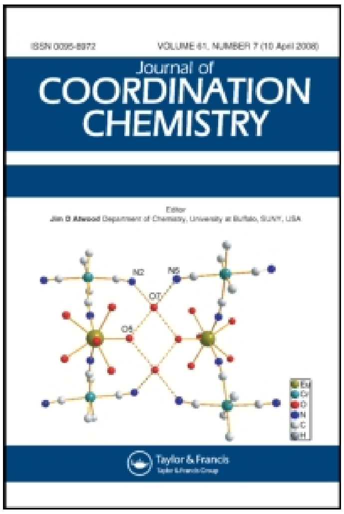

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

PSEUDOTETRAHEDRAL METAL (II) COMPLEXES OF TRIS- (t-BUTYL) PHOSPHINE

Elmer C. Alyea[a]; George T. Fey[a]; Ram G. Goel[a]
[a] Guelph-Waterloo Centre for Graduate Work in Chemistry Department of Chemistry, University of Guelph, Guelph, Ontario, Canada

To cite this Article Alyea, Elmer C. , Fey, George T. and Goel, Ram G.(1976) 'PSEUDOTETRAHEDRAL METAL (II) COMPLEXES OF TRIS- (t-BUTYL) PHOSPHINE', Journal of Coordination Chemistry, 5: 3, 143 — 152

To link to this Article: DOI: 10.1080/00958977608073001

URL: http://dx.doi.org/10.1080/00958977608073001

J. Coord. Chem.
1976, vol. 5, pp. 143–152

Printed in Great Britain

PSEUDOTETRAHEDRAL METAL (II) COMPLEXES OF TRIS-(t-BUTYL) PHOSPHINE

ELMER C. ALYEA, GEORGE T. FEY[1] and RAM G. GOEL

Guelph–Waterloo Centre for Graduate Work in Chemistry
Department of Chemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1

(Received June 5, 1975; in final form August 25, 1975)

The synthesis of divalent metal complexes of the type $[\mathrm{Bu}^t_3\mathrm{PH}]$ $[(\mathrm{Bu}^t_3\mathrm{P})\mathrm{MX}_3]$ (M = Ni; X = Cl, Br, I; M = Co; X = Br; M = Zn; X = Cl) is reported. Characterization of the solids by conductivity, magnetic susceptibility, electronic and vibrational spectral measurements indicate that the structures are similar and unchanged in solution from the solid state. On the basis of an earlier X-ray single crystal analysis of $[\mathrm{Bu}^t_3\mathrm{PH}]$ $[(\mathrm{Bu}^t_3\mathrm{P})\mathrm{NiBr}_3]$ and a comparison of the physical measurements for the series of complexes, the inner coordination geometry of the anions can be represented as pseudotetrahedral with C_{3v} local symmetry. The unexpected formation of these ionic complexes is attributed to the bulkiness of tris-(*t*-butyl) phosphine. The isolation and probable geometry of the anion are also discussed for an orange-brown $[\mathrm{Bu}^t_3\mathrm{PH}]$ $[\mathrm{Ni(NCS)}_3]$ complex.

INTRODUCTION

The coordination complexes of transition metal ions and phosphines is an extensively investigated field of chemistry. Nickel(II) complexes of monodentate phosphines have received particular interest because of the variety of coordination numbers and stereochemistries that have been proved possible[2,3]. The various factors which influence the adoption of a planar (diamagnetic) or a tetrahedral (paramagnetic) geometry in complexes of the type $[\mathrm{Ni(PR_3)_2X_2}]$, which are the commonest type of nickel(II)–phosphine complexes, have been studied by a number of spectroscopic techniques[2,3]. In general, it is expected that aryldialkyl- and trialkylphosphines will form planar diamagnetic complexes both in the solid state and in solution whereas triarylphosphines give tetrahedral paramagnetic structures. A number of four-coordinate nickel(II) complexes, including bis(n-alkyldiphenylphosphine)nickel dihalides[4–7], participate in a structural equilibrium between the planar and tetrahedral forms and their characterization has led to considerable understanding of the steric and electronic factors that determine which structural isomer is more stable.

In initiating an investigation of transition metal complexes of the little-studied tris(*t*-butyl) phosphine[8], the stereochemistry adopted in the nickel(II) complexes $\mathrm{Ni(PBu^t_3)_2X_2}$ appeared worthy of study because steric ligand-ligand interactions would favor the tetrahedral configuration whereas the strong ligand field of the trialkylphosphine would supposedly stabilize the planar isomer. The square-planar geometry has been established by X-ray single-crystal analysis for $\mathrm{Ni(Cy_3P)_2Cl_2}$[9] and tris(*t*-butyl)phosphine apparently[10] has similar steric and electronic properties to tricyclohexylphosphine. The addition of $\mathrm{Bu^t_3P}$ in a 2:1 molar ratio to an alcoholic solution of $\mathrm{NiBr_2}$ led to the isolation of a green paramagnetic complex which was found to be $[\mathrm{Bu}^t_3\mathrm{PH}]$ $[(\mathrm{Bu}^t_3\mathrm{P})\mathrm{NiBr}_3]$ by a X-ray crystal structure determination[11]. Although the existence of pseudotetrahedral anions of this type was recognized many years ago[12], the formation of $[(\mathrm{Bu}^t_3)\mathrm{NiBr}_3]^-$ in the above reaction was unexpected. In order to establish the generality of the synthetic route we examined the reaction of tris(*t*-butyl)phosphine with halides of nickel, cobalt and zinc. In each case the reaction led to the formation of the complexes of the type $[\mathrm{Bu}^t_3\mathrm{PH}]$ $[(\mathrm{Bu}^t_3\mathrm{P})\mathrm{MX}_3]$, where M = Ni, Co or Zn and X = Cl or Br. Metathetical reactions of $[\mathrm{Bu}^t_3\mathrm{PH}]$ $[(\mathrm{Bu}^t_3\mathrm{P})\mathrm{NiBr}_3]$ with excess KI and KCNS in n-butanol solution give $[\mathrm{Bu}^t_3\mathrm{PH}]$ $[(\mathrm{Bu}^t_3)\mathrm{NiI}_3]$ and $[\mathrm{Bu}^t_3\mathrm{PH}]$ $[\mathrm{Ni(NCS)_3}]$ respectively. This paper reports the synthesis and characterization of the complexes of the type $[\mathrm{Bu}^t_3\mathrm{PH}]$ $[(\mathrm{Bu}^t_3\mathrm{P})\mathrm{MX}_3]$ (M = Ni; X = Cl,Br, I; M = Co; X = Br; M = Zn; X = Cl) and of the species $[\mathrm{Bu}^t_3\mathrm{PH}]$ $[\mathrm{Ni(NCS)_3}]$.

