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Phosphorus Chalcogenides as Ligands in d^{10} Metal Complexes

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The reaction of the complexes $[(np_3)M]$ (M = Ni or Pd, np_3 = tris(2-(diphenylphosphino)ethyl)amine) with the P_4X_3 (X = S, Se) phosphorus chalcogenides affords compounds of the formula $[(np_3)M(P_4X_3)]\cdot nC_6H_6$ (M = Ni, X = S or Se, n = 2; M = Pd, X = S, n = 0). The molecular structure of $[(np_3)Ni(P_4S_3)]\cdot 2C_6H_6$ was determined by single-crystal X-ray diffraction methods. The compound crystallizes in the cubic space group $P2_13$ with $Z = 4$ and unit cell dimension a = 17.310 (4) Å. The metal atom is in a distorted-tetrahedral environment formed by the three P atoms of the np_3 ligand and by the P_4S_3 apical P atom. A similar structure is assigned to the isomorphous P_4Se_3 adduct $[(np_3)Ni(P_4Se_3)]\cdot 2C_6H_6$ and to the $[(np_3)Pd(P_4S_3)]$ complex.

Introduction

We have recently found that the phosphorus chalcogenides P_4S_3 and P_4Se_3 react with nickel(II) and cobalt(II) tetrafluoroborate salts in the presence of the tridentate tripod ligand 1,1,1-tris((diphenylphosphino)methyl)ethane, triphos, to give complexes having the P_3 homocyclic unit[1] or the P_2X (X = S[2] or Se[3]) heterocyclic unit η^3 bonded to the metal.

As a part of a study on the reactivity of these cage molecules toward several transition-metal systems, we have investigated the reactions of P_4S_3 and P_4Se_3 with d^{10} metal complexes formed by the tetradentate tripod ligand tris(2-(diphenylphosphino)ethyl)amine, np_3.

The complexes $[(np_3)Ni(P_4X_3)]\cdot 2C_6H_6$ (X = S or Se) and $[(np_3)Pd(P_4S_3)]$, in which the P_4X_3 intact molecule is coordinated to the metal, have been synthesized, and the structure of the compound $[(np_3)Ni(P_4S_3)]\cdot 2C_6H_6$ has been determined by X-ray diffraction methods. The P_4S_3 molecule has been previously shown to act as a ligand only toward chromium group carbonyls.[4,5] To the best of our knowledge, the P_4Se_3 molecule has never been used as a ligand in transition-metal complexes.

Experimental Section

Materials. The complexes $[(np_3)M]$ (M = Ni[6] or Pd,[7] np_3 = tris(2-(diphenylphosphino)ethyl)amine) were prepared as previously described. Tetraphosphorus trisulfide, P_4S_3, was purchased from Fluka AG and used after recrystallization from benzene. Tetraphosphorus triselenide was prepared according to the published procedure.[8]

Preparation of Complexes. All the reactions were carried out under dry nitrogen and in freshly distilled oxygen-free solvents.

$[(np_3)Ni(P_4X_3)]\cdot 2C_6H_6$ (X = S or Se). A warm solution of the tetraphosphorus chalcogenide (P_4S_3, P_4Se_3) (0.5 mmol) in benzene (50 mL) was slowly added to a solution of $[(np_3)Ni]$ (0.5 mmol) in tetrahydrofuran (40 mL) at 35–40 °C. The complexes were deposited after bubbling a slow stream of inert gas through the resulting solution for 3–4 h. The crystals were separated from the solution, then washed with benzene, filtered off, and dried in a current of nitrogen at room temperature. The complexes crystallize with two molecules of benzene as indicated by the elemental analysis data and by the mass spectrometric and X-ray investigations (yield ca. 50–55%). Anal. Calcd for $[(np_3)Ni(P_4S_3)]\cdot 2C_6H_6$: C, 59.57; H, 5.00; N, 1.29; Ni, 5.39; P, 19.91; S, 8.83. Found: C, 59.42; H, 5.11; N, 1.22; Ni, 5.25; P, 19.83; S, 8.65. Calcd for $[(np_3)Ni(P_4Se_3)]\cdot 2C_6H_6$: C, 52.75; H, 4.43; N, 1.14; Ni, 4.78; P, 17.63. Found: C, 52.68; H, 4.51; N, 1.12; Ni, 4.70; P, 17.41.

