condensation of phosphoric acid in the interlayer spaces with the host layers in a different manner under different preparative conditions. The results obtained here indicate a possibility that compounds with various sequences of $NbO(H_2O)PO_4$ layers can be prepared by condensation with PO_4 groups and other oxoacid groups.

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Infrared Spectra of P_4S_{10} and Its Decomposition Products in Solid Argon

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The vapor from solid molecular P_4S_{10} in a stainless steel Knudsen cell at 175 °C was trapped in solid argon for infrared spectroscopic study. Comparison with infrared spectra of solid P_4S_{10} and P_4S_9 provides a basis for identification of molecular P_4S_{10} and P_4S_9, which were isolated in comparable yields. A similar fraction of product absorptions is identified as phosphorus sulfides (PS, PS_2) and diphosphorus sulfides (P_2S_4, P_2S_5), with P_2S_5 being the major diphosphorus species in the equilibrium vapor and in superheated vapor. Photolysis of P_4S_{10} and O_3 mixtures produced new infrared absorptions for SO_2 and the terminal oxide P_4S_9O.

Introduction

Tetraphosphorus decasulfide, P_4S_{10}, was first synthesized by Berzelius in 1843 by the violent reaction of white phosphorus and sulfur, but the reaction of red phosphorus and sulfur is more controlled.[1] This compound is an important industrial chemical, used in the production of additives for lubricants, insecticides, and flotation agents.[2] Although P_4S_{10} is a molecular solid, on evaporation some of the parent molecules decompose, but apparently the decomposition is reversible because the compound may be purified by distillation.[3] The infrared spectrum of the solid has been reported by several groups,[4-7] and the Raman spectrum of the vapor (at 550 °C) is different from the solid spectrum.[6] In order to complement matrix studies of small phosphorus–sulfur transient species formed from the elements in a microwave discharge,[8] P_4S_{10} and its thermal decomposition products were trapped in solid argon for spectroscopic study.

Experimental Section

The cryogenic refrigerator, Perkin-Elmer 983 spectrometer, and vacuum apparatus have been described earlier.[9] Tetraphosphorus decasulfide, obtained from Fluka, was evaporated from a stainless steel Knudsen cell at 175–215 °C into a 2 mmol/h argon stream and condensed on a cesium iodide window maintained at 12 K. Infrared spectra were recorded from 2000 to 200 cm^{-1} on a Perkin-Elmer 983 spectrometer with sufficient resolution to give a wavenumber accuracy of ±0.5 cm^{-1}. Similar experiments were performed with a double oven, which allowed superheating of the effusing vapors in a 50-mm alumina tube 6 mm in diameter.[10]

Results

Tetraphosphorus decasulfide was evaporated from a stainless steel Knudsen cell at several temperatures. The spectrum illustrated in Figure 1 for P_4S_{10} from a 175 °C Knudsen cell contains a strong doublet at 711.3 and 707.8 cm^{-1}, three strong bands at 552.9, 540.8, and 499.2 cm^{-1}, a sharp band at 750.6 cm^{-1}, weak bands at 743.7 and 728.3 cm^{-1}, and other weaker bands listed in Table I. Also observed was a sharp trio of bands at 861.3, 765.8, and 647.7 cm^{-1} (labeled T) and a structured feature around 1000 cm^{-1}, which diminished markedly in subsequent experiments using the same sample. These latter bands arise from more volatile impurities believed to be P_4S_{10} hydrolysis products; the trio is particularly prominent in phosphine/sulfur discharge experiments where it is identified as $HSPS_2$.[11]

In the next experiment with a 185 °C cell temperature, the 707.8-cm^{-1} band was stronger than the 711.3-cm^{-1} absorption and the 540.8-cm^{-1} band was likewise stronger than the 552.9- and 499.2-cm^{-1} bands (Figure 1b). A subsequent experiment with a 215 °C cell temperature favored the 707.8- and 540.8-cm^{-1} bands even more. More sample was deposited, and a weaker band at 268.0 cm^{-1} tracked with the stronger 707.8- and 540.8-cm^{-1} bands, which are identified by arrows in Figure 1a. The 750.6- and 508.5-cm^{-1} bands were observed with the same intensity relative to each other in all of these experiments.

