

the following equation can be derived.

$$K_2 = \left(\frac{A_i - A}{A - A_f} \right) \frac{1}{(\text{Hg}^{2+})_{\text{eq}}^2} (\text{H}^+)^2$$

$$(\text{Hg}^{2+})_{\text{eq}} = (\text{Hg}^{2+})_{\text{total}} - 2 \left(\frac{A_i - A}{A_1 - A_f} \right) C_p$$

The equilibrium constants ($\log K_2$) computed employing the above equation for this system at 512 and 616 nm are -6.57 ± 0.03 and -6.51 ± 0.05 , respectively.

Discussion

Among the divalent ions of group 2B, mercury is unique in that it forms thermodynamically very stable complexes with N-donor ligands.⁸ The preferred coordination of these mercury(II) complexes appears to be two with a linear configuration.^{10,11} On comparing the formation constants of N-donor complexes of mercury(II) ion, there is a big gap in these constants after the addition of two monodentate ligands. For example, the successive formation constants of ammonia complexes¹² of Hg^{2+} are 6.0×10^8 , 5.0×10^8 , 10, and 6. Similarly, the successive formation constants of pyridine complexes¹² are 1.2×10^5 , 8.0×10^4 , and 2. Even the common bidentate ligand ethylenediamine coordinates¹⁰ at only one position, indicating that chelate effects of N-donor ligands for Hg^{2+} are minimal, if any. On the basis of this information, one would expect that Hg^{2+} would prefer a linear configuration with the porphyrin ligand also. Among the porphyrins, synthetic porphyrins such as tetraphenylporphyrin (TPP) exhibit a remarkable ability to deform.¹³ This deformation, with alternative pyrrole rings pointing above or below the mean plane of porphyrin, has been observed in crystals of the diacid form of TPP.¹⁴ Such a buckling of the ring system has been proposed in solution studies of water-soluble porphyrins.^{15,16} If there is a dynamic equilibrium between the deformed and undeformed forms, the deformed form would provide the necessary configuration for binding with mercury(II) ions, though the two N-Hg bonds would still be under strain to attain a bond angle of 180° . This probably accounts for the relatively low formation constants observed in this case in comparison to that of pyridine or aniline complexes.¹¹

A consequence of such a labile equilibrium is that it was found to be impractical to isolate this compound in the pure crystalline form and study its solution properties. Currently, work is in progress on kinetic aspects of this system.

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Registry No. H_2TPPS , 35218-75-8; Hg^{2+} , 14302-87-5; $\text{Hg}_2\text{TPPS}^{2+}$, 64475-51-0.

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- Note: There is considerable ambiguity as to the exact nature of mercury species in basic solutions. By potentiometric studies, Hietanen and Sillen⁹ concluded the hydrolyzed mercury(II) species to be monomeric and determined the hydrolysis constants. This technique would not indicate the exact nature of the species in solution, whether the mercury(II) is in the form of $\text{Hg}(\text{OH})_2$, HgO , or $\text{Hg}^{2+}(\text{aq})$. But in ref 8, p 517, it is stated that there is no evidence for any hydroxo complex, even in 2 M NaOH. So we assumed the species to be aquo ions and computed the

- equilibrium constants. The exact nature of the mercury(II) ion species does not affect the fact that there is a complex ion equilibrium in this system. Though the magnitude of the constants would be affected depending upon the number of hydrogen or hydroxide ions in reactions 1 and 2, the change can be computed from the data presented herein.
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Structure of Uranyl Nitrate-Bis(tetrahydrofuran)¹

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Uranyl nitrate is soluble in a variety of organic solvents and forms various crystalline phases with them.^{2,3} Extraction into ether was the classical method of purification of this salt, and today extraction with various nonaqueous solvents remains an important industrial technique. To extend our knowledge of the molecular basis for this solubility, we prepared the tetrahydrofuran complex $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{C}_4\text{H}_8\text{O}$ and determined its crystal structure. Feder, Ross, and Vogel³ have reported a 1:1 addition compound of $\text{UO}_2(\text{NO}_3)_2$ with tetrahydrofuran.

