correction was applied (see Table I). Atomic scattering factors of Doyle and Turner[9] were used, and anomalous scattering corrections[10] were applied.

Three-dimensional Patterson maps indicated the positions of the Mo atoms. Subsequent least-squares refinements and difference Fourier maps revealed all of the nonhydrogen atoms. Most of the hydrogen atom peaks were not resolved in the Fourier maps, and none were included in the least-squares refinements. All of the atoms with the exception of the carbon atoms in isomer A were assigned anisotropic thermal parameters in the final refinements. Because of the poor resolution of the ethyl groups in the A isomer, restraints were imposed on the geometry of the triethylphosphine groups by a procedure suggested by Waser,[11] and described in a previous paper.[12]

(9) Doyle, P. A.; Turner, P. S. *Acta Crystallogr., Sect. A* **1968**, *A24*, 390.
(10) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.
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For the A isomer, the C–C and P–C bond distances were restrained to 1.54 and 1.82 Å, respectively. The full-matrix least-squares program minimizes the function $\sum w(\Delta F)^2/\sum wF_o^2$. After the last cycle of refinement, the largest shift of the parameter was 0.03 and 0.01 of its esd for the A and B isomer, respectively. *R* factors and other statistical results of the least-squares refinement are given in Table I.

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Registry No. C_2-$Mo_2Cl_2(O_2CCMe_3)_2(PEt_3)_2$, 81276-73-5; C_{2h}-$Mo_2Cl_2(O_2CCMe_3)_2(PEt_3)_2$, 81339-50-6; $Mo_2Cl_4(PEt_3)_4$, 59780-36-8; $Mo_2(O_2CCMe_3)_4$, 55946-68-4; Me_3SiCl, 75-77-4.

Supplementary Material Available: Listings of thermal parameters and observed structure factors (26 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry, University of California, and the Materials and Molecular Research Division, Lawrence Berkeley Laboratory, Berkeley, California 94720

Organouranium Complexes of Pyrazole and Pyrazolate. Synthesis and X-ray Structures of $U(C_5Me_5)_2Cl_2(C_3H_4N_2)$, $U(C_5Me_5)_2Cl(C_3H_4N_2)$, and $U(C_5Me_5)(C_3H_3N_2)_2$

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The title compounds have been prepared by the reaction between $U(C_5Me_5)_2Cl_2$ and pyrazole ($C_3H_4N_2$), or sodium pyrazolate ($NaC_3H_3N_2$), in THF. The new compounds are characterized by their infrared, ^{1}H NMR visible–near-IR, and mass spectra and by single-crystal X-ray diffraction (monochromatic Mo Kα radiation). The molecular structure of $U(C_5Me_5)_2Cl_2(C_3H_4N_2)$ consists of discrete mononuclear units at positions of *mm* (C_{2v}) symmetry. The U^{4+} ion is coordinated by two η^5-pentamethylcyclopentadienide rings, two chloride ions, and one nitrogen atom from the neutral pyrazole ring, for a total coordination number of 9. Red-brown crystals from toluene conform to space group *Cmcm* with a = 13.697 (4) Å, b = 11.496 (2) Å, c = 15.555 (2) Å, and four molecules per unit cell. For the 924 independent reflections with $F^2 > 3\sigma(F^2)$, the final weighted and unweighted *R* factors are 3.48 and 2.45%, respectively. The average U–C bond distance is 2.74 (2) Å, the U–N bond distance is 2.607 (8) Å, and the U–Cl distance is 2.696 (2) Å. This compound exhibits Curie–Weiss behavior with C = 1.46, Θ = 43.3 K, and μ_{eff} (from the slope of $1/\chi$ vs. T) = 3.24 μ_B. The molecular structure of $U(C_5Me_5)_2Cl(C_3H_3N_2)$ consists of discrete U^{4+} ions coordinated by two η^5-pentamethylcyclopentadienide rings, one chloride ion, and both nitrogen atoms from the pyrazolate anion, for a total coordination number of 9. Red-brown crystals from toluene conform to space group $P2_1/n$ with a = 8.737 (1) Å, b = 18.068 (1) Å, c = 15.229 (1) Å, β = 92.38 (1)°, and four molecules per unit cell. For the 2566 independent reflections with $F^2 > 3\sigma(F^2)$, the final weighted and unweighted *R* factors are 4.50 and 3.27%, respectively. The average U–C bond distance is 2.73 (3) Å, the U–N distances are 2.351 (5) and 2.349 (5) Å, and the U–Cl distance is 2.611 (2) Å. This compound exhibits Curie–Weiss behavior with C = 0.73, Θ = 5.95 K, and μ_{eff} = 2.42 μ_B. The molecular structure of $U(C_5Me_5)_2(C_3H_3N_2)_2$ consists of discrete mononuclear U^{4+} ions coordinated by two η^5-pentamethylcyclopentadienide rings and four nitrogen atoms from the two pyrazolate anions, for a total coordination number of 10. Red-brown crystals from toluene conform to space group $C2/c$ with a = 33.326 (2) Å, b = 10.450 (2) Å, c = 16.646 (1) Å, β = 117.09 (1)°, and eight molecules per unit cell. For the 2706 independent reflections with $F^2 > 3\sigma(F^2)$, the final weighted and unweighted *R* factors are 3.31 and 2.43%, respectively. The average U–C bond distance is 2.75 (2) Å, and the U–N distances are 2.403 (4), 2.360 (5), 2.363 (5), and 2.405 (5) Å. This compound does not exhibit simple magnetic behavior.

Introduction

As part of our effort to create, examine, and explain structural[1] and magnetic[2] probes of the bonding in organolanthanide and actinide compounds, we have sought the synthesis and magnetic characterization of an appropriate dimeric uranium complex. Our recent report of the synthesis and structure of $UCp_3(pz^-)$[3] (pz^- = pyrazolate) revealed that our attempt to form a dimer (based on a precedent in titanium chemistry, $[TiCp_2(pz^-)]_2$)[4] resulted instead in the formation of a monomeric species, allowing us to characterize a new mode of pyrazolate bonding. To investigate what role, if any, steric factors played in the formation of the monomeric compound, and to learn more about the pyrazolate ion as a ligand, we have adjusted the size and number of the Cp (C_5H_5) ligands. We anticipated that a reduction in the total steric bulk of the other ligands might lead to the formation of one or more dimeric species. The compound UCp''_2Cl_2 (Cp'' = C_5Me_5) has proven to be a useful starting material for other studies[5,6]

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(2) Baker, E. C.; Raymond, K. N. *Inorg. Chem.* **1977**, *16*, 2710.
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Table I. Magnetic Susceptibility Data

$UCp''_2Cl_2(pz)$		$UCp''_2Cl(pz^-)$		$UCp''_2(pz^-)_2$	
T, K	$10^3\chi_M^{cor}$, cm³/mol	*T*, K	$10^3\chi_M^{cor}$, cm³/mol	*T*, K	$10^3\chi_M^{cor}$, cm³/mol
5.4	30.26	4.2	93.17	6.1	2.57
9.0	27.16	9.1	57.89	8.6	4.37
17.9	23.83	17.9	31.47	17.9	7.56
27.8	21.46	27.8	21.23	27.5	9.29
37.4	52.18	37.4	16.20	37.2	9.42
46.4	58.52	46.4	12.82	46.3	8.82
60.2	73.69	60.2	10.69	60.2	8.58
		77.6	9.34	77.6	8.73

but does not produce dimers. Instead, the compounds $U(C_5Me_5)_2Cl(pz^-)$ and $U(C_5Me_5)_2(pz^-)_2$ are formed by the reaction between $U(C_5Me_5)_2Cl_2$ and stoichiometric amounts of $Na(pz^-)$. In the course of this study, an adduct of neutral pyrazole, $U(C_5Me_5)_2Cl_2(pz)$ (pz = pyrazole) was also characterized.