Table I. Infrared Absorptions (cm^{-1}) from a Sample Produced by Condensing Argon and Vapor from a 175 °C Knudsen Cell Containing Solid P_4S_{10}

absorption	identification	absorption	identification
861.3	($HSPS_2$)	552.9	P_4S_9
765.8	($HSPS_2$)	540.8	P_4S_{10}
750.6	P_2S_5	528	(P_4S_8)
748.3	P_2S_4	508.5	P_2S_5
743.7	PS_2	499.2	P_4S_9
733.3	(P_2S_4)	485.0	?
728.3	PS	460.1	?
716 sh	?	418.0	?
711.3	P_4S_9	406.2	?
707.8	P_4S_{10}	383.9	?
701	(P_4S_8)	358.9	?
647.7	($HSPS_2$)	268.0	P_4S_{10}

A similar sample was deposited from a 195 °C Knudsen cell, and 0.5-cm^{-1} resolution spectra are shown in Figure 2a. The strong 707.8- and 540.8-cm^{-1} bands dominate this spectrum. The sample was photolyzed by visible radiation (380–1000 nm) without effect, but Pyrex-filtered radiation (290–1000 nm) for 10 min decreased the 711.3-, 552.0-, and 499.2-cm^{-1} bands together, decreased the weaker 750.6-, 748.3-, and 743.7-, 733.3-, and 728.3-cm^{-1} bands, produced a new band at 716 cm^{-1}, and left the 707.8- and 540.8-cm^{-1} bands unchanged. Exposure to the full arc (220–1000 nm) for 2 min continued this trend and produced the spectrum shown in Figure 2b.

Experiments were also done by using a quartz finger to evaporate P_4S_{10} into a short tube with argon carrier gas.[8] In this case, the 750.6- and 733.3-cm^{-1} bands were much stronger than the 711.3- and 707.8-cm^{-1} bands, the 743.7-cm^{-1} absorption was observed, and the 508.5-cm^{-1} band tracked with the 750.6-cm^{-1}

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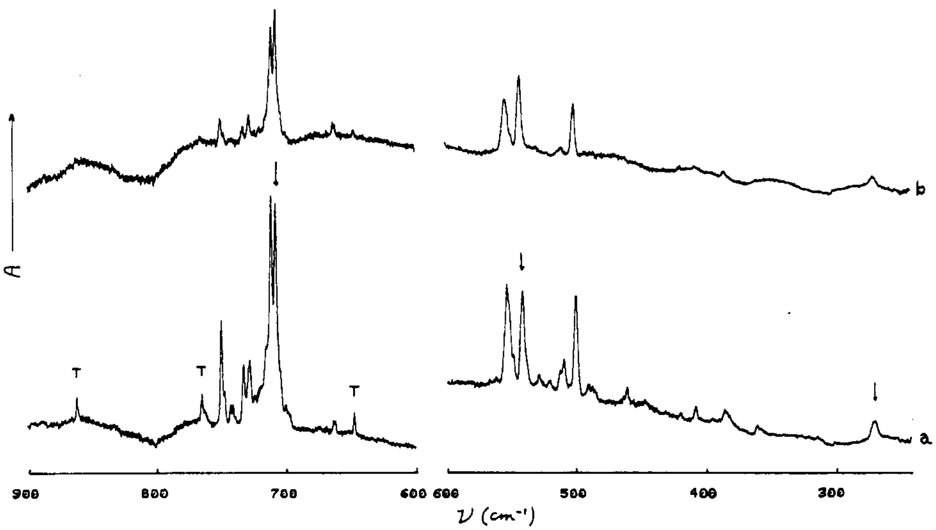

Figure 1. Infrared spectra in the 900–200-cm^{-1} range for a sample prepared by condensing the vapor from solid P_4S_{10} with excess argon at 12 K: (a) 175 °C Knudsen cell, 5-h deposition; (b) 185 °C Knudsen cell, 3-h deposition. Spectra were recorded by using a 1.0-cm^{-1} resolution and plotted on an A = 0.0–1.5 absorbance scale. Arrows denote absorptions assigned to P_4S_{10}.