Experimental Section

Uranyl nitrate hexahydrate was dissolved in tetrahydrofuran at room temperature to form a saturated solution. As the nitrate salt dissolved, the formation of an aqueous layer was evident. Upon saturation, the layers were separated and the ether layer was dried over anhydrous MgSO_4 . After ~ 30 min, the solution was filtered into an Erlenmeyer flask equipped with an airtight seal. It was placed in a quiet place for crystal formation, and after 2 days large platelike yellow crystals had formed. Due to the high ether vapor pressure, the crystals had to be loaded in a glovebag with an atmosphere saturated with THF. The large crystals were fragmented with a pestle and loaded into 0.3-mm quartz capillaries. These were sealed temporarily with stopcock grease and then fire-sealed outside the glovebag.

After considerable effort, a crystal suitable for data collection was found that was irregularly shaped with poorly defined facets and had dimensions approximately $0.25 \times 0.25 \times 0.20$ mm. It was examined with a Picker FACS-I automatic diffractometer equipped with a graphite monochromator and a Mo x-ray tube ($\lambda(\text{K}\alpha_1)$ 0.709 26 Å). ω scans of several low-angle reflections showed peaks with half-widths of $0.1-0.2^\circ$. A unit cell was found that fit the space group $P2_1/a$. The setting angles of 12 manually centered reflections ($42^\circ < 2\theta < 45^\circ$) were used to determine by least squares the cell parameters $a = 9.412$ (7) Å, $b = 12.649$ (9) Å, $c = 7.237$ (5) Å, $\beta = 117.12$ (6)°, and $V = 766.8$ Å³. For $Z = 2$ and a molecular weight of 538.25 the calculated density is 2.33 g cm⁻³.

Intensity data were collected using the $\theta-2\theta$ scan technique with a scan speed of $2^\circ/\text{min}$ on 2θ . Each reflection was scanned from 1° before the $\text{K}\alpha_1$ peak to 1° after the $\text{K}\alpha_2$ peak, and backgrounds were counted for 10 s at each end of the scan range, offset by 0.5° . The temperature during data collection was $23 \pm 1^\circ\text{C}$. Preliminary investigations of the intensities showed a very pronounced pseudo-C-centering which was indicative of the uranium atom on a special

Table I. Positional and Thermal Parameters^a with Estimated Standard Deviations^b for $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{C}_4\text{H}_8\text{O}$

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
U	0	0	0	3.33 (1)	2.30 (1)	2.149 (9)	0.04 (2)	1.282 (7)	0.01 (2)
O(1)	-0.0125 (6)	0.0896 (4)	-0.1905 (7)	5.6 (2)	3.6 (2)	3.2 (2)	-0.0 (2)	2.1 (2)	0.7 (2)
O(2)	0.2934 (7)	0.0317 (5)	0.199 (1)	3.9 (2)	5.9 (3)	5.3 (3)	-0.1 (2)	1.8 (2)	-2.1 (2)
O(3)	0.4750 (7)	-0.0613 (6)	0.172 (1)	3.8 (2)	8.1 (4)	8.5 (4)	0.6 (3)	2.3 (3)	-1.7 (4)
O(4)	0.2239 (6)	-0.0935 (4)	-0.0227 (8)	4.0 (2)	4.8 (3)	5.3 (3)	-0.0 (2)	2.1 (2)	-1.5 (2)
O(5)	0.0767 (6)	0.1410 (4)	0.2524 (7)	4.7 (2)	3.1 (2)	2.9 (2)	-0.1 (2)	1.5 (2)	-0.6 (2)
N	0.3373 (8)	-0.0417 (6)	0.118 (1)	3.7 (3)	4.8 (3)	4.7 (3)	0.2 (2)	1.7 (2)	-0.5 (3)
C(1)	0.138 (1)	0.1214 (6)	0.478 (1)	8.9 (5)	4.1 (3)	2.6 (2)	-1.4 (4)	2.1 (3)	-1.0 (2)
C(2)	0.177 (1)	0.2304 (9)	0.571 (2)	10.2 (7)	6.4 (6)	6.4 (5)	-3.3 (5)	4.4 (5)	-3.5 (5)
C(3)	0.144 (1)	0.3069 (8)	0.408 (2)	9.5 (7)	3.5 (4)	5.3 (5)	-0.1 (4)	0.6 (4)	-0.9 (3)
C(4)	0.068 (1)	0.2525 (6)	0.207 (1)	9.4 (6)	3.1 (3)	5.0 (4)	-1.6 (4)	2.5 (4)	-0.1 (3)

^a The anisotropic temperature factor has the form $\exp(-0.25(B_{11}h^2a^{*2} + 2B_{12}hka^*b^* + \dots))$. ^b Here and in the following tables the numbers in parentheses are the estimated standard deviations in the least significant digit.

