

description, the complex might be expected to give a spectrum rather similar to the imino form of 1-MeAdo, IX, by analogy with the spectra of $[\text{CH}_3\text{HgUrdH}_{-1}]$ and $[\text{CH}_3\text{HgGuoH}_{-1-5'-\text{P}}]$. Except for the appearance of a band at 1656 cm^{-1} in the complex in the region of a weak band of 1-MeAdo at 1642 cm^{-1} , the complex spectrum resembles 1-MeAdoH⁺.

It is conceivable that mercuriation of 1-MeAdoH⁺ could occur without displacement of a proton to give X or XI. The charge distribution of XI does not appear to be particularly favorable. Mercuriation at N₍₇₎ might be expected to have an effect similar to that assigned to mercuriation of Guo-5'-P at N₍₇₎, pH 2. In that case, shifts occurred in almost all of the bands compared either to $[\text{GuoH-5'-P}]^+$ or Guo-5'-P, unlike what is observed for coordination to $[\text{1-MeAdoH}]^+$. This also is the only system examined so far where coordination of $\text{CH}_3\text{Hg}^{\text{II}}$ to a nucleic acid base does not give a significant hyperchromic effect in $\nu(\text{Hg-C})$. This suggests that coordination occurs to a weakly polarizable site on the base and is consistent with a weak interaction without proton transfer, X or XI, of which the former seems more likely.

A summary of the Raman information on the $\text{CH}_3\text{-Hg}^{\text{II}}$ coordination to nucleosides and nucleotides is given in Table IV. Frequencies of difference spectra marker bands characteristic of metalation of particular bases also are tabulated. These are suitable for use in Raman spectrophotometric titrations of mixed polynucleotides.

Although a number of questions concerning the structure of these heavy metal nucleoside and nucleotide complexes can be settled on the basis of the Raman spectra alone, it is clear that a few model compounds of known structure would be of great help in further interpretations of the spectra. We are attempting to synthesize crystalline products which have spectra analogous to the solution species.

Supplementary Material Available. Reproductions of Raman spectra 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 \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-74-6874.

Bis(cyclooctatetraenyl)neptunium(III) and -plutonium(III) Compounds^{1,2}

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Abstract: Potassium bis(cyclooctatetraenyl)neptunium(III) ($\text{KNp}(\text{COT})_2$, $\text{COT} = \text{C}_8\text{H}_8^{2-}$) and $\text{KPu}(\text{COT})_2$ were prepared as bis(tetrahydrofuran) (THF) solvates by treating the trivalent actinide bromides or iodides with K_2COT in THF solution. X-Ray powder patterns indicate that these compounds are isostructural, and the similarity of the powder patterns of $\text{KPu}(\text{COT})_2 \cdot (\text{CH}_3\text{OCH}_2)_2\text{O}$ with the Ce^{3+} analog suggests that the Pu^{3+} ion is in a D_{8d} ("sandwich") site in the molecule. The Mössbauer spectrum of the $\text{Np}(\text{III})$ compound has an isomer shift (δ) of +3.92 cm/sec, which confirms a +3 valence with only slight covalency, and a quadrupole splitting constant ($eqQ/4$) of 0.72 cm/sec with zero asymmetry. Magnetic susceptibility measurements on both compounds are reported and discussed in terms of crystal field models.

Mares, Hodgson, and Streitwieser have prepared and studied two series of compounds between the cyclooctatetraenyl dianion and trivalent lanthanide ions, $\text{KLn}(\text{COT})_2^3$ and $[\text{Ln}(\text{COT})\text{Cl} \cdot 2\text{THF}]^4$ ($\text{Ln} = \text{La}^{3+}$, Ce^{3+} , Pr^{3+} , Nd^{3+} , Sm^{3+} , Gd^{3+} , Tb^{3+} ; $\text{COT}^{2-} = \text{C}_8\text{H}_8^{2-}$, the cyclooctatetraenyl dianion). The structure determination by single-crystal X-ray⁵ of the mono-"diglyme" $[\text{CH}_3\text{OCH}_2)_2\text{O}]$ solvate of $\text{KCe}(\text{COT})_2$ showed that the Ce^{3+} ion is at a site of D_{8d} symmetry between the two planar COT rings. In this structure, the carbon atoms

of the COT rings are staggered, instead of eclipsed, like U^{4+} in $\text{U}(\text{COT})_2$.^{6,7} This paper reports synthesis and study of the analogous compounds $\text{KNp}(\text{COT})_2$ and $\text{KPu}(\text{COT})_2$.