EXPERIMENTAL

Chemicals

Di-*t*-butylphosphine chloride was obtained from

Orgmet, Inc. It was fractionally distilled at 70°C/10 mm. Hg as described previously[13]. *t*-Butyl lithium (2M in pentane) was purchased from Research Organic/Inorganic Chemical Corp. Tris(*t*-butyl)phosphine was synthesized by adding the Bu^{t}Li solution to the Bu$^t_2$PCl dissolved in benzene by previously described methods[8a,13a]. The colorless liquid collected at 50–52°/2 mm. Hg [lit. 102–103°/13 mm. Hg][8a] was sealed under nitrogen in ampoules until required. It was further characterized by conversion to the sulfide[8a] and hydrochloride and stored in the dry box in serum-capped bottles. Other solvents were purified and dried following standard procedures. 2,2-Dimethoxy propane was distilled at 83°. Metal salts were used as received from commercial sources.

Physical Measurements

Elemental analyses were performed by M-H-W Laboratories, Garden City, Michigan, or by Galbraith Laboratories, Knoxville, Tenn. Infrared spectra were obtained in the region 4000–250 cm^{-1} using a Beckman IR-12 spectrophotometer and in the 350–140 cm^{-1} range using a Perkin-Elmer 180 instrument. Solid state spectra were recorded as Nujol or Halocarbon mulls between KRS-5 plates or polythene discs. Solution spectra were recorded using matched NaCl cells of 0.1 mm. path length. Raman spectra were obtained with a Jarrell-Ash spectrophotometer using the 514.5 nm line of a Spectra-Physics 165 laser. Nmr spectra were recorded at ambient temperatures on a Varian A-60 spectrometer with TMS as reference standard. Electronic spectra in solution in the region 5,000–35,000 cm^{-1} were measured in CH_2Cl_2 using matched solution cells on a Cary 14 recording spectrophotometer. Spectra of solid samples were obtained by the diffuse transmittance technique[14] employing Nujol mulls on filter paper. Magnetic susceptibility measurements[15a] were obtained on solid samples by the Faraday method[15b] and on CH_2Cl_2 or CH_3CN solutions by the Evans nmr method[15c]. Diamagnetic corrections were made employing Pascal's constants[15a]. Conductivity measurements were obtained for CH_3CN solutions with a Beckman RC-16B2 conductivity bridge using a conductivity cell with

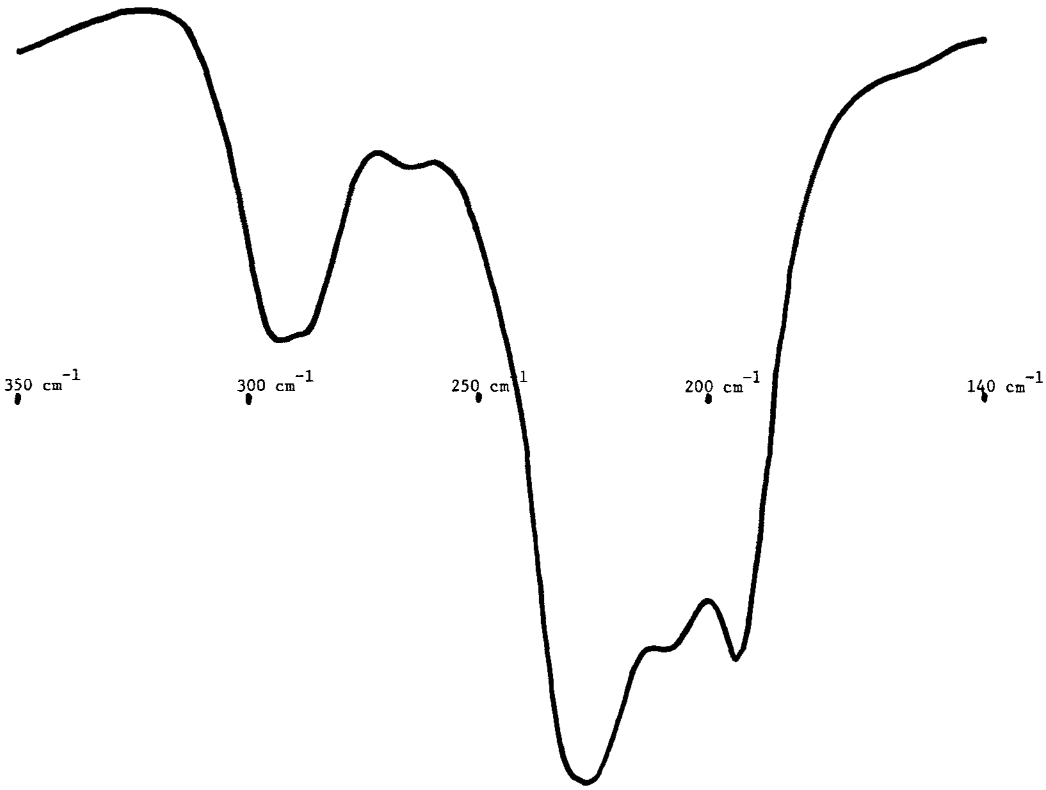

FIGURE 1 The far infrared spectrum of [Bu$^t_3$PH] [(Bu$^t_3$P)NiBr$_3$].

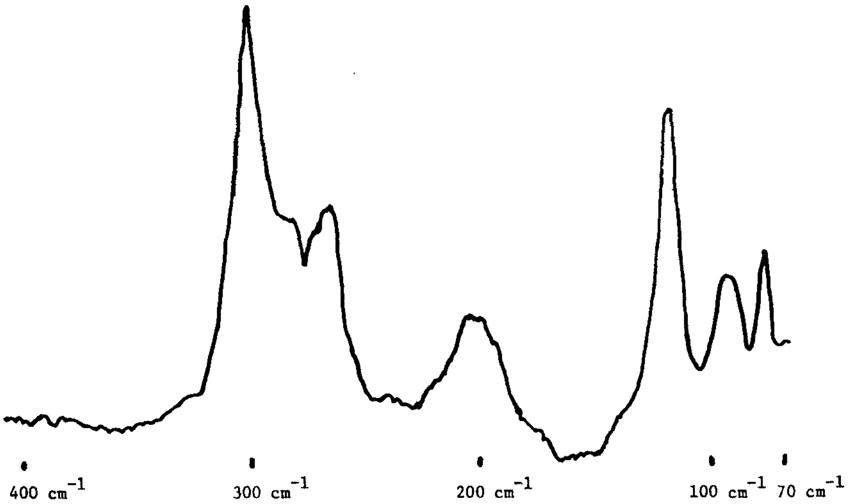

FIGURE 2 The Raman spectrum of [Bu$^t_3$PH] [(Bu$^t_3$P)ZnCl$_3$] in the 400–70 cm^{-1} region.

platinum electrodes. Melting points were determined with a Gallenkamp melting point apparatus in sealed capillary tubes and are uncorrected.

