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References and Notes

(1) R. E. Drew and F. W. B. Einstein, *Inorg. Chem.*, **11**, 1079 (1972).
(2) G. Mathern and R. Weiss, *Acta Crystallogr., Sect. B.*, **27**, 1572 (1971).
(3) R. Stomberg, *Ark. Kemi.*, **22**, 49 (1964).
(4) R. Stomberg, *Ark. Kemi.*, **23**, 401 (1965).
(5) R. Stomberg, *Ark. Kemi.*, **24**, 47 (1965).
(6) R. Stomberg and I.-B. Ainalem, *Acta Chem. Scand.*, **22**, 1439 (1968).
(7) R. Stomberg, *Ark. Kemi.*, **24**, 111 (1965).
(8) R. Stomberg, *Ark. Kemi.*, **22**, 29 (1964).
(9) R. Stomberg, *Acta Chem. Scand.*, **24**, 2024 (1970).
(10) We prefer to regard the peroxo group as a bidentate ligand, though we recognize that an alternative description of the peroxo group as a π-bonded monodentate ligand is possible.[11]
(11) D. G. Tuck and R. M. Walters, *Inorg. Chem.*, **2**, 428 (1963).
(12) G. Mathern and R. Weiss, *Acta Crystallogr., Sect. B*, **27**, 1572 (1971).
(13) G. Mathern and R. Weiss, *Acta Crystallogr., Sect. B*, **27**, 1598 (1971).
(14) R. Stomberg, *Acta Chem. Scand.*, **17**, 1563 (1963).
(15) J. D. Swalen and J. A. Ibers, *J. Chem. Phys.*, **37**, 17 (1962).
(16) N. Vuletic and C. Djordjevic, *J. Chem. Soc., Dalton Trans.*, 1137 (1973).
(17) A. R. Davis and F. W. B. Einstein, *Inorg. Chem.*, **13**, 1880 (1974).
(18) S. A. Goldfield and K. N. Raymond, *Inorg. Chem.*, **10**, 2604 (1971).
(19) J. Karle and I. L. Karle, *Acta Crystallogr.*, **21**, 849 (1966).
(20) D. Sayre, *Acta Crystallogr.*, **5**, 60 (1952).
(21) R is defined as $\sum(|F_o| - |F_c|)/\sum|F_o|$. R_w is defined as $[\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$.
(22) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).
(23) "International Tables of X-Ray Crystallography", Vol. III, Kynoch Press, Birmingham, England, 1965, Section 3.3.
(24) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
(25) R. E. Drew and F. W. B. Einstein, *Inorg. Chem.*, **12**, 829 (1973).
(26) Supplementary material.
(27) I.-B. Svensson and R. Stomberg, *Acta Chem. Scand.*, **25**, 898 (1971).
(28) F. W. B. Einstein, E. Enwall, D. M. Morris, and D. Sutton, *Inorg. Chem.*, **10**, 678 (1971).
(29) (a) R. Stomberg, *Acta Chem. Scand.*, **22**, 1076 (1968); (b) I. Larking and R. Stomberg, *ibid.*, **24**, 2043 (1970).
(30) R. J. Gillespie and R. S. Nyholm, *Q. Rev., Chem. Soc.*, **11**, 339 (1957).
(31) R. Stomberg, *Ark. Kemi.*, **24**, 283 (1965), and references therein.
(32) D. M. P. Mingos, *Nature (London)*, **230**, 154 (1971).
(33) W. P. Griffith, *J. Chem. Soc.*, 5248 (1964).
(34) L. Pauling, "The Nature of the Chemical Bond", 3rd ed, Cornell University Press, Ithaca, N.Y., 1960.
(35) J. L. Hoard, *Struct. Chem. Mol. Biol.*, 573, 582 (1968).
(36) M. D. Lind, M. J. Hamor, T. A. Hamor, and J. L. Hoard, *Inorg. Chem.*, **3**, 34 (1964).
(37) T. G. Appleton, H. C. Clark, and L. E. Manzer, *Coord. Chem. Rev.*, **10**, 335 (1973).
(38) W. R. Scheidt, C. C. Tsai, and J. L. Hoard, *J. Am. Chem. Soc.*, **93**, 3867 (1971).
(39) See ref 9 and references therein.
(40) (a) R. E. Drew, F. W. B. Einstein, and S. E. Gransden, *Can. J. Chem.*, **52**, 2184 (1974); (b) G. L. Glen, J. V. Silverton, and J. L. Hoard, *Inorg. Chem.*, **2**, 250 (1963).
(41) W. C. Hamilton and J. A. Ibers, "The Hydrogen Bond", W. A. Benjamin, New York, N.Y., 1968.

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Reactions of the Tripod Ligand Tris(2-diphenylphosphinoethyl)phosphine with Cobalt(II) and Nickel(II) Salts and Sodium Borohydride. Structural Characterization of a Five-Coordinate Cobalt(I) Hydride Complex

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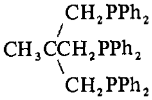
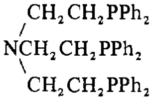
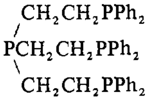
The potentially tetradentate tripod ligand tris(2-diphenylphosphinoethyl)phosphine, pp$_3$, reacts with cobalt(II) salts in the presence of sodium borohydride to give low-spin five-coordinate cobalt(I) complexes [CoX(pp$_3$)], where X = halide, thiocyanate, and hydride. With nickel(II) salts five-coordinate hydrido complexes of the general formula [NiH(pp$_3$)]Y (Y = iodide, tetrafluoroborate, tetraphenylborate) are formed. The cobalt–hydrido complex [CoH(pp$_3$)]·$^1/_2$(CH$_3$)$_2$CO has been characterized by an X-ray structure analysis (trigonal with hexagonal dimensions a = 13.573 (3) Å, c = 36.404 (8) Å, Z = 6, space group $R\bar{3}$) and has been found to have a trigonal-bipyramidal geometry with C_{3v} symmetry. On the basis mainly of the electronic spectra the same geometry must be attributed to all of the cobalt(I) complexes.