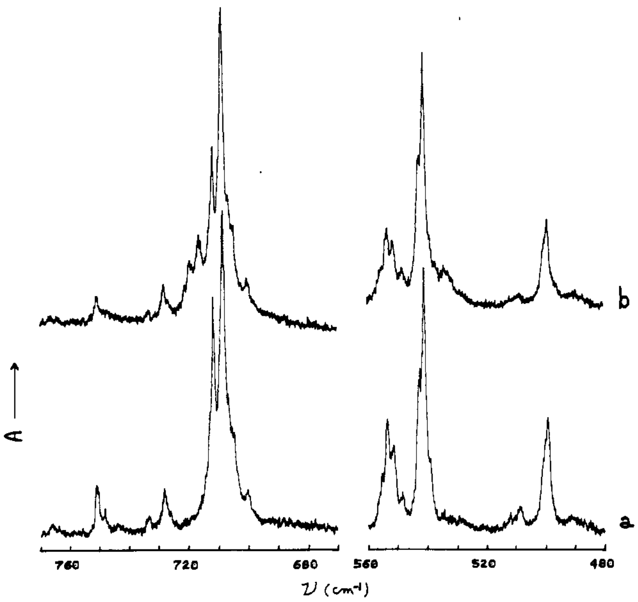

Figure 2. Infrared spectra of the vapor from solid P_4S_{10} at 195 °C recorded by using a 0.5-cm^{-1} resolution and plotted on an A = 0.0–2.0 absorbance scale: (a) sample deposited with excess argon for 2 h at 12 K; (b) sample after ultraviolet photolysis, 10 min at $\lambda > 290$ nm and 2 min at $\lambda > 220$ nm.

band. When this flowing Ar/P_4S_{10} stream was subjected to microwave discharge, the above absorptions were replaced by strong 748.9-, 743.7-, and 729.2-cm^{-1} bands in the infrared spectrum of the resulting deposit.[8]

Several superheater experiments were performed with P_4S_{10} vapor. The results are summarized in Figure 3. The first spectrum in Figure 3a follows deposition of P_4S_{10} from a 175 °C reservoir through an alumina tube heated to approximately 350 °C; the 711.3-, 707.8-, 552.9-, 540.8-, and 499.2-cm^{-1} bands dominate, but weak absorptions were observed at 750.6 and 728.3 cm^{-1}. Sample deposition was continued for 1 h while the reservoir was maintained at 175 °C and the alumina tube was heated to 450 °C, and the spectra are shown in Figure 3b. The weaker 750.6-, 728.3-, and 508.5-cm^{-1} bands increased at a faster rate than the 711.3-, and 707.8-, 552.9-, 540.8-, and 499.2-cm^{-1} bands, but the last five bands maintain their original relative intensity distribution. This procedure was continued for an additional 3 h, and the spectrum is illustrated in Figure 3c; major growth in the 750.6- and 508.5-cm^{-1} bands is obvious. A shoulder was also observed at 748.3 cm^{-1} along with weak 743.7-, 733.3-, 728.3-, and 716-cm^{-1} bands. This experiment was continued with 175 and 530 °C temperatures on the reservoir and superheater tubes, respectively, and several points are noteworthy: the 750.6-cm^{-1} band increased with the 508.5-cm^{-1} band, the 750.6-cm^{-1} band became the strongest absorption in the spectrum, the original five bands did not increase, and the weak 743.7- and 716-cm^{-1} bands grew substantially. It must also be pointed out that thermal equilibrium was not attained in the superheater tube.

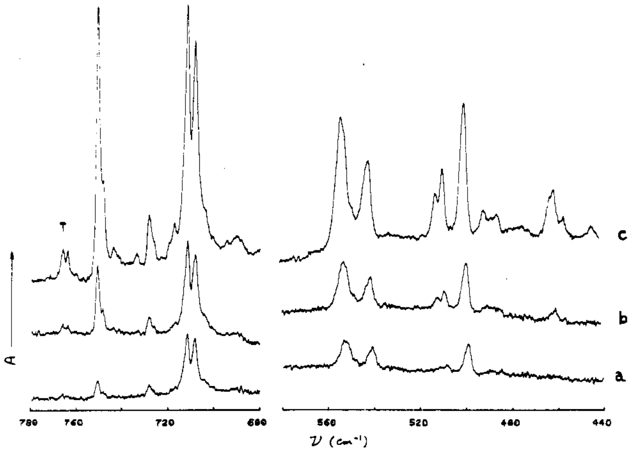

Figure 3. Infrared spectra of the vapor from solid P_4S_{10} at 175 °C passed through a superheated tube and condensed with excess argon at 12 K: (a) 1 h through a 350 °C tube; (b) 1 h through a 450 °C tube; (c) additional 3 h through a 450 °C tube. Spectra were recorded by using a 1.0-cm^{-1} resolution and plotted on an A = 0.0–1.5 absorbance scale.