Preparation of Complexes

Since tris(*t*-butyl)phosphine and some of the complexes are very air-sensitive (in solution), all operations involved in synthesis, purification, and subsequent handling of these compounds were conducted under an oxygen-free dry nitrogen atmosphere.

[Bu$^t_3$PH] [(Bu$^t_3$P)NiBr$_3$]. Anhydrous nickel(II) bromide (1.87g, 8.55 mmol) was dissolved in n-butanol[16] (60 ml) and filtered into a hot solution of Bu$^t_3$P (3.23g, 16.0 mmol) in n-butanol (10 ml). A green solid soon separated; this was collected and dried *in vacuo* over phosphorus pentoxide in an Alderhalden pistol at 56°. Recrystallization of the powder from dichloromethane gave dark green crystals; m.p. 195–196° (dec). *Anal.* Calcd. for $C_{24}H_{55}Br_3P_2Ni$:C, 40.94; H, 7.87; Br, 34.05. Found: C, 40.85; H, 7.70; Br, 34.46.

[Bu$^t_3$PH] [(Bu$^t_3$P)NiCl$_3$]. Anhydrous nickel(II) chloride (1.28g, 9.9 mmol) was refluxed in n-butanol[16] (60 ml) containing 6 ml of 2,2-dimethoxypropane. Transfer of this yellow-orange solution to a solution of Bu$^t_3$P (2.00g, 9.9 mmol) in n-butanol (5 ml) gave immediately a bright blue solution. Filtration removed a yellow residue; concentration of the filtrate gave a blue solid that was collected and dried *in vacuo*. Combination of the latter filtrate with the yellow residue removed previously and subsequent refluxing of the mixture led to the isolation of another fraction of the product. Recrystallization of the blue solid from dichloromethane gave a deep blue crystalline product; m.p. 189–190° (dec). *Anal.* Calcd. for $C_{24}H_{55}Cl_3P_2Ni$: C, 50.51; H, 9.71; Cl, 18.64. Found; C, 50.64; H, 9.83; Cl, 18.51.

[Bu$^t_3$PH] [(Bu$^t_3$P)NiI$_3$]. A mixture of [Bu$^t_3$PH] [(Bu$^t_3$P)NiBr$_3$] (0.24g, 0.34 mmol) and KI (0.52g, 3.1 mmol) was refluxed in 20 ml of n-butanol[16]. The red-black mixture was warmed and stirred overnight before filtration. The solvent was completely removed from the filtrate under reduced pressure and the residue recrystallized from dichloromethane. The dark red solid was collected and dried *in vacuo*; m.p. 209–210° (dec). *Anal.* Calcd. for $C_{24}H_{55}I_3P_2Ni$: C, 34.41; H, 6.56; I, 45.05. Found: C, 34.05; H, 6.70; I, 44.87.

[Bu$^t_3$PH] [Ni(NCS)$_3$]. A mixture of [Bu$^t_3$PH] [(Bu$^t_3$P)NiBr$_3$] (0.45g, 0.64 mmol) and KSCN (0.21g, 2.2 mmol) was refluxed in 20 ml of n-butanol[16]. After filtration to remove a white precipitate, the solvent was completely removed from

the green filtrate. Recrystallization of the residue from dichloromethane-hexane gave an orange-brown solid; m.p. 205–206° (dec). *Anal.* Calcd. for $C_{15}H_{28}N_3PS_3Ni$: C, 41.30; H, 6.42; N, 9.63. Found: C, 41.30; H, 6.51; N, 9.46.

$[Bu^t_3PH]$ $[(Bu^t_3P)CoBr_3]$. Anhydrous cobalt(II) bromide (0.62g, 2.84 mmol) dissolved in 15 ml of n-butanol[16] was added to Bu^t_3P (1.15g, 5.70 mmol), giving a dark blue mixture. After heating the mixture for 3 hr. and filtration, the dark blue product was recovered from the filtrate and dried *in vacuo* at 56°, in a drying-pistol, for several hours. Recrystallization from dichloromethane gave blue crystals; m.p. 199–200°. *Anal.* Calcd. for $C_{24}H_{55}Br_3P_2Co$: C, 40.93; H, 7.87; Br, 34.04. Found: C, 40.70; H, 7.63; Br, 34.19.

$[Bu^t_3PH]$ $[(Bu^t_3P)ZnCl_3]$. Anhydrous zinc(II) chloride (0.75g, 5.5 mmol) and Bu^t_3P (2.60g, 12.9 mmol) were added to 25 ml of n-butanol[16] and the mixture stirred for 30 min. with heating. Filtration gave a colorless solution from which a white solid precipitated on standing. Recrystallization of this product from dichloromethane gave white crystals; m.p. 198–199°. *Anal.* Calcd for $C_{24}H_{55}Cl_3P_2Zn$: C, 49.93; H, 9.60; Cl, 18.92. Found: C, 49.73; H. 9.66; Cl, 18.67.

RESULTS AND DISCUSSION

Synthesis of the Complexes

In general, all of the complexes are stable toward air in the solid state but display differing stabilities in solution, the iodo-derivative decomposing rapidly even under an anhydrous nitrogen atmosphere. All of the complexes are reasonably soluble in dichloromethane, nitromethane and acetonitrile but are insoluble in hexane.