Introduction

In recent years many reactions of 3d transition metal ions with tertiary phosphines and a reducing agent such as borohydride have been reported.[1-11] Most reactions involved mono- or bidentate phosphines.[1-3,9] In this laboratory we have investigated the reactions of ligands with three phosphorus atoms in order to examine the effect of increasing denticity. The two ligands used so far have a "tripod" structure. 1,1,1-Tris(diphenylphosphinomethyl)ethane, p$_3$, I, reacts with cobalt(II) and nickel(II) halides to give, in the presence of borohydride, tetrahedral complexes of the monovalent metal ions with the formula [MX(p$_3$)].[4,12] Tris(2-diphenylphosphinoethyl)amine, np$_3$, II, reacts in an analogous way to give the trigonal-bipyramidal complexes [MX(np$_3$)].[10] When an anion is used which does not coordinate strongly to the metal ion, complexes of the zerovalent metal, such as [Ni(np$_3$)], are obtained.[6,10] This complex is the first one known to have a trigonal-pyramidal structure. Alternatively, the first coordination sphere may become filled by a hydride ion as in the nonstoichiometric compounds [NiH$_x$(np$_3$)]Y (Y = BF$_4$, ClO$_4$, NO$_3$)[8] or the triply bridged dimer [(p$_3$)CoH$_3$Co(p$_3$)BPh$_4$.[11] Iron(II) forms an analogous dimer.[5,11]


$CH_3C(CH_2PPh_2)_3$
I


$N(CH_2CH_2PPh_2)_3$
II


$P(CH_2CH_2PPh_2)_3$
III

In this work we describe the reactions of the tetraphosphine tris(2-diphenylphosphinoethyl)phosphine, pp$_3$, III, which is similar to the ligand np$_3$ but has a phosphorus atom in the apical position instead of a nitrogen atom. We have prepared and characterized 11 compounds of cobalt and nickel and have determined the X-ray structure of one of them, [CoH(pp$_3$)]·$^1/_2$(CH$_3$)$_2$CO.

Some metal complexes of this ligand have been recently described;[7,13-15] as far as the 3d transition metals are concerned, pentacoordinate complexes of iron(II), cobalt(II), and nickel(II) have been reported,[13] along with carbonyl derivatives

Table I. Analytical Data and Molar Conductance Values for the Cobalt and Nickel Complexes

Compd	Color	% C		% H		% M		Λ_M,[a] cm^2 ohm^{-1} mol^{-1}
		Calcd	Found	Calcd	Found	Calcd	Found	
$[\mathrm{CoCl(pp_3)}]$[b]	Dark green	65.93	65.83	5.53	5.62	7.70	7.89	
$[\mathrm{CoBr(pp_3)}]$	Dark green	62.31	61.50	5.23	5.26	7.28	7.36	
$[\mathrm{CoI(pp_3)}]$[c]	Dark green	58.89	59.10	4.94	5.01	6.88	6.80	
$[\mathrm{CoNCS(pp_3)}]$[d]	Red	65.26	64.04	5.38	5.28	7.49	7.22	
$[\mathrm{CoCN(pp_3)}]$[e]	Orange	68.35	68.76	5.60	5.48	7.80	7.76	
$[\mathrm{Co(CO)(pp_3)}]\mathrm{BPh_4}$	Yellow	74.70	73.43	5.81	6.10	5.50	5.60	23
$[\mathrm{CoH(pp_3)}]\cdot{}^1/_2\mathrm{(CH_3)_2CO}$	Yellow	68.78	68.79	6.10	6.27	7.76	7.54	
$[\mathrm{CoH(pp_3)}]\cdot{}^1/_2\mathrm{DMF}$[f]	Yellow	68.09	68.05	5.98	6.12	7.68	7.60	
$[\mathrm{NiH(pp_3)}]\mathrm{I}$[g]	Pale yellow	58.83	58.60	5.05	5.30	6.84	6.58	24
$[\mathrm{NiH(pp_3)}]\mathrm{BF_4}$	Pale yellow	61.70	61.32	5.30	5.56	7.21	7.13	27
$[\mathrm{NiH(pp_3)}]\mathrm{NO_3}$[h]	Brown	63.60	63.84	5.46	5.54	7.42	7.42	27
$[\mathrm{NiH(pp_3)}]\mathrm{BPh_4}$[i]	Yellow-green	75.52	75.25	6.05	6.26	5.59	5.68	24

[a] Molar conductance values for 10^{-3} *M* 1,2-dichloroethane solutions. [b] Calcd: Cl, 4.63. Found: Cl, 4.32. [c] Calcd: I, 14.47. Found: I, 14.59. [d] Calcd: N, 1.77. Found: N, 1.79. [e] Calcd: N, 1.85; mol wt 756. Found: N, 1.83; mol wt 682. [f] Calcd: N, 0.91. Found: N, 1.00. [g] Calcd: I, 14.80. Found: I, 14.64. [h] Calcd: N, 1.77. Found: N, 1.77. [i] Calcd: P, 11.80. Found: P, 11.98.

of cobalt(I) (also pentacoordinate)[14] and hydride and dinitrogen complexes of iron with the formulas $[\mathrm{FeH(pp_3)}]\mathrm{BPh_4}$ and $[\mathrm{FeHN_2(pp_3)}]\mathrm{BPh_4}$.[7]

Experimental Part

Reagents. Cobalt(II) and nickel(II) salts, sodium borohydride, sodium tetraphenylborate, and all solvents were reagent grade quality and were used without further purification. The ligand tris(2-diphenylphosphinoethyl)phosphine (pp3) was acquired from the Pressure Chemical Co., Pittsburgh, Pa., and was used without further purification.

Preparation of the Complexes. All the reactions were carried out under dry nitrogen, using deoxygenated solvents. The solid compounds were collected on a glass frit in a closed system and were generally washed with ethanol, water, ethanol, and petroleum ether before being dried in a stream of nitrogen.

$[\mathrm{CoX(pp_3)}]$. X = Cl, Br, I, NCS. The ligand (1 mmol) in 10 ml of dichloromethane was added at ambient temperature to a solution of the cobalt(II) salt (1 mmol) in 25 ml of ethanol. Sodium borohydride (1 mmol in 20 ml of ethanol) was added slowly and with stirring to the resulting brown solution. Crystals were obtained by isothermal evaporation of solvent.

X = CN. This compound was prepared in an exchange reaction between equimolar quantities of NaCN and $[\mathrm{Co(pp_3)I}]$.

$[\mathrm{CoH(pp_3)}]\cdot{}^1/_2\mathrm{DMF}$. A solution of anhydrous $\mathrm{CoCl_2}$ (1 mmol) in 1-butanol (5 ml) was added to a solution of the ligand (1 mmol) in dimethylformamide (DMF). $\mathrm{NaBH_4}$ (2 mmol, 15 ml of DMF) was then added and the resulting solution was boiled and concentrated to half-volume. Large yellow-brown crystals were obtained on slow-cooling (ν(C–O) 1670 cm^{-1}).