Experimental Section

All reactions were carried out under an inert atmosphere of argon on a Schlenk or vacuum line. Transfer and some handling were facilitated by a Vacuum Atmospheres HE-93-A glovebox with recirculating moisture and oxygen-free argon atmosphere. Elemental analyses were performed by the Microanalytical Laboratory, UC, Berkeley. Infrared spectra were recorded on a Perkin-Elmer 597 spectrophotometer (Nujol mulls, reported in cm^{-1}), mass spectra were obtained on an AEI-MS12 mass spectrometer [reported as *m/e* (relative abundance (%))], electronic spectra were recorded on a Cary 14 spectrophotometer (in toluene vs. toluene reported in nm), and ^1H NMR spectra were obtained with the UCB-250 NMR spectrometer (in toluene-d_8, shifts in δ vs. Me_4Si, s = singlet, line width at half-height, integrated intensity, assignment). Magnetic susceptibilities were determined as described elsewhere[3] and are corrected for underlying diamagnetism.[7] Crystalline samples for X-ray diffraction were mounted in glass capillaries under a He atmosphere in a horizontal-format inert-atmosphere glovebox equipped with a binocular microscope.

Materials. Toluene and tetrahydrofuran (THF) were distilled from potassium benzophenone ketyl. Pyrazole was obtained from Aldrich (98%) and recrystallized from toluene at −15 °C before use. Sodium pyrazolate was prepared from NaH and pyrazole in THF;[8] UCl_4 was prepared by the literature procedure.[9]

To a green solution of 5.00 g (13.2 mmol) of UCl_4 in THF was added 6.87 g (39.5 mmol) of $K(C_5Me_5)$ (prepared by the reaction between KH and HC_5Me_5 in THF). A total of 200 mL of THF was maintained at reflux under argon for 24 h. After removal of solvent, the residue was extracted several times with 200 mL of toluene. The separation of suspended particulate and solvent was facilitated by centrifugation. The volume of toluene was reduced and cooling overnight to −15 °C yielded crystals of $U(C_5Me_5)_2Cl_2$ in moderate yield.

$UCp''_2Cl_2(pz)$. To a red-brown solution of 0.55 g (0.9 mmol) of $U(C_5Me_5)_2Cl_2$ in 75 mL of THF was added 0.06 g (0.9 mmol) of pyrazole. The solution was stirred overnight at room temperature. After solvent removal, the red-brown residue was washed with hexane and then dissolved in toluene and this solution cooled to −15 °C. After 12 h, the large crystals that had formed were filtered and an IR spectrum clearly revealed an N–H stretch at 3100 cm^{-1}. Anal. Calcd for $UC_{23}H_{34}N_2Cl_2$: C, 42.66; H, 5.29; N, 4.33. Found: C, 43.26; H, 5.55; N, 4.38. IR: 3265 (st), 3115 (shp), 2720 (shp), 1424 (st), 1337 (st), 1149 (sh), 1132 (st), 1052 (sh), 1040 (st), 1018 (st), 930, 910, 776 (st), 723 (sh), 598. Mass spectrum: 624 (9.5), 622 (7.4), 578 (93.4), 542 (34.3), 443 (98.6), 407 (73.1), 403 (79.3), 308 (100), 135 (37.6), 119 (75.1), 105 (42.5). Electronic spectrum: 1607 (sh), 1590 (st), 1423 (st), 1400 (sh), 1168 (st), 1133 (shp), 1118 (shp), 1095 (shp), 1049 (st), 990 (w), 908 (w), 880 (w), 858 (w), 817 (w), 790 (w), 730 (w), 718 (w), 708 (w), 691 (shp), 680 (sh). ^1H NMR spectrum: at 22 °C, 11.49 (s, ~40 Hz, 30 H, methyl), −9.58 (s, ~200 Hz, 2 H, pz), −28.63 (~1500 Hz, 1 H, N–H); at −10 °C, 12, −16, −47, −65; at −25 °C, 13, −17, −19, −52, −72; at −40 °C, 13.9 (s, ~40 Hz, 30 H, methyl), −20.0 (s, ~80 Hz, 1 H, pz), −21.2 (s, ~90 Hz, 1 H, pz), −58.1 (s, ~205 Hz, 1 H, pz), −80.2 (s, ~250 Hz, 1 H, pz). Magnetic susceptibility: this compound exhibits Curie–Weiss behavior with *C* = 1.46 and Θ = 42.34 K. Table Ia includes χ_M^{corr} vs. *T* data. The slope of $1/\chi_M^{cor}$ vs. *T* yields μ_{eff} = 3.42 μ_B.

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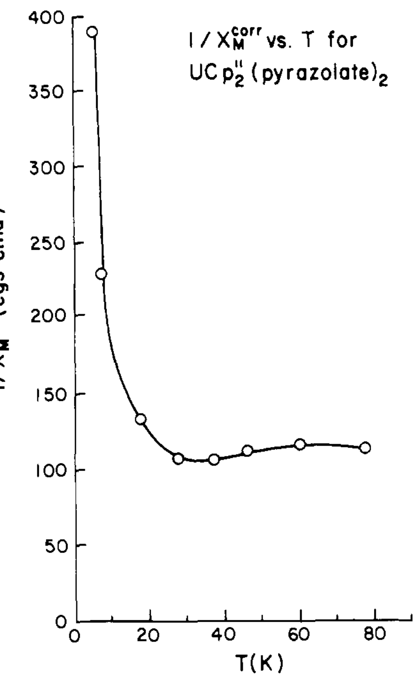

Figure 1. Graph of $1/\chi_M^{cor}$ vs. *T* for $UCp''_2(pz^-)_2$.

$U(C_5Me_5)_2Cl(pz^-)$. About 150 mL of THF was vacuum distilled from potassium benzophenone ketyl onto a mixture of 1.00 g (1.7 mmol) of UCp_2Cl_2 and 0.16 g (1.8 mmol) of $Na(pz^-)$. The reaction was warmed to room temperature and stirred 12 h. The THF was distilled away under vacuum. A hexane solution was filtered through diatomaceous earth, concentrated, and cooled to −15 °C overnight, yielding large crystals. Anal. Calcd for $UC_{23}H_{33}N_2Cl$: C, 45.21; H, 5.44; N, 4.58; Cl, 5.80. Found: C, 45.35; H, 5.57; N, 4.54; Cl, 6.06. IR: 2730 (w), 1418 (shp), 1348 (w), 1286 (st), 1066 (w), 1023 (w), 968 (st), 922 (shp), 782 (st), 771 (shp), 726 (w), 609 (shp). Mass spectrum: 610 (6.8), 542 (1.0), 475 (38.7), 407 (5.6), 403 (4.8), 340 (7.3), 137 (19.6), 121 (28.2), 105 (63.3), 91 (57.0), 77 (31.3), 68 (100). Electronic spectrum: 1648 (st), 1635 (st), 1562 (sh), 1440 (s), 1290 (w), 1259 (sh), 1175 (st), 1122 (st), 1095 (st), 1040 (shp), 967 (w, shp), 920 (sh), 907 (sh), 872 (w), 855 (w), 826 (w), 773 (w), 721 (sh), 713 (st, shp), 700 (st, shp), 660 (w), 600 (st). ^1H NMR: 12.956 (s, ~84 Hz, 2 H, pz^-), 8.098 (s, ~30 Hz, 30 H, Me). Magnetic susceptibility: this compound exhibits Curie–Weiss behavior with *C* = 0.73 and Θ = 5.95 K. Table Ib includes χ_M^{corr} vs. *T* data. The slope of $1/\chi_M^{corr}$ vs. *T* yields μ_{eff} = 2.42 μ_B.

