(HPR$_2$)$_4$X]$^+$ species, which are formed only with diethylphosphine.

Steric arguments could provide the most obvious interpretation of this trend. However, we believe that this fact alone cannot explain entirely the drastic col-

(15) P. Rigo and M. Bressan, unpublished results.

lapse of the stability of the five-coordinate adducts, going from diethylphosphine to dicyclohexylphosphine.

Probably, as already suggested for the case of tertiary phosphine complexes,[2–5] the stabilization of five-coordinate species depends on a favorable balance of electronic as well steric factors.

# Dithiotropolonates. III.[1] Ring-Alkylation Reactions of Bis(dithiotropolonato)nickel(II) and -zinc(II) Complexes

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Bis(dithiotropolonato)nickel(II) and -zinc(II) have been found to undergo reactions consistent with electrophilicity of the seven-membered ring. Reaction of M(SST)$_2$ (**2, 3**) with methyllithium in THF has been shown to yield the anionic methylated complexes [Ni(H,Me-SST)$_2$]$^{2-}$ (**6**), [Zn(H,Me-SST)(SST)]$^-$ (**9**), and [Zn(H,Me-SST)$_2$]$^{2-}$. Controlled oxidation of the nickel dianion gave the spin-doublet complex [Ni(H,Me-SST)$_2$]$^-$ (**7**). Pure salts of the anions **6**, **7**, and **9** were isolated. Exhaustive oxidation of the nickel mono- or dianion afforded the methyl-substituted dithiotropolonate complex Ni(Me-SST)$_2$ (**8**). Electrochemical, epr, and spectral studies of the nickel complexes have revealed the existence of the electron-transfer series [Ni(H,Me-SST)$_2$]^z, where $z = 2-$, $1-$, 0, and other familiar electronic characteristics of nickel dithiolenes. These findings together with the results obtained from spin-decoupled pmr spectra of the zinc dianion establish that methylation has occurred at the α carbon of the seven-membered ring. Certain parallels are pointed out between the reactions of azulene and M(SST)$_2$ complexes with organolithium reagents. Methylation reactions of the complexes are considered to proceed by direct nucleophilic attack rather than by a free-radical process.

Introduction

In parts I[1a] and II[1b] of this series we have reported the synthesis of dithiotropolone (2-mercaptocycloheptatrienethione, **1**) and certain of its bis(chelate)-metal(II) complexes, M(SST)$_2$ (**2, 3**). These complexes
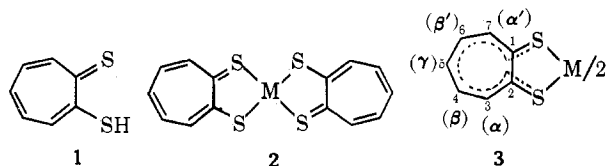
are of particular interest because, like the thoroughly studied bis-dithiolene complexes,[3–5] they contain unsaturated five-membered chelate rings with sulfur donor atoms. However, the dithiotropolonates of the nickel group do not possess ground-state electronic structures equivalent or analogous to the corresponding neutral dithiolenes, a situation which is most simply expressed in VB terms. The dithiotropolonate chelate ring lacks the dithiolate–dithione resonance properties strictly analogous to those considered responsible for the relatively high electron affinities of the neutral dithiolenes.[3–5] The most nearly analogous resonance

(1) (a) Part I: C. E. Forbes and R. H. Holm, *J. Amer. Chem. Soc.*, **90**, 6884 (1968); (b) part II: C. E. Forbes and R. H. Holm, *ibid.*, **92**, 2297 (1970).
(2) National Institutes of Health Predoctoral Fellow, 1968–1971.
(3) J. A. McCleverty, *Progr. Inorg. Chem.*, **10**, 49 (1968).
(4) G. N. Schrauzer, *Transition Metal Chem.*, **4**, 299 (1968); *Accounts Chem. Res.*, **2**, 72 (1969).
(5) E. Hoyer and W. Dietzsch, *Z. Chem.*, **11**, 41 (1971).

forms are obtainable only with invocation of presumably excited ligand structures which involve charge separation or unpairing of electrons[1b] and, therefore, would make only small contributions to the ground-state electronic structure. Consistent with this situation are the considerably more negative (0.75–1.0 V) half-wave potentials for the electrochemically irreversible reductions of the nickel group dithiotropolonates compared to the values for the reversible reductions of the dithiolenes of this group. The electronic structures of dithiotropolonate complexes are best described by **2** and its symmetry-related form, which lead to the delocalized structure **3**. Dithiotropolonates are therefore examples of complexes containing odd-atom mono-anionic ligands with an even number of π electrons[4] and do not possess low-energy vacant orbitals. In contrast, the dithiolenes (*e.g.*, M(S$_2$C$_2$R$_2$)$_2^z$, M(S$_2$C$_6$H$_4$)$_2^z$) are of the even–odd types,[4] leading to dithiolate-dithione resonance contributions in the neutral species which impart partial α-dithione character to each coordinated ligand, thereby accounting for the relatively high electron affinities of these complexes.

This view of the electronic structure of M(SST)$_2$ complexes has been confirmed in substantial part by the recent X-ray structural determination of Ni(SST)$_2$.[6] The complex is planar (overall D_{2h} symmetry), consistent with its diamagnetism,[2] and has an average Ni–S distance of 2.147 Å, indicating some metal–ligand

(6) G. P. Khare, A. J. Shultz, and R. Eisenberg, *J. Amer. Chem. Soc.*, **93**, 3597 (1971).