of the van der Waals radii for light atoms[16] and for mercury[17] were used.

As noted previously,[14,15] the methyl group at N(9) is a serious barrier to metal binding to N(3). Indeed, in the bisecting position, mercury would overlap appreciably with the methyl group, and the closeness of H(2) would make it impossible to cancel the overlap by moving the metal in that direction. Steric hindrance is obviously less severe at positions N(1) and N(7), but it is difficult to determine which position is sterically favored. The extent of amino hydrogen–metal overlap is marginally smaller for N(1). However, since small departures from bisecting positions are probably not detrimental to bond strength, the larger gap between H(8) and Hg(7) than between H(2) and Hg(1) would tend to favor the former site. Consequently, direct steric effects with the exocyclic groups are not expected to create major differences between N(1) and N(7).

This leaves factor i (intrinsic basicity) as the determining effect. Also consistent with this conclusion is the fact that H^+, the least bulky Lewis acid, also reacts with N(1). Furthermore, since the hard H^+ ion and the soft CH_3Hg^+ ion both interact with N(1) in the first place, appreciable difference in softness between N(1) and N(7) has to be ruled out. The present results reinforce previous conclusions that stabilizing or repulsive effects between the amino group and other ligands in the coordination sphere may play a determining role.

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Registry No. $[CH_3Hg(m^9Ade)]NO_3$, 72827-58-8; CH_3HgNO_3, 2374-27-8.

Supplementary Material Available: Listings of temperature factors, observed and calculated structure factors, and hydrogen coordinates (11 pages). Ordering information is given on any current masthead page.

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Contribution from the Materials and Molecular Research
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Structure of Di-μ-aquo-bis(dioxobis(nitrato)uranium(VI))-Diimidazole, $[UO_2(NO_3)_2(H_2O)]_2 \cdot 2C_3H_4N_2$, a Water-Bridged Dimer of Uranyl Nitrate

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While a large number of uranium complexes have been postulated as dimers, trimers, or polymers, relatively few of them have been corroborated by X-ray crystallography. Several of these compounds are connected by oxygen-containing bridging units such as carboxylates or hydroxy groups; uranyl acetate dihydrate, for example, is a dimer with both bridging and terminal acetate groups.[2] Uranyl oxalate trihydrate[3] contains bridging, coordinated oxalate groups (with both coordinated and uncoordinated hydrogen-bonded water molecules) that contribute to the formation of a pentagonal-bipyramidal structure. Hydrogen bonding also plays a role in the dimerization of uranyl complexes involving thiocarboxylic-like donor centers.[4,5] Dimeric, trimeric, and tetrameric complexes of uranium(IV) have recently been reported.[6-9]

One of the reasons for interest in the coordination properties of imidazole is the important role its derivatives play in coordinating transition-metal ions in biological systems.[10] Presumably, for example, three of the four ligands of cobalt(II) in carbonic anhydrase are nitrogen donors, most likely imidazole nitrogens of histidine residues.[11] Important systems containing imidazole as a ligand include hemoglobin which has Fe^{2+} attached octahedrally with the four nitrogens of heme, a histidine molecule, and either a water or oxygen molecule also coordinated;[12] myoglobin,[12b] histidine deaminase,[13] cytochrome *c*,[14] and cytochrome oxidase[15] are other examples.

In forming chemical systems with metal ions, imidazole, which is somewhat more basic than pyridine and slightly more acidic than pyrrole, can exist in several forms.[10] First, the pyridine-like nitrogen (N(3)) possesses a pair of electrons for coordination with metal ions, thus effectively acting as a monodentate ligand. Second, the N(3) nitrogen can be protonated in acidic solutions to form the imidazolium cation which forms salts with metal ions such as the uranyl ion.[16] Third, the neutral imidazole can undergo deprotonization in strongly basic solutions to form the imidazolate anion which possesses two equivalent nitrogen coordination sites and is thus a potential bridging ligand.[10]

Imidazole, however, also participates in the formation of hydrogen bonds in a number of systems,[10] and it is this property which is utilized in still another mode of bonding in the compound $[UO_2(NO_3)_2(H_2O)] \cdot 2C_3H_4N_2$ which is reported here. The molecules of imidazole act as secondary ligands in the complex, since they are not directly bonded to the uranium species but are hydrogen bonded to the bridging water molecules.

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0020-1669/80/1319-1067$01.00/0

Experimental Section

All solvents were reagent grade and were used as received. Commercially obtained reagent grade imidazole (Aldrich Chemicals) and uranyl nitrate hexahydrate (Alfa Ventron) were also used without further purification.

Infrared spectra were obtained in the 400–4000-cm^{-1} region on a Perkin-Elmer Model 283 infrared spectrometer. The samples were prepared as Nujol mulls between KBr plates.