$[(np_3)Pd(P_4S_3)]$. The complex was prepared by the same procedure as the above compounds. The microcrystalline precipitate was washed with benzene, filtered off, and dried in a current of nitrogen (yield ca. 55–60%). Anal. Calcd for $[(np_3)Pd(P_4S_3)]$: C, 51.47; H, 4.32; N, 1.43; P, 22.12; Pd, 10.86. Found: C, 51.33; H, 4.35; N, 1.36; P, 21.96; Pd, 10.74.

Physical Measurements. Infrared and electronic spectra were obtained as already described.[9] Mass spectra were recorded on a Kratos MS80 mass spectrometer with an ionizing voltage of 70 eV. A direct-insertion probe was employed with source temperatures ranging from 100 to 200 °C.

X-ray Data Collection and Reduction for $[(np_3)Ni(P_4S_3)]\cdot 2C_6H_6$. The compound crystallizes in the cubic $P2_13$ space group with tetrahedral morphology. A crystal with a 0.35-mm edge was used for crystal data and intensity data collection. A Philips PW 1100 automated diffractometer and graphite-monochromated Mo Kα radiation (λ = 0.71069 Å) were used for all operations. The lattice constant determined from the setting angles of 12 pairs of reflections with $12° < \theta < 16°$, and other crystal data are as follows: a = 17.310 (4) Å, V = 5186.7 Å^3, Z = 4, M_r = 1088.76, D_{calcd} = 1.394 g cm^{-3}, μ(Mo Kα) = 7.40 cm^{-1}. The intensities of 2249 symmetry-independent reflections were measured in the interval $5° < 2\theta < 54°$, with a symmetric scan range of $(1.20 + 0.30 \tan \theta)°$ and a scan speed of 5°/min in 2θ. Stationary-background countings were taken at each end of the scan for a time equal to half the scan time. The intensities of three standard reflections, monitored every 120 min, showed no significant fluctuation during the collection procedure. The raw intensity data were corrected for Lorentz–polarization effects and for absorption (transmission coefficients ranging from 0.79 to 0.84). A total of 1030 reflections with $I > 3\sigma(I)$ were used for structure solution and refinement. The principal computer programs used in the crystallographic calculations are listed in ref 10.

Structure Solution and Refinement for $[(np_3)Ni(P_4S_3)]\cdot 2C_6H_6$. The structure was solved by the heavy-atom method. The position of the nickel atom was determined from a Patterson map. All other nonhydrogen atoms were located in subsequent Fourier maps. The complex molecule and both benzene solvate molecules reside in special positions of 3 symmetry so that the asymmetric unit consists of one-third of each of the above molecules. Full-matrix least-squares refinement was based on minimization of the function $\sum w(|F_o| - |F_c|)^2$ with weights $w = 1/\sigma^2(F_o)$. Anisotropic thermal parameters were used for atoms heavier than carbon and isotropic parameters for the carbon atoms, overall values being applied within each benzene solvate molecule. Hydrogen atoms were introduced in calculated positions (C–H = 1.00 Å) as fixed contributions, each with a temperature factor ca. 20% larger than that of the respective carbon atom. The scattering factors of the neutral atoms were taken from ref 11 and the anomalous dispersion corrections for nickel from ref 12. With a total of 107 parameters, the refinement converged at R = 0.056 and R_w = 0.056.[13]

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(12) Reference 11, p 148 ff.
(13) $R = \sum ||F_o| - |F_c|| / \sum |F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w(F_o)^2]^{1/2}$.