$[\mathrm{CoH(pp_3)}]\cdot{}^1/_2\mathrm{(CH_3)_2CO}$. A solution of $\mathrm{Co(BF_4)_2\cdot 6H_2O}$ or $\mathrm{Co(acac)_2}$ (1 mmol) in ethanol (10 ml) was added to the ligand (1 mmol) in 10 ml of acetone. $\mathrm{NaBH_4}$ (2 mmol) in 5 ml of ethanol was then added. Yellow-brown crystals were obtained by isothermal evaporation (ν(C–O) 1710 cm^{-1}).

$[\mathrm{NiH(pp_3)}]\mathrm{I}$. The ligand (1 mmol) in dichloromethane (10 ml) was added to a solution of anhydrous nickel(II) iodide (1 mmol) in ethanol (10 ml). The methylene chloride was removed by distillation, and $\mathrm{NaBH_4}$ (1 mmol) in ethanol (10 ml) was added slowly to the cooled mixture. Fine yellow crystals appeared immediately.

$[\mathrm{NiH(pp_3)}]\mathrm{Y}$. Y = $\mathrm{BF_4}$, $\mathrm{NO_3}$. A solution of $\mathrm{NaBH_4}$ (1 mmol in 15 ml of ethanol) was added slowly to a mixture obtained from the ligand (1 mmol in 20 ml of acetone) and $\mathrm{Ni(BF_4)_2\cdot 6H_2O}$ or $\mathrm{Ni(NO_3)_2\cdot 6H_2O}$ (1 mmol in 15 ml of ethanol). Crystals were obtained by isothermal evaporation.

$[\mathrm{NiH(pp_3)}]\mathrm{BPh_4}$. A mixture obtained from 1 mmol of $[\mathrm{NiX(pp_3)}]\mathrm{BPh_4}$ (X = Cl, Br, or I)[16] suspended in 25 ml of absolute alcohol and 1.5 mmol of $\mathrm{NaBH_4}$ in 15 ml of ethanol was stirred for ca. 12 hr at room temperature until the initially violet solid became completely yellow-green.

Deuterated Complexes. These were prepared in the same manner as the protic complexes, using $\mathrm{NaBD_4}$ and deuterated solvents.

Physical Measurements. Physical methods have been described previously.[17]

The analytical and conductometric data of the cobalt and nickel complexes are reported in Table I; the maxima and extinction coefficients for the electronic spectra of the complexes are reported in Table II.

Table II. Maxima and Extinction Coefficients for the Electronic Spectra of the Cobalt and Nickel Complexes

Compd	Absorption max,[a] kK (ϵ_M for soln)
$[\mathrm{CoCl(pp_3)}]$	a: 9.5, 18, 26.65 sh b: 9.5 (28), 18.35 (2600)
$[\mathrm{CoBr(pp_3)}]$	a: 9.5, 17.85, 26.65 sh b: 9.5 (51), 18 (1850)
$[\mathrm{CoI(pp_3)}]$	a: 9.05, 17.85, 26.65 sh b: 9.3 (46), 18 (2480)
$[\mathrm{CoNCS(pp_3)}]$	a: 9.6, 20 sh, 25 sh b: 9.6 (45), 20.6 (3080)
$[\mathrm{CoCN(pp_3)}]$	a: 27 sh b: 27 (11, 700)
$[\mathrm{Co(CO)(pp_3)}]\mathrm{BPh_4}$	a: 25 sh b: 25.6 (3750)
$[\mathrm{CoH(pp_3)}]\cdot{}^1/_2\mathrm{(CH_3)_2CO}$	a: 18.2 sh, 27 sh b: 18.2 sh, 27 sh
$[\mathrm{NiH(pp_3)}]\mathrm{I}$	a: 17.7, 27 sh b: 18.2 sh
$[\mathrm{NiH(pp_3)}]\mathrm{BF_4}$	a: 18.35, 28.5 sh b: 18.5 (1346)
$[\mathrm{NiH(pp_3)}]\mathrm{NO_3}$	a: 18.5, 28.15 b: 18.2 sh
$[\mathrm{NiH(pp_3)}]\mathrm{BPh_4}$	a: 17.85, 25.65 b: 17.8 sh

[a] Key: a, solid at room temperature; b, 1,2-dichloroethane solution.

Collection and Reduction of X-Ray Intensity Data. The crystal used for data collection was an irregular tetragonal bipyramid whose edges ranged from 0.25 to 0.28 mm. The specimen was mounted in an arbitrary orientation on a Philips computer-controlled diffractometer PW 1100. Cell constants and the Bravais lattice were determined using a procedure described elsewhere.[10] On the basis of systematic extinctions the space group was found. The crystals are trigonal, space group $R\bar{3}$, with hexagonal dimensions a = 13.573 (3) Å and c = 36.404 (8) Å. The observed density of 1.31 g cm^{-3} (by flotation) agrees with the value of 1.30 g cm^{-3} calculated assuming six formula units of $[\mathrm{CoH(pp_3)}]\cdot{}^1/_2\mathrm{(CH_3)_2CO}$ per cell.

The intensity data were collected using Mo Kα radiation monochromatized with a flat graphite crystal at a takeoff angle of 4.5°. Reflections for which $2\theta \leq 40°$ were collected by the ω–2θ scan technique over a 2θ interval of 1.6° at a scan speed of 0.14°/sec. Stationary-background counts were taken before and after each scan for a time equal to half the scan time. As a check three standard reflections were monitored every 90 min and showed no drop in intensity during the data collection. The total peak counts were corrected for background and the standard deviation of the resulting intensity I was calculated according to $\sigma(I) = [P + 0.25(B_1 + B_2)(T_p/T_b)^2 + (KI)^2]^{1/2}$ where P is the peak count, B_1 and B_2 are the background counts, T_p and T_b are the count times on the peak and background, respectively, and K is the instability factor.[18] A value of 0.014 was used for K. After correction for Lorentz and polarization

