TABLE I

TENTATIVE FAR-INFRARED BAND ASSIGNMENTS (CM^{-1}) OF PHOSPHITES AND THEIR COMPLEXES

Compound	Ligand mode	Shifted ligand mode or F_2 species	νM–P
$CH_3C(CH_2O)_3P$	265		
$(CH_3C(CH_2O)_3P)_4Ni$	271		157
$(CH_3C(CH_2O)_3P)_4Pd$	272	192	142
$(CH_3C(CH_2O)_3P)_4Pt$	274	191	160
$[(CH_3C(CH_2O)_3P)_4Ag]ClO_4$	268		112
$[(CH_3C(CH_2O)_3P)_4Cu]ClO_4$	269		132
$(CH_2)_3(CHO)_3P$	321		
$((CH_2)_3(CHO)_3P)_4Ni$	349		162
$((CH_2)_3(CHO)_3P)_4Pd$	333	193	145
$((CH_2)_3(CHO)_3P)_4Pt$	338	194	170
$(C_2H_5O)_3P$	330		
$((C_2H_5O)_3P)_4Ni$	330		299

Myers, *et al.*,[1] for the complex $((C_2H_5O)_3P)_4Ni$, though we did observe the bands at 299 and 330 cm^{-1} (Figure 3c) in essential agreement with the two absorptions described by these workers at 305 and 335 cm^{-1}. Our observation on this complex may be indicative of a single M–P vibration at 299 cm^{-1} if the 330-cm^{-1} band can be assigned to the ligand mode we observed at 330 cm^{-1} in free $(C_2H_5O)_3P$ (see Figure 3). Although this conclusion would be consistent with that reached for our bicyclic phosphite–nickel(0) complexes, we regard it only as a very tentative possibility inasmuch as it rests on the presently moot question of the existence of the weak 210-cm^{-1} band reported by Myers, *et al.*[1] Furthermore it leads to an unexpectedly large difference between the metal–phosphorus frequencies in the nickel(0) polycyclic phosphites (157, 162 cm^{-1}) and the analogous triethyl phosphite complex (299 cm^{-1}). Further investigations are necessary to test the validity of these assignments.

The assignment of the absorption in the 142–170-cm^{-1} region in the four platinum(0) and palladium(0) complexes to an M–P mode is made somewhat difficult by the presence of a band in the 191–194-cm^{-1} range. It is surprising that this latter absorption is so constant from the palladium to the platinum complex (1 cm^{-1}) while the M–P mode varies as much as 18 and 25 cm^{-1} in the $CH_3C(CH_2O)_3P$ and $(CH_2)_3(CHO)_3P$ complexes, respectively. Although this band may be a ligand mode which has moved to lower energy upon coordination, an F_2 species of an M–P mode arising out of a distortion from T_d symmetry cannot be ruled out. If distortion occurs, however, the second member of the split F_2 species as described by Myers, *et al.*,[1] for the $(C_2H_5O)_3P$ complexes is not apparent. The coincidence of the missing F_2 member with the ligand band in the 270–338-cm^{-1} range for both ligands would be fortuitous and somewhat unlikely in view of the extremely large splitting of 80–140 cm^{-1} which would then be the case for this mode. It should be recognized, however, that there is some evidence for suggesting[8] that three of the M–P bonds may be different from the fourth in Pt(0) complexes of this type. The powder patterns of the $CH_3C(CH_2O)_3PNi^0$ and -Pt^0 complexes were not identical and so isomorphism arguments cannot be used to favor the conclusion that these compounds have identical geometries. Single-crystal studies are planned hopefully to shed light on this problem. Our provisional assignments are summarized in Table I.