Table II. Interatomic Distances (Å)

U-O(1)	1.75 (2)	N-O(4)	1.27 (2)
U-O(2)	2.50 (3)	O(5)-C(1)	1.48 (2) ^a
U-O(4)	2.49 (2)	O(5)-C(4)	1.44 (2)
U-O(5)	2.42 (2)	C(1)-C(2)	1.51 (2)
N-O(2)	1.26 (2)	C(2)-C(3)	1.44 (2)
N-O(3)	1.20 (2)	C(3)-C(4)	1.47 (2)

^a The tetrahydrofuran molecule is represented by atoms C(1) through C(5) and O(5). Because of the disorder in this molecule these distances are foreshortened.

position. Approximately three-fourths of the *C*-centered reflections between 3 and 62° of 2θ were collected first, 4024 scans including standards. Then all of the non-*C*-centered reflections between 3 and 37° of 2θ were collected, 1182 scans including standards. The non-*C*-centered reflections above 37° were too weak to be observed. Three standard reflections were measured after every 200th scan. The 5035 scans, not including standards, resulted in 1573 unique intensities, 1486 of which were greater than σ . Because of the irregular shape of the crystal and the lack of facets an absorption correction was not made; the absorption coefficient is estimated to be 101 cm⁻¹.

The strong pattern of *C*-centered reflections is clear evidence of a uranium atom at the origin. The Fourier map, calculated with all phases positive, resulted in a map from which the full trial structure was deduced. A series of least-squares refinements in which the function $\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2$ was minimized converged rapidly to the final structure. The expressions that were used in processing the data and estimating the weights are given in the supplementary material; the "ignorance factor", *p*, was set to 0.04. Scattering factors from Doyle and Turner⁴ were used, and anomalous dispersion corrections⁵ were applied. Hydrogen atoms could not be identified in the final difference maps and were not included in the least-squares refinement; all significant peaks could be identified either as disorder effects on the THF or as ripples in the vicinity of the uranium atom. Anisotropic thermal parameters were included for all atoms refined but due to the lack of an absorption correction have little chemical significance. The discrepancy indices for 1486 data where $I > \sigma$ are

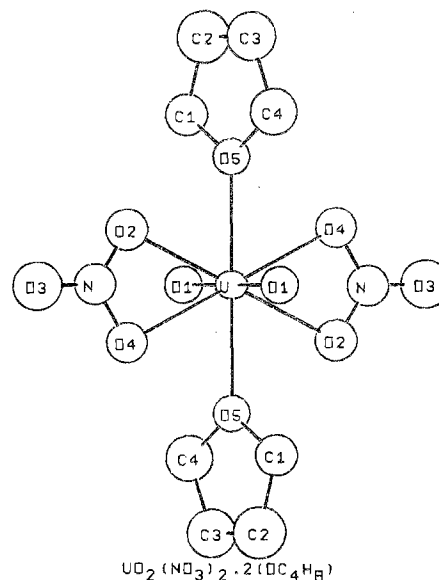
$$R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.028$$

$$R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w |F_o|^2]^{1/2} = 0.032$$

R for all 1568 data is 0.030. The error in an observation of unit weight is 1.17. In the last cycle no parameter changed more than 0.03σ.

Results and Discussion

Atomic parameters, distances, and angles are listed in Tables I-III. The molecular structure (Figure 1) consists of a uranium atom on a center of symmetry coordinated to eight oxygen atoms. The two uranyl oxygen atoms are perpendicular to the plane of the remaining coordinating oxygen atoms and with them form a hexagonal bipyramid about the uranium atom. This coordination geometry is typical of uranyl nitrate and is the same as that found in $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$,^{6,7} $\text{UO}_2(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$,⁸ $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$,⁹ $\text{UO}_2(\text{NO}_3)_2 \cdot 2[\text{O}-\text{P}(\text{OC}_2\text{H}_5)_3]$,¹⁰ and $\text{UO}_2(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O} \cdot (18\text{-crown-6})$.¹¹ The agreement of corresponding distances and angles in these structures in most cases is within the quoted estimated errors.