Table III. Positional Parameters with Estimated Standard Deviations

Atom	x/a	y/b	z/c
Co	0.0	0.0	0.23647 (3)
P(1)	0.0	0.0	0.17909 (6)
P(2)	0.1435 (1)	0.1673 (1)	0.23543 (3)
C(1)	0.0998 (4)	0.1403 (4)	0.1596 (1)
C(2)	0.1970 (4)	0.2027 (4)	0.1870 (1)
C(3)	0.1360 (4)	0.2949 (4)	0.2491 (1)
C(4)	0.0718 (5)	0.3281 (5)	0.2279 (2)
C(5)	0.0613 (6)	0.4201 (6)	0.2379 (2)
C(6)	0.1124 (6)	0.4805 (5)	0.2692 (2)
C(7)	0.1743 (5)	0.4479 (5)	0.2904 (2)
C(8)	0.1854 (5)	0.3564 (5)	0.2807 (1)
C(9)	0.2749 (4)	0.1974 (4)	0.2593 (1)
C(10)	0.3807 (5)	0.2852 (5)	0.2491 (1)
C(11)	0.4784 (4)	0.3019 (5)	0.2666 (2)
C(12)	0.4699 (5)	0.2313 (6)	0.2946 (2)
C(13)	0.3660 (6)	0.1448 (5)	0.3058 (1)
C(14)	0.2687 (4)	0.1279 (4)	0.2881 (1)
H	0.0	0.0	0.276 (2)
AC	0.100	0.010	0.493
AO	0.175	0.020	0.475

effects, out of the total 1299 independent reflections, 1044 having $I \geq 3\sigma(I)$ were considered observed. No attempt was made to correct for absorption owing to the shape of the crystal and to the low value of the linear absorption coefficient μ of 6.57 cm^{-1}. An empirical estimation of the effects of absorption was made considering a dozen reflections whose intensity was measured as the crystal was rotated about its azimuthal angle ψ: the maxima changes in intensity ranged from ±1 to ±4%.

Solution and Refinement of the Structure. All calculations were performed using the XRY72 crystallographic system kindly supplied by J. M. Stewart, adapted for the University of Florence CII 10070 computer. The atomic scattering factors for cobalt, phosphorus, and carbon atoms were those calculated by Cromer and Waber[19] while those for hydrogen were those calculated by Stewart, Davidson, and Simpson.[20] The effects of anomalous dispersion of the cobalt and phosphorus atoms were included in the calculation of F_c, the values of $\Delta f'$ and $\Delta f''$ being those calculated by Cromer.[21]

Since there are six molecules per cell, the molecule must lie on a threefold axis; a three-dimensional Patterson map gave the position of the cobalt and phosphorus atoms. Successive three-dimensional Fourier syntheses showed all the other monohydrogen atoms. Several cycles of full-matrix least-squares refinement using isotropic thermal parameters, followed by others where anisotropic thermal parameters for cobalt and phosphorus atoms and isotropic ones for the carbon were used, reduced the conventional R factor to 0.074. The function minimized was $\sum w(|F_o| - |F_c|)^2$; the weights w were taken as $1/\sigma(F_o)$.

At this point a difference Fourier map, calculated in an attempt to locate the hydride ligand, clearly showed a peak of 0.7 e/Å^3, 1.4 Å below the metal atom. The positional parameters of the hydride ligand were included in further refinement with a starting thermal parameter B = 3 Å^2 and a unit population parameter. The other hydrogen atoms, calculated in idealized positions (C–H = 1.0 Å), were introduced in subsequent calculations with temperature factors equal to those of their own carbon atoms. Positional and thermal parameters were not refined but were recalculated according to the new parameters of the carbon atoms. Two cycles of refinement, where all the parameters as described before were allowed to vary together with x_H, y_H, z_H, and B_H, gave a conventional R factor of 0.058.

On the basis of the analytic and infrared data acetone should be present in the sample. A difference Fourier map calculated at this stage without the contribution of the hydride ligand showed three peaks whose electronic density was between 0.7 and 0.6 e/Å^3. The most prominent one was that corresponding to the hydride atom and the other two were thought to belong to the solvent. Because the two peaks were in the proximity of the special position $\bar{3}$ at 0, 0, $^1/_2$, they give rise to other ten peaks at bond distance from each other. On the basis of bond distances and angles these peaks were interpreted as the nonhydrogen atoms of the acetone molecule and of the other five symmetry-related molecules overlapping each other.[22] Two cycles of refinement led to positions of the solvent atoms different from those derived from the difference Fourier map and to very poor bond distances and angles. The solvent atoms were then introduced in the following calculations as a fixed contribution with parameters derived from the difference Fourier map. Two cycles of refinement led to a conventional R factor of 0.050.

Since a difference Fourier map showed residual electronic density attributable to the anisotropic motion of the carbon atoms, three cycles of full-matrix least-squares refinement using anisotropic thermal parameters also for the carbon atoms were performed. The final discrepancy indices R_w and R are 0.032 and 0.034, respectively. $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$. In the last cycle the largest shift for the hydride atom was 0.04 of the standard deviation and the Co–H bond distance was 1.43 (6) Å. It is worth noting that the position of the hydride ligand derived from the Fourier methods is identical with that from the least squares. The final values of the atomic parameters with their estimated standard deviations are given in the Tables III and IV.

Results and Discussion

Cobalt Complexes. Equimolar quantities of sodium borohydride, pp$_3$, and cobalt(II) halides react in ethanol–methylene chloride at ca. 20° under nitrogen to give air-sensitive crystals with the formula [CoX(pp$_3$)], X = Cl, Br, I. The compounds are nonconductors in 1,2-dichloromethane (Table I); the solutions are not sufficiently stable to permit a molecular weight determination. The decomposition of the solutions can be limited to a considerable extent by the addition of free ligand to the solutions. An analogous thiocyanate complex [Co(NCS)(pp$_3$)] has also been made.