The title compound was prepared by *very slowly* evaporating (in 1 or 2 weeks) a 1:1 millimolar ratio of uranyl nitrate hexahydrate and imidazole in 500 mL of water. The complex, which appeared as greenish yellow crystals, was then washed with diethyl ether and air-dried for several hours. The rate of evaporation seems to be quite critical, with other products and mixtures of other products sometimes being formed. The infrared spectrum of the complex in the 2500–3500-cm^{-1} region, however, is quite distinctive (see discussion below) and provides a good "fingerprint" identification.

A small green-yellow fluorescent crystal, approximately 0.11 × 0.10 × 0.06 mm in size, was glued to a glass fiber and examined with a Picker FACS-I automated diffractometer equipped with a graphite monochromator and a Mo X-ray tube ($\lambda(K\alpha_1)$ 0.709 30 Å). ω scans of several low-angle reflections showed peaks with half-widths of ~0.15°. The space group is $P2_1/c$. The setting angles of 12 manually centered reflections ($40° < 2\theta < 48°$) were used to determine by least squares the following cell parameters: $a = 9.314$ (4) Å, $b = 16.230$ (16) Å, $c = 7.053$ (3) Å, $\beta = 100.72(4)°$, and $V = 1047.6$ Å^3. For $Z = 4$ and a molecular weight of 480.13, the calculated density is 3.04 g/cm^3.

Intensity data were collected by using a θ–2θ scan technique with a scan speed of 2°/min on 2θ. Each peak was scanned 0.6° before the $K\alpha_1$ peak to 0.6° after the $K\alpha_2$ peak, and backgrounds were counted for 4 s at each end of the scan range offset by 0.3°. The temperature during the data collection was 22 ± 1 °C. Three standard reflections were measured every 250th scan. A total of 6418 scans ($4° < 2\theta < 60°$) yielded 3064 unique reflections of which 2012 had $F^2 > 3\sigma$. An absorption correction ($\mu = 147$ cm^{-1}) was applied[17] which ranged from 2.4 to 3.1. The variation of the three standard reflections was about 1% from the mean values, and no correction for decay was indicated.

A three-dimensional Patterson calculation showed the uranium atom and three oxygen atom positions, and subsequent least-squares refinements and Fourier calculations revealed all of the nonhydrogen atoms in the structure. After several least-squares refinements of the structure, in which the atoms were given anisotropic thermal parameters, a difference Fourier map was calculated. Positive peaks were observed in regions where hydrogen atoms were expected to be but were scattered among a larger number of "noise" peaks of comparable size. Isotropic hydrogen atoms at calculated positions, 0.95 Å from the atoms to which they are bonded, were included in the final least-squares refinements but not refined. The least-squares function used minimizes the function $\sum w(|F_o| - |F_c|)^2/\sum wF_o^2$. The expressions that were used in processing the data and estimating weights are given in the supplementary material; the "ignorance factor" p was set to 0.06. Scattering factors from Doyle and Turner[18] were used, and anomalous dispersion corrections[19] were applied.

The discrepancy indices for 2009 data where $F^2 > 3\sigma$ are

$$R = \sum||F_o| - |F_c||\sum|F_o| = 0.042$$

$$R_w = [\sum w(|F_o| - |F_c|)^2/\sum|F_o|^2]^{1/2} = 0.049$$

R for all 3063 data is 0.073. The error in an observation of unit weight is 1.16. In the last cycle, no parameter changed more than 0.02σ. The three largest peaks in the final difference Fourier were 2.5–3.9 e/Å^3 and are associated with ripples near the uranium atom.

Results and Discussion

Positional parameters, distances, and angles are listed in Tables I–III. Figure 1 shows an ORTEP view of two formula units that form the water-bridged dimer.

The structure is a dimer of two formula units related to each other by a center of symmetry. Two $UO_2(NO_3)_2$ units are bridge bonded via the oxygen atoms of two water molecules. The water molecule is hydrogen bonded to the nonprotonated nitrogen atom (N(3)) of the imidazole and to a nitrate oxygen (O(5)) of an adjacent dimer. The nitrate to water bond links the dimers together into an infinite chain.