Finally, P_4S_{10} and O_3 samples were photolyzed as described previously.[12,13] Weak new bands were observed at 1342 and 1149 cm^{-1} near SO_2 isolated in solid argon (1355, 1152 cm^{-1});[12] sharp 1244-cm^{-1} and broad 1228-cm^{-1} bands and a new 579-cm^{-1} absorption were observed after 20 min of full arc photolysis. An analogous $^{18}O_3$ experiment produced $S^{18}O_2$ bands at 1300 and 1099 cm^{-1} and product absorptions at 1201, 1185, and 578 cm^{-1}.

Discussion

Infrared spectra of the vapor from solid P_4S_{10} will be assigned to P_4S_{10} and its decomposition products.

P_4S_{10} and P_4S_9. The five strong bands at 711.3, 707.8, 552.9, 540.8, and 499.2 cm^{-1} in Figure 1 are clearly due to the major evaporation products from solid P_4S_{10}. Since the infrared spectrum

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Table II. Infrared Absorptions (cm^{-1}) Due to Solid- and Matrix-Isolated P_4O_{10} and P_4S_{10}

P_4O_{10}		P_4S_{10}		P_4S_9	
solid[a]	matrix[b]	solid[c]	matrix	solid[d]	matrix
1390	1408	690	708	694, 677	712
1015	1026	533	541	546	553
764	767	264	268	492	499
573	576	192			
424	412	138			
278	272				

[a] Reference 14. [b] Reference 15. [c] Reference 7. [d] Reference 6.

of solid P_4S_{10} contains only two strong bands in this region (690 and 533 cm^{-1}),[6,7] some decomposition must accompany evaporation, even at the lowest temperature (175 °C) that gave observable matrix spectra. Increasing the Knudson cell temperature over the range employed here (175–215 °C) increased the 707.8- and 540.8-cm^{-1} band intensities relative to the 711.3-, 552.9-, and 449.2-cm^{-1} band intensities and clearly demonstrated that the first two bands are due to one species and the last three bands are all due to another similar species.

Solid P_4S_9 exists in two modifications that have similar infrared spectra, a strong band with peaks at 694 and 677 cm^{-1} and two strong bands at 546 and 492 cm^{-1}.[6] Considering the solid-to-matrix shifts found for P_4O_{10} (Table II), the comparison with the spectra of solid P_4S_{10} and P_4S_9 identifies the 707.8- and 540.8-cm^{-1} bands as P_4S_{10} and the 711.3-, 552.9-, 540.8-cm^{-1} bands as P_4S_9.

The 707.8- and 540.8-cm^{-1} bands are assigned to the strongest two t_2 modes of the tetrahedral P_4S_{10} cage molecule, which is isostructural with P_4O_{10}.[2] These antisymmetric vibrations involve terminal P–S and cage P–S–P stretching motions, respectively. The sharp weaker band at 268.0 cm^{-1} also correlates with a band for the solid sample at 264 cm^{-1}, which has been assigned to another t_2 cage mode.[7] The P_4S_9 molecule left by dissociation of one terminal sulfur atom has C_{3v} symmetry. The t_2 bands of P_4S_{10} will therefore split into e and a_1 bands. In the terminal PS stretching region the 711.3-cm^{-1} band is assigned to the e mode; the weaker a_1 mode is probably obscured by the red tail of the 707.8-cm^{-1} P_4S_{10} band. In the sulfur bridge stretching region, the 552.9-cm^{-1} band is assigned to the e mode and the 449.2-cm^{-1} band to the a_1 mode. The larger separation between the latter bands is verified by the spectrum of the solid compound.[6]

It appears that P_4S_9 is more reactive than P_4S_{10}. This is the case with respect to hydrolysis.[2] The unsaturated molecule is also more photosensitive, as Figure 2 indicates.