These complexes are substantially diamagnetic though they almost always contain paramagnetic impurities, probably cobalt(II) compounds, and show slight ferromagnetism at-

Table IV. Thermal Parameters with Their Standard Deviations (All × 10^3)

Atom	U_{11} or U	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co	35.9	35.9	33.5 (0.7)	18.0 (0.2)	0	0
P(1)	44.0	44.0	36.9 (1.4)	22.0 (0.5)	0	0
P(2)	36.5 (0.9)	37.4 (0.9)	39.4 (0.8)	18.0 (0.7)	0.3 (0.7)	1.9 (0.7)
C(1)	58 (4)	53 (4)	38 (3)	29 (3)	2 (3)	4 (3)
C(2)	49 (4)	45 (3)	48 (3)	19 (3)	8 (3)	8 (3)
C(3)	39 (3)	40 (3)	50 (3)	20 (3)	−3 (3)	5 (3)
C(4)	84 (5)	63 (5)	72 (4)	47 (4)	−15 (4)	−13 (4)
C(5)	113 (6)	76 (5)	97 (5)	71 (5)	−14 (5)	−4 (4)
C(6)	102 (6)	57 (5)	99 (5)	49 (4)	−3 (5)	−12 (4)
C(7)	86 (5)	70 (5)	83 (5)	48 (4)	−19 (4)	−28 (4)
C(8)	62 (4)	59 (4)	62 (4)	36 (4)	−13 (4)	−13 (3)
C(9)	38 (4)	39 (3)	46 (3)	20 (3)	−1 (3)	−3 (3)
C(10)	39 (4)	62 (4)	48 (3)	14 (4)	3 (3)	7 (3)
C(11)	27 (4)	85 (5)	59 (4)	13 (3)	−1 (3)	−9 (4)
C(12)	51 (5)	87 (5)	59 (4)	41 (4)	−15 (3)	−19 (4)
C(13)	62 (5)	58 (4)	62 (4)	34 (4)	−15 (4)	−4 (3)
C(14)	41 (4)	45 (4)	55 (3)	19 (3)	−4 (3)	−1 (3)
H	38 (20)					
AC	190					
AO	190					

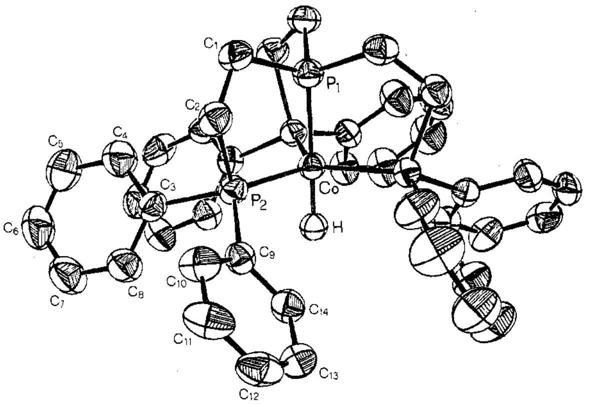


Figure 1. Perspective view of the $[CoH(pp_3)]$ complex (ORTEP diagram showing 30% probability ellipsoids).

tributable to the presence of colloidal cobalt metal which cannot be separated by filtration. The magnetic susceptibility of samples of the chloro complex was the highest, but extrapolation to infinite field gave the negative limiting susceptibility. Thus the compounds $[CoX(pp_3)]$ should be considered as low-spin complexes of cobalt(I), d^8.

The complex $[CoCl(pp_3)]$ shows an infrared-active Co–Cl stretching band at 260 cm^{-1}. The infrared spectrum of $[Co(NCS)(pp_3)]$ shows a C–N stretching band at 2100 cm^{-1} indicative of an N-bonded thiocyanated complex. Treatment of $[CoX(pp_3)]$ with sodium cyanide or carbon monoxide in the presence of sodium tetraphenylborate, gives the substitution reactions

$$[CoX(pp_3)] + NaCN \rightarrow [Co(CN)(pp_3)] + NaX$$

$$[CoX(pp_3)] + NaBPh_4 + CO \rightarrow [Co(CO)(pp_3)]BPh_4 + NaX$$

The cyano derivative yields orange, air-stable, diamagnetic crystals and is monomeric and nonelectrolytic in 1,2-dichloroethane (Table I). An infrared-active band at 2060 cm^{-1} indicates a terminally coordinated cyanide group. The carbonyl derivative has been obtained previously from the reaction of pp_3 with dicobalt octacarbonyl and has been assigned a trigonal-bipyramidal structure.[14]

Cobalt(II) halides and pp_3 in the presence of ca. 2 mol of sodium borohydride react in boiling dimethylformamide to yield yellow crystals with the formula $[CoH(pp_3)]\cdot{}^1/_2DMF$. An analogous acetone solvate can be obtained by treating cobalt(II) acetylacetonate or tetrafluoroborate with pp_3 and borohydride. The solid acetone solvate is moderately air stable and diamagnetic and has well-formed crystals. In 1,2-dichloroethane it is more air sensitive but is a nonconductor of electric current. It reacts with an excess of hydrochloric acid at 60° to yield ca. 1.5 mol of hydrogen per mole of complex consumed, according to the reaction

$$2[CoH(pp_3)] + 4HCl \rightarrow 2CoCl_2 + 2pp_3 + 3H_2$$

The molecular structure of $[CoH(pp_3)]\cdot{}^1/_2(CH_3)_2CO$ consists of discrete molecules of $[CoH(pp_3)]$ and acetone. Figure 1 shows a perspective view of $[CoH(pp_3)]$. Interatomic distances and selected angles are reported in Table V. The coordination polyhedron is an almost regular trigonal bipyramid in which the metal atom is five-coordinated by the four phosphorus atoms of the ligand and by the hydride atom.

A threefold crystallographic axis of symmetry passes through the apical phosphorus atom, the metal atom, and the hydride ligand. The metal atom lies 0.04 Å below the equatorial plane with the angle P(1)–Co–P(2) equal to 89.0 (1)°. The near planarity of the CoP_3 group allows the equatorial angles to attain a value of 120.0 (1)°. The axial and equatorial Co–P bond lengths are 2.089 (2) and 2.128 (1) Å, within the range of values previously reported for Co–P distances in five-coordinate cobalt(I) complexes.[10,23,24] The difference between axial and equatorial bonds is significant, however. A similar shortening of the axial Co–P bond has been found in the compound $[CoH(QP)]$ which also contains four donor phosphorus atoms in a tetradentate ligand.[24] On the other hand, the five-coordinate complex $CoH(P(Ph)(OEt)_2)_4$ which has the same set of donor atoms, but only monodentate ligands, exhibits an axial bond length which is comparable to the equatorial.[23]

Table V. Distances (Å) and Angles (deg)