Table I. Positional Parameters with Estimated Deviations[a]

atom	x	y	z
U	0.12027 (4)	0.06380 (2)	0.20731 (5)
O(1)	0.2646 (8)	0.0649 (5)	0.075 (1)
O(2)	−0.0243 (8)	0.0640 (5)	0.337 (1)
O(3)	0.0481 (8)	−0.0685 (4)	0.090 (1)
O(4)	0.2137 (9)	0.2052 (5)	0.331 (1)
O(5)	0.127 (1)	0.3233 (5)	0.227 (1)
O(6)	0.0270 (9)	0.2098 (5)	0.102 (1)
O(7)	0.303 (1)	0.0706 (5)	0.522 (1)
O(8)	0.2552 (9)	−0.0503 (5)	0.408 (1)
O(9)	0.407 (1)	−0.0330 (6)	0.679 (1)
N(1)	0.121 (1)	0.2485 (5)	0.220 (2)
N(2)	0.325 (1)	−0.0051 (6)	0.544 (1)
N(3)	0.295 (1)	−0.1653 (6)	0.059 (2)
N(4)	0.524 (1)	−0.1888 (7)	0.090 (2)
C(1)	0.426 (1)	−0.1310 (8)	0.087 (2)
C(2)	0.313 (1)	−0.2483 (8)	0.049 (2)
C(3)	0.454 (1)	−0.2634 (8)	0.069 (2)
H(1)	0.6259	−0.1805	0.1034
H(2)	0.4450	−0.0735	0.1017
H(3)	0.2366	−0.2885	0.0302
H(4)	0.4994	−0.3162	0.0699
H(5)	−0.0099	−0.1043	0.1506
H(6)	0.1313	−0.1010	0.0796

[a] In this and the following tables the number in parentheses is the estimated standard deviation for the least significant figures.

Table II. Distances (Å)

U–U	3.927 (2)	N(2)–O(7)	1.25 (2)
–O(1)	1.78 (1)	–O(8)	1.28 (2)
–O(2)	1.76 (1)	–O(9)	1.19 (2)
–O(3)	2.35 (1)	O(3)–O(3)[a]	2.63 (2)
–O(3)[a]	2.37 (1)	–O(5)[b]	2.87 (2)
–O(4)	2.55 (1)	–N(3)	2.83 (2)
–O(6)	2.59 (1)	C(1)–N(3)	1.32 (2)
–O(7)	2.54 (1)	–N(4)	1.31 (2)
–O(8)	2.52 (1)	C(2)–N(3)	1.36 (2)
N(1)–O(4)	1.26 (2)	C(3)–N(4)	1.37 (2)
–O(5)	1.22 (2)	C(2)–C(3)	1.32 (2)
–O(6)	1.26 (2)		

[a] At position $-x, -y, -z$. [b] At position $-x, y - {}^1/_2, {}^1/_2 - z$.

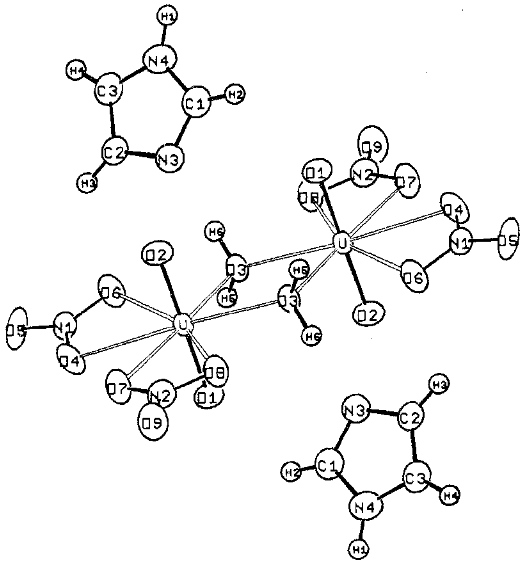

Figure 1. ORTEP drawing of two formula units in the dimer configuration.

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Table III. Selected Angles (Deg)

O(1)-U-O(2)	179.1 (4)	O(7)-U-O(8)	49.9 (3)
O(1)-U-O(3)	91.0 (3)	U-O(3)-U	112.3 (3)
O(1)-U-O(3)[a]	88.6 (3)	O(5)-O(3)-N(3)	103.6 (4)
O(1)-U-O(4)	85.9 (3)	O(5)-N(1)-O(4)	121 (1)
O(1)-U-O(6)	95.0 (3)	O(5)-N(1)-O(6)	123 (1)
O(1)-U-O(7)	90.5 (4)	O(4)-N(1)-O(6)	116 (1)
O(1)-U-O(8)	87.5 (3)	O(7)-N(2)-O(8)	115 (1)
O(2)-U-O(3)	89.3 (4)	O(7)-N(2)-O(9)	123 (1)
O(2)-U-O(3)[a]	90.8 (3)	O(8)-N(2)-O(9)	123 (1)
O(2)-U-O(4)	93.8 (4)	C(1)-N(3)-C(2)	108 (1)
O(2)-U-O(6)	84.2 (4)	N(3)-C(2)-C(3)	108 (1)
O(2)-U-O(7)	90.1 (4)	C(2)-C(3)-N(4)	107 (1)
O(2)-U-O(8)	93.3 (4)	C(3)-N(4)-C(1)	109 (1)
O(3)-U-O(3)	67.7 (3)	N(3)-C(1)-N(4)	109 (1)
O(4)-U-O(6)	49.3 (3)		

[a] At position $-x, -y, -z$.