Experimental Section

The methods used to purify solvents, analyze compounds, measure magnetic susceptibility, and obtain Mössbauer spectra have been previously reported.⁸ All syntheses, transfer of compounds, and measurements of their properties were performed in a dry argon atmosphere. Qualitative tests for halides were performed by adding solid compounds to dilute HNO_3 under argon, filtering insoluble material, and adding AgNO_3 to the clear filtrate.

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(2) This paper was prepared in connection with work under Contract No. AT(07-2)-1 with the U. S. Atomic Energy Commission.

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Actinide(III) chlorides, bromides, and iodides were prepared by standard methods.⁹ NpCl_3 was prepared by reducing NpCl_4 with powdered zinc at 550°; PuCl_3 was prepared by treating PuO_2 with CCl_4 vapor at 600°. PuBr_3 was prepared by treating plutonium metal with HgBr_2 at 350°; PuI_3 was prepared by treating plutonium metal with HgI_2 at 350°. NpBr_3 and NpI_3 were prepared by treating 35 wt % Np -65 wt % Al alloy with the proper mercuric halide.

Preparation of $\text{KPu}(\text{COT})_2 \cdot 2\text{THF}$ and $\text{KNp}(\text{COT})_2 \cdot 2\text{THF}$. $\text{KPu}(\text{COT})_2 \cdot 2\text{THF}$ was prepared by adding a stoichiometric quantity of either PuBr_3 or PuI_3 to a -10 to -20° THF solution of K_2COT . The solution was allowed to warm to room temperature and was stirred for at least 1 hr. The reaction mixture was filtered to remove precipitated potassium halide, and the filtrate was vacuum evaporated to recover turquoise-green $\text{KPu}(\text{COT})_2 \cdot 2\text{THF}$. (Calculated plutonium is 37.88%; determined plutonium was 37.9, 36.8, and 39.1%.) A test for halides was negative. $\text{KPu}(\text{COT})_2 \cdot 2\text{THF}$ was dissolved in diglyme, and the solution was evaporated by vacuum to produce $\text{KPu}(\text{COT})_2 \cdot \text{diglyme}$.

By the same procedure, burgundy colored $\text{KNp}(\text{COT})_2 \cdot 2\text{THF}$ was prepared from NpBr_3 and K_2COT solution. (Calculated neptunium was 37.7%; determined neptunium was 40.4%.) A test for bromide was negative. The X-ray powder diffraction pattern was identical with that of $\text{Pu}(\text{COT})_2 \cdot 2\text{THF}$. The Mössbauer spectrum showed only Np^{3+} in the compound.

Properties of $\text{KM}(\text{COT})_2 \cdot 2\text{THF}$. These compounds are extremely air- and water-sensitive, like the corresponding $\text{KLn}(\text{COT})_2 \cdot n\text{THF}$ compounds.^{3,4} Traces of oxidizing agents rapidly oxidize solutions to $\text{Pu}(\text{COT})_2$ or $\text{Np}(\text{COT})_2$. $\text{KM}(\text{COT})_2$ compounds were quite soluble in THF but almost insoluble in benzene or toluene. In some preparations, the $\text{M}(\text{COT})_2$ impurity was separated by extraction with toluene from the solid $\text{KM}(\text{COT})_2 \cdot 2\text{THF}$. Attempts to measure the absorption spectra in THF solution were unsuccessful because the strong absorption by $\text{Np}(\text{COT})_2$ or $\text{Pu}(\text{COT})_2$ impurities obscured the spectra of the trivalent actinide compounds.

Attempts to prepare $\text{KU}(\text{COT})_2 \cdot n\text{THF}$ by the reaction of UBr_3 or UI_3 with K_2COT solution yielded only $\text{U}(\text{COT})_2$. Attempts to reduce $\text{U}(\text{COT})_2$ with potassium, sodium amalgam, or potassium naphthenide yielded either a pyrophoric powder, assumed to be uranium, or no reaction. Attempts to produce $\text{KPu}(\text{COT})_2$ or $\text{KNp}(\text{COT})_2$ by the reaction of K_2COT with PuCl_3 or NpCl_3 were unsuccessful, possibly because of a very low solubility for the actinide(III) chlorides in THF.