	Distances		
Co–P(1)	2.089 (2)	C(5)–C(6)	1.37 (1)
Co–P(2)	2.128 (1)	C(6)–C(7)	1.37 (1)
Co–H	1.43 (6)	C(7)–C(8)	1.37 (1)
P(1)–C(1)	1.839 (4)	C(8)–C(3)	1.38 (1)
P(2)–C(2)	1.876 (5)	C(9)–C(10)	1.38 (1)
P(2)–C(3)	1.852 (6)	C(10)–C(11)	1.38 (1)
P(2)–C(9)	1.837 (6)	C(11)–C(12)	1.37 (1)
C(1)–C(2)	1.53 (1)	C(12)–C(13)	1.37 (1)
C(3)–C(4)	1.40 (1)	C(13)–C(14)	1.38 (1)
C(4)–C(5)	1.37 (1)	C(14)–C(9)	1.38 (1)
	Angles		
P(1)–Co–P(2)	89.0 (1)	P(2)–C(9)–C(10)	122.7 (4)
P(2)–Co–P(2′)	120.0 (1)	P(2)–C(9)–C(14)	119.0 (3)
C(1)–P(1)–C(1′)	106.1 (1)	C(4)–C(3)–C(8)	117.2 (6)
Co–P(1)–C(1)	112.7 (1)	C(3)–C(4)–C(5)	120.9 (5)
Co–P(2)–C(2)	108.7 (1)	C(4)–C(5)–C(6)	120.7 (8)
Co–P(2)–C(3)	122.9 (2)	C(5)–C(6)–C(7)	119.0 (8)
Co–P(2)–C(9)	119.8 (2)	C(6)–C(7)–C(8)	120.8 (6)
C(2)–P(2)–C(3)	102.1 (2)	C(7)–C(8)–C(3)	121.5 (6)
C(2)–P(2)–C(9)	100.3 (2)	C(10)–C(9)–C(14)	118.3 (5)
C(3)–P(2)–C(9)	99.6 (3)	C(9)–C(10)–C(11)	121.0 (5)
P(1)–C(1)–C(2)	107.9 (3)	C(10)–C(11)–C(12)	119.5 (5)
P(2)–C(2)–C(1)	110.7 (3)	C(11)–C(12)–C(13)	120.8 (6)
P(2)–C(3)–C(4)	119.2 (4)	C(12)–C(13)–C(14)	119.5 (6)
P(2)–C(3)–C(8)	123.5 (5)	C(13)–C(14)–C(9)	120.8 (4)

The Co–H distance of 1.43 (6) Å agrees well with the values of 1.45 and 1.38 Å which have been obtained by refinement of the hydrogen atom's position in other five-coordinate cobalt(I) complexes.[10,23] In the present case, refinement of the hydrogen atom's position did not change the bond length from its initial value given by the Fourier synthesis. The other bond distances and angles are normal.

The infrared spectra of $[CoH(pp_3)]\cdot{}^1/_2solv$ (solv = $(CH_3)_2CO$, DMF) show two intense bands, which must be associated with the hydride ligand, at 1780 and 602 cm^{-1}. Both bands are absent in the deuterio complex, and new bands are present at 1288 cm^{-1} [$\nu(H)/\nu(D) = 1.38$] and 450 cm^{-1} [$\nu(H)/\nu(D) = 1.34$]. The band at higher frequency must be assigned to a Co–H stretching vibration. The frequency is lower than in the corresponding complex $[CoH(np_3)]$ (1870 cm^{-1})[10] as a result of changing the trans ligand from nitrogen to phosphorus. The second band at ca. 602 cm^{-1} corresponds, at least in frequency, to the infrared bands previously observed in $[NiH_x(np_3)]BF_4$ (596 cm^{-1})[8] and $[CoH(np_3)]$[10] (607–620 cm^{-1}). This band may possibly be assigned to a M–H deformation vibration even though it lies some 100 cm^{-1} lower than other M–H deformation vibrations.[25]

The electronic spectra of the solids and of the 1,2-dichloroethane solutions of the compounds $[CoX(pp_3)]$ with X = Cl, Br, NCS, and H are all similar. They show an intense band at 18–20 kK with a shoulder at ca. 27 kK (Table II, Figure 2). The very weak band at 9.5 kK which is present in the spectra of the halo and thiocyanate derivatives increases in intensity with the compound being exposed to air and would seem to correspond to the first band in the spectrum of $[CoI(pp_3)]BPh_4$[16] (Figure 2); its presence in the cobalt(I) spectra is therefore to be attributed to cobalt(II) impurities in line with the observed paramagnetism. The spectra of the complexes $[Co(CN)(pp_3)]$ and $[Co(CO)(pp_3)]BPh_4$ are

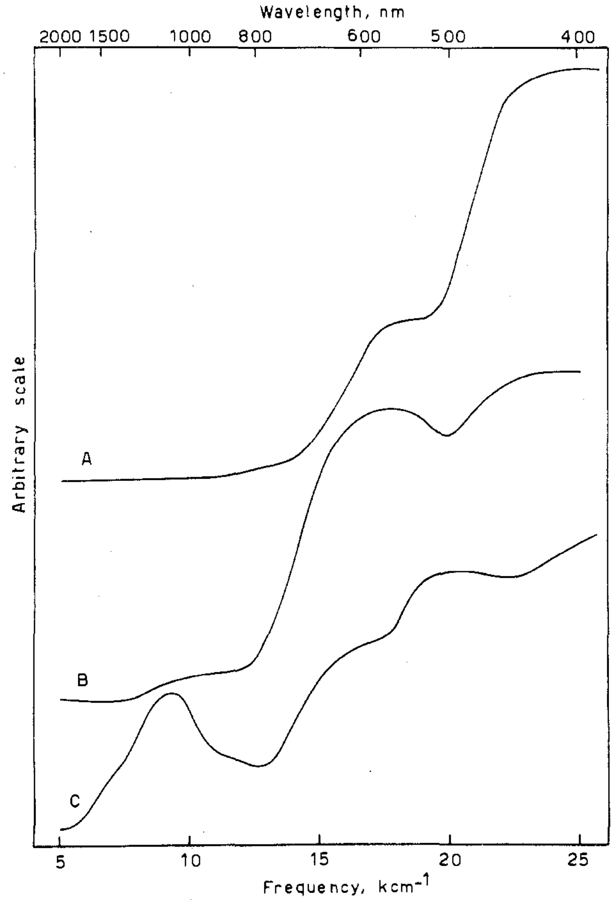


Figure 2. Reflectance spectra of $[CoH(pp_3)]\cdot{}^1/_2(CH_3)_2CO$ (A), $[CoI(pp_3)]$ (B), and $[CoI(pp_3)]BPh_4$ (C).

practically identical with each other and basically analogous to the previous spectra. The shift to higher frequencies of the highest electronic transitions is to be expected in view of the π-bonding character of the CN^- and CO ligands.

In conclusion, a trigonal-bipyramidal structure can be assigned to all these cobalt(I) complexes, bearing in mind also the particular geometry of the ligand.