$U(C_5Me_5)_2(pz^-)_2$. Onto a mixture of 1.35 g (2.3 mmol) of $U(C_5Me_5)_2Cl_2$ and 0.42 g (4.7 mmol) of Na (pz^-) was distilled about 200 mL of THF from potassium benzophenone ketyl. The resulting red-brown solution was stirred at room temperature for 24 h with the development of a fine precipitate. The solvent was removed under vacuum and the residue extracted with a small volume of hexane (ca. 30 mL). The volume was reduced and the solution cooled overnight to −15 °C, whereupon large crystals formed. Anal. Calcd for $UC_{26}H_{36}N_4$: C, 48.59; H, 5.65; N, 8.72. Found: C, 48.72; H, 5.71; N, 8.80. IR: 3125 (w), 3100 (w), 2720 (w), 1731 (w), 1696 (w), 1590 (w), 1410, 1349, 1280 (st), 1230 (w), 1052, 1018, 985 (st), 921 (st), 866, 800 (w), 759 (st), 725 (w), 616 (st), 591 (w), 550 (w), 382. Mass spectrum: 642 (67.35), 575 (3.13), 508 (73.93), 597 (91.79), 412 (66.92), 372 (42.65), 136 (34.74), 119 (57.09), 105 (32.69), 91 (27.69), 77 (15.02), 68 (99.15). Electronic spectrum: 1464 (w), 1317 (w), 1262 (w), 1183 (sh), 1124 (st), 1089 (st, shp), 982 (w), 950 (w), 930 (w), 855 (w), 834 (w), 745 (w), 691 (shp), 661 (shp), 582 (w). ^1H NMR: 29.09 (s, ~30 Hz, 2 H 27.44 (s, ~200 Hz, 4 H, pz^-),

Table II. Cell Parameters for $UCp''_2Cl_2(pz)$, $UCp''_2Cl(pz^-)$, and $UCp''_2(pz^-)_2$[a]

	HPYZ	1:1	1:2
space group	*Cmcm*	$P2_1/n$	*C2/c*
a, Å	13.697 (4)	8.737 (1)	33.326 (2)
b, Å	11.496 (2)	18.068 (1)	10.450 (2)
c, Å	15.555 (2)	15.229 (2)	16.646 (1)
β, deg		92.38 (1)	117.09 (1)
Vol, Å^3	2449.4 (14)	2401.9 (6)	5160.8 (17)
2θ range (lattice constants), deg	26–40	27–30	26–35
molecules/cell	4	4	8
d_{calcd}, g/cm^3	1.75	1.69	1.65
d_{obsd}, g/cm^3	1.77	1.68	1.66
2θ range (intens data), deg	4–52	4–45	4–45
obsns	924	2566	2706
parameters	75	201	280
R, %	2.45	3.27	2.43
R_w,[c] %	3.48	4.50	3.31

[a] HPYZ is $UCp''_2Cl_2(pz)$, 1:1 is $UCp''_2Cl(pz^-)$, and 1:2 is $UCp''_2(pz^-)_2$. [b] All data are for monochromatic Mo Kα radiation, λ = 0.710 73 Å, at 22 °C. [c] In each case a *p* factor of 0.03 was used; see ref 15.

−0.20 (s, ~7 Hz, 30 H, methyl). Magnetic susceptibility: this compound does not exhibit simple behavior. Table Ic includes χ_M^{corr} vs. *T* data, and Figure 1 illustrates $1/\chi_M^{corr}$ vs. *T*.

Data Collection, Solution, and Refinement[10–18]

$UCp''_2Cl_2(pz)$. Suitable crystals for diffraction were grown by cooling a saturated hexane or toluene solution to −15 °C. Precession photographs revealed orthorhombic symmetry and the conditions *hkl*, $h + k = 2n$, and *h0l*, $l = 2n$. These are consistent with the space groups *Cmcm*, $Cmc2_1$, and *Ama*2. The crystal was oriented, and lattice parameters were accurately determined by 25 automatically centered reflections (Table II).

A total of 1071 data were collected between 4 and 52° in 2θ for +*h*,+*k*,+*l*, and $h + k = 2n$. During data collection, one reorientation was required. Azimuthal scans on five reflections with θ between 7 and 21° revealed an intensity variation of ±17%. The crystal faces were identified on the diffractometer and their dimensions measured at 7X under a binocular microscope. The distances of the eight planes identified from a common center were adjusted incrementally until the calculated edge lengths agreed most closely with those observed. An absorption correction ranging between 2.15 and 2.67 was then applied (μ = 65.82 cm^{-1}). No crystal decay was observed during data collection. There were 924 reflections with $F^2 > 3\sigma(F^2)$ used in the structure solution and refinement. The initial Patterson map confirmed the space group *Cmcm*, and the structure was solved by heavy-atom techniques. The pyrazole was found to be lying across the mirror plane at *x* = 0, disordering the NH and CH ortho to the metal-bound nitrogen. The structure was refined with only the carbon atom position varied (at. 0.25 occupancy), with the parameters of the mirror-related nitrogen being reset to those of the carbon after each least-squares cycle. (This is an excellent approximation, given the similar scattering power of these two elements.) The model converged to weighted and unweighted *R* factors of 3.48% and 2.45%, respectively. During the final least-squares cycle, the largest parameter shift was 0.18σ. The largest peak in the final difference Fourier was 0.4 e/Å^3 and was less than 1 Å from the uranium. Hydrogen atoms were not found, nor were calculated positions included in the final calculations. The residuals showed no anomalies. Positional and thermal parameters appear in Tables III and IIIa.[19]

Table III. Positional Parameters and Their Estimated Standard Deviations for $UCp''_2Cl_2(pz)$

atom	*x*	*y*	*z*
U	0.0000 (0)	0.22632 (3)	0.2500 (0)
Cl	0.1893 (2)	0.2904 (2)	0.2500 (0)
N(1)	0.0000 (0)	0.4531 (8)	0.2500 (0)
N(2)	0.0776 (12)	0.5222 (16)	0.2500 (0)
C(11)	0.0515 (5)	0.2273 (5)	0.0810 (4)
C(21)	0.0835 (5)	0.1173 (6)	0.1119 (4)
C(31)	0.0000 (0)	0.0516 (8)	0.1287 (5)
C(71)	0.4495 (8)	0.1397 (9)	0.2500 (0)
C(80)	0.0776 (12)	0.5222 (16)	0.2500 (0)
C(41)	0.1135 (6)	0.3255 (9)	0.0442 (6)
C(61)	0.0000 (0)	−0.0791 (10)	0.1457 (7)
C(51)	0.1891 (6)	0.0728 (9)	0.1145 (5)

$UCp''_2Cl(pz^-)$. Crystals suitable for diffraction studies were obtained by cooling a concentrated hexane or toluene solution at −15 °C overnight. The polycrystalline solids that formed were fractured into large single crystal fragments. Precession photographs revealed the conditions *h0l*, $h + l = 2n$, and *0k0*, $k = 2n$, indicating space group $P2_1/n$ (an alternative setting of $P2_1/c$). Cell parameters are given in Table II.

A total of 3513 +*h*,+*k*,±*l* data were collected between 4 and 45° in 2θ. Azimuthal scans on 6 reflections between 5° and 22° in θ revealed an intensity variation of ±17%. Because the data crystal was of a particularly irregular shape, an empirical absorption correction was applied; it ranged from 1.00 to 1.49 (μ = 66.00 cm^{-1}). No decay was observed during data collection. The averaging of equivalent reflections left 3134 unique data, 2566 of which were greater than 3σ and were used in the least-squares refinement. The initial Patterson map confirmed the space group, and subsequent difference Fourier least-squares cycles revealed the pyrazolate and the two Cp″ rings. Residual electron density and some poor atomic relationships suggested a second orientation for both the Cp″ rings, so primed carbon atom positions and isotropic thermal parameters were refined. The relative occupancy factors of the two orientations refined to about 50/50 for Cp''_2 and about 60/40 for Cp''_1. Fourier maps showed these ligands consisted of diffuse rings of electron density, with some localized peaks. This observation leads us to conclude that further attempts to improve the moderately poor atomic relationships in the ring were unwarranted. In the final refinements, only the thermal parameters of uranium and chlorine were treated anisotropically. The model converged to weighted and unweighted *R* factors of 4.50% and 3.27%, respectively. On the final least-squares cycle, the largest parameter shift was 0.29σ, while for those seven atoms not involved in the disorder the largest shift was 0.02σ. The residual peaks in the final difference Fourier (largest

(10) Mo Kα radiation was used throughout. The intensity of three standard reflections was measured every 7200 s of X-ray exposure, and the position of three orientation standards was checked every 250 reflections.

(11) Roof, R. B. "A Theoretical Extension of the Reduced-Cell Concept in Crystallography", Publication LA-4038; Los Alamos Scientific Laboratory: Los Alamos, NM, 1969.

