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ORGANOURANIUM COMPLEXES OF PYRAZOLE AND PYRAZOLATE. SYNTHESIS AND X-RAY STRUCTURES OF U(C5Me5)2 Cl2(C3H4N2), U(C5Me5)2C1(C3H4N2), AND U(C5Me5)2 (C3H3N2)2

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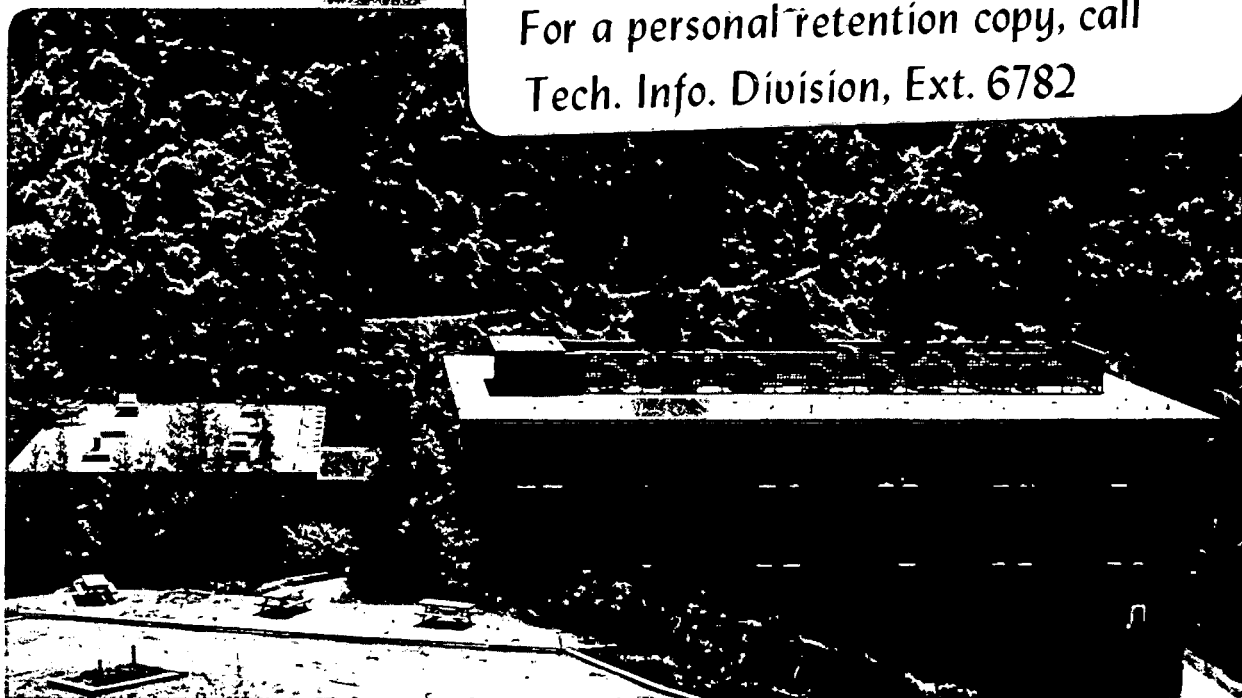
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ORGANOURANIUM COMPLEXES OF PYRAZOLE AND PYRAZOLATE.
SYNTHESIS AND X-RAY STRUCTURES OF $U(C_5Me_5)_2Cl_2(C_3H_4N_2)$,
$U(C_5Me_5)_2Cl(C_3H_4N_2)$, AND $U(C_5Me_5)_2(C_3H_3N_2)_2$

Charles W. Eigenbrot, Jr. and Kenneth N. Raymond

July 1981

DISCLAIMER

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 $U(C_5Me_5)_2(C_3H_3N_2)_2$

By

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Running Title: Organouranium Pyrazole and Pyrozolate Complexes