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Table I. Positional Parameters for the Structure of $[(np_3)Ni(P_4S_3)]\cdot 2C_6H_6$[a]

atom	*x/a*	*y/b*	*z/c*
Ni	0.0332 (1)	0.0332 (1)	0.0332 (1)
S	−0.1485 (2)	−0.0678 (2)	0.0022 (2)
P1	0.0511 (2)	−0.0223 (2)	0.1490 (2)
P2	−0.0359 (2)	−0.0359 (2)	−0.0359 (2)
P3	−0.1920 (2)	−0.1362 (2)	−0.0872 (2)
N	0.1388 (5)	0.1388 (5)	0.1388 (5)
C1	0.1393 (6)	0.0114 (7)	0.1991 (7)
C2	0.1440 (7)	0.0959 (6)	0.2111 (7)
C11	0.0578 (6)	−0.1290 (6)	0.1547 (6)
C12	−0.0083 (7)	−0.1716 (7)	0.1387 (6)
C13	−0.0064 (8)	−0.2523 (7)	0.1433 (7)
C14	0.0636 (8)	−0.2881 (8)	0.1599 (8)
C15	0.1276 (8)	−0.2490 (8)	0.1769 (8)
C16	0.1260 (7)	−0.1678 (7)	0.1714 (7)
C21	−0.0208 (6)	−0.0098 (6)	0.2235 (6)
C22	−0.0942 (6)	0.0124 (6)	0.2055 (6)
C23	−0.1528 (8)	0.0204 (8)	0.2603 (7)
C24	−0.1385 (7)	−0.0013 (7)	0.3357 (7)
C25	−0.0665 (8)	−0.0244 (8)	0.3572 (9)
C26	−0.0073 (7)	−0.0324 (7)	0.3020 (7)
C31	0.338 (1)	0.231 (1)	0.270 (1)
C32	0.290 (1)	0.222 (1)	0.333 (1)
C41	0.447 (2)	0.358 (1)	0.453 (2)
C42	0.385 (2)	0.391 (2)	0.473 (2)

[a] Standard deviations of the least significant digits are in parentheses. Atoms C11–C16 and C21–C26 belong to the phenyl groups of the np_3 ligand. Atoms C31, C32 and, respectively, C41, C42 belong to the two solvate benzene molecules.

In the last cycle of refinement, the largest shift/error ratio was 0.02. The highest peak in the final difference map (0.5 e Å^{-3}) lay close to the metal atom position. Neither this or lower peaks in the map could be assigned any chemical significance. The final positional parameters for the non-hydrogen atoms are given in Table I. Listings of thermal parameters and of the observed and calculated structure amplitude are available as supplementary material.[14]

Crystal Data for $[(np_3)Ni(P_4Se_3)]\cdot 2C_6H_6$. Crystals of this compound are similar in morphology to those of the P_4S_3 derivative, with which they are isomorphous (a = 17.413 (7) Å). At variance with the latter, however, they do not provide good material for X-ray diffraction. The intensities fall off rather rapidly with θ, so that the number of reflections with $I > 3\sigma(I)$ was only half as large as that obtained for the P_4S_3 derivative. Probably due to some degree of disordering in the structure, refinement on the P_4Se_3 derivative was not successful. However, it was evident from the distribution of intensities and from the form of the Patterson map that the two isomorphous compounds are also isostructural.

The $[(np_3)Pd(P_4S_3)]$ compound was not obtained in crystalline form suitable for X-ray diffraction.