That the pp3 complexes are low spin whereas the corresponding np3 complexes are high spin[10] results from the changing nature of the apical ligand. Phosphorus has a higher overall nucleophilicity constant than nitrogen[26] and so tends to produce low-spin complexes. Clearly the compounds $[CoX(pp_3)]$ and $[CoX(np_3)]$ lie on either side of, but close to, the magnetic crossover point.

Nickel Complexes. When nickel(II) iodide reacts with equimolar quantities of pp3 and $NaBH_4$, a yellow crystalline compound is obtained whose empirical formula is $NiH(pp_3)I$. The compound is air sensitive and diamagnetic and is a 1:1 electrolyte in 1,2-dichloroethane (Table I). Treatment with concentrated hydrochloric acid liberates 1 mol of hydrogen/mol of compound consumed. The compound is therefore a hydride and should be formulated as $[NiH(pp_3)]I$. The iodide is anionic and not coordinated.

The analogous compounds $[NiH(pp_3)]Y$ ($Y = BF_4, NO_3, BPh_4$) can also be prepared—the first two in the same way as the iodide and the last by borohydride reduction of the compound $[NiX(pp_3)]BPh_4$ (X = Cl, Br, I).

The infrared spectra of the complexes $[NiH(pp_3)]Y$ ($Y = I, BF_4, NO_3, BPh_4$) show bands due to the anions [$\nu(BF_4^-)$ 1050 cm^{-1}, $\nu(NO_3^-)$ 1330 cm^{-1}] but apart from that are virtually identical. The bands which must be associated with the hydride ligand are found at ca. 1880 and 595 cm^{-1}. These bands are not present in the infrared spectra of the deuterated complexes where three new bands appear at 500, 460, and 435 cm^{-1}.

The electronic spectra of the solids and 1,2-dichloroethane solutions of the nickel(II) hydrides are all similar and show one band at 17.7–18.5 kK with a shoulder at 27–28 kK. These spectra are comparable to the spectra of the isoelectronic trigonal-bipyramidal hydride $[CoH(pp_3)]\cdot{}^1/_2(CH_3)_2CO$ (Table II).

Conclusions

The reactions of borohydride with cobalt(II) and nickel(II) salts in the presence of pp3 may follow three alternative paths: (1) simple reduction of the metal ion

$$MX_2 + L + BH_4^- \rightarrow [M(L)X] + X^- + {}^1/_2B_2H_6 + {}^1/_2H_2$$

(2) formation of metal hydride, without reduction of the metal

$$MX_2 + L + BH_4^- \rightarrow [MH(L)]X + X^- + {}^1/_2B_2H_6$$

(3) simultaneous reduction of the metal and formation of hydride

$$MX_2 + L + 2BH_4^- \rightarrow [MH(L)] + 2X^- + B_2H_6 + {}^1/_2H_2$$

With cobalt(II), reduction to cobalt(I) always takes place, but depending on factors such as temperature, amount of borohydride, and counterion, the third reaction may also occur. With nickel(II), reduction does not take place—only the metal hydride formation (second reaction). Since cobalt(I) and nickel(II) are both d^8 ions, pentacoordination results in the full utilization of the nine valence orbitals (effective atomic number 36). Thus the compounds formed seem to depend on the attainment of this rather stable electronic configuration, helped by the phosphorus ligands which concentrate the d electrons into four orbitals, leaving d_{z^2} free for σ bonding.

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Registry No. $[CoCl(pp_3)]$, 55297-75-1; $[CoBr(pp_3)]$, 55236-46-9; $[CoI(pp_3)]$, 55236-47-0; $[CoNCS(pp_3)]$, 55236-48-1; $[CoCN(pp_3)]$, 55236-49-2; $[CoH(pp_3)]$, 55088-11-4; $[CoH(pp_3)]\cdot{}^1/_2(CH_3)_2CO$, 55236-50-5; $[NiH(pp_3)]I$, 55236-51-6; $[NiH(pp_3)]BF_4$, 55236-53-8; $[NiH(pp_3)]NO_3$, 55236-54-9; $[NiH(pp_3)]BPh_4$, 55236-55-0; $[Co(CO)(pp_3)]BPh_4$, 41777-22-4.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number AIC50197Y.

References and Notes

(1) J. Chatt, F. A. Hart, and H. R. Watson, *J. Chem. Soc.*, 2537 (1962).
(2) M. Aresta, M. Rossi, and A. Sacco, *Inorg. Chim. Acta*, **3**, 227 (1969).
(3) M. Aresta, P. Giannoccaro, M. Rossi, and A. Sacco, *Inorg. Chim. Acta*, **5**, 115 (1971).
(4) L. Sacconi and S. Midollini, *J. Chem. Soc., Dalton Trans.*, 1213 (1972).
(5) P. Dapporto, G. Fallani, S. Midollini, and L. Sacconi, *J. Am. Chem. Soc.*, **95**, 2021 (1973).
(6) C. Mealli and L. Sacconi, *J. Chem. Soc., Chem. Commun.*, 886 (1973).
(7) P. Stoppioni, F. Mani, and L. Sacconi, *Inorg. Chim. Acta*, **11**, 227 (1974).
(8) L. Sacconi, A. Orlandini, and S. Midollini, *Inorg. Chem.*, **13**, 2850 (1974).
(9) D. G. Holach, A. N. Hughes, B. C. Hui, and K. Wright, *Can. J. Chem.*, **52**, 2990 (1974).
(10) L. Sacconi, C. A. Ghilardi, C. Mealli, and F. Zanobini, *Inorg. Chem.*, **14**, 1380 (1975).
(11) P. Dapporto, S. Midollini, and L. Sacconi, *Inorg. Chem.*, **14**, 1643 (1975).
(12) P. Dapporto, G. Fallani, and L. Sacconi, *Inorg. Chem.*, **13**, 2847 (1974).
(13) R. B. King, R. N. Kapoor, M. S. Saran, and P. N. Kapoor, *Inorg. Chem.*, **10**, 1815 (1971).
(14) R. L. Peterson and K. L. Watters, *Inorg. Chem.*, **12**, 3009 (1973).
(15) M. M. T. Khan and A. F. Martell, *Inorg. Chem.*, **13**, 2961 (1974).
(16) The complexes $[MX(pp_3)]BPh_4$ (M = Co, Ni; X = Cl, Br, I) were prepared using a method analogous to that described for the [MCl-

(pp3)]PF$_6$ (M = Co, Ni) complexes.[13]

(17) L. Sacconi and R. Morassi, *J. Chem. Soc. A*, 2997 (1968); L. Sacconi, I. Bertini, and F. Mani, *Inorg. Chem.*, **7**, 1417 (1968).