In these experiments, solid P_4S_{10} was heated to the lowest temperature (175 °C) that gave infrared matrix spectra. The above (Table II) correlation with solid P_4S_{10} spectra and observation of the molecular ion in the mass spectrum of P_4S_{10} vapor[16] demonstrate that a substantial portion of the equilibrium vapor at 175 °C is molecular P_4S_{10}. It is also interesting to note that the $P_4S_9^+$ peak is 80% as strong as the $P_4S_{10}^+$ peak in the mass spectrum.

P_4S_8. The spectra of P_4S_{10} and P_4S_9 suggest slightly lower bands for the P_4S_8 molecule. The weak 701- and 528-cm^{-1} bands are in accord with this trend and are tentatively assigned to P_4S_8, analogous to P_4O_8 in structure. The fact that these bands are very weak and no other bands are in this region for alternative assignment to P_4S_8 indicates that thermal dissociation of two sulfur atoms from P_4S_{10} is an unfavorable reaction and/or that any P_4S_8 formed decomposes readily. Cleavage of the parent molecular cage framework is an important dissociation process.

PS and PS_2. The most abundant ion in the mass spectrum of P_4S_{10} is PS^+.[16] Although the PS diatomic molecule, prepared by discharge of P_4 and S_8 has been observed at 729.3 cm^{-1} in solid argon,[8] the weak 728.3-cm^{-1} band in the present samples containing substantial concentrations of P_4S_{10} and P_4S_9 is most probably due to the PS molecule. In the earlier study, a sharp 744.1-cm^{-1} band was identified as PS_2 on the basis of a mixed sulfur isotopic triplet.[8] The present weak 743.7-cm^{-1} band is therefore assigned to PS_2.

P_2S_5 and P_2S_4. In the P_4 + S_8 discharge work, a sharp 748.9-cm^{-1} band that exhibited a mixed isotopic triplet and increased on sample annealing at the expense of PS and PS_2 was assigned to P_2S_4. According to experimental and theoretical work on P_2O_4,[17,18] the most stable structure is the oxo-bridged isomer O_2P–O–PO, and it follows that the most stable structure for P_2S_4 is probably the sulfo-bridged S_2P–S–PS isomer. The present 748.4-cm^{-1} shoulder is assigned to the same S_2P–S–PS species.

Although the much stronger 750.6-cm^{-1} band could be due to a different structural conformation or matrix site of P_2S_4, its clear dominance as the major higher temperature decomposition product in superheater experiments (Figure 3) strongly suggests the P_2S_5 identification. This is supported by vapor density measurements at 600 °C, which are appropriate for the P_2S_5 formula.[2] In all experiments, the 508.5-cm^{-1} band is associated with the stronger 750.6-cm^{-1} absorption by relative intensity. This band is clearly due to an antisymmetric P–S–P vibration, and its observation confirms the sulfo-bridged structure for P_2S_5, which is presumed to have the structure of molecular P_2O_5.[18,19]

In the series of terminal PO_2 antisymmetric stretching vibrations, the P_2O_5 fundamental comes above the P_2O_4 value, which appears above the PO_2 frequency. The 750.6-cm^{-1} band is the highest frequency due to a thermal decomposition product of P_4S_{10}. This band is accordingly assigned to the antisymmetric PS_2 stretching fundamental in S_2P–S–PS_2, which is the strongest infrared absorption for the P_2S_5 molecule. We also note that $P_2S_5^+$ is the second most abundant ion in the mass spectrum of P_4S_{10}.[16]

Other Absorptions. The weaker 733.3-cm^{-1} band is also due to a decomposition product, and this product appears to be more reactive than P_2S_5 at higher temperatures, as comparison of spectra in Figures 1 and 3 shows. Our best suggestion for the 733.3-cm^{-1} band is another structural isomer of P_2S_4, possibly one that involves weak bonding between terminal sulfur atoms. Finally, the observation of the 750.6- and 733.3-cm^{-1} bands in preference to the 711.3- and 707.8-cm^{-1} bands, when P_4S_{10} was distilled from a finger through an unheated tube, indicates that the former are due to more volatile lower molecular weight species, which supports the above assignments.

All of the above absorptions were photosensitive except those of P_4S_{10} and the absorption at 716 cm^{-1}, which was produced by photolysis. The 716-cm^{-1} absorption is probably due to the terminal P–S vibration of a fragment species that cannot be identified from the present data. The remaining absorptions in the 350–490-cm^{-1} region are likely due to predominantly P–S–P vibrations in other fragments, which cannot be identified.