Results and Discussion

The reaction of the $[(np_3)M]$ (M = Ni or Pd) complexes with the P_4X_3 (X = S or Se) chalcogenides affords compounds of the formula $[(np_3)M(P_4X_3)]\cdot nC_6H_6$. (M = Ni, X = S or Se, n = 2; M = Pd, X = S, n = 0). All of the compounds are air stable for several days in the solid state and completely insoluble in common organic solvents and in liquid ammonia. For this reason their NMR spectra could not be recorded. The reflectance spectra of the $[(np_3)Ni(P_4X_3)]\cdot 2C_6H_6$ complexes exhibit strong bands at 16 400 and 25 600 cm^{-1} (X = S) and at 15 800 and 22 200 cm^{-1} (X = Se). A band at 21 750 cm^{-1} is observed in the spectrum of $[(np_3)Pd(P_4S_3)]$ before the onset of charge-transfer bands. The P_4X_3 bands in the IR spectra of the compounds are obscured by those due to the tripod ligand so that no unambiguous assignment of important IR transitions could be made. The mass spectra of the $[(np_3)Ni(P_4X_3)]\cdot 2C_6H_6$ complexes show, up to ca. 200 °C, the peaks recorded[15] for the free P_4X_3 (X = S, Se) phosphorus chalcogenides in analogous conditions, in addition to those of the benzene solvate molecules. Only the P_4S_3 peaks are observed in the same temperature range for $[(np_3)Pd(P_4S_3)]$. The ion abundances agree in each case with values reported for the uncoordinated P_4X_3 molecules,[15] indicating that the same fragmentation patterns occur as for the free molecules. This in turn suggests that the undecomposed P_4X_3 unit is released by the solid compound, particularly at temperatures >150 °C.

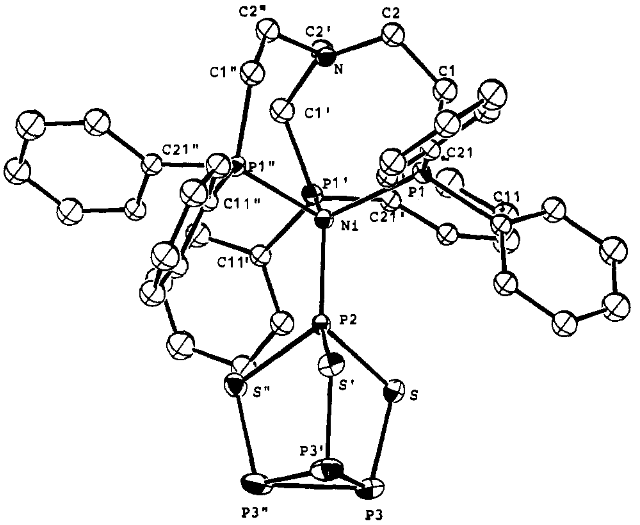

Figure 1. Perspective view of the $[(np_3)Ni(P_4S_3)]$ molecule, with 20% probability ellipsoids. Primed and double-primed atoms are related to the corresponding unprimed ones by a threefold symmetry axis.

Table II. Selected Bond Lengths (Å) and Angles (deg) for the Structure of $[(np_3)Ni(P_4S_3)]\cdot 2C_6H_6$[a]

Ni–P1	2.245 (3)	P1–C11	1.85 (1)
Ni–P2	2.072 (5)	P1–C21	1.81 (1)
S–P2	2.129 (4)	N–C2	1.46 (1)
S–P3	2.090 (5)	C1–C2	1.48 (2)
P3–P3′	2.223 (7)	Ni· · ·N	3.166 (8)
P1–C1	1.85 (1)		
P1–Ni–P1′	108.5 (1)	Ni–P1–C11	118.9 (4)
P1–Ni–P2	110.4 (1)	Ni–P1–C21	119.4 (3)
Ni–P2–S	119.9 (1)	C1–P1–C11	103.8 (5)
S–P2–S′	97.3 (2)	C1–P1–C21	101.3 (5)
P2–S–P3	104.3 (2)	C11–P1–C21	97.2 (5)
S–P3–P3′	103.4 (2)	P1–C1–C2	115.0 (9)
S–P3–P3″	103.5 (2)	N–C2–C1	112.3 (1.0)
P3′–P3–P3″ [b]	60.0	C2–N–C2′	114.5 (1.0)
Ni–P1–C1	113.4 (4)		

[a] Primed and double-primed atoms are related to the corresponding unprimed ones by a threefold symmetry axis.
[b] Symmetry-determined value.