Results

X-Ray Diffraction Data. Partial X-ray diffraction data for $\text{KPu}(\text{COT})_2 \cdot 2\text{THF}$ and $\text{KNp}(\text{COT})_2 \cdot 2\text{THF}$ (Table I) indicate that the two compounds are isostructural. The powder sample data for the Pu compound were indexed by computer¹⁰ to have an orthorhombic cell, $a = 9.03$, $b = 6.65$, and $c = 5.52 \text{ \AA}$, with standard deviations of 0.01 \AA for all cell constants. The X-ray diffraction pattern of $\text{KPu}(\text{COT})_2 \cdot \text{diglyme}$, compared in the calculated diffraction pattern of $\text{KCe}(\text{COT})_2 \cdot \text{diglyme}$ in Table II, shows a strong similarity, indicating that the diglyme solvates probably have the same structures for the $\text{KM}(\text{COT})_2 \cdot \text{diglyme}$ compounds. Using the hkl values for the three distinct lines with 2θ values of 16.49, 18.64, and 20.89, the calculated constants for an orthorhombic cell of $\text{KPu}(\text{COT})_2 \cdot \text{diglyme}$ are $a = 16.80$, $b = 13.79$, and $c = 9.04 \text{ \AA}$. These values are all slightly smaller than the cell constants for $\text{KCe}(\text{COT})_2 \cdot \text{diglyme}$ and are consistent with a 3% smaller ionic radius for Pu^{3+} compared to Ce^{3+} .

Mössbauer Spectrum of $\text{KNp}(\text{COT})_2 \cdot 2\text{THF}$. The spectrum (Figure 1) is split by an electric quadrupole interaction and shows an isomer shift of +3.92 cm/sec, which establishes the tripositive valence of the neptunium ion in this compound.¹¹ The quadrupole coupling con-

Table I. X-Ray Diffraction Data for $\text{KM}(\text{COT})_2 \cdot 2\text{THF}$ Compounds

hkl^a	$\text{KPu}(\text{COT})_2 \cdot 2\text{THF}$		$\text{KNp}(\text{COT})_2 \cdot 2\text{THF}$	
	$d, \text{ \AA}$	I^b	$d, \text{ \AA}$	I
100	8.35	M	8.16	W
010	6.52	S	6.69	M
001	5.53	S	5.53	M
101	4.71	W		
011	4.14	W	4.13	W
111	3.81	M	3.82	W
201	3.53	W	3.54	W
020	3.33	W	3.30	W
120	3.14	S	3.14	S
102	2.63	W		
311	2.45	W	2.45	W
400	2.27	W		
030	2.23	W	2.22	W
401	2.09	M	2.10	M
302	2.03	W		
222	1.92	W		
003	1.84	W	1.82	W
330	1.78	W		
501	1.71	W	1.83	W
213	1.65	W	1.65	W
303	1.57	W		
223	1.52	W		
530	1.40	W		

^a Orthorhombic cell. ^b Key: S, strong; M, medium; W, weak.

Table II. Partial X-Ray Diffraction Data for $\text{KM}(\text{COT})_2 \cdot \text{diglyme}$

hkl	$\text{KCe}(\text{COT})_2 \cdot \text{diglyme}$		$\text{KPu}(\text{COT})_2 \cdot \text{diglyme}$	
	2θ	I^a	2θ	I^b
200	10.47	79		
101	10.81	244	10.84	S
011	11.37	100		
210	12.23	84		
111	12.52	60	12.44	S
020	12.63	404		
211	15.48	322	15.59	VS
220	16.43	141		
121	16.65	165	16.49	S
301	18.38	105	18.64	M
112	20.69	80	20.89	M
400	21.03	43		
031	21.26	55		
321	22.37	55	22.54	W
420	24.61	61	24.89	W
132	27.49	81	27.69	M
332	31.37	36	31.49	W
341	31.56	42		
123	31.84	46	32.09	W
611	33.85	22	33.69	VW
620	34.32	31		VW
033	34.57	14	34.69	VW
233	36.22	26		
413	36.77	22	36.59	W
152	37.79	39		
143	39.03	21	38.94	W
352	40.80	20		
702	41.12	20	40.94	W

^a Calculated by computer from the crystal structure. See ref 5.
^b Key: S, strong; M, medium; W, weak.

stant, $1/4\epsilon qQ$, equals 0.75 cm/sec with an asymmetry parameter of zero within the resolution of the measurement.