Abstract

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, pmr, visible near-IR, and mass spectra; and by single crystal X-ray diffraction (monochromatic MoK_α 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 nine. Red-brown crystals from toluene conform to space group Cmcm with a = 13.697(4), b = 11.496(2), 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 nine. Red-brown crystals from toluene conform to space group $P2_1/n$ with a = 8.737(1), b = 18.068(1), 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 disance is 2.73(3) Å, the U-N

distances are 2.351(5) Å and 2.349(5) Å, and the U–Cl distance is 2.611(2) Å. This compound exhibits Curie–Weiss behavior with $C = 0.73$, $\theta = 5.95$ K, and $\mu_{eff} = 2.42$ 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 ten. Red–brown crystals from toluene conform to space group C2/c with $a = 33.326(2)$, $b = 10.450(2)$, $c = 16.646(1)$ Å, $\beta = 117.09(1)°$, and eight molecules per unit cell. For the 2706 indpendent 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(pyrazolate)[3] revealed that our attempt to form a dimer (based on a precedent in titanium chemistry, $[TiCp_2$(pyrazolate)$]_2$),[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 compund UCp''_2Cl_2 ($Cp''=C_5Me_5$) has proven to be a useful starting material for other studies,[5,6] but does not produce dimers. Instead, the compounds $U(C_5Me_5)_2Cl$(pyrazolate) and $U(C_5Me_5)_2$(pyrazolate)$_2$ are formed by the reaction between $U(C_5Me_5)_2Cl_2$ and stoichiometric amounts of Na(pyrazolate). In the course of this study, an adduct of neutral pyrazole, $U(C_5Me_5)_2Cl_2$(pyrazole) was also characterized.

Experimental

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 Atmostphere HE-93-A glove box with recirculating moisture and oxygen-free argon atmosphere. Elemental analyses were performed by the Microanalytical Laboratory UC Berkeley. Infra-red 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 pmr spectra obtained with the UCB-250 nmr spectrometer (in d^8-toluene, shifts in δ ppm vs. TMS). Magnetic susceptibilities were determined as described elsewhere,[3] and are corrected for under-lying diamagnetism.[7] Crystalline samples for X-ray diffraction were mounted in glass capillaries under a He atmosphere in a horizontal-format inert atmosphere glove box 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) UCl_4 in THF was added 6.87 g (39.5 mmol) $K(C_5Me_5)$ (prepared by the reaction between KH and HC_5Me_5 in THF). The total of 200 ml THF was maintained at reflux under Argon for 24 h. After removal of solvent, the residue was extracted several times with a total of 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"$_2$Cl$_2$(pyrazole)

To a red-brown solution of 0.55 g (0.9 mmol) U(C$_5$Me$_5$)$_2$Cl$_2$ in 75 ml THF was added 0.06 g (0.9 mmol) pyrazole. The solution was stirred overnight at room temperature. After solvent removal, the red-brown residue was washed with hexane, then dissolved in toluene and this solution cooled to -15°C. After 12 hours, the large crystals that had formed were filtered and an IR spectrum clearly revealed an N-H stretch at 3100 cm^{-1}. Analysis UC$_{23}$H$_{34}$N$_2$Cl$_2$-- found: %C, 43.26; %H, 5.55; %N, 4.38; calculated: %C, 42.66; %H, 5.29; %N, 4.33.

Infra-red spectrum

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, 1590, 1423, 1400, 1168, 1133, 1118, 1095, 1049, 990, 908, 880, 858, 817, 790, 730, 718, 708, 691, 680.

PMR spectrum

At 22°C. 11.49 (s, ~40 Hz, 30H, methyl); -9.58 (s, ~200 Hz, 2H, pyrazole); -28.63 (~1500 Hz, 1H, 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, 30H, methyl); -20.0 (s, ~80 Hz, 1H,

pyrazole); -21.2 (s, ~90 Hz, 1H, pyrazole); -58.1 (s, ~205 Hz, 1H, pyrazole); -80.2 (s, ~250 Hz, 1H, pyrazole).

Magnetic susceptibility

This compound exhibits Curie-Weiss behavior with C = 1.46 and Θ = 42.34 K. Table Ia includes χ_M^{corr} versus T. The slope of $1/\chi_M^{corr}$ versus T yields μ_{eff} = 3.42 μ_B.

$U(C_5Me_5)_2Cl$(pyrazolate).

About 150 ml THF was vacuum distilled from potassium benzophenone ketyl onto a mixture of 1.00 g (1.7 mmol) UCp_2Cl_2 and 0.16 g (1.8 mmol) Na(pyrazolate). The reaction was warmed to room temperature and stirred 12 hours. 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. Analysis $UC_{23}H_{33}N_2Cl$— calculated: %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.

Infra-red spectrum

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, 1635, 1562, 1440, 1290, 1259, 1175, 1122, 1095, 1040, 967, 920, 907, 872, 855, 826, 773, 721, 713, 700, 660, 600.