P_2S_{10} + O_3. Photolysis of ozone and tetraphosphorus decasulfide was performed to see if oxygen would replace a terminal or bridged sulfur atom. The observation of SO_2 and $S^{18}O_2$ verifies the removal and trapping of sulfur by oxygen. The sharp 1244-cm^{-1} band is appropriate for a terminal PO vibration (P_4O absorbs at 1240 cm^{-1}),[9] and the 43-cm^{-1} ^{18}O shift confirms this assignment. The 578-cm^{-1} band is in the region for a P–S–P cage vibration blue-shifted from 553 cm^{-1} by replacement of a terminal sulfur by oxygen; the small (1 cm^{-1}) ^{18}O shift shows that oxygen is only minimally involved in this vibration. No absorptions were observed in the 800–900-cm^{-1} region where oxo-bridged motions are expected. It is therefore concluded that oxygen replaces a terminal rather than bridged sulfur in P_4S_{10} to give the new P_4S_9O species. In analogous experiments with P_4S_3 and O_3, the primary products were the two terminally bound isomers of P_4S_3O.[13]

Conclusions

The vapor effusing from solid P_4S_{10} at 175 °C was trapped in solid argon. The five strongest infrared absorptions at 711.3, 707.8, 552.9, 540.8, and 499.2 cm^{-1} correlate with infrared spectra of

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solid P_4S_{10} and P_4S_9 and show that the major vapor components are molecular P_4S_{10} and the terminal sulfur decomposition product P_4S_9. Another sharp 750.6-cm^{-1} band, with an associated 508.5-cm^{-1} absorption, is dominant in superheated vapor; these bands are probably due to molecular P_2S_5, which likely has the same structure as molecular P_2O_5. Additional weaker bands are identified as PS and PS_2.

The present infrared matrix experiments with P_4S_{10} suggest that at 175 °C P_4S_{10} evaporates into three comparable fractions—molecular P_4S_{10}, the terminal sulfur dissociation product P_4S_9, and smaller phosphorus and diphosphorus sulfides—on the basis of the reasonable assumption of similar infrared extinction coefficients for these species. The spectra further suggest that the cage dissociation reactions (2a) and (2b) together are as important as the terminal sulfur dissociation reaction (1).

The thermal decomposition of P_4S_{10} follows the pyrolysis of P_4O_{10} in several ways: the major decomposition products (P_4S_9

$$P_4S_{10} \longrightarrow P_4S_9 + S \tag{1}$$

$$P_4S_{10} \longrightarrow 2P_2S_5 \longrightarrow 2P_2S_4 + 2S \tag{2a}$$

$$P_4S_9 \longrightarrow P_2S_5 + P_2S_4 \tag{2b}$$

$$P_2S_5 \longrightarrow PS + PS_2 + S_2 \tag{2c}$$

$$P_2S_4 \longrightarrow 2PS_2 \tag{2d}$$

and P_4O_9) involve the loss of a simple terminal atom, and the loss of two terminal atoms plays only a minor role.[10] Although P_2S_5 is a major thermolysis product of P_4S_{10}, little P_2O_5 was observed from P_4O_{10} whereas PO_2 was a major product from P_4O_{10}, but PS_2 was only a minor product from P_4S_{10}.

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Stability and Stereochemistry of Tetrahedral Nickel Nitrosyl Complexes: Crystal and Molecular Structures of (R^*,S^*)-*anti*-[NiNCS(NO){1,2-C$_6$H$_4$(PMePh)$_2$}] and (R^*,S^*)-*anti*-[NiNO{P(OMe)$_3$}{1,2-C$_6$H$_4$(PMePh)$_2$}]PF$_6$