Magnetic Susceptibilities. The magnetic susceptibilities of $\text{KPu}(\text{COT})_2 \cdot 2\text{THF}$ and $\text{KNp}(\text{COT})_2 \cdot 2\text{THF}$ were measured from 2.2 to 80°K, and the data below 50°K are shown in Figures 2 and 3. The Pu^{3+} ion in $\text{KPu}(\text{COT})_2 \cdot 2\text{THF}$ showed a magnetic susceptibility

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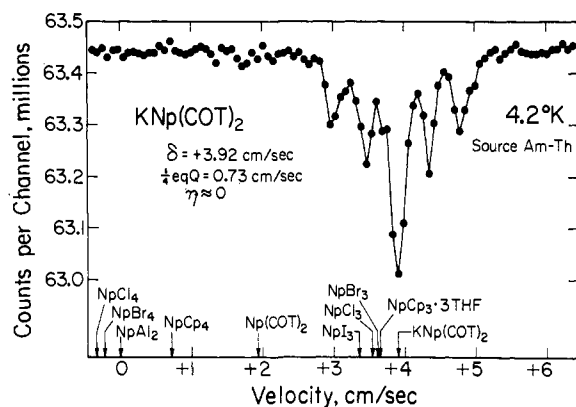


Figure 1. Mössbauer spectrum of $\text{KNp}(\text{COT})_2 \cdot 2\text{THF}$.

of $\mu_{\text{eff}} = 1.25 \text{ BM}$, $\theta = 3.7^\circ$. The result would be relatively unaffected by an impurity of diamagnetic $\text{Pu}(\text{COT})_2$. The magnetic susceptibility of $\text{KNp}(\text{COT})_2 \cdot 2\text{THF}$ has a region of temperature-independent paramagnetism (TIP) from 2.2 to 5.5°K , where $\chi_m = 1.10 \times 10^{-2} \text{ emu/mol}$, and two regions of temperature-dependent paramagnetism from 5.5 to 19°K , $\mu_{\text{eff}} = 1.04 \text{ BM}$, $\theta = 6.4^\circ$, and from 19 to 80°K , $\mu_{\text{eff}} = 1.39 \text{ BM}$, $\theta = 26^\circ$. The magnetic susceptibility of $\text{KNp}(\text{COT})_2 \cdot 2\text{THF}$ could be severely affected by an impurity of the strongly paramagnetic $\text{Np}(\text{COT})_2$, but this result is considered reliable since Np^{4+} ($J = 9/2$) cannot show TIP behavior. A Mössbauer spectrum of the $\text{KNp}(\text{COT})_2 \cdot 2\text{THF}$ also showed that Np^{4+} was below the detection limit of 5%.

Discussion

Although X-ray powder diffraction patterns do not definitely establish identical structures for actinide(III) and lanthanide(III) $\text{KM}(\text{COT})_2 \cdot 2\text{THF}$ compounds, the probability of the trivalent actinide ion having "sandwich" site in $\text{KM}(\text{COT})_2 \cdot 2\text{THF}$ is very high. Because the asymmetry parameter is zero for the quadrupole-split Mössbauer spectrum of $\text{KNp}(\text{COT})_2 \cdot 2\text{THF}$, the Np^{3+} ion must be at a site with an n -fold axis, where n is greater than three. When possible ways to arrange the planar COT rings around the Np^{3+} ion are considered, a "sandwich" structure with a D_{8h} or D_{8d} site for the Np^{3+} ion appears the most probable. The differences in X-ray powder patterns might be explained by differences in self-absorption between lanthanide and actinide ions.