PMR spectrum

12.956 (s, ~84 Hz, 2H, pyrazolate); 8.098 (s, ~30 Hz, 30H, Me).

Magnetic susceptibility

This compound exhibits Curie-Weiss behavior with C = 0.73 and

Θ = 5.95 K. Table Ib includes χ_M^{corr} versus T. The slope of $1/\chi_M^{corr}$

versus T yields μ_{eff} = 2.42 μ_B.

$U(C_5Me_5)_2(pyrazolate)_2$

Onto a mixture of 1.35 g (2.3 mmol) $U(C_5Me_5)_2Cl_2$ and 0.42 g (4.7

mmol) Na(pyrazolate) was distilled about 200 ml THF from potassium

benzophenone ketyl. The resulting red-brown solution was stirred at

room temperature for 24 hours 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.

Analysis $UC_{26}H_{36}N_4$—calculated: %C, 48.59; %H, 5.65; %N, 8.72; found:

%C, 48.72; %H, 5.71; %N, 8.80.

Infra-red spectrum

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, 1317, 1262, 1183, 1124, 1089, 982, 950, 930, 855, 834, 745, 691, 661, 582.

PMR spectrum

29.09 (s, ~30 Hz, 2H, pyrazolate); 27.44 (s, ~200 Hz, 4H, pyrazolate); -0.20 (s, 30H, ~7 Hz, methyl).

Magnetic susceptibility

This compound does not exhibit simple behavior. Table Ic includes χ_M^{corr} vs. T, and Figure 1 illustrates $1/\chi_M^{corr}$ vs. T.

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

UCp''_2Cl_2 (pyrazole)

Suitable crystals for diffraction were grown by cooling a saturated hexane solution to -15°C. Precession photographs revealed orthorhomblic symmetry and the conditions: hkl, h + k = 2n and h0l, l = 2n. These are consistent with the space groups: Cmcm, Cmc2$_1$, and Ama2. The crystal was oriented and lattice parameters accurately determined by 25 automatically centered reflections (Table II).

A total of 1071 data were collected between 4° and 52° 2θ, for +h, +k, +l, and h + k = 2n. During data collection, one reorientation was required. Azimuthal scans on 5 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 8 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 refine-

ment. 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 .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

.18σ. The largest peak in the final difference Fourier was .4$\frac{e^-}{A^3}$ and was

less than one Angstrom 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 Table III.

UCp"$_2$Cl(pyrazolate)

Crystals suitable for diffraction studies were obtained by cooling

a concentrated hexane 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 in Table II.

A total of 3513 +h, +k, ±1 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 .29σ, while for those 7 atoms not involved in the disorder the largest shift was .02σ. The residual peaks in the final difference Fourier (largest = .525 $\frac{e^-}{A^3}$) 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 Table IV.

UCp"$_2$(pyrazolate)$_2$

Crystals suitable for diffraction experiments were obtained by slow
cooling of a hexane solution to -15°C. Precession photographs revealed
conditions indicating space groups Cc or C2/c (hkl, h + k = 2n, and
hol, l = 2n). Lattice parameters are in Table II. A total of 3737
+h, +k, l data (for h + k = 2n) were collected between 4° and 45° 2Θ.
Twice during data collection reorientation of the crystal was required.
Azimuthal scans on 7 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 C2/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 dif-
ference Fourier map the largest peak at a grid point was 0.36$\frac{e}{A^3}$, and was
more than 1.6 A from any atom or other peak. Hydrogen atoms were not
found, nor were calculated positions included in the final calculations.
The residuals showed no anomalies. Positional and thermal parameters
are listed in Table V.

Description of the Structures

UCp"$_2$Cl$_2$(pyrazole)

The crystal structure consists of discrete mononuclear units at positions of mm symmetry (Fig 2). The closest intermolecular contact is 3.68(1)A 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(3), C(6), 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)A, the U-Cl bond is 2.696(2)A, and U-N bond is 2.607(8)A long. The closest intramolecular non-bonded contact is 3.07(1)A between Cl and C(80). 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 angle is 111.4°. Pertinent bond angles and distances are listed in Table VI.