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The tetrahedral complexes (R^*,R^*)-(±)- and (R^*,S^*)-*anti*-[NiX(NO){1,2-C$_6$H$_4$(PMePh)$_2$}] rearrange in nitrobenzene-d_5 at 25 °C with inversion at the metal stereocenter [$t_{1/2}$ ca. 5 s (X = Cl), 9 s (X = NCS), and 3.5 h (X = CN)] and intermolecular exchange of X [$t_{1/2}$ ca. 8 h (X = CN)]. The salts (R*,R^*)-(±)- and (R^*,S^*)-*anti*-[NiL(NO){1,2-C$_6$H$_4$(PMePh)$_2$}]PF$_6$ rearrange with $t_{1/2}$(inversion) of ca. 6 min and $t_{1/2}$(redistribution) of ca. 12 h (L = PMe$_2$Ph). The crystal structures of (R^*,S^*)-*anti*-[NiNCS(NO){1,2-C$_6$H$_4$(PMePh)$_2$}] [(R^*,S^*)-*anti*-**1** (X = NCS)] and (R^*,S^*)-*anti*-[NiNO{P(OMe)$_3$}{1,2-C$_6$H$_4$(PMePh)$_2$}]PF$_6$ [(R^*,S^*)-*anti*-**2** [L = P(OMe)$_3$]] at 21 ± 1 °C have been determined. Crystal data: for (R^*,S^*)-*anti*-**1** (X = NCS), monoclinic, $a = 10.336$ (3) Å, $b = 17.663$ (5) Å, $c = 11.743$ (3) Å, $\beta = 91.51$ (2)°, $Z = 4$, $R(F_o) = 0.041$, $R_w(F_o) = 0.043$; for (R^*,S^*)-*anti*-**2** [L = P(OMe)$_3$], monoclinic, $a = 15.547$ (4) Å, $b = 11.191$ (3) Å, $c = 19.137$ (6) Å, $\beta = 107.04$ (2)°, $Z = 4$, $R(F_o) = 0.051$, $R_w(F_o) = 0.054$. The stereochemistry around the nickel atom in each complex is distorted tetrahedral with the bond angle Ni–N–O being equal to 159.5 (3)° in the isothiocyanato complex and equal to 178.0 (5)° in the phosphite complex. The ligand redistribution studies were conducted with use of isotopically labeled substances and NMR spectroscopy.

Introduction

Although many pseudotetrahedral[1] (pseudooctahedral)[2] complexes of the type [(η^5-C$_5$H$_5$)MABC] are known to be configurationally stable at the stereogenic metal center (indeed, the enantiomers of (±)-[(η^5-C$_5$H$_5$)FeCO(COMe)(PPh$_3$)] are available commercially for use in asymmetric synthesis[3]), little is known about the configurational stability or the stereochemistry of substitution of purely tetrahedral transition-metal complexes containing one or more unidentate ligands.[4,5] Of relevance to the present work, however, are the observations that the complexes [Co(AsPh$_3$)CO(NO)(PPh$_3$)] and [Ni(phen)$_3$][CoCN(CO)NO(PPh$_3$)]$_2$ have been isolated (as racemates),[6] [CoCO(NO)(PMe$_2$Ph)$_2$] is configurationally stable in solution up to 100 °C,[7] and diastereomers of complexes of the type (±)-[Fe(CO)(NNAr)(NO){PPh$_2$(NRR*)}] have been separated.[5] In an attempt to identify tetrahedral complexes with metal–halogen bonds for use in asymmetric synthesis, we have characterized (R^*,R^*)-(±)- and (R^*,S^*)-*anti*-[NiX(NO){1,2-C$_6$H$_4$(PMePh)$_2$}] (where X = Cl, Br, I, CN, or NCS) [(R^*,R^*)- and (R^*,S^*)-*anti*-**1**] and (R^*,R^*)-(±)- and (R^*,S^*)-*anti*[NiL(NO){1,2-C$_6$H$_4$(PMePh)$_2$}]PF$_6$ [where L = PMe$_3$, PMe$_2$Ph, PMePh$_2$, PPh$_3$, or P(OMe)$_3$] [(R^*,R^*)- and (R^*,S^*)-*anti*-**2**].[8,9]

Results

The compounds described in this work are listed in Tables I and II. The crystal and molecular structures of two of the complexes, neutral (R^*,S^*)-*anti*-**1** (X = NCS) and ionic (R^*,S^*)-*anti*-**2** [L = P(OMe)$_3$], have been determined; the results are presented in Tables III–VI. The solution behavior of the complexes has been investigated with use of NMR spectroscopy. The various aspects of the work will be introduced in the sections that follow.

(a) The Neutral Complexes [NiX(NO){1,2-C$_6$H$_4$(PMePh)$_2$}]. The complexes (R^*,R^*)- and (R^*,S^*)-**1** (X = Cl) were prepared

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