Taking into account the changing mass of the metal, the progression of the M–P mode in the 140–170-cm^{-1} range to increasing energy in the order Pd < Ni < Pt suggests that the bond order is greatest for platinum if the trend in M–P stretching force constants parallels their associated frequencies. The M–P stretching frequency in $[(CH_3C(CH_2O)_3P)_4Cu]ClO_4$ and the silver(I) analog appears at a distinctly lower energy than in the nickel(0) and palladium(0) complexes, respectively, in spite of the nearly identical masses involved in the third- and fourth-row metal pairs. Moreover the presence of a positive charge on the silver and copper complexes might have been expected to increase rather than decrease the M–P stretching frequency because of an increase in the polarity of the M–P bond. It is tentatively suggested that the weak σ basicity of phosphites may result in a subordination of this effect to a substantial weakening of metal to phosphorus π bonding from the zerovalent to the monovalent d^{10} complexes. The decrease in M–P from the copper(I) to the silver(I) complex parallels that observed for the nickel(0) to the palladium(0) compounds.

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The Enthalpy of the Solid Decomposition Reaction $Cs_3NiCl_5(s) = CsNiCl_3(s) + 2CsCl(s)$

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An investigation by Iberson, Gut, and Gruen[1] of the nickel(II) chloride–cesium chloride phase diagram has shown that this system exhibits two congruently melting compounds, the blue Cs_3NiCl_5 (mp 547°) and the orange-yellow $CsNiCl_3$ (mp 768°). In the former compound Ni^{2+} is in tetrahedral coordination; in the latter it is in octahedral coordination. At 417° a solid-state transformation of Cs_3NiCl_5 results in a decomposition according to the equation

$$Cs_3NiCl_5(s) = 2CsCl(s) + CsNiCl_3(s) \qquad (\Delta H^D) \qquad (1)$$

Cs_3NiCl_5 is stable above 417°, and the mixture of $2CsCl + CsNiCl_3$ below 417°. We wish to report

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[1] E. Iberson, R. Gut, and D. M. Gruen, *J. Phys. Chem.*, **66**, 65 (1962).

here a calorimetric determination of the enthalpy change associated with this decomposition reaction at 25° and at 445°.

The Cs_3NiCl_5 compound and its solid products of decomposition (*i.e.*, the solid mixture of $2CsCl-CsNiCl_3$) were prepared in the form of small rods (10–15 mm long × 3 mm in diameter) by mixing the solid anhydrous $NiCl_2$[2a] with the appropriate amount (1:3 ratio) of solid CsCl.[2b] The mixture was melted at 900° in an evacuated and sealed tube made from fused silica (~3-mm i.d.). Rapid cooling of the melt to room temperature gave (blue) rods of Cs_3NiCl_5. An intimate mixture of the solid products of decomposition of this compound was prepared in the form of (yellow) rods by keeping the Cs_3NiCl_5 rods at 400° for several hours[1] and then cooling to room temperature.

The calorimetric experiments reported here were performed in a twin calorimeter assembly described before.[3] In order to protect the salts against water vapor and oxygen, the assembly was suitably modified[4] and the experiments were conducted in an inert atmosphere of dry argon. The calibration of the apparatus was by the gold-drop method.[3] The enthalpy of the solid-state reaction of $2CsCl + CsNiCl_3$ to form Cs_3NiCl_5 at 25° ($-\Delta H^{D}{}_{25}$) was measured as follows.

In the first series of experiments the (yellow) rods of the solid mixture were dropped from room temperature (25 ± 1°) into the calorimeter which was maintained at 445°. At this temperature the Cs_3NiCl_5 was formed rapidly (in the form of blue rods). Thus the total enthalpy, ΔH^{T}, measured in these experiments represented the sum of the heat content of the salts involved and the enthalpy of formation of Cs_3NiCl_5 from $CsNiCl_3 + 2CsCl$. Removal of the Cs_3NiCl_5 from the calorimeter and (rapid) cooling to room temperature gave quenched (blue) rods of Cs_3NiCl_5.

In a second series of experiments the Cs_3NiCl_5 rods obtained from the first series of experiments were dropped from room temperature into the calorimeter at 445°. The measured enthalpy change, ΔH^{I}, represents the heat content of this compound at 445° (referred to 25°). The average values of ΔH^{T} (in kilocalories per mole of solid mixture) and of ΔH^{I} (in kilocalories per mole of compound) are given in Table I.