The structure of $[(np_3)Ni(P_4S_3)]\cdot 2C_6H_6$ was investigated by X-ray diffraction procedures in order to determine the exact mode of coordination of the P_4S_3 molecule and draw possible comparisons with the dimensions of the same moiety coordinated in the molybdenum carbonyl $Mo(CO)_5P_4S_3$[4] as well as with those of the free molecule.[16] The structure consists of molecules of the nickel(0) complex in which the P_4S_3 ligand is coordinated to the metal through its apical P atom and of interposed benzene molecules from the solvent. Each of these lies in a special position of 3 symmetry; in particular, in the molecule of the complex a threefold axis passes through the metal atom, the apical P atom of the P_4S_3 cage, and the N atom of the tripod ligand. A perspective view of the $[(np_3)Ni(P_4S_3)]$ molecule is shown in Figure 1. Values of selected bond lengths and angles are listed in Table II.

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(14) Supplementary material.

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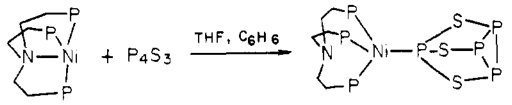
Table III. Structural Data for the Coordinated and Uncoordinated P_4S_3 Molecule[a,b]

compd	P_2-S	P_3-S	P_3-P_3'	S-P_2-S′	P_2-S-P_3	S-P_3-P_3[c]
$[(np_3)Ni(P_4S_3)]\cdot 2C_6H_6$[d]	2.129 (4)	2.090 (5)	2.223 (7)	97.3 (2)	104.3 (2)	103.4 (2)
$Mo(CO)_5P_4S_3$[e]	2.11 (3)	2.13 (1)	2.24 (1)	99.5 (6)	102.7 (8)	103 (1)
P_4S_3[f]	2.088 (9)	2.093 (3)	2.235 (11)	99.4 (3)	103.0 (3)	103.1 (1)

[a] Averages over chemically equivalent bond distances (Å) and angles (deg) are reported; standard deviations are calculated by the formula $[\Sigma_i \Delta_i^2/(n-1)]^{1/2}$, where n is the number of bonds or angles and Δ_i are deviations of individual values from the mean. [b] Atomic labels are as in Figure 1. [c] Averages over S-P_3-P_3' and S-P_3-P_3'' values. [d] Present work. [e] Reference 4. [f] Reference 16.

Scheme I



The metal atom is in a distorted tetrahedral environment formed by the three P atoms of the np_3 ligand and by the P_4S_3 apical P atom. The Ni–P(np_3) distance (2.245 (3) Å) matches that found in the *tetrahedro*-tetraphosphorus adduct $[(np_3)Ni(P_4)]$[17] (2.24 (2) Å) having similar geometry to that of the present compound, whereas the Ni–P(P_4S_3) bond length (2.072 (5) Å) is longer than that of Ni–P(P_4) (1.99 (1) Å), formed by the smaller coligand in the P_4 derivative. The nitrogen atom is uncoordinated and lies 3.166 (8) Å apart from the metal center. Such a distance is in the range of values previously determined for complexes in which the np_3 nitrogen atom is not coordinated.[18]

The easy detachment of the np_3 nitrogen from the metal atom is of crucial importance to the formation of the present P_4S_3 adduct in mild conditions. Indeed, as already noted[19] for the similar cases of the $[(np_3)M(P_4)]$ (M = Ni[17] or Pd[20]) *tetrahedro*-tetraphosphorus adducts, owing to the flexibility of the ancillary np_3 ligand lengthening of the Ni–N bond with formation of the new Ni–P bond by the coligand according to the simplest reaction path (Scheme I) involves only a modest conformational rearrangement of the tripod ligand. Moreover, further transformations of the cage molecule are probably prevented by the fact that (a) the coordination number and the oxidation number of the metal atom do not change in the process and (b) the P_4S_3 molecule finally enters the protective environment of the np_3 phenyl groups.