UCp"$_2$Cl(pyrazolate)

The crystal structure consists of discrete mononuclear units at general positions in the unit cell (Fig 4). The closest intermolecular contact is 3.41(3)A between C(17) and C(20'). The molecular strucure consists of a uranium ion coordinated by two η^5-pentamethylcyclopenta-dienyl 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 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)A and 2.78(1)A, averaging 2.73(3)A. The U-N distances are 2.351(5)A and 2.349(5)A. The U-Cl distance is 2.611(2)A. Within a molecule, the closest inter-ligand non-bonded contact is 3.00(2)A between N(1) and C(16'). Selected bond lengths and angles appear in Table VII.

Least-squares planes for the 4 Cp" rings show all but that of C's 11-15 are planar to about one sigma; C's 13 and 14 are about two sigma from their least-squares plane. The methyl carbons generally are tilted away from the uranium by tenths of an Angstrom (5-15 sigma); 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 one sigma, and the three pyrazolate carbon atoms are about one sigma from the UN_2 plane.[19]
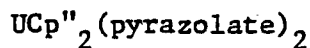
$UCp"_2(pyrazolate)_2$

The crystal structure consists of discrete mononuclear units at general positions in the unit cell (Fig 6). The closest intermolecular contacts are 3.638(8) and 3.637(9)A between C(10) and C(2) and C(7)

respectively. The molecular structure consists of the uranium ion coordinated by two η^5-pentamethylcyclopentadiene rings from 4 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 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-carbon distances range from 2.724(6)A to 2.786(5)A, averaging 2.75(2)A. The U-N distances are 2.403(4)A, 2.360(5)A, 2.363(5)A, and 2.405(5)A. The closest intramolecular non-bonded contact is 3.006(6)A between N's 2 and 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 on one σ.[19] Again, the methyl carbons all bend away from the uranium ion by a few tenths of an Angstrom. Both pyrazolates are planar. The average deviation from the UN_4 least squares plane is 0.003A (ca. 5 σ). The angles between the least squares planes of the Cp" rings is 41.4°, between the pyrazolates is 5.6°, and between the Cp"s and the pyrazolates 20.2°, 25.3°, 21.6°, and 16.1° (Cp"1-pyz1,2;;Cp"2-pyz1,2).

Discussion

These structures constitute the first formal reports of bis-pentamethylCp uranium 4+ compounds. Marks has presented unpublished results on the structure of $UCp"_2(CONMe_2)_2$[20] and has published structural results on $[UCp"_2Cl]_3$,[6] $[ThCp"_2H_2]_2$,[21] and $[ThCp"_2O_2C_2Me_2]_2$.[22] More unpublished results include the structure of $ThCp"_2Cl(COCH_2CMe_3)$ and $ThCp"_2Cl(CONEt_2)$.[20]

In addition, the structure of numberous Ti^{4+} and Zr^{4+} compounds of the type MCp_2X_2 have been reported.[23,24]

In comparison with Cp itself, the larger size of the methylated Cp rings means fewer of them are able to share a coordination sphere, as in the numerous compounds with unsubstituted Cp rings of general formula MCp_3X.[25] 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 $UCp''_2Cl(pyrazolate)$ (2.611 A) is similar to those found in other U^{4+} organometallics,[26-29] but the U-Cl distance in $UCp''_2Cl_2(pyrazole)$ (2.696(2)A) is considerably longer. This is probably best attributed to the relatively greater crowding the chloride in $Cp''_2Cl_2(pyrazole)$ – one might also consider this complex to have a higher coordination number than the pyrazolate, in which the $\eta^2 N_2$ 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 $UCp''_2Cl_2(pyrazole)$, 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 $UCp''_2Cl(pyrazolate)$, the angles from the Cp"'s to the other ligands is increased from 95° by the removal of one ligand. Also as a result of fewer ligands, the Cl-U-(N-N) angles relaxes to 103° from the 148° for the Cl-U-Cl angle in $UCp''_2Cl_2(pyrazole)$. In going to $UCp''_2(pyrazolate)_2$,

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(pyrazolate), 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 decreases in going from the small bridging hydride ligands to the larger bridging enediolate ligands, and the monomeric species, where crowding is decreased, exhibit the largest angles. We see, then, that the interligand relationships in these compounds can be explained by ligand repulsion.

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

The disorder in UCp''_2Cl(pyrazolate) can also be explained in terms of intermolecular contacts. Although the closest intermolecular contact is shorter than in UCp''_2(pyrazolate)$_2$ (3.413(3)A vs. 3.638(8)A), in UCp''_2Cl(pyrazolate), Cp''(2) and Cp''(2') have only 34 contacts within 4.5 A, 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.