The addition of a tertiary phosphine ligand in a 2:1 molar ratio to a nickel(II) salt in alcoholic solution is expected[3] to lead to formation of a neutral species of stoichiometry $NiX_2(PR_3)_2$. Accordingly, isolation of a green paramagnetic solid $[Bu^t_3PH]$ $[(Bu^t_3P)NiBr_3]$ was unexpected from the reaction between Bu^t_3P and nickel(II) bromide. Although Cotton and co-workers[12] reported the existence of salts containing $[(R_3P)NiX_3]^-$ anions several years ago, the earlier preparation of this type of pseudotetrahedral nickel(II) complex involved significantly different experimental conditions. Either the tertiary phosphine, organic halide and nickel halide in mole ratio of 2:1:1 were heated in a sealed tube or solutions of the tertiary phosphine, cation salt and nickel halide in molar ratio of 1:1:1 were allowed to crystallize. In the present work, the reaction between Bu^t_3P and nickel(II) bromide in a 2:1 mole ratio always led to the isolation of $[Bu^t_3PH]$ $[(Bu^t_3P)NiBr_3]$ as the only characterizable nickel-containing species regardless of the order of addition of the reagents or the duration of mixing or reflux. Similarly, our isolation of other $[Bu^t_3PH]$ $[(Bu^t_3P)MX_3]$ complexes under varying conditions (see Experimental) indicates that their

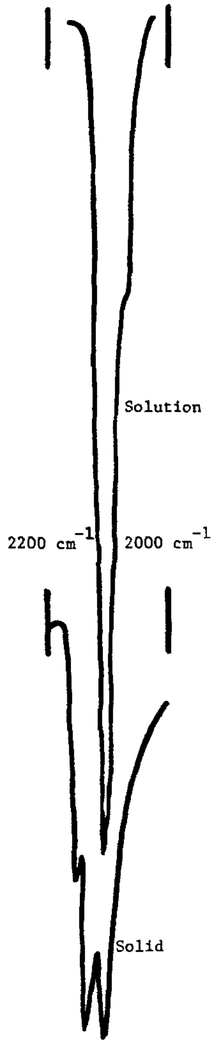

FIGURE 3 The infrared spectrum of $[Bu^t_3PH]$ $[Ni(NCS)_3]$ in the 2000–2200 cm^{-1} region.

formation is characteristic of the interaction of Bu^t_3P with divalent metal halides in alcoholic solution.

The unexpected ionic nature of the complexes requires some consideration of a feasible reaction pathway to the observed products. The question of the source of the phosphonium hydrogen atom is particularly intriguing. Since all of the reactions were carried out under anhydrous conditions, the hydrogen is most likely abstracted from the solvent or from another phosphine molecule. The absence of water was assured by the use of anhydrous dry box conditions including prior drying of the butanol[16] solvent by fractional distillation from calcium hydride and of the metal halides *in vacuo* or by refluxing with 2,2-dimethoxypropane. It might be noted that no reaction occurs between Bu^t_3P and a $NiBr_2$-dimethoxyethane solution, thus offering some support for the first alternative involving the participation of the alcohol in the reaction scheme. Hydrogen abstraction from an alcohol solvent has been shown to occur in the formation of metal hydrides[17].

The formation of the iodo-derivative from $[Bu^t_2PH]$ $[(Bu^t_3P)NiBr_3]$ takes place in a straightforward metathetical reaction bur the product isolated after refluxing KCNS with the bromo-derivative corresponds to the formulation $[Bu^t_3PH]$ $[Ni(NCS)_3]$, i.e., displacement of Bu^t_3P from the anion occurs as well as exchange of the bromo-atoms. Since steric interaction of the linear isothiocyanato-groups with the coordinated Bu^t_3P would not be any greater than in the iodo complex, electronic factors must have a major influence in formation of the $[Ni(NCS)_3]^-$ anion. It is worth nothing here that prevous attempts[12] to isolate $[(R_3P)NiCl_3]^-$ (R = Ph, n-Bu) and $[(Ph_3P)Ni(CNS)_3]^-$ yielded instead $[NiCl_3]^-$ and $(Ph_3P)_2Ni(CNS)_2$, respectively. Similarly, attempts to prepare $[Cy_3P)NiX_3]^-$anions were also unsuccessful[12].

Characterization of the Complexes

An X-ray single crystal analysis[11] of the green complex $[Bu^t_3PH]$ $[(Bu^t_3P)NiBr_3]$ has shown that the solid state structure consists of discrete $[Bu^t_3PH]^+$ cations and $[(Bu^t_3P)NiBr_3]^-$ anions, with the latter having nearly C_{3v} symmetry (excluding the *t*-butyl groups). Table I lists the magnetic and conductance data for the complexes. Table II lists the infrared spectral bands observed in the far infrared region whilst Figure 1 shows the infrared spectrum of $[Bu^t_3PH]$ $[(Bu^t_3P)NiBr_3]$ in the 350–140 cm^{-1} region. The Raman spectrum of $[Bu^t_3PH]$ $[(Bu^t_3P)ZnCl_3]$ is shown in Figure 2 and Figure 3 illustrates the solid and solution infrared spectra of the isothiocyanato-derivative near 2100 cm^{-1}. Details of the electronic spectra are recorded in Table III and illustrated in Figure 4 for the nickel halide complexes.

Conductivity Measurements

Molar conductances of the new compounds in acetonitrile or nitromethane are indicative of uni-univalent electrolytes[18]. The value of Λ_M iodo-derivative is well above the normal range

TABLE I

Magnetic and conductance data

Complex	μ_{eff}, B.M.[a] solid-state	μ_{eff}, B.M. CH_2Cl_2 solution	Conductance[b] (in ohm^{-1} cm^2 $mole^{-1}$)
$[Bu^t_3PH]$ $[(Bu^t_3P)NiCl_3]$	4.02	4.09	141
$[Bu^t_3PH]$ $[(Bu^t_3P)NiBr_3]$	3.73	3.87	223
$[Bu^t_3PH]$ $[(Bu^t_3P)NiI_3]$	3.07	(2.8)[c]	(432)[c]
$[Bu^t_3PH]$ $[(Bu^t_3P)CoBr_3]$	4.70	4.52	153
$[Bu^t_3PH]$ $[(Bu^t_3P)ZnCl_3]$	diam.	diam.	55
$[Bu^t_3PH]$ $[Ni(NCS)_3]$	3.66	3.74[d]	191

[a] At 296°K, corrected for diamagnetism and, for the cobalt complex, an assumed T.I.P. contribution of 500 x 10^{-6} c.g.s. units.
[b] Λ_M for *ca.* 10^{-3} M acetonitrile solutions, except nitromethane solution for zinc complex.
[c] Decomposition was obvious on standing.
[d] Acetonitrile solution.