(18) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).

(19) D. T. Cromer and J. A. Waber, *Acta Crystallogr.*, **18**, 104 (1965).

(20) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

(21) D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).

(22) Owing to the proximity of the special position $\bar{3}$ there is no room to accommodate more than one molecule of acetone; therefore the carbon atom (AC) and the oxygen atom (AO) were allotted population parameters of 0.5 and 0.167, respectively.

(23) D. D. Titus, A. A. Orio, R. E. Marsh, and H. B. Gray, *Chem. Commun.*, 322 (1971).

(24) A. Orlandini and L. Sacconi, *Cryst. Struct. Commun.*, **4**, 107 (1975).

(25) H. D. Kaesz and R. B. Saillant, *Chem. Rev.*, **72**, 231 (1972).

(26) L. Sacconi, *J. Chem. Soc. A*, 248 (1970).

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Single-Crystal Raman Evidence for and X-Ray Analysis of the Distorted Square-Pyramidal Pentachlorothallate and Pentachloroindate Complexes in $[(C_2H_5)_4N]_2[TlCl_5]$ and $[(C_2H_5)_4N]_2[InCl_5]$

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Detailed single-crystal vibrational data and X-ray space group determinations reveal that the tetraethylammonium salts of $InCl_5^{2-}$ and $TlCl_5^{2-}$ are isomorphous and isostructural. High-quality single-crystal Raman data were collected on well-formed crystals with polished faces. This new data in conjunction with low-temperature infrared and Raman spectroscopy had led to a major reinterpretation of the previous vibrational assignments for $[(C_2H_5)_4N]_2[InCl_5]$ and in the process clarified an ambiguity in the previous vibrational work. The new assignments, which indicate that the $InCl_5^{2-}$ ion does not have full C_4 symmetry, and second harmonic generation experiments, which indicate that the crystal may not be centrosymmetric, prompted reassessment of the published X-ray data. An alternate refinement is presented which is based on C_2 symmetry for the $InCl_5^{2-}$ ion.

Introduction

Although many five-coordinate complexes are known among the main-group elements, only two systems having monodentate ligands and lacking lone electron pairs on the central atom have been shown to have square-pyramidal structures by X-ray diffraction studies. These are $(C_6H_5)_5Sb$[1] and $InCl_5^{2-}$ in the salt $[(C_2H_5)_4N]_2[InCl_5]$,[2] the last of which has been studied in greater detail because of its simplicity and reported rigorous fourfold symmetry. The general motivation for structural and vibrational work on these systems is the lack of a ready explanation of their geometry and the implication of the square-pyramidal configuration in the Berry pseudorotation mechanism for the stereochemical nonrigidity of trigonal-bipyramidal compounds.[3]

In addition to the crystal structure determination, $InCl_5^{2-}$ has been investigated in solution,[4,5] various salts have been prepared,[5-7] and two single-crystal vibrational studies have appeared,[8,9] which form the basis of normal-coordinate vibrational analyses.[3,10] In both papers on the single-crystal spectra, one more E symmetry vibration was observed than would be expected for a square-pyramidal C_4 symmetry $InCl_5^{2-}$ ion, and, for want of a better assignment, this extra vibration was attributed to a lattice mode.[8,9]

We undertook the present work on $[(C_2H_5)_4N]_2[TlCl_5]$ in the hope that the results might help to clarify the ambiguities in the $InCl_5^{2-}$ vibrational data. In addition, we sought a positive test of the contention that the indium and thallium salts are isostructural.[5] The results led us to question the rigorous C_4 symmetry previously assigned to these complexes and therefore prompted a reinvestigation of the $[(C_2H_5)_4N]_2[InCl_5]$ X-ray structure.

Experimental Section

$[(C_2H_5)_4N]_2[TlCl_5]$ and $[(C_2H_5)_4N]_2[InCl_5]$ were prepared by the published methods[5] and crystallized from acetonitrile—containing a 50% excess of $(C_2H_5)_4NCl$—by slow evaporation of the solvent at room temperature. The crystals used for vibrational data collection had polished perpendicular faces, ca. 3 × 3 × 1.5 mm on a side, and were oriented by the aid of a polarizing microscope and their morphology.

Raman spectra were obtained on a 0.85-m Spex 1401 double monochromator with sampling optics of our own design and extensively modified Spex photon-counting electronics. A 1-cm^{-1} band pass was employed in all experiments. Data on the single crystals were collected on magnetic tape at 0.17-cm^{-1} intervals and were processed on the CDC 6400 computer by the program RAMAN.[11] Among its various functions, RAMAN allows least-squares fitting of component bands via a modified version of the Pitha and Jones routine.[12] The 647.1-nm line of a light-feedback-stabilized Kr-ion laser (Spectra Physics 164) was used for sample illumination. Laser power, ca. 100 mW, was measured at the sample and was readjusted to a fixed value for both orientations of the incident electric vector. Plasma lines were removed by a premonochromator in the laser beam, and peak positions were accurately located relative to Ne atomic lines, introduced by a Ne bulb close to the sample.

For low-temperature runs, a cylindrical laser focusing lens (f = 90 mm) was used to minimize local heating and an oblique (ca. 160°) back-scattering geometry was employed. The polycrystalline sample in the form of a pressed disk was attached to a copper block by Eccotherm TC-4 (Emerson and Cummings, Northbrook, Ill.) and cooled by a transfer gas in a double-chamber helium dewar. Temperature of the sample was monitored by a Au–Fe vs. Cu thermocouple attached to the side of the sample by Eccotherm. The absolute temperatures are estimated to be known to ±4° and relative temperatures are ±2°. Peak positions were measured relative to the exciting line, 647.089 nm, and two Kr-plasma lines, 651.095 and 657.007 nm.

Infrared spectra of Nujol mulls between polyethylene plates were obtained using a Perkin-Elmer 180 far-infrared spectrometer which was calibrated using water vapor lines and is accurate to ±1 cm^{-1}; however, the breadth of the infrared bands leads to a greater uncertainty than this.

Precession, Laue, and Weissenberg photographs taken with both Mo and Cu radiation were employed to assign the Laue class, lattice type, and apparent space group. Lattice constants at 22° were

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