The U-N distance in UCp''_2Cl_2(pyrazole) is much longer than those reported in UCp_3(pyrazolate)[3]; undoubtedly due to the neutral charge of the pyrazole ligand. In UCp''_2(pyrazolate)$_2$, the same U-N distances obtain as in UCp_3(pyrazolate): 2.36A and 2.40A. This difference of 0.04A in UCp_3(pyrazolate) is difficult to explain, but even more mystifying is the pattern of the U-N bond lengths in UCp''_2(pyrazolate)$_2$. 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(pyrazolate) the U-N distances are identical, as we expect.

Of the other physical properties of these compounds, a few are worthy of mention. The pmr spectrum of UCp''_2Cl_2(pyrazole) reveals a fluxionality of the pyrazole ligand. At low temperature, 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(pyrazole) and UCp''_2Cl(pyrazolate) is as one expects for U^{4+} ions. However, UCp''_2(pyrazolate)$_2$ 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(pyrazolate)$_2$ has its minimum at low temperature

and _increases_ as the temperature increases, until it becomes relatively
invariant with temperature.

Acknowledgment

Supplemental Material

Ordering information is given on any current masthead page.

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$$F_o^2 = \frac{\omega(C - 2B)}{Lp}$$

$$F_o = (F_o^2)^{1/2}$$

$$\sigma_o(F_o^2) = \frac{\omega(C + 4B)^{1/2}}{Lp}$$

$$\sigma_o(F_o) = \frac{\sigma_o(F_o^2)}{2F_o}$$

where C is the total count in the scan, B is the sum of the 2 back-
ground counts, ω is the scan speed in degrees per minute, and

$$\frac{1}{Lp} = \frac{\sin2\theta(1 + \cos^2 2\theta_m)}{1 + \cos^2 2\theta_m - \sin^2 2\theta}$$

is the correction for Lorentz and polarization effects for a reflec-
tion with scattering angle 2θ and radiation monocromatized with a
50% perfect single-crystal monochromator with scattering angle $2\theta_m$.

15. $$R = \frac{\Sigma||F_o| - |F_o||}{\Sigma|F_o|}$$

$$R_w = \left|\frac{\Sigma w(|F_o| - |F_c|)^2}{\Sigma w F_o^2}\right|^{1/2}$$

$$GOF = \left|\frac{\Sigma w(|F_o| - |F_c|)^2}{(n_o - n_v)}\right|^{1/2}$$

where n_o is the number of observations and n_v is the number of

variable parameters, and the weights w are given by $w = \dfrac{4F_o^2}{\sigma^2(F_o^2)}$,

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.

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Table I. Magnetic Susceptibility Data

a) UCp''_2Cl_2(pyrazole)		b) UCp''_2Cl(pyrazolate)		c) UCp''_2(pyrazolate)$_2$	
T (K)	$\chi_M^{corr} \times 10^3$ (cm^3/mol)	T (K)	$\chi_M^{corr} \times 10^3$ (cm^3/mol)	T (K)	$\chi_M^{corr} \times 10^3$ (cm^3/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

Table II. Cell Parameters for UCp''_2Cl_2(pyrazole),

UCp''_2Cl(pyrazolate), and UCp''_2(pyrazolate)$_2$[a]

	HPYZ	1:1	1:2
space group	Cmcm	$P2_1/n$	C2/c
a(A)	13.697(4)	8.737(1)	33.326(2)
b(A)	11.496(2)	18.068(1)	10.450(2)
c(A)	15.555(2)	15.229(2)	16.646(1)
$\beta(°)$		92.38(1)	117.09(1)
Vol.(A^3)	2449.4(14)	2401.9(6)	5160.8(17)
2θ range(lattice constants)	26–40°	27–30°	26–35°
molecules/cell	4	4	8
$d_{calc}(g/cm^3)$	1.75	1.69	1.65
$d_{obs}(g/cm^3)$	1.77	1.68	1.66
2θ range(intensity data)	4–52°	4–45°	4–45°
observations	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(pyrazole), 1:1 is UCp''_2Cl(pyrazolate), and 1:2 is

   UCp''_2(pyrazolate)$_2$.

b) All data for monochromatic MoK_α radiation, λ = .71073 Å, at 22°C.

c) In each case a p factor of 0.03 was used, see reference 15.