The isomer shift of $+3.92 \text{ cm/sec}$ for Np^{3+} in $\text{KNp}(\text{COT})_2 \cdot 2\text{THF}$ is the largest positive shift yet observed for a $\text{Np}(\text{III})$ ion and is slightly more positive than NpCl_3 ($\delta = 3.54 \text{ cm/sec}$) or $\text{Np}(\text{C}_5\text{H}_5)_3 \cdot 3\text{THF}$ ($\delta = 3.64 \text{ cm/sec}$). This isomer shift suggests some degree of covalency of Np^{3+} in $\text{KNp}(\text{COT})_2 \cdot 2\text{THF}$, probably from the contribution of π -electron density from the COT^{2-} ligands. However, the covalent contribution is minor in comparison with $\text{Np}(\text{COT})_2$, whose isomer shift is $+1.94 \text{ cm/sec}$ compared with -0.34 cm/sec for NpCl_4 (Table III). The small covalency of Np^{3+} in actinide(III)-COT compounds, compared with the much larger covalent contributions to Np^{4+} in $\text{Np}(\text{COT})_2$, conforms to the pattern established in NpCp_4 and $\text{NpCp}_3 \cdot 3\text{THF}$ ¹⁰ and again indicates that covalency in actinide organometallic compounds depends principally on the valence of the actinide ion.

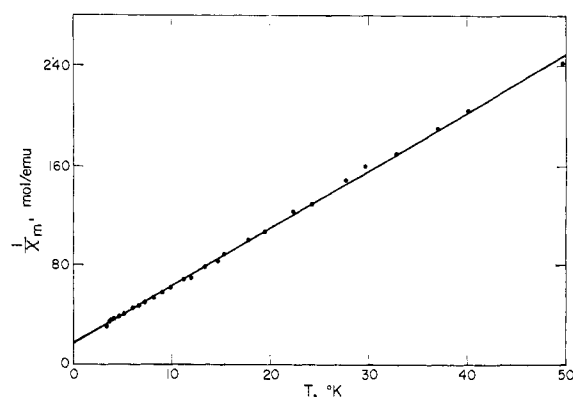


Figure 2. Inverse magnetic susceptibility of $\text{KPu}(\text{COT})_2 \cdot 2\text{THF}$.

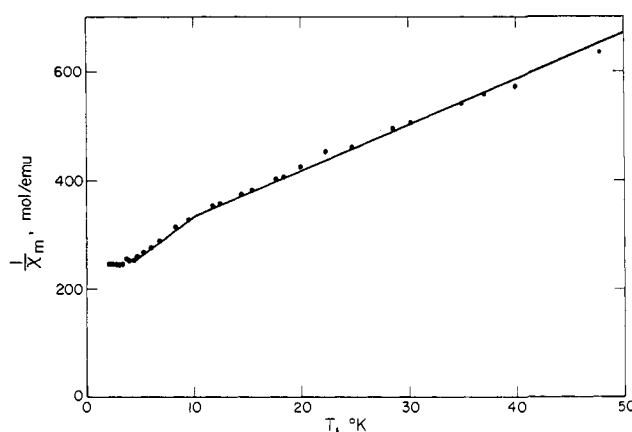


Figure 3. Inverse magnetic susceptibility of $\text{KNp}(\text{COT})_2 \cdot 2\text{THF}$.

Table III. Isomer Shifts of Neptunium(III) and Neptunium(IV) Compounds at 4.2°K

Compound	Isomer shift, ^a cm/sec
NpO_2	-0.56
NpCl_4	-0.34
NpAl_2	0.00
NpCp_4	+0.72
$\text{Np}(\text{COT})_2^b$	+1.94
NpCl_3	+3.54
$\text{NpCp}_3 \cdot 3\text{THF}$	+3.64
$\text{KNp}(\text{COT})_2 \cdot 2\text{THF}$	+3.92

^a Relative to NpAl_2 at 77°K . ^b COT = cyclooctatetraenyl ion, $\text{C}_8\text{H}_8^{2-}$.

A possible explanation for the lack of covalency for trivalent actinide COT and Cp compounds, compared to the quadrivalent actinide compounds with the same ligands, probably lies in the difference in size between the $+3$ and $+4$ actinide ions. For $+3$ ions, the $5f$ orbitals are sufficiently shielded that interaction with ligand orbitals is hindered. For the smaller $+4$ ions the shielding of the $5f$ orbitals is less, and metal orbital-ligand orbital interactions are possible. Extending this argument, $+5$ and $+6$ actinides should show a still greater tendency toward covalency. Unfortunately, the synthesis of $+5$ or $+6$ compounds with strongly reducing organic ligands appears extremely improbable.