(12) All calculations were performed with a PDP 11/60 equipped with 128 kilowords of memory, twin RK07 20 MByte disk drives, Versatec printer/plotter, and a TU10 tape drive using locally modified Enraf-Nonius SDP software operating under RSX-11M (see ref 13).

(13) "Structure Determination Package User's Guide"; Molecular Structure Corp.: College Station, TX 77840.

(14) The data reduction formulae are $F_o^2 = (\omega(C - 2B)/(Lp)$, $F_o = (F_o^2)^{1/2}$, $\sigma_o(F_o^2) = \omega(C + 4B)^{1/2}/(Lp)$, and $\sigma_o(F_o) = \sigma_o(F_o^2)/2F_o$, where *C* is the total count in the scan, *B* is the sum of the two background counts, ω is the scan speed in deg/min, and $1/(Lp) = (\sin 2\theta)(1 + \cos^2 2\theta_m)/(1 + \cos^2 2\theta_m - \sin^2 2\theta)$ is the correction for Lorentz and polarization effects for a reflection with scattering angle 2θ and radiation monochromatized with a 50% perfect single-crystal monochromator with scattering angle $2\theta_m$.

(15) $R = (\sum||F_o| - |F_c||)/\sum|F_o|$, $R_w = [(\sum w(|F_o| - |F_c|)^2)/\sum wF_o^2]^{1/2}$, and $GOF = [(\sum w(|F_o| - |F_c|)^2)/(n_o - n_v)]^{1/2}$, where n_o is the number of observations, n_v is the number of variable parameters, and the weights *w* are given by $w = 4F_o^2/\sigma^2(F_o^2)$, and $\sigma^2(F_o^2) = \sigma_o^2(F_o^2) + (pF^2)^2$, where *p* is the factor used to lower the weight of intense reflections. The form of the anisotropic thermal correction is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

(16) Atomic scattering factors are from: Cromer, D. T.; Weber, J. T. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2B. Cromer, D. T. *Ibid.*, Table 2.3.1.

(17) Instrumentation at the University of California Chemistry Department X-ray Crystallography Facility (CHEXRAY) consists of two Enraf-Nonius CAD-4 diffractometers, one controlled by a DEC PDP 8/a with an RK05 disk and the other by a DEC PDP 8/e with an RL01 disk. Both use Enraf-Nonius software as described in: "CAD-4 Operation Manual"; Enraf-Nonius: Delft, Amsterdam, 1977 (updated in Jan 1980).

(18) Johnson, C. K. Report ORNL-3794; Oak Ridge National Laboratory: Oak Ridge, TN, 1965.

(19) For data which appear in the supplementary material, see the paragraph at the end of this paper.

Table IV. Positional Parameters and Their Estimated Standard Deviations for $UCp''_2Cl(pz^-)$

atom	x	y	z	atom	x	y	z
U	0.40954 (3)	0.10361 (2)	0.26343 (2)	C(21)	0.306 (1)	−0.0210 (6)	0.4456 (7)
Cl	0.6845 (3)	0.1054 (1)	0.3375 (2)	C(22)	0.154 (1)	−0.0347 (6)	0.4421 (7)
N(1)	0.2119 (8)	0.0393 (4)	0.3307 (5)	C(23)	0.102 (1)	0.0009 (6)	0.3714 (7)
N(2)	0.3419 (8)	0.0251 (4)	0.3785 (5)	C(1)′	0.464 (2)	−0.0302 (9)	0.1850 (11)
C(1)	0.370 (1)	−0.0220 (7)	0.1671 (9)	C(2)′	0.322 (2)	−0.0040 (11)	0.1442 (13)
C(2)	0.310 (2)	0.0352 (8)	0.1147 (10)	C(3)′	0.346 (3)	0.0524 (12)	0.0942 (15)
C(3)	0.430 (1)	0.0771 (7)	0.0882 (8)	C(4)′	0.518 (2)	0.0665 (12)	0.1018 (14)
C(4)	0.569 (1)	0.0528 (7)	0.1262 (9)	C(5)′	0.561 (2)	0.0176 (12)	0.1580 (14)
C(5)	0.535 (2)	−0.0099 (8)	0.1766 (9)	C(11)′	0.238 (2)	0.2070 (9)	0.3460 (11)
C(6)	0.250 (2)	−0.0020 (11)	0.1909 (14)	C(12)′	0.197 (11)	0.2142 (7)	0.2499 (9)
C(7)	0.150 (3)	0.0527 (13)	0.0709 (15)	C(13)′	0.326 (2)	0.2420 (8)	0.2051 (10)
C(8)	0.458 (2)	0.1379 (12)	0.0132 (14)	C(14)′	0.434 (2)	0.2521 (10)	0.2785 (11)
C(9)	0.740 (3)	0.0655 (13)	0.1201 (16)	C(15)′	0.390 (2)	0.2320 (10)	0.3520 (12)
C(10)	0.626 (3)	−0.0659 (17)	0.2304 (16)	C(6)	0.475 (6)	−0.1010 (19)	0.2369 (30)
C(11)	0.207 (2)	0.2118 (8)	0.3018 (10)	C(7)′	0.157 (5)	−0.0395 (22)	0.1312 (28)
C(12)	0.276 (2)	0.2364 (9)	0.2198 (10)	C(8)′	0.327 (5)	0.1123 (19)	0.0111 (30)
C(13)	0.430 (2)	0.2536 (9)	0.2379 (10)	C(9)′	0.684 (4)	0.1087 (15)	0.0852 (24)
C(14)	0.454 (2)	0.2453 (9)	0.3314 (11)	C(10)′	0.739 (4)	−0.0235 (20)	0.2027 (23)
C(15)	0.328 (2)	0.2178 (9)	0.3657 (10)	C(16)′	0.102 (3)	0.1820 (13)	0.4075 (16)
C(16)	0.021 (3)	0.1955 (15)	0.2833 (18)	C(17)′	0.031 (3)	0.1969 (12)	0.2092 (14)
C(17)	0.224 (3)	0.2589 (13)	0.1204 (16)	C(18)′	0.334 (3)	0.2595 (13)	0.1140 (16)
C(18)	0.555 (3)	0.2900 (2)	0.1904 (16)	C(19)′	0.585 (3)	0.2934 (18)	0.2684 (22)
C(19)	0.576 (3)	0.2683 (14)	0.3881 (17)	C(20)′	0.466 (4)	0.2375 (17)	0.4458 (20)
C(20)	0.253 (4)	0.1938 (19)	0.4497 (24)				

Table V. Positional Parameters and Their Estimated Standard Deviations for $UCp''_2(pz^-)_2$

atom	x	y	z	atom	x	y	z
U	0.12839 (1)	0.28541 (2)	0.05748 (1)	C(12)	0.0668 (2)	0.4794 (8)	0.0150 (5)
N(1)	0.1729 (2)	0.4758 (5)	0.0819 (3)	C(13)	0.0417 (2)	0.3742 (10)	−0.0229 (5)
N(2)	0.1613 (2)	0.4332 (6)	−0.0823 (3)	C(14)	0.0453 (2)	0.2931 (7)	0.0511 (7)
N(3)	0.1028 (2)	0.2849 (5)	−0.0904 (4)	C(15)	0.0724 (2)	0.3621 (10)	0.1296 (5)
N(4)	0.0884 (2)	0.1190 (5)	−0.0489 (3)	C(16)	0.1134 (3)	0.5738 (11)	0.1762 (7)
C(1)	0.2168 (2)	0.2062 (6)	0.1445 (4)	C(17)	0.0712 (3)	0.5965 (10)	−0.0339 (7)
C(2)	0.1918 (2)	0.0965 (6)	0.0991 (4)	C(18)	0.0119 (3)	0.3494 (15)	−0.1230 (7)
C(3)	0.1662 (2)	0.0588 (6)	0.1438 (4)	C(19)	0.0282 (3)	0.1650 (12)	0.0404 (11)
C(4)	0.1749 (2)	0.1453 (7)	0.2157 (4)	C(20)	0.0793 (3)	0.3277 (14)	0.2280 (6)
C(5)	0.2065 (2)	0.2377 (7)	0.2149 (4)	C(21)	0.1991 (2)	0.5822 (8)	0.0981 (5)
C(6)	0.2523 (2)	0.2739 (8)	0.1269 (5)	C(22)	0.2038 (2)	0.6108 (7)	0.0200 (5)
C(7)	0.1941 (2)	0.0264 (8)	0.0229 (4)	C(23)	0.1798 (2)	0.5153 (8)	−0.0408 (5)
C(8)	0.1393 (3)	−0.0640 (8)	0.1272 (6)	C(24)	0.0891 (3)	0.1670 (9)	−0.1766 (5)
C(9)	0.1628 (2)	0.1232 (9)	0.2938 (4)	C(25)	0.0653 (2)	0.0531 (9)	−0.1914 (5)
C(10)	0.2259 (2)	0.3482 (8)	0.2821 (4)	C(26)	0.0654 (2)	0.0253 (9)	−0.1103 (6)
C(11)	0.0845 (2)	0.4716 (8)	0.1044 (5)				