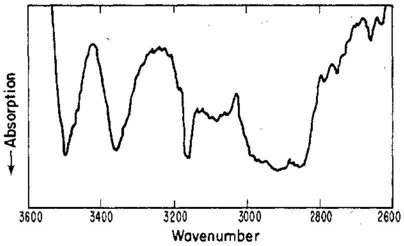

Figure 2. Infrared spectrum of the title compound taken as a Nujol mull.

Uranium is eight-coordinate at the center of a distorted hexagonal bipyramid which has the uranyl oxygen atoms at the apices. The O–U–O axis is more or less perpendicular to the distorted equatorial plane; the largest deviation from orthogonality of the O–U–O axis to any U–O bond in the equatorial plane is 6°. A slight twist of the nitrate groups out of the equatorial plane indicates some crowding in the coordination environment about UO_2^{2+}. The geometry and bond distances of the water-bridged uranyl dimer in this structure are remarkably similar to the hydroxy-bridged uranyl dimer found in $[(NO_3)_2UO_2(OH)_2UO_2(H_2O)_3]\cdot H_2O$,[20] in which hydroxide instead of H_2O is the bridging group and three waters occupy one end of the dimer rather than two nitrate groups. Another similar type of uranyl dimer is found in the $Cl(H_2O)_3UO_2(OH)_2UO_2(H_2O)_3Cl$ structure,[21] which has heptacoordinate rather than octacoordinate uranium. The U–U distance in the title compound is 3.927 Å and compares to 3.939 Å[20] and 3.944 Å[21] in the two other compounds mentioned above. The bridging U–O(water) distances are about 0.2 Å shorter than the U–O(nitrate) distances, and this is consistent with what is observed in the other compounds.[20,21] The double oxygen bridging of the uranyl ion is somewhat rare, but several examples exist for thorium in which the Th–Th distances vary from 3.97 to 4.09 Å in a series of double hydroxo-bridged thorium(IV) complexes.[22]

The imidazole molecules are associated by hydrogen bonds to the bridging water molecules and are not directly bonded to the uranyl cations. The bond distances and angles of the imidazole molecules are in agreement with previous structural studies.[23,24]

The infrared spectrum of the complex is quite distinctive in the O–H and N–H stretching region and is shown in Figure 2. Rather than the broad band in the 3500-cm^{-1} region which is customarily seen for metal-ion complexes involving water, a single, considerably sharpened peak is found at 3500 cm^{-1}. An N–H stretching band, similar in contour to the O–H band, is found at 3350 cm^{-1}, while a second, sharper N–H frequency lies at 3160 cm^{-1}. These values compare quite favorably with those of transition-metal–imidazole complexes.[25]

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Registry No. $[UO_2(NO_3)_2(H_2O)]_2\cdot 2C_3H_4N_2$, 72827-60-2.

Supplementary Material Available: Data processing formulas, the table of anisotropic thermal parameters, the calculated powder pattern, and the listing of structure factor amplitudes (15 pages). Ordering information is given on any current masthead page.

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Interaction of Carbon Dioxide with Coordinatively Unsaturated Rhodium(I) Complexes with the Ligand 1,2-Bis(diphenylphosphino)ethane

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The activation of CO_2 through coordination to transition-metal complexes[2] has received considerable attention in the last few years as these complexes can be involved in CO_2 fixation into organic substrates.

A number of CO_2 complexes of Rh(I) with monodentate phosphines have been isolated,[3] and reports on the interaction of CO_2 with Rh(I) complexes with chelating ligands such as 1,2-bis(dimethylphosphino)ethane or 1,2-bis(diethylphosphino)ethane[4] can be found in the literature, but no evidence of CO_2 coordination to Rh(I) or to other transition-metal complexes with the ligand 1,2-bis(diphenylphosphino)ethane (diphos) has been reported to date.

In this note we report the results of our studies on the interaction of CO_2 with unsaturated Rh(I) complexes with diphos and the synthesis, structure, and reactivity of the covalent complex Rh(diphos)(η-BPh_4).

Experimental Section

Reactions were carried out in an atmosphere of purified gases. The solvents were dried as reported in the literature and stored under nitrogen. Infrared spectra were run with a Perkin-Elmer 577 spectrophotometer. Molecular weights were determined with the Hewlett-Packard 302 VP osmometer, and gas chromatographic analyses were performed with a Hewlett-Packard 5750 instrument.

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