Table III. Positional and Thermal Parameters and Their Estimated Standard Deviations for UCp″$_2$Cl$_2$(pyrazole)

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
U	0.0000(0)	0.22632(3)	0.2500(0)	0.00421(2)	0.00532(3)	0.00350(2)	0.0000(0)	0.0000(0)	0.0000(0)
Cl	0.1893(2)	0.2904(2)	0.2500(0)	0.00448(9)	0.0131(3)	0.0087(1)	−0.0004(3)	0.0000(0)	0.0000(0)
N1	0.0000(0)	0.4531(8)	0.2500(0)	0.0089(7)	0.0041(7)	0.0093(7)	0.0000(0)	0.0000(0)	0.0000(0)
N2	0.0776(0)	0.5222(0)	0.2500(0)	0.0066(0)	0.0002(0)	0.0121(0)	−0.0035(0)	0.0000(0)	0.0000(0)
C11	0.0515(5)	0.2273(5)	0.0810(4)	0.0077(4)	0.0114(6)	0.0038(3)	−0.0028(7)	0.0017(6)	0.0018(6)
C21	0.0835(5)	0.1173(6)	0.1119(4)	0.0096(4)	0.0123(6)	0.0042(3)	0.0070(9)	0.0012(6)	−0.0008(7)
C31	0.0000(0)	0.0516(8)	0.1287(5)	0.0160(9)	0.0077(7)	0.0035(3)	0.0000(0)	0.0000(0)	−0.0021(9)
C71	0.4495(8)	0.1397(9)	0.2500(0)	0.0104(7)	0.0069(8)	0.0165(11)	0.0022(14)	0.0000(0)	0.0000(0)
C80	0.0776(12)	0.5222(16)	0.2500(0)	0.0066(10)	0.0002(16)	0.0121(16)	−0.0035(23)	0.0000(0)	0.0000(0)
C41	0.1135(6)	0.3255(9)	0.0442(6)	0.0134(6)	0.0205(9)	0.0067(4)	−0.0120(13)	0.0041(8)	0.0071(10)
C61	0.0000(0)	−0.0791(10)	0.1457(7)	0.0412(25)	0.0063(9)	0.0063(6)	0.0000(0)	0.0000(0)	−0.0036(12)
C51	0.1891(6)	0.0728(9)	0.1145(5)	0.0121(5)	0.0318(12)	0.0088(5)	0.0250(11)	0.0013(9)	−0.0063(13)

The form of the anisotropic thermal parameter is: $\exp[-(\beta_{11}*H*H + \beta_{22}*K*K + \beta_{33}*L*L + \beta_{12}*H*K + \beta_{13}*H*L + \beta_{23}*K*L)]$.

Table IV. Positional and Thermal Parameters and Their Estimated Standard Deviations for UCp"$_2$Cl(pyrazolate)