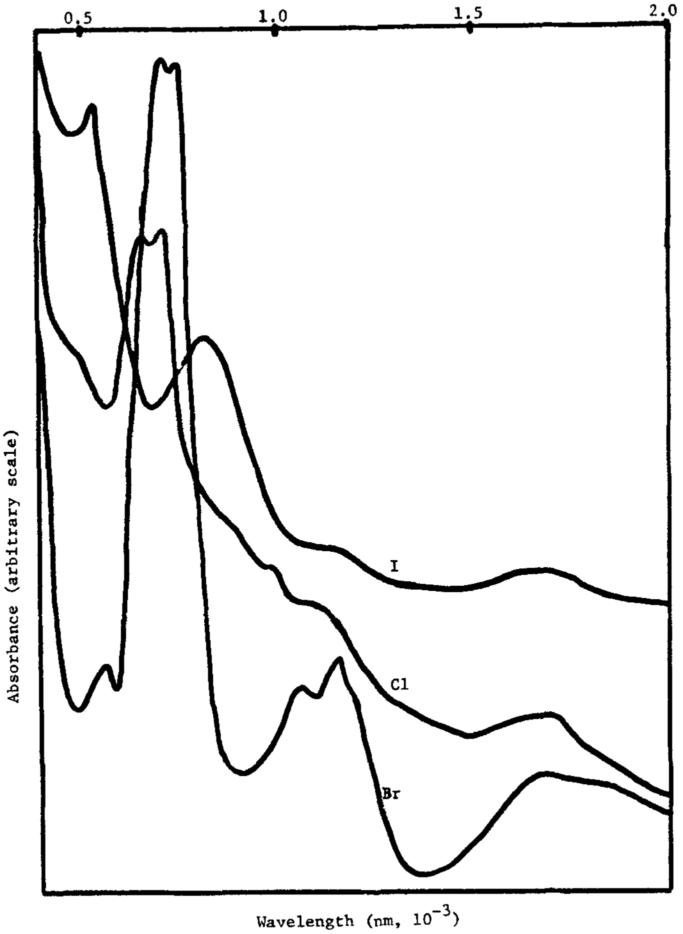

FIGURE 4 The solid-state electronic spectra of the [Bu$^t_3$PH] [(Bu$^t_3$P)NiX$_3$] complexes.

TABLE II

Far infrared spectra bands of the complexes

Complex	ν(M−X)	ν(M−P)	Other frequencies
[Bu$^t_3$PH] [(Bu$^t_3$P)ZnCl$_3$]	325w,sh, 300w,sh 274vs	210w,b	494m, 479m, 242w,sh, 222w
	(328vs)^a, (290sh), (272s)	(206m)	(122s), (96m), (80m)
[Bu$^t_3$PH] [(Bu$^t_3$P)NiCl$_3$]	295vs, 276vs	211w	496w, 479m, 242w, 161m
[Bu$^t_3$PH] [(Bu$^t_3$P)NiBr$_3$]	232vs, 214s	199s^b	495m, 477m, 298w,
[Bu$^t_3$PH] [(Bu$^t_3$P)NiI$_3$]	201s	201s^b	497m, 476m, 298w, 230sh
[Bu$^t_3$PH] [(Bu$^t_3$P)CoBr$_3$]	238vs	201s^b	494m, 476m, 300w, 272vs, 214w
[Bu$^t_3$PH] [(Ni(NCS)$_3$]	292s, 256vs, 244vs	——	501w, 480m, 464w, 456w, 213w, 188w, 172w

[a] Raman spectrum in 400–70 cm^{-1} region in parentheses.
[b] Intensity mainly due to a ν(M−X) component.

(150–200 ohm^{-1} cm^2 mol^{-1}) observed for uni-univalent electrolytes in acetonitrile and reflects the instability of this product towards dissociation and decomposition. Solutions of this dark red complex in dichloromethane and nitromethane gave precipitates on standing.

TABLE III

Electronic absorption spectra of the metal(II) complexes of tris(*t*-butyl)phosphine

Complex	E_{max}, nm CH_2Cl_2 solution(ϵ)[a]	E_{max}, nm Nujol mulls at ~300°K
$[Bu^t_3PH][(Bu^t_3P)NiCl_3]$	350(1570)	350
	460(7)	460
	630(136)	635
	685(141)	680
	975(26)	975
	1085(41)	1080
	1660(21,b)	1675(b)
$[Bu^t_3PH][(Bu^t_3P)NiBr_3]$	320	338
	382(3217)	388
	540(13)	544
	675(198)	690
	720(194)	720
	1040(45)	1040
	1140(55)	1138
	1700(27,b)	1670(b)
$[Bu^t_3PH][(Bu^t_3P)NiI_3$	340(1210)	
	400(1430)	
	510(1210)	510
	780(155)	800
	1130(35)	1120
	1380(26)	1700(b)
	1680(19,b)	
$[Bu^t_3PH][(Bu^t_3P)CoBr_3]$	307(2300)	325
	415(16)	415
	455(19)	458
	490(16)	492
	560(26)	567
	650(775)	650
	682(1005)	675
	715(1020)	710
	1450(111,b)	1490(b)
	2135(93,b)	2140(b)
$[Bu^t_3PH][(Bu^t_3P)ZnCl_3]$	300	322
$[Bu^t_3PH][Ni(NCS)_3]$[b]	360(436)	390
	625(30)	465
	910(15)	785
	980(22)	900(sh)
		980(sh)
		1750(b)

[a] Molar extinction coefficient in parenthesis.
[b] Acetonitrile solution.

Magnetic Data

Truly tetrahedral nickel(II) complexes exhibit effective magnetic moments near 4.0 B.M. whereas pseudotetrahedral nickel(II) complexes having C_{2v} symmetry [i.e., $(R_3P)_2NiX_2$] show moments at *ca.* 3.2 B.M.^{2,3}. In the present complexes, which have local C_{3v} symmetry in the anion the magnetic moments of the chloro- and bromo-anions are only slightly below the expected value for regular tetrahedral nickel(II) complexes. Splitting of the $^3T_1$ orbital ground state of T_d symmetry by the low symmetry component of the ligand field thus does not exceed a few hundred wave numbers. The magnetic moment of $[Bu^t_3PH]$ $[(Bu^t_3P)NiBr_3]$ agrees well with that previously reported for $[Et_4N]$ $[(Ph_3P)NiBr_3]$ ($\mu_{eff} = 3.68$ B.M.)^{12} The lower moment of the iodo-derivative than the bromo- and chloro-derivatives is expected, as the iodide must differ most from Bu^t_3P in the spectrochemical series, but the extent of lowering is initially surprising since μ_{eff} for the $[(Ph_3P)NiI_3]^-$ ion was reported to be 3.46 B.M.^{12}. Thus, in addition to the low symmetry field due to the disparity of the ligands and covalency effects which would be expected to split the orbital triplet (of T_d symmetry), an additional influence seems apparent. In view of the steric crowding that is evident in the $[(Bu^t_3P)NiBr_3]^-$ anion^{11} even greater distortion of bond angles and bond distances from regular tetrahedral values is to be expected in the iodo-anion, and hence a greatly lowered magnetic moment.