**Figure 1.** ORTEP view of $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{THF}$. Isotropic thermal parameters were used in preparing this figure.**Table III.** Selected Angles (deg)

O(1)-U-O(1) ^a	180.0	O(4)-U-O(4) ^a	180.0
O(1)-U-O(2)	90.6 (5)	O(4)-U-O(5)	115.5 (5)
O(1)-U-O(4)	90.6 (5)	O(5)-U-N	90.1 (3)
O(1)-U-O(5)	90.4 (9)	O(2)-N-O(3)	122.3 (8)
O(2)-U-O(2) ^a	180.0	O(2)-N-O(4)	114.7 (9)
O(2)-U-O(4)	50.7 (6)	O(3)-N-O(4)	123.0 (9)
O(2)-U-O(5)	64.8 (3)		

^a Atoms in positions $\bar{x}, \bar{y}, \bar{z}$.

The tetrahydrofuran molecule in this structure appears disordered as it does in most crystallographic determinations,¹²⁻¹⁶ presumably as a result of "pseudorotation";¹⁷ therefore interatomic distances in this ligand do not represent the true values for a single conformation.

Registry No. $\text{UO}_2(\text{NO}_3)_2 \cdot 2(\text{C}_4\text{H}_8\text{O})$, 64413-67-8.

Supplementary Material Available: Data processing formulas and the listing of structure factor amplitudes (8 pages). Ordering information is given on any current masthead page.

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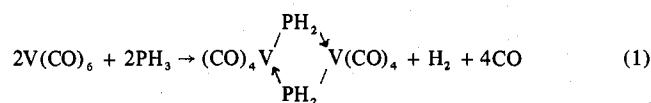
A Novel Phosphorus-Centered Heterometallic Cluster

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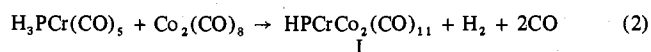
The reactivity of the silicon-hydrogen bond in a variety of silanes can be exploited in convenient syntheses for several silicon-centered heterometallic clusters. These syntheses, previously described,¹ are more usefully applied to clusters involving the odd-numbered transition metals. The isosteric identity of $H_3SiMn(CO)_5$ and $H_3PCr(CO)_5$ suggested the possibilities of synthesizing phosphorus-centered heterometallic clusters incorporating even-numbered transition metals. Syntheses obviously could be effected in reactions analogous to the reactions of isosteric silanes if the phosphorus-hydrogen bond displayed similar chemical reactivity. Such a possibility is indicated in a reaction reported by Hieber and Winter:²



The evolution of hydrogen in this reaction has its parallel in silane chemistry already mentioned.¹

Results and Discussion

The treatment of a tetrahydrofuran solution of pentacarbonylphosphinochromium, $H_3PCr(CO)_5$, with a deficiency of cobalt octacarbonyl, $Co_2(CO)_8$, results in a steady evolution of a mixture of hydrogen and carbon monoxide. The reaction



is complete after 60 h at room temperature. The amount of pentacarbonylphosphinochromium remaining after completion is consistent with the equation given. The yield of product I is quantitative. The dark red crystalline solid I is quite soluble in methylene chloride and tetrahydrofuran, yet only sparingly soluble in *n*-hexane. The new compound is indefinitely stable in vacuo at room temperature and does not visibly change upon exposure to air for short periods of time. It is apparently slightly volatile in vacuo at elevated temperatures but decomposes at temperatures in excess of 90 °C as evidenced by the deposition of a metallic mirror on the walls of the reaction vessel. The volatile products of this decomposition have yet to be examined.