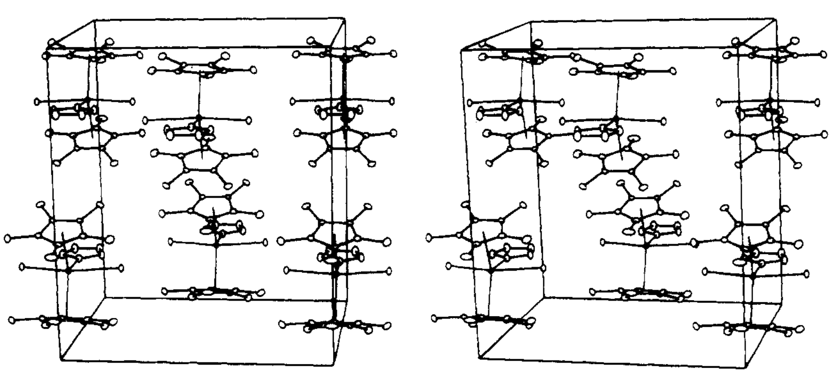

Figure 2. Stereoscopic drawing of the unit cell of $UCp''_2Cl_2(pz)$.

= 0.525 e/Å^3) were near the methyl carbons of the Cp″ rings. Hydrogen atoms were not found, nor were calculated positions included in the final calculations. The residuals showed no anomalies. Positional and thermal parameters appear in Tables IV and IVa.[19]

$UCp''_2(pz^-)_2$. Crystals suitable for diffraction experiments were obtained by slow cooling of a toluene solution to −15 °C. Precession photographs revealed conditions indicating space groups *Cc* or *C*2/*c* (hkl, $h + k = 2n$, and $h0l$, $l = 2n$). Lattice parameters are in Table II. A total of 3737 $+h,+k,\pm l$ data (for $h + k = 2n$) were collected between 4 and 45° in 2θ. Twice during data collection reorientation of the crystal was required. Azimuthal scans on seven reflections with θ between 5 and 22° revealed an intensity variation of ±10%. The crystal faces were identified and measured as described before. The absorption correction applied ranged from 1.91 to 2.77 (μ = 60.52 cm^{-1}). No crystal decay was observed during data collection.

The initial Patterson map confirmed the space group *C*2/*c*, and the structure was solved by heavy-atom techniques. In the final refinements, the temperature factors of all atoms were treated anisotropically, the model converging to weighted and unweighted *R* factors of 3.31% and 2.43%, respectively. On the final cycle, the largest parameter shift was 0.63σ for one of the methyl carbons on Cp''_2. This ring has generally greater thermal motion than the other parts of the molecule. In the final difference Fourier map the largest peak at a grid point was 0.36 e/Å^3 and was more than 1.6 Å from any atom or other peak. Hydrogen atoms were not found, nor were calculated positions included in the final calculations. The residuals showed no

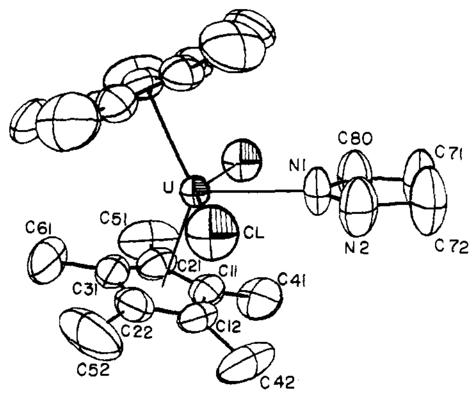

Figure 3. ORTEP drawing of the molecular unit of $UCp''_2Cl_2(pz)$.

anomalies. Positional and thermal parameters are listed in Tables V and Va.[19]

Description of the Structures

$UCp''_2Cl_2(pz)$. The crystal structure consists of discrete mononuclear units at positions of *mm* symmetry (Figure 2). The closest intermolecular contact is 3.68 (1) Å between C(60) and C(71). The molecular structure consists of a uranium ion bound by two η^5-pentamethylcyclopentadienyl rings, two chloride ions, and one nitrogen from the pyrazole ring, for a formal coordination number of 9. Both the uranium and the bound nitrogen lie at the intersection of mirror planes, while the chlorides, C(31), C(61), and the remaining atoms of the pyrazole ring lie in the mirror planes.[19] All the other atoms are in general positions. A perspective drawing of the molecular unit is illustrated in Figure 3.

The uranium–carbon distances average 2.74 (2) Å, the U–Cl bond is 2.696 (2) Å, and the U–N bond is 2.607 (8) Å long. The closest intramolecular nonbonded contact is 3.07 (1) Å between Cl and C(80) and N(2). The Cl–U–Cl angle of 148.29(8)° is (by symmetry) bisected by the U–N bond. The Cl–U–Cp″ (centroid) angle is 95.7°, and the Cp″–U–Cp″ angle is 137.1°. The Cp″–U–N(1) angle is 111.4°. Pertinent bond angles and distances are listed in Table VI.

$UCp''_2Cl(pz^-)$. The crystal structure consists of discrete mononulcear units at general positions in the unit cell (Figure 4). The closest intermolecular contact is 3.41 (3) Å between C(17) and C(20′). The molecular structure consists of a uranium ion coordinated by two η^5-pentamethylcyclopentadienyl rings, one chloride ion, and two nitrogens from the pyrazolate ion for a formal coordination number of 9. The coordination geometry is very roughly tetrahedral—when considering the chloride, the Cp″ centroids, and the midpoint of the N–N bond as the ligands. The angles from both the

Table VI. Bond Distances (Å) and Angles (Deg) for $UCp''_2Cl_2(pz)$

U–Cl	2.696 (2)	C(71)–C(72)	1.384 (16)
U–C(11)	2.722 (5)	U–C(av)	2.74 (2)
U–C(21)	2.737 (5)	C(11)–C(12)	1.410 (11)
U–C(31)	2.756 (7)	C(11)–C(21)	1.422 (7)
U–N(1)	2.607 (8)	C(11)–C(41)	1.525 (8)
C(31)–C(61)	1.525 (12)	C(21)–C(31)	1.396 (7)
N(1)–C(80)	1.327 (14)	C(21)–C(51)	1.535 (7)
C(80)–C(71)	1.401 (17)		
Cl–U–Cl	148.29 (8)	Cp–U–N(1)	111.44 (1)
Cl–U–N(1)	74.14 (4)	Cp–U–Cp	137.1
Cl–U–Cp	95.73 (1)		
C(12)–C(11)–C(21)	108.0 (3)	C(21)–C(31)–C(61)	124.5 (3)
C(12)–C(11)–C(41)	123.9 (4)	C(21)–C(31)–C(22)	110.1 (7)
C(41)–C(11)–C(21)	127.8 (6)	N(2)–N(1)–C(80)	106 (1)
C(11)–C(21)–C(51)	126.6 (6)	N(1)–C(80)–C(71)	111 (1)
C(11)–C(21)–C(31)	107.0 (5)	C(80)–C(71)–C(72)	105.4 (6)
C(51)–C(21)–C(31)	125.9 (6)		

N–N midpoint and the chloride to each of the other three ligands are approximately equal; either serves as the apex of a tetrahedron in which the basal angles are distorted by the 136° angle between the Cp″ centroids. Figure 5 illustrates the molecular structure utilizing one nominal orientation for each Cp″ ring.