For the enthalpy of decomposition according to (1) at room temperature we have

$$\Delta H^{D}{}_{25} = \Delta H^{I} - \Delta H^{T} = -7.35 \pm 0.41 \text{ kcal/mol}$$

In order to measure the enthalpy of this decomposition at 445°, $\Delta H^{D}{}_{445}$, we also prepared small rods made from CsCl and from the 1:1 compound $CsNiCl_3$. These rods were dropped from 25° into the calorimeter at 445° and the enthalpy changes were measured. The average values of these enthalpies for cesium chloride, ΔH^{II}, and for $CsNiCl_3$, ΔH^{III}, are also listed in Table I. The measured value for CsCl (5.65 kcal/mol) is in very good agreement with the value (5.67 kcal/mol) calculated from the heat content data given in the literature.[5]

TABLE I

ENTHALPY MEASUREMENTS IN THE SYSTEM $CsNiCl_3-CsCl-Cs_3NiCl_5$ (25–445°; IN KCAL/MOL)

$\Delta H^{T}(CsNiCl_3 + 2CsCl)$	32.60 ± 0.30 (9)[a]
$\Delta H^{I}(Cs_3NiCl_5)$	25.25 ± 0.27 (6)
$\Delta H^{II}(CsCl)$	5.65 ± 0.03 (5)
$\Delta H^{III}(CsNiCl_3)$	13.25 ± 0.15 (5)

[a] The quoted uncertainties are standard deviations from the mean. The numbers in parentheses are the number of calorimetric experiments performed.

For the enthalpy change $\Delta H^{D}{}_{445}$ we can write

$$\Delta H^{D}{}_{445} = \Delta H^{D}{}_{25} - \Delta H^{I} + 2\Delta H^{II} + \Delta H^{III} = 2\Delta H^{II} + \Delta H^{III} - \Delta H^{T}$$

$$\Delta H^{D}{}_{445} = -8.05 \pm 0.44 \text{ kcal/mol}$$

From the values of ΔH^{D} at 25 and 445° we interpolate a value for ΔH^{D} at equilibrium (417°) of approximately −8.0 kcal/mol. This implies that eq 1, as written, is associated with an entropy change, ΔS^{D}, of about −11.6 ± 0.7 cal/deg mol.

In closing this communication, we take note of the fact that ΔH^{D} may be considered to arise from the sum of (1) the appropriate difference in the lattice energies of the three solid salts involved and (2) the energy associated with the octahedral-site stabilization of the d^8 electrons of the Ni^{2+} cation. Since the latter energy has been found to be of the order of 21 kcal/mol (for Cl^- anions as ligands[6]), we should be able to estimate the enthalpy change arising from the difference in the lattice energies proper to be about $-8 + 21 \approx +13$ kcal/mol. Hence reactions similar to (1) are not expected to be spontaneous in binary systems in which the octahedral-site stabilization energy is small or absent. This is consistent with the work of Iberson, Gut, and Gruen[1] and with preliminary enthalpy data for other $CsMCl_3$ and Cs_3MCl_5 (M = Mn, Fe, Co) compounds determined by high-temperature solution calorimetry.[7]

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(2) (a) Prepared by removing water from the hydrated $NiCl_2 \cdot 6H_2O$ (Mallinckrodt AR) in an $HCl-N_2$ atmosphere at temperatures up to 850°. (b) Kawecki Chemical Co., 99.9% pure. Dried at 150° for several hours.

(3) O. J. Kleppa, *J. Phys. Chem.*, **64**, 1937 (1960).

(4) G. N. Papatheodorou and O. J. Kleppa, *J. Chem. Phys.*, **47**, 2014 (1967).

(5) K. K. Kelley, Bureau of Mines Bulletin 584, U. S. Government Printing Office, Washington, D. C., 1960, p 55.

(6) The value of 21 kcal/mol was derived from the values of Dq_{tet} for the $NiCl_4^{2-}$ configuration and the well-known relation: $Dq_{tet} = {}^4/_9 Dq_{oct}$. A value of Dq_{tet} is listed by A. B. Blake and F. A. Cotton, *Inorg. Chem.*, **3**, 5 (1964).

(7) G. N. Papatheodorou and O. J. Kleppa, unpublished results.