The magnetic moment of the Co(II) derivative, after correction for temperature independent paramagnetism (assumed to be 500 x 10^{-6} c.g.s. units)^{19,20}, compares well with the values of μ_{eff} found for other tetrahedral Co(II) complexes^{20}, and indeed is nearly identical to that calculated for $[CoBr_4]^{2-}$. The implication that the ligand field strength of Bu^t_3P is similar to Br^- is misleading, since all the other magnetic and spectral evidence in this work is consistent with a high ligand field strength for Bu^t_3P. Nevertheless the high values of μ_{eff} for the $[(Bu^t_3P)MX_3]^-$ (M = Ni; X = Cl,Br; M = Co; X = Br) anions could be a manifestation of a long M-P bond distance in these complexes (Ni-P is 2.48 Å in the bromo-derivative)^{11} since that would have the effect of reducing the normal ligand field strength of Bu^t_3P.

The effective magnetic moment of $[\mathrm{Bu}^t_3\mathrm{PH}]$ $[\mathrm{Ni(NCS)_3}]$ is 3.66 B.M. Although this value normally corresponds to a tetrahedral geometry[2], the spectroscopic data for this complex can be interpreted in favour of an octahedral structure (*vide infra*). Lever[21a] has pointed out that certain tetragonal nickel complexes have magnetic moments above 3.3 B.M. Additionally, we note that complexes of the type $\mathrm{(Cat)NiX_3}$ where Cat is a relatively large unipositive cation and X = Cl or Br, are known[2,21b,c] to contain octahedral Ni(II). The magnetic moments of the latter complexes, after allowance for antiferromagnetic interactions suggested by measurements in the range of 85–600°K, fall between 3.3 and 3.5 B.M.[21d]. Thus, the magnetic moment of the yellow-orange $[\mathrm{Bu}^t_3\mathrm{PH}]$ $[\mathrm{Ni(NCS)_3}]$ complex is not incompatible with an octahedral structure involving bridging thiocyanato groups.

The magnetic moments measured by the Evans n.m.r. method of solutions of the complexes are in good agreement with the Faraday solid state measurements, providing evidence that the same configuration is found in both the solid state and solution. The solution determination of μ_{eff} for the iodo-complex is of marginal accuracy because decomposition was apparent (i.e., precipitation on standing) in all solvents that were employed.

Vibrational Spectra

No significant changes in the infrared spectrum of $\mathrm{Bu}^t_3\mathrm{P}$ are observed upon its complexation and hence only the far infrared bands attributable to M-X and M-P vibrations contribute information about the geometry of the anion. The bands observed in the 500–140 cm^{-1} region and the assignments for the metal-ligand stretching frequencies are listed in Table II. With reference to previous assignments[22-24] for $[\mathrm{(Ph_3P)MX_3}]^-$, $[\mathrm{(R_3P)_2MX_2}]$ and $[\mathrm{MX_4}]^{2-}$ complexes it is possible to assign bands in the 200–330 cm^{-1} region to metal-ligand stretching modes. These metal-ligand frequencies are consistent with the formulation of the $[(\mathrm{Bu}^t_3\mathrm{P})\mathrm{MX_3}]^-$anions as C_{3v} pseudotetrahedral complexes.

The infrared spectra of the $[\mathrm{Bu}^t_3\mathrm{PH}]$ $[(\mathrm{Bu}^t_3\mathrm{P})\mathrm{MX_3}]$ complexes show two medium to weak bands at *ca.* 200 cm^{-1}. Only one of these bands is also observed in the spectra of $\mathrm{Bu}^t_3\mathrm{PHCl}$ and $[\mathrm{Bu}^t_3\mathrm{PH}]$ $[\mathrm{Ni(NCS)_3}]$ and therefore we assign the other band to the metal-phosphorus stretching frequency. Confirmation of this assignment in the case of the Zn(II) complex is provided by the Raman spectrum (Figure 2), which shows a medium-strong band at 206 cm^{-1}. Since this band is not observed in the Raman spectrum of either $\mathrm{Bu}^t_3\mathrm{P}$ or $\mathrm{Bu}^t_3\mathrm{PHCl}$, there can be little doubt that it is due to the Zn-P stretching mode.

Other Raman bands observed for the $[(\mathrm{Bu}^t_3\mathrm{P})\text{-}\mathrm{ZnCl_3}]^-$ anion in the region below 400 cm^{-1} are in accord with a C_{3v} skeletal symmetry[22]. The most intense band at 328 cm^{-1} can be assigned to the symmetric Zn-Cl stretching mode (A_1) and the less intense band at 272 cm^{-1} is assigned to the antisymmetric Zn-Cl mode (E). Similarly, the strong band at 122 cm^{-2} can be assigned to the Zn-Cl bending mode (A_1) and the less intense bands at 96 and 80 cm^{-1} are due to the $\mathrm{ZnCl_3}$ rocking mode (E) and the Zn-Cl bending mode (E), respectively. Attempts to measure the Raman spectra of the colored complexes failed due to the decomposition of the samples in the laser beam.

In the case of the $[\mathrm{Ni(NCS)_3}]^-$ anion, the infrared bands at 292, 256 and 244 cm^{-1} are most likely due to the metal-ligand vibrations since none of these bands appears in the spectrum of $\mathrm{Bu}^t_3\mathrm{PHCl}$. Bands at 890 cm^{-1} and at 464, 456 cm^{-1} may be assigned[22,25] to ν(C-S) and δ(NCS), respectively, of bridging NCS groups. The high ν(CN) frequencies (2152 cm^{-1}, 2134 cm^{-1}, 2102 cm^{-1}) observed in the Nujol mull spectrum (Figure 3) indicate the presence of bridging thiocyanato-groups [22,25]. The bridging ν(CN) bands disappear entirely upon dissolution in acetonitrile, only N-bonded groups remaining. Equivalence of the NCS groups is indicated by the sharpness of the intense band at 2104 cm^{-1} in the solution spectrum but the extent of solvation is of course not apparent from the infrared spectrum.

We did not observe the ν(PH) frequency of the cation in any of the metal complexes though a medium band at 2284 cm^{-1} was observed in the infrared spectrum of $\mathrm{Bu}^t_3\mathrm{PH}^+\mathrm{Cl}^-$. However, it is worth noting that the phosphonium hydrogen atom was located in the X-ray single crystal analysis[11] of the bromo-derivative.