The uranium–carbon distances range between 2.69 (1) and 2.78 (1) Å, averaging 2.73 (3) Å. The U–N distances are 2.351(5) and 2.349 (5) Å. The U–Cl distance is 2.611 (2) Å. Within a molecule, the closest interligand nonbonded contact is 3.00 (2) Å between N(1) and C(16′). Selected bond lengths and angles appear in Table VII.

Least-squares planes for the four Cp″ rings show all but those of C(11)–C(15) are planar to about one sigma; C(13) and C(14) are about 2σ from their least-squares plane. The methyl carbons generally are tilted away from the uranium by 0.1 Å (5–15σ); one methyl carbon from each ring, however, is much more nearly coplanar with the internal carbons of the ring to which it belongs. The pyrazolate ring is planar to within 1σ, and the three pyrazolate carbon atoms are about 1σ from the UN_2 plane.[19]

$UCp''_2(pz^-)_2$. The crystal structure consists of discrete mononuclear units at general positions in the unit cell (Figure 6). The closest intermolecular contacts are 3.638 (8) and 3.637 (9) Å between C(10) and C(2) and C(2) and C(7), respectively. The molecular structure consists of the uranium ion coordinated by two η^5-pentamethylcyclopentadienyl rings and four nitrogens from the two pyrazolate rings, for a total formal coordination number of 10. The pyrazolates are adjacent and nearly coplanar while they oppose the two Cp″ rings, whose least-squares planes are about 40° from each

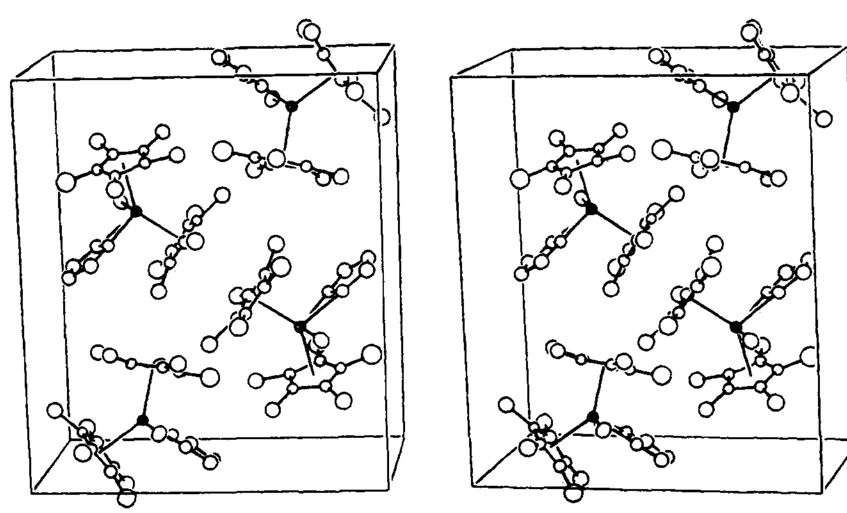

Figure 4. Stereoscopic drawing of the unit cell of $UCp''_2Cl(pz^-)$.

Table VII. Bond Distances (Å) and Angles (Deg)

a. For $UCp''_2Cl(pz^-)$

	U-X Distances		
C(1), C(1′)	2.72 (1), 2.75 (1)	C(11), C(11′)	2.72 (1), 2.73 (1)
C(2), C(2′)	2.69 (1), 2.75 (2)	C(12), C(12′)	2.74 (1), 2.73 (1)
C(3), C(3′)	2.72 (1), 2.77 (2)	C(13), C(13′)	2.75 (1), 2.74 (1)
C(4), C(4′)	2.72 (1), 2.76 (2)	C(14), C(14′)	2.78 (1), 2.70 (1)
C(5), C(5′)	2.70 (1), 2.73 (2)	C(15), C(15′)	2.70 (1), 2.69 (2)
N(1), N(2)	2.351 (5), 2.349 (5)	Cl	2.611 (2)
U-C(av)	2.73 (3)		
	Pyrazolate Distances and Angles		
N(1)-C(23)	1.354 (9)	around N(1)	104.5 (5)
C(23)-C(22)	1.318 (10)	around N(2)	107.7 (5)
C(22)-C(21)	1.343 (10)	around C(21)	109.9 (7)
C(21)-N(2)	1.367 (9)	around C(22)	104.4 (7)
N(2)-N(1)	1.348 (7)	around C(23)	113.4 (7)
	Interligand Angles		
Cp″-U-Cp″	136.2	Cp″(2)-U-(N-N)	107.4
Cp″(1)-U-Cl	102.5	Cl-U-(N-N)	103.2
Cp″(1)-U-(N-N)	104.6	N(1)-U-N(2)	33.3 (2)
Cp″(2)-U-Cl	98.4		

b. For Cp″(1) and Cp″(1′) in $UCp''_2Cl(pz^-)$

C(1)-C(2)	1.39 (2), 1.44 (2)	C(1)-C(6)	1.57 (2), 1.52 (3)
C(2)-C(3)	1.37 (2), 1.30 (3)	C(2)-C(7)	1.55 (2), 1.58 (3)
C(3)-C(4)	1.40 (2), 1.52 (3)	C(3)-C(8)	1.61 (2), 1.67 (4)
C(4)-C(5)	1.41 (2), 1.33 (3)	C(4)-C(9)	1.52 (2), 1.67 (3)
C(5)-C(1)	1.46 (2), 1.41 (3)	C(5)-C(10)	1.51 (2), 1.68 (3)
C(5)-C(1)-C(2)	107 (1), 107 (1)	C(5)-C(1)-C(6)	139 (2), 130 (2)
C(1)-C(2)-C(3)	108 (1), 91 (1)	C(2)-C(1)-C(6)	114 (2), 123 (2)
C(2)-C(3)-C(4)	112 (1), 106 (2)	C(1)-C(2)-C(7)	135 (2), 133 (3)
C(3)-C(4)-C(5)	106 (1), 108 (2)	C(3)-C(2)-C(7)	116 (2), 115 (3)
C(4)-C(5)-C(1)	107 (1), 108 (2)	C(2)-C(3)-C(8)	137 (2), 160 (3)
C(3)-C(4)-C(9)	140 (2), 158 (3)	C(4)-C(3)-C(8)	111 (1), 91 (3)
C(5)-C(4)-C(9)	113 (2), 94 (3)	C(1)-C(5)-C(10)	117 (2), 102 (2)
C(4)-C(5)-C(10)	136 (2), 149 (3)		

c. For Cp″(2) and Cp″(2′) of $UCp''_2Cl(pz^-)$

C(11)-C(12)	1.48 (2), 1.50 (2)	C(11)-C(16)	1.67 (2), 1.61 (2)
C(12)-C(13)	1.40 (2), 1.44 (2)	C(12)-C(17)	1.61 (2), 1.58 (2)
C(13)-C(14)	1.44 (2), 1.44 (2)	C(13)-C(18)	1.49 (2), 1.48 (2)
C(14)-C(15)	1.34 (2), 1.25 (2)	C(14)-C(19)	1.40 (2), 1.53 (3)
C(15)-C(11)	1.41 (1), 1.40 (2)	C(15)-C(20)	1.53 (3), 1.55 (3)
C(15)-C(11)-C(12)	104 (1), 103 (1)	C(15)-C(11)-C(16)	146 (2), 141 (2)
C(11)-C(12)-C(13)	109 (1), 110 (1)	C(12)-C(11)-C(16)	110 (2), 116 (2)
C(12)-C(13)-C(14)	106 (1), 100 (1)	C(11)-C(12)-C(17)	140 (2), 123 (1)
C(13)-C(14)-C(15)	110 (1), 116 (2)	C(13)-C(12)-C(17)	111 (2), 127 (1)
C(14)-C(15)-C(11)	112 (1), 113 (2)	C(12)-C(13)-C(18)	136 (2), 129 (2)
C(13)-C(14)-C(19)	131 (2), 121 (2)	C(14)-C(13)-C(18)	117 (2), 129 (2)
C(15)-C(14)-C(19)	119 (2), 122 (2)	C(11)-C(15)-C(20)	103 (2), 117 (2)
C(14)-C(15)-C(20)	146 (2), 132 (2)		

other (vide infra). A perspective drawing of the molecule appears in Figure 7, where one can see relatively high thermal motion in Cp''_2.