The small covalent contribution of the actinide(III) ions and their probable high site symmetry in KNp -

(COT)₂·2THF and KPu(COT)₂·2THF presents the possibility that the crystal field model originally proposed⁸ for the actinide(IV)-COT compounds could be applied to the actinide(III)-COT compounds to predict their magnetic properties. In this model, the Np³⁺ ion ($J = 4$) in KNp(COT)₂·2THF would have $J_z = 0$ in a magnetic field and thus would be diamagnetic, analogous to Pu⁴⁺ in Pu(COT)₂. The experimental magnetic susceptibility shows a nonmagnetic ground state and two higher magnetically degenerate levels at ~ 5 and ~ 15 cm⁻¹. In general, this conforms to the predicted ordering of the levels of $J_z = 0$ as the lowest level and $J_z = \pm 1$ and $J_z = \pm 2$ as the next levels. Further, the magnetic susceptibility is greater for the $J_z = \pm 2$ level than for $J_z = \pm 1$. The TIP observed for the lowest level can be accounted for by either weak second-order crystal fields or the magnetic field mixing the $J_z = 0$ wave functions with $J_z = \pm 1$ wave functions. The MO model of Hayes and Edelstein¹² predicts $J_z = 0$, $J_z = \pm 1$, and $J_z = \pm 2$ for the three lowest levels of the isoelectronic Pu⁴⁺ ion in Pu(COT)₂, with the magnetic susceptibilities of 0, 1.47, and 1.35 BM, respectively. Adjustments of this calculation for Np³⁺ might lead to a reasonable fit with experimental results.

Although it is not yet necessary to discard the crystal field model,^{8,12} this model assumes no mixing of J states by the crystal field and small intermediate coupling. Neither of these assumptions is strictly true for the Np³⁺ ion, as comparison of measured and calculated magnetic susceptibilities for Cs₂NaNpCl₆ in-

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dicates.¹³ The predicted ordering of crystal field levels from first-order wave functions¹³ for a $J = 4$ ion in an eightfold cubic O site also predicts a nonmagnetic Γ_1 lowest level with Γ_4 and Γ_5 triplet levels higher in energy.¹⁴ Considering the environment of anion in a D_{8d} site not too different from an O site also yields a qualitative agreement with experiment.

The magnetic susceptibility of Pu³⁺ in KPu(COT)₂·2THF, $\mu_{\text{eff}} = 1.25$ BM, agrees with the free ion moment for Pu³⁺ with intermediate coupling taken into account.¹⁵ However, it is difficult to rationalize three crystal field levels below 70°K for Np³⁺ in KNp(COT)₂·2THF and a KPu(COT)₂·2THF magnetic susceptibility that implies all crystal field levels for Pu³⁺ are below 2.2°K. It appears probable that there is an accidental agreement between the magnetic susceptibility of the ground crystal field level and the free ion value. Further experimental and theoretical studies are considered necessary to explain the properties of these compounds adequately.

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Crystal and Molecular Structure of a Dioxadiazaspirophosphorane Derived from (-)-Ephedrine

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Abstract: The structural analysis of a spirophosphorane produced in the reaction between (-)-ephedrine and tris(dimethylamino)phosphine has been carried out *via* single-crystal X-ray diffraction analysis. Crystals of the spirophosphorane are orthorhombic with $a = 14.101$ (3), $b = 6.797$ (1), and $c = 20.394$ (4) Å and space group $P2_12_1$. The molecules contain an approximate noncrystallographic twofold axis parallel to the P-H bond. The phosphorus geometry is essentially trigonal bipyramidal, and the nitrogen and attached atoms are coplanar.

Various spirophosphoranes containing P-H bonds have been synthesized by reaction of the 2-dimethylamino derivatives of 1,3,2-dioxo- or oxazaphospholanes with diols or β -amino alcohols.² Symmetrical

dioxadiazaspirophosphoranes can be synthesized directly from the amino alcohol hydrochlorides and tris(dimethylamino)phosphine.³ The formation of the spirophosphorane presumably occurs *via* initial formation of the trivalent phosphite derivative followed by cyclization. When (-)-ephedrine⁴ (I) is used as the β -

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