The P_4S_3 unit is so oriented about the molecular threefold axis that its S and basal P atoms lie in staggered positions with respect to the P atoms of the tripod ligand. Although bond lengths and angles within the coordinated P_4S_3 moiety in the present nickel compound are not considerably different from those existing in the free molecule,[16] or in the previously reported $Mo(CO)_5P_4S_3$ complex,[4] a few significant differences exist, as appears from the values listed in Table III. The P–S bond distances are more affected by coordination than the P–P ones. As already noted[4] all P–S bonds in the Mo complex are longer than those in the uncoordinated P_4S_3 molecule. In the Ni compound, on the other hand, only the P_{ap}–S distance exhibit an appreciable increase. The S–P_{ap}–S angles are smaller in the latter compound than in the former or in the free molecule.

Such small differences should be ascribed to different "bonding capabilities" of the L_5M vs. the L_3M conical fragment[21] and/or to effects of intramolecular nonbonded interactions. The d^6 $(CO)_5Mo$ moiety has essentially one σ-type empty orbital at suitable energy for interaction with the P_4S_3 unit, whereas a d^{10} L_3M fragment with the geometry of the present $(np_3)Ni$ moiety has one σ orbital and one degenerate pair of π orbitals, all occupied.[21] Coordination by the P_4S_3 unit in the Ni compound is probably allowed by σ-type metal 4s and 4 p contributions to the Ni–P_{ap} bond as in the similar $[(np_3)Ni(P_4)]$ molecule.[17,19] In analogy with such an η^1-P_4 derivative and with η^3-P_3 complexes,[19] an overall shift of negative charge toward the P_4S_3 group is expected, so that the observed increase in the P–S bond lengths upon coordination may be due to increased contributions to antibonding orbitals within the cage molecule. Finally, repulsive four-electron interactions with the filled π orbitals of the $(np_3)Ni$ moiety may cause the decrease in the S–P_{ap}–S angles found for the Ni complex, although such a decrease may also be caused by some S···C nonbonded approaches in the range 3.6–4.0 Å. The overall picture of the interaction between the two fragments in the Ni compound is such that the P_4S_3 molecule does not appear to be as strongly coordinated as in the Mo complex.[4] This is in keeping with the present mass spectrometric results.

Atoms of the P_4S_3 moiety in the structure of $[(np_3)Ni(P_4S_3)]\cdot 2C_6H_6$ form no intermolecular contact with other non-hydrogen atoms shorter than 3.7 Å. The solvate benzene molecules are not involved in particularly short approaches to other parts of the structure, although the distance of 4.1 Å between their planes is suggestive of some interactions. The presence of such solvate molecules is certainly important to the overall stability of the lattice.

A structure similar to that of the P_4S_3 derivative described above may be safely assigned to the complex molecule in the isomorphous P_4Se_3 adduct $[(np_3)Ni(P_4Se_3)]\cdot 2C_6H_6$ on the basis of the elemental analysis, mass spectrometric, UV–visible, and partial X-ray diffraction data (see Experimental Section). Also the $[(np_3)Pd(P_4S_3)]$ derivative is assigned this type of structure, mainly on the basis of analytical and mass spectrometric data.

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Registry No. $[(np_3)Ni(P_4S_3)]\cdot 2C_6H_6$, 86013-18-5; $[(np_3)Ni(P_4Se_3)]$, 86013-19-6; $[(np_3)Pd(P_4S_3)]$, 86013-20-9; $(np_3)Ni$, 52633-73-5; $(np_3)Pd$, 86013-21-0.

Supplementary Material Available: Tables of anisotropic thermal parameters for non-hydrogen atoms and calculated and observed structure factor amplitudes for $[(np)_3Ni(P_4S_3)]\cdot 2C_6H_6$ (7 pages). Ordering information is given on any current masthead page.

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