The U–C distances range from 2.724 (6) to 2.786 (5) Å, averaging 2.75 (2) Å. The U–N distances are 2.403 (4), 2.360 (5), 2.363 (5), and 2.405 (5) Å. The closest intramolecular nonbonded contact is 3.006 (6) Å between N(2) and N(3). Selected bond lengths and angles appear in Table VIII.

The internal carbons of both Cp″ rings are essentially planar, deviations from the least-squares plane being on the order of 1σ.[19] Again, the methyl carbons all bend away from the uranium ion by a few tenths of an Å. Both pyrazolates are planar. The average deviation from the UN_4 least-squares plane is 0.003 Å (ca. 5σ). The angles between the least-squares planes of the Cp″ rings is 41.4°, that between the pyrazolates is 5.6°, and those between the Cp″ rings and the pyrazolates are 20.2, 25.3, 21.6, and 16.1° (Cp″(1)–pz⁻(1,2); Cp″(2)–pz⁻(1,2)).

Table VIII. Bond Distances (Å) and Angles (Deg) for $UCp''_2(pz^-)_2$

U-X Distances

C(1)	2.753 (5)	C(11)	2.753 (6)	N(1)	2.403 (4)
C(2)	2.740 (5)	C(12)	2.738 (6)	N(2)	2.360 (5)
C(3)	2.759 (5)	C(13)	2.735 (6)	N(3)	2.363 (5)
C(4)	2.786 (5)	C(14)	2.724 (6)	N(4)	2.405 (5)
C(5)	2.763 (5)	C(15)	2.757 (6)	U-C(av)	2.75 (2)

Pyrazolate Distances

N(1)-N(2)	1.349 (6)	N(3)-N(4)	1.348 (7)
N(1)-C(21)	1.362 (8)	N(3)-C(24)	1.352 (8)
C(21)-C(22)	1.411 (9)	C(24)-C(25)	1.388 (11)
C(22)-C(23)	1.386 (10)	C(25)-C(26)	1.380 (11)
C(23)-N(2)	1.373 (8)	C(26)-N(4)	1.371 (8)

Angles of Interest[a]

Cp″(1)-U-Cp″(2)	137.2	Cp″(2)-U-N(3,4)	101.7
Cp″(1)-U-N(1,2)	101.2	N(1,2)-U-N(3,4)	112.2
Cp″(1)-U-N(3,4)	103.1	N(1)-U-N(2)	32.9
Cp″(2)-U-N(1,2)	100.9	N(3)-U-N(4)	32.8

[a] N(*x*,*y*) is the midpoint of the N(*x*)-N(*y*) bond.

Discussion

Recently several dipentamethylcyclopentadienylactinide structures have been reported, principally of Th^{4+} and U^{3+} compounds. These include $UCp''_2(CONMe_2)_2$,[20] $[UCp''_2Cl]_3$,[6] $[ThCp''_2H_2]_2$,[21] $[ThCp''_2O_2C_2Me_2]_2$,[22] $ThCp''_2Cl(COCH_2CMe_3)$,[23] and $ThCp''_2Cl(CONEt_2)$.[20] In addition,

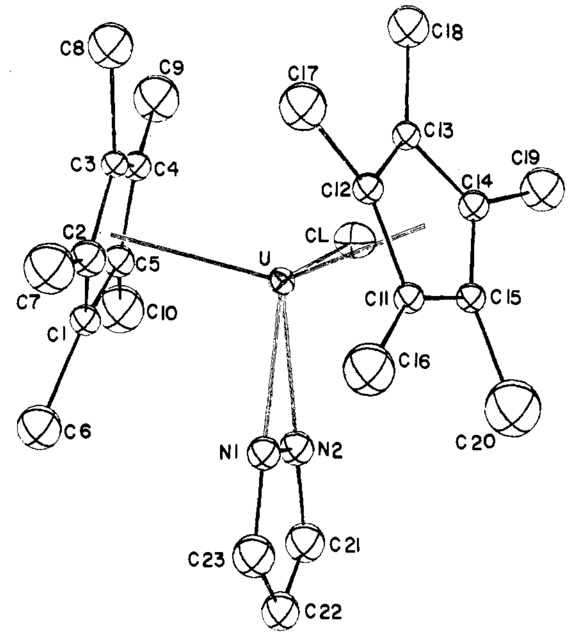

Figure 5. ORTEP drawing of the molecular unit of $UCp''_2Cl(pz^-)$.

the structure of a number of Ti^{4+} and Zr^{4+} compounds of the type MCp_2X_2 have been reported.[24,25]

In comparison with Cp itself, the larger size of the methylated Cp rings means fewer of the latter are able to share a coordination sphere, as occurs in the numerous compounds with unsubstituted Cp rings of general formula MCp_3X.[26] The Cp–U–Cp angles in the latter are less than 120°, whereas the present compounds share a value for this angle of about 137°. All the Cp″ ligands characterized here exhibit the outward bending of the methyl groups, as is quite common for this ligand. The U–Cl distance in $UCp''_2Cl(pz^-)$ (2.611 Å) is similar to those found in other U^{4+} organometallic compounds,[27-30] but the U–Cl distance in $UCp''_2Cl_2(pz)$ [2.696 (2) Å] is considerably longer. This is probably best attributed to the relatively greater crowding the chloride in $UCp''_2Cl_2(pz)$ experiences—one might also consider this complex to have a higher coordination number than $UCp''_2Cl\ (pz^-)$, in which the η^2-N_2 coordination is intermediate between a mono- and bidentate ligand in steric bulk.

The average U–C(ring) distances are nearly identical for the three compounds, and the two Cp rings bear a constant relationship to each other of 137°. In $UCp''_2Cl_2(pz)$, the two Cp″ centroids and N(1) are coplanar by symmetry. The 137° angle between centroids leaves 111.5° between each of the centroids and N(1); the Cp″–U–Cl angle is 95° (Table IX).

In $UCp''_2Cl(pz^-)$, the angles from the Cp rings to the other ligands is increased from 95° by the removal of one ligand.

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Table IX. Comparisons between $UCp''_2Cl_2(pz)$, $UCp''_2Cl(pz^-)$, and $UCp''_2(pz^-)_2$[a]

	HPYZ	1:1	1:2
coord number	9	9	10
U-C(av), Å	2.74 (2)	2.73 (3)	2.75 (2)
U-Cl, Å	2.696 (2)	2.611 (2)	
U-N, Å	2.607 (8)	2.351 (5) 2.349 (5)	2.403 (4) 2.360 (5) 2.363 (5) 2.405 (5)
Cp″-U-Cp″, deg	137	136	137
Cp″-U-N, deg	111.4		
Cp″-U-(N-N), deg		107.4 104.6	101.2 103.1 100.9 101.7
X-U-(N-N),[b] deg	74.14 (X = Cl)	103.2 (X = Cl)	112.2 (X = N-N)
Cp″-U-Cl, deg	95.7 (X = Cl)	102.5 (X = Cl) 98.4 (X = Cl)	

[a] HPYZ is $UCp''_2Cl_2(pz)$, 1:1 is $UCp''_2Cl(pz^-)$, and 1:2 is $UCp''_2(pz^-)_2$. [b] These angles represent Cl-U-N(1) for $UCp''_2Cl_2(pz)$, Cl-U-(N-N) for $UCp''_2Cl(pz^-)$, and (N-N)-U-(N-N) for $UCp''_2(pz^-)_2$.