It is of interest that the infrared spectrum of this new cluster does not indicate the presence of any bridging carbonyl ligands, especially so since the most closely similar known silicon-centered cluster, μ -pentacarbonylchlorosilyl- μ -carbonyl-bis(tricarbonyl)cobalt, $Cl[Mn(CO)_5]_2SiCo_2(CO)_7$, involves such

Table I. Mass Spectrum of $HPCrCo_2(CO)_{11}$

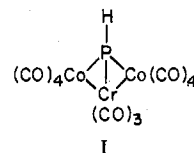
Ion	Rel intens	Ion	Rel intens
$HPCrCo_2(CO)_{11}^+$	2	$HPCrCo_2(CO)_3^+$	1
$PCrCo_2(CO)_{11}^+$	13	$PCrCo_2(CO)_3^+$	14
$HPCrCo_2(CO)_{10}^+$	3	$PCo_2(CO)_4^+$	10
$PCrCo_2(CO)_{10}^+$	19	$HPCrCo_2(CO)_2^+$	3
$HPCrCo_2(CO)_9^+$	2	$PCrCo_2(CO)_2^+$	31
$PCrCo_2(CO)_9^+$	16	$PCrCo_2(CO)^+$	9
$HPCrCo_2(CO)_8^+$	2	$PCrCo_2^+$	17
$PCrCo_2(CO)_8^+$	13	$CrCo_2^+$	5
$HPCrCo_2(CO)_7^+$	2	PCo_2^+	24
$PCrCo_2(CO)_7^+$	20	$Cr(CO)_3^+$	4
$PCo_2(CO)_8^+$	3	$PCo(CO)^+$	9
$HPCrCo_2(CO)_6^+$	2	$Co(CO)_2^+$	9
$PCrCo_2(CO)_6^+$	16	$Cr(CO)_2^+$	28
$PCo_2(CO)_7^+$	4	$HPCo^+$	14
$HPCrCo_2(CO)_5^+$	1	$Co(CO)_5^+$	28
$PCrCo_2(CO)_5^+$	16	$HPCr^+$	50
$PCo_2(CO)_6^+$	5	PCr^+	5
$HPCrCo_2(CO)_4^+$	2	$Cr(CO)^+$	58
$PCrCo_2(CO)_4^+$	17	Co^+	14
$PCo_2(CO)_5^+$	8	Cr^+	100

a bridging carbonyl. Apparently, in this silicon-centered cluster more CO ligands also are required for stability.

The fragmentation of I in the mass spectrometer clearly shows the parent ion and fragments resulting from the successive loss of CO ligands without significant loss of the underlying cluster structure. The fragmentation pattern is informative. The family of ions including the parent molecular ion, $HPCrCo_2(CO)_x^+$ (where $x = 0-11$), are observed, but the family of ions where hydrogen is lost, $PCrCo_2(CO)_x$ (where $x = 0-11$), is approximately four-five times more intense. In this family, formed by successive loss of carbon monoxide ligands, the abundance of each is essentially constant. The cluster, $PCrCo_2^+$, is as abundant as the average of all members this family. These facts suggest that the loss of hydrogen from the cluster is relatively facile and that coordinatively unsaturated clusters possess moderate stability. Both of these properties should be useful in catalytic applications.

The phosphorus-hydrogen bond in I has so far proved intractable to further metallic substitution. Treatment of I with an excess of cobalt octacarbonyl and manganese pentacarbonyl hydride under a variety of conditions did not effect further metalation of the phosphorus.

The most probable structure for I in agreement with its infrared, NMR, and mass spectra is³



This structure utilizes the electron pairs on each $-Co(CO)_4$ group which usually are "nonbonding". While this is unusual, the mass fragmentation pattern, shown in Table I, furnishes sound support for this proposal. The ions $PCo_2(CO)_8^+$ and $PCo_2(CO)_7^+$ appear in reasonable intensities and only those ions, containing chromium in the absence of cobalt, possessing fewer than three CO ligands, $Cr(CO)_3^+$, $Cr(CO)_2^+$, and $Cr(CO)^+$, are observed.

Experimental Section

All reactions reported here were carried out in the absence of air and moisture, using standard vacuum apparatus and procedures, unless otherwise noted. Proton NMR data were obtained using the Varian HA 100 spectrometer, infrared spectra on the Perkin-Elmer 180 spectrometer, and mass spectra on the Hitachi RMU-6L spectrometer. All reactants and solvents were cryogenically degassed before use.

Analyses not performed in our laboratory were reported to us by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.