Electronic Spectra

For tetrahedral Ni(II) complexes, three electronic transitions are spin-allowed and, in addition, some spin-forbidden transitions from the $^3T_1(F)$ ground state to singlet states derived from the field-free terms ^1D and ^1G may be observed[2,19]. Considering that spin-orbit coupling and low symmetry fields would both split the ^3T levels by several hundred wavenumbers, the electronic spectrum for the $[(\mathrm{Bu}^t_3\mathrm{P})\mathrm{NiX_3}]^-$ anions might be expected to be difficult to interpret. However, the electronic spectra tabulated in Table IV are readily explicible in terms of tetrahedral symmetry by comparison with the spectra of truly tetrahedral and other pseudotetrahedral complexes[2,12,19].

In the case of $[Bu^t_3PH][(Bu^t_3P)NiBr_3]$, in which the bond angles around the Ni(II) atom are known to depart only slightly from 109.5° [Br–Ni–Br, 108.7° (avg); P–Ni–Br, 110.3° (avg)] the absorption at *ca.* 700 nm, which is split into two components, may be assigned to the $^3T_1(P) \leftarrow {}^3T_1(F)$ (ν_3) transition, using T_d notation. The absorption at 1040 nm or 1140 nm thus corresponds to the $^3A_2 \leftarrow {}^3T_1(F)$ transition (ν_2) and is weaker, being more forbidden than the higher energy band. Since the upper state for the ν_2 transition is an orbital singlet and cannot be split by any ligand field, either the 1040 nm or the 1140 nm band must be attributed to a spin-forbidden transition to a singlet state (derived from ^1D). The third expected transition, $^3T_2$ (F) $\leftarrow$ $^3T_1$ (F) (ν_1), may be assigned to the broad absorption band centered at 1700 nm. The energies of the ν_3 transition, in particular, decrease in accord with the well-known spectrochemical sequence (Cl > Br > I) for the halide ions. Comparison of the observed bands for the bromo- and iodo-derivatives with those previously reported for $[(Ph_3P)NiX_3]^-$ (X = Br,I)[12] indicate a significantly lower ligand field strength for Bu^t_3P than for Ph_3P, though the opposite trend might be expected due to the greater basicity of aliphatic phosphines[26,27]. Since π-bonding is not significant in Ni(II)-P bonds, then the lower apparent position of Bu^t_3P than Ph_3P in the spectrochemical series is a consequence of its inability to approach the Ni(II) atom at a normal covalent bond distance[11].

Similarly the electronic spectrum of the $[(Bu^t_3P)CoBr_3]^-$ ion can be interpreted in terms of tetrahedral sysmmetry. The $^4T_1$ (P) $\leftarrow$ $^4A_2(\nu_3)$ transition is expected to be split into several components by the effects of spin-orbit coupling and asymmetry in the ligand field[19,20]. In the present case the band centered at 690 nm corresponds to ν_3 and it has a halfwidth of almost 2000 wavenumbers. The band position and splitting compares well with the earlier observations for the $[(Ph_3P)CoBr_3]^-$ ion[20]. In addition, in our work we can assign the bands at 1490 nm and 2100 nm as ν_2 and ν_1, respectively. The latter transition, $^4T_2 \leftarrow {}^4A_2$, corresponds to 10 Dq in tetrahedral sysmmetry and thus the value for the $[(Bu^t_3P)CoBr_3]^-$ ion (4760 cm^{-1}), as compared to 3500 cm^{-1} for $[CoBr_4]^{2-}$[28], reflects the expected high ligand field strength of the Bu^t_3P ligand. Since the ground state is an orbital singlet, the disparity of the ligand environment does not appreciably affect the magnetic behavior of the $[(Bu^t_3P)CoBr_3]^-$ion (vide supra).

In all of the above cases there are no significant differences between the electronic spectra of the complexes in solution and in the solid state. Since pseudotetrahedral symmetry has been proved by X-ray analysis for $[(Ph_3P)NiI_3]^-$[29] and $[(Bu^t_3P)NiBr_3]^-$[11], the close similarity of the solution and solid state spectra for all of the nickel complexes strongly supports pseudotetrahedral geometry for these complexes both in the crystal and in solution. Assuming the validity of the electronic spectral assignments for the $[(Bu^t_3P)CoBr_3]^-$ ion, together with the other physical evidence presented in this paper, the same configuration is found for the cobalt complex in both the solid state and in solution.

In contrast to the above cases, the electronic spectrum of the $[Ni(NCS)_3]^-$ ion does change significantly from the solid state to an acetonitrile solution. A change in coordination number is not necessarily implied, since the bridging isothiocyanato--groups present in the solid-state (*vide supra*) may be replaced, in the coordination sphere of the nickel(II) ion, by molecules of acetonitrile. The low molar extinction coefficients and the band positions for the acetonitrile solution are more explicable in terms of octahedral geometry {perhaps $[(CH_3CN)_3Ni(NCS)_3]^-$}than a tetrahedral configuration. If the broad band at 1750 nm in the solid state spectrum were taken as ν_1 in tetrahedral symmetry, then the band at 785 nm attributable to the ν_3 transition would be lower in energy than anticipated. Comparison of the solid state electronic spectrum of the $[Ni(NCS)_3]^-$ anion with the spectrum reported[30] for the tetrahedral form and the olive-yellow six-coordinate tetragonal form of $[Ni(NCS)_4]^{2-}$ shows better agreement with the latter spectrum. This fact, together with the well established tendency for the NCS^- ligand to bridge, suggests an assignment in terms of a polymeric octahedral geometry (at least for the solid state) for $[Ni(NCS)_3]^-$. In that case, the bands at 785 nm and 465 nm would correspong to ν_1 and ν_2 transitions respectively, of octahedral symmetry $(\nu_2/\nu_1 = 1.68)$ and are compatible with the spectrum reported for the known polymeric $[NiCl_3]^-$ ion[12] since NCS^- is appreciably higher in the spectrochemical series than the Cl^- ion.

Nuclear Magnetic Resonance Spectra

The ^1H nmr spectrum of Bu^t_3P (neat liquid) consists of a doublet resonance centered at $\delta 1.21$ ppm ($J_{PCCH} = 9.0$ Hz). This resonance shifts downfield in the sulfide ($\delta 1.50$, $J_{PCCH} = 13.5$ Hz) and the hydrochloride ($\delta 1.67$, $J_{PCCH} = 15.0$ Hz), as expected. In the ^{1}H n.m.r. spectrum of the zinc derivative, peaks of approximately equal intensity occur at $\delta 1.43$, 1.60, 1.63 and 1.83. We interpret these peaks as two doublets arising from the methyl hydrogen atoms of the $[Bu^t_3PH]^+$ ion ($\delta 1.71$, $J_{PCCH} = 15$ Hz) and the $[(Bu^t_3P)ZnCl_3]^-$ ion ($\delta 1.53$, $J_{PCCH} = 12$ Hz), respectively. The isotropic shifts exhibited by these resonances in the corresponding Co^{2+} and Ni^{2+} complexes are under further investigation as they are particularly relevant to other nmr studies of ion pairing in solution[29,31]. The solution structures are of considerable interest because the solid state structure proved for $[Bu^t_3PH]$ $[(Bu^t_3P)NiBr_3]$ revealed a Ni——P(2) (phosphonium) distance of 4.48 Å with P(2)——Br contacts of 4.27–4.31 Å, indicating strong ion-pairing interaction[11].