Table X. Distances (Å) and Angles (Deg) from Some Reported Structures

compd	Cp″-M-Cp″	M-C(ring)(av)	coord no.	ref
$(ThCp''_2H_2)_2$	130	2.83 (1)	9	21
$(ThCp''_2O_2C_2Me_2)_2$	129	2.83 (6)	8	22
$ThCp''_2Cl(COCH_2CMe_3)$	138	2.80 (3)	9	23
$ThCp''_2Cl(CONEt_2)$	138	2.78 (4)	9	20
$UCp''_2(CONMe_2)_2$	138	2.79 (4)	10	20

Also as a result of fewer ligands, the Cl–U–(N–N) [where N–N represents the midpoint of the N–N bond] angle relaxes to 103 from the 148° for the Cl–U–Cl angle in $UCp''_2Cl_2(pz)$. In going to $UCp''_2(pz^-)_2$, substitution of a sterically larger pyrazolate for the remaining chloride results in an increase in the (N–N)–U–(N–N) angle relative to the Cl–U–(N–N) angle in $UCp''_2Cl(pz^-)$, while also the Cp″–U–(N–N) angles decrease slightly, on average. This behavior is the same as that seen in the thorium compounds (Table X). The Cp″–Th–Cp″ angle is nearly constant in going from the bridging hydride ligands to the larger bridging enediolate ligands; however in the monomeric species, where crowding is decreased, much larger angles were found. We see, in general, that the interligand relationships in these compounds can be explained by ligand repulsion.

In $UCp''_2(pz^-)_2$, Cp″(2) exhibits much more thermal motion than Cp″(1). This is probably the result of the fact that Cp″(2) has fewer nonbonded neighbors than Cp″(1). For instance, the closest intermolecular contact in this compound is 3.64 Å and involves atoms of Cp″(1) (vide supra). The closest such contact for Cp″(2) is 3.72 Å [C(19)–C(19)]. In addition, Cp″(1) has 33 intermolecular contacts within 4.5 Å, while Cp″(2) has only 29.

The disorder in $UCp''_2Cl(pz^-)$ can also be explained in terms of intermolecular contacts. Although the closest intermolecular contact is shorter than in $UCp''_2\ (pz)_2$ [3.413 (3) vs. 3.638 (8) Å], in $UCp''_2Cl(pz^-)$, Cp″(2) and Cp″(2′) have only 34 contacts within 4.5 Å, or 17 contacts per 5 methyl carbons. The occupancy factors (%) for Cp″(1) refined to 62/38, while for Cp″(2) they refined to 50/50. The fact that Cp″(1) has many more contacts (32 per 5 methyl carbons) explains its greater preference for one orientation over the other, inasmuch as the orientation is determined by the intermolecular environment.

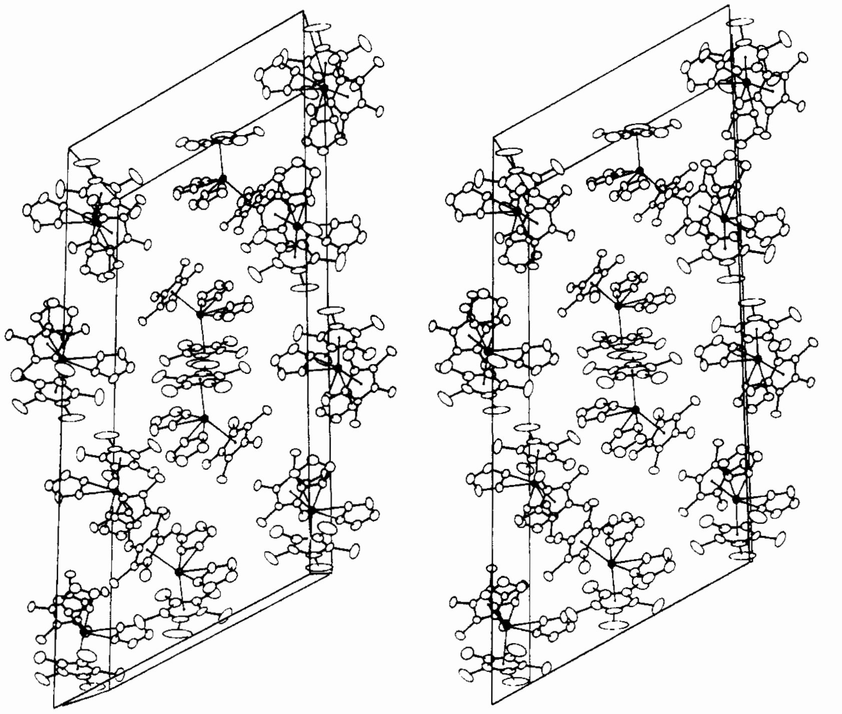

Figure 6. Stereoscopic drawing of the unit cell of $UCp''_2(pz^-)_2$.

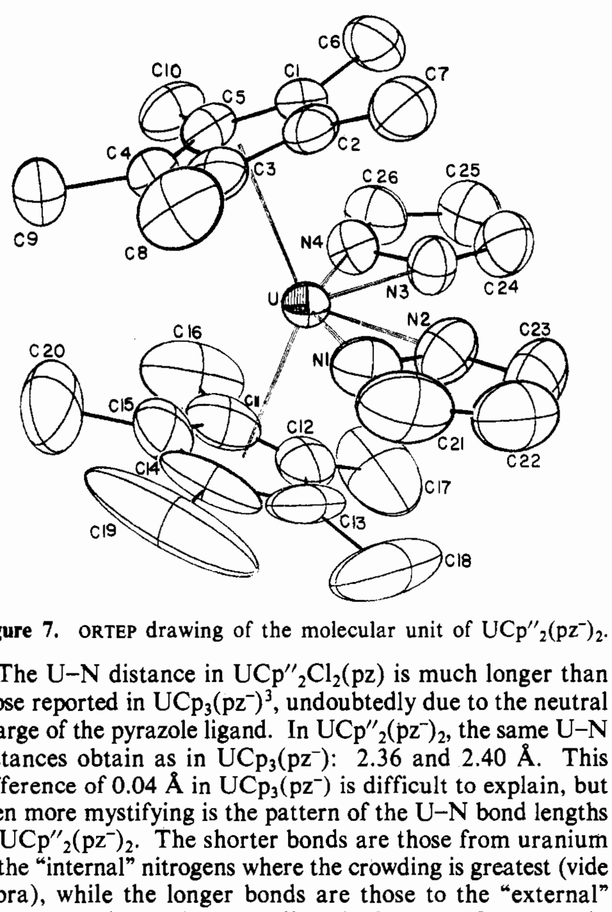

Figure 7. ORTEP drawing of the molecular unit of $UCp''_2(pz^-)_2$.

The U–N distance in $UCp''_2Cl_2(pz)$ is much longer than those reported in $UCp_3(pz^-)^3$, undoubtedly due to the neutral charge of the pyrazole ligand. In $UCp''_2(pz^-)_2$, the same U–N distances obtain as in $UCp_3(pz^-)$: 2.36 and 2.40 Å. This difference of 0.04 Å in $UCp_3(pz^-)$ is difficult to explain, but even more mystifying is the pattern of the U–N bond lengths in $UCp''_2(pz^-)_2$. The shorter bonds are those from uranium to the "internal" nitrogens where the crowding is greatest (vide supra), while the longer bonds are those to the "external" nitrogens where the crowding is least. However, in $UCp''_2Cl(pz^-)$ the U–N distances are identical, as we expected.

Of the other physical properties of these compounds, a few are worthy of mention. The ^1H NMR, spectrum of $UCp''_2Cl_2(pz)$ reveals a fluxionality of the pyrazole ligand. At low temperatures, four resonances are resolved that can be assigned to the pyrazole. Those most strongly shifted can be assigned to the C–H and N–H adjacent to the metal-bound nitrogen, while those less strongly shifted are the protons further from the uranium. By room temperature, the four resonances collapse into a broad singlet and a very broad resonance, indicative of a fluxional U–N bond that makes all the carbon bound protons nearly equivalent and leaves the remaining proton's resonance quite broad and less strongly shifted than previously.

The magnetic behavior of both $UCp''_2Cl_2(pz)$ and $UCp''_2Cl(pz^-)$ is as one expects for U^{4+} ions. However, $UCp''_2(pz^-)_2$ does not exhibit similar magnetic behavior. Instead of decreasing with increasing temperature from an initial high value as the others, the susceptibility of $UCp''_2(pz^-)_2$ has its *minimum* at low temperature and *increases* as the temperature increases, until it becomes relatively invariant with temperature.

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Supplementary Material Available: Listings of thermal parameters (Tables IIIa, IVa, and Va), least-squares planes (Tables XI–XIII), and structure factors (40 pages). Ordering information is given on any current masthead page.