ACKNOWLEDGEMENTS

This research was supported by the National Research Council of Canada. The authors are grateful to Drs. D.E. Irish and A.J. Carty, Department of Chemistry, University of Waterloo, for providing assistance in obtaining the Raman and far infrared data, and to Dr. S. Goldman of this department for the Karl Fischer titrations.

REFERENCES

1. Teaching postdoctoral fellow, 1973–74.
2. L. Sacconi in *Transition Metal Chemistry*, Vol. 4, R.L. Carlin, Ed., Marcel Dekker, Inc., 1968, p. 199, and references cited therein.
3. K. K. Chow, W. Levason and C. A. McAuliffe in *Transition Metal Complexes of Phosphorus, Arsenic and Antimony Ligands*, C. A. McAuliffe, Ed., MacMillan, 1973, p. 33, and references cited therein.
4. G. N. LaMar and E. O. Sherman, *J. Chem. Soc.*, 92, 2691 (1970).
5. R. G. Hayter and F.S. Humiec, Inorg. Chem., 4, 1701 (1965).
6. C. R. Coussmaker, M. H. Hutchinson, J. R. Mellor, D. J. Morgan, S.A.J. Pratt, L. E. Sutton and L. M. Venanzi, *J. Chem. Soc.*, 2705 (1961).
7. M. C. Browning, J. R. Mellor, D. J. Morgan, S.A.J. Pratt, L E. Sutton and L.M. Venanzi, *J. Chem. Soc.*, 693 (1962).
8. (a) H. Hoffman and P. Schellenbeck, *Chem. Ber*,. **100**, 692 (1967). (b) H. Schumann, O. Stelzer and U. Niederreuther, *J. Organomet. Chem.*, **16**, 64 (1969).
9. P. L. Bellon, V. Albano, V. D. Bianco, F. Pompa and V. Scatturin, *Ricerca Sci.*, **33**, 1213 (1963).
10. C. A. Tolman, *J. Amer. Chem. Soc.*, **92**, 2956 (1970).
11. E. C. Alyea, A. Costin, G. T. Fey, G. Ferguson, R. G. Goel and R. J. Restivo, *J. Chem. Soc., Dalton*, 1294(1975).
12. F. A. Cotton, O. D. Faut and D.M.L. Goodgame, *J. Amer. Chem. Soc.*, **83**, 344 (1961).
13. (a) G. T. Fey, Ph. D. Dissertation, University of Massachusetts, 1973.
    (b) M. Fild, O. Stelzer and R. Schmutzler, *Inorg. Syn.*, **14**, 4 (1973).
14. R. H. Lee, E. Griswold and J K. Kleinberg, *Inorg. Chem.*, 3, 1278 (1964).
15. (a) L N. Mulay, *Physical Methods of Chemistry*, Vol. 1, Part IV, A. Weissberger and B. W. Rossiter, Eds., Wiley-Interscience, New York, 1972, p. 430.
    (b) L. F. Lindoy, V. Katovic and D. H. Busch, *J. Chem. Educ.*, **49**, 117 (1972).
    (c) T. H. Crawford and J. Swanson, *ibid*, 382 (1971).
16. Concentration of water by the Karl Fischer method was 80 ppm, corresponding to 0.3 mmol in 60 ml butanol.
17. H. D. Kaesz and R. B. Saillant, *Chem, Rev.*, **72**, 231 (1972).
18. (a) E. C. Alyea and D.W. Meek, *Inorg. Chem.*, **11**, 1029 (1972).
    (b) M. O. Workman, G. Dyer and D. W. Meek, *ibid*, **6**, 1543 (1967).
    (c) W. J. Geary, *Coord. Chem. Rev.*, 7, 81 (1971).
19. B. N. Figgis, *Introduction to Ligand Fields*, Interscience Publishers, 1966.
20. F. A. Cotton, O. D. Faut, D. M. L. Goodgame and R. H. Holm, *J. Amer. Chem. Soc.*, **83**, 1780 (1961).
21. (a) A. B. P. Lever, *Inorg. Chem.*, **4**, 763 (1965).
    (b) G. N. Tishchenko, Tr. Inst. Kristallogr. *Akad. Nauk. SSSR*, **11**, 93 (1955).
    (c) R. W. Asmussen and O. Bostrup, *Acta Chem. Scand.*, **11**, 745 (1957).
    (d) R. W. Asmussen and H. Soling, *Z. Anorg. Allgem. Chem.*,**283**, 3 (1956).
22. (a) K. Nakamoto, *Infrared Spactra of Inorganic and Coordination Compounds*, Wiley-Interscience, New York, 1970
    (b) T. V. Long, A. W. Herlinger, E. F. Epstein and I. Bernal, *Inorg. Chem.*, **9**, 459 (1970).
23. K. Shobatake and K. Nakamoto, *J. Amer. Chem. Soc.*, **92**, 3332 (1970).
24. J. Bradbury, K. P. Forest, R. H. Nuttall and D. W. A. Sharp, *Spectrochim. Acta*, **23A**, 2701 (1967).
25. John L. Burmeister, T.P. O'Sullivan, K.A. Johnson, *Inorg. Chem.*, **10**, 1803 (1971).
26. M. A. Bennett, R. J. H. Clark and A. D. J. Goodwin, *Inorg. Chem.*, **6**, 1625 (1967).
27. C. A. Streuli, *Anal. Chem.*, **32**, 985 (1960).
28. R. H. Holm and F. A. Cotton, *J. Chem. Phys.*, **31**, 788 (1959).
29. R. P. Taylor, D. H. Templeton, A. Zalkin and W. De. W. Horrocks, *Inorg. Chem.*, 7, 2629 (1968).
30. D. Forster and D. M. L. Goodgame, *Inorg. Chem.*, 4, 823 (1965).
31. G. N. LaMar, *Nuclear Magnetic Resonance of Paramagnetic Molecules*, G. N. LaMar, W. De. W. Horrocks, Jr., R. H. Holm, Eds., Academic Press, New York, 1973, p. 387.