Atom	x	y	z	β_{11} or β_{iso}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
U	0.40954(3)	0.10361(2)	0.26343(2)	0.00976(4)	0.00221(1)	0.00367(1)	0.00030(4)	0.00044(4)	-0.00000(2)
Cl	0.6845(3)	0.1054(1)	0.3375(2)	0.0123(3)	0.0062(1)	0.0073(1)	-0.0014(3)	-0.0043(4)	0.0024(2)
N1	0.2119(8)	0.0393(4)	0.3307(5)	4.5(1)					
N2	0.3419(8)	0.0251(4)	0.3785(5)	5.2(2)					
C1	0.0370(1)	-0.0220(7)	9.1671(9)	4.2(3)					
C2	0.310(2)	0.0352(8)	0.1147(10)	5.5(3)					
C3	0.430(1)	0.0771(7)	0.0882(8)	3.1(2)					
C4	0.569(1)	0.0528(7)	0.1262(9)	4.1(3)					
C5	0.535(2)	-0.0099(8)	0.1766(9)	4.9(3)					
C6	0.250(2)	-0.0020(11)	0.1909(14)	8.3(5)					
C7	0.150(3)	0.0527(13)	0.0709(15)	9.6(6)					
C8	0.458(2)	0.1379(12)	0.0132(14)	8.0(5)					
C9	0.740(3)	0.0655(13)	0.1201(16)	9.9(6)					
C10	0.626(3)	-0.0659(17)	0.2304(16)	11.3(7)					
C11	0.207(2)	0.2118(8)	0.3018(10)	3.6(3)					
C12	0.276(2)	0.2364(9)	0.2198(10)	3.6(3)					
C13	0.430(2)	0.2536(9)	0.2379(10)	3.3(3)					
C14	0.454(2)	0.2453(9)	0.3314(11)	3.9(3)					
C15	0.328(2)	0.2178(9)	0.3657(10)	3.5(3)					
C16	0.021(3)	0.1955(15)	0.2833(18)	9.2(7)					
C17	0.224(3)	0.2589(13)	0.1204(16)	7.6(6)					
C18	0.555(3)	0.2900(2)	0.1904(16)	6.9(5)					
C19	0.576(3)	0.2683(14)	0.3881(17)	8.5(6)					
C20	0.253(4)	0.1938(19)	0.4497(24)	12.7(10)					
C21	0.306(11)	-0.0210(6)	0.4456(7)	7.0(3)					
C22	0.154(1)	-0.0347(6)	0.4421(7)	6.2(2)					
C23	0.102(1)	0.0009(6)	0.3714(7)	7.0(3)					
C1'	0.464(2)	-0.0302(9)	0.1850(11)	2.1(3)					
C2'	0.322(2)	-0.0040(11)	0.1442(13)	3.3(4)					
C3'	0.346(3)	0.0524(12)	0.0942(15)	4.2(5)					
C4'	0.518(2)	0.0665(12)	0.1018(14)	4.0(4)					
C5'	0.561(2)	0.0176(12)	0.1580(14)	4.2(4)					
C11'	0.238(2)	0.2070(9)	0.3460(11)	4.0(3)					
C12'	0.197(11)	0.2142(7)	0.2499(9)	2.7(3)					
C13'	0.326(2)	0.2420(8)	0.2051(10)	3.6(3)					
C14'	0.434(2)	0.2521(10)	0.2785(11)	4.6(4)					
C15'	0.390(2)	0.2320(10)	0.3520(12)	5.2(4)					
C6'	0.475(6)	-0.1019(19)	0.2369(30)	9.8(11)					
C7'	0.157(5)	-0.0395(22)	0.1312(28)	10.8(11)					
C8'	0.327(5)	0.1123(19)	0.0111(30)	10.1(11)					
C9'	0.684(4)	0.1087(15)	0.0852(24)	7.4(8)					
C15'	0.739(4)	-0.0235(20)	0.2027(23)	9.1(9)					
C16'	0.102(3)	0.1820(13)	0.4075(16)	7.9(6)					
C17'	0.031(3)	0.1969(12)	0.2092(14)	6.8(5)					
C18'	0.334(3)	0.2595(13)	0.1140(16)	8.2(6)					
C19'	0.585(3)	0.2934(18)	0.2684(22)	11.7(9)					
C20'	0.466(4)	0.2375(17)	0.4458(20)	11.2(8)					

The form of the anisotropic thermal parameter is: $\exp[-(\beta_{11}*H*H + \beta_{22}*K*K + \beta_{33}*L*L + \beta_{12}*H*K + \beta_{13}*H*L + \beta_{23}*K*L)]$.

Table V. Positional and Thermal Parameters and Their Estimated Standard Deviations for UCp"$_2$(pyrazolate)$_2$

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
U	0.12839(1)	0.28541(2)	0.05748(1)	0.00083(0)	0.00654(2)	0.00370(1)	0.00011(1)	0.00147(1)	-0.00022(3)
N1	0.1729(2)	0.4758(5)	0.0819(3)	0.00135(6)	0.0085(6)	0.0055(2)	-0.0007(3)	0.0027(2)	-0.0002(6)
N2	0.1613(2)	0.4332(6)	-0.0823(3)	0.00146(6)	0.0108(6)	0.0047(2)	-0.0015(3)	0.0025(2)	-0.0008(7)
N3	0.1028(2)	0.2849(5)	-0.0904(4)	0.00170(7)	0.0113(7)	0.0048(2)	0.0000(4)	0.0018(2)	-0.0014(7)
N4	0.0884(2)	0.1190(5)	-0.0489(3)	0.00125(6)	0.0099(6)	0.0064(3)	-0.0009(3)	0.0019(2)	-0.0041(7)
C1	0.2168(2)	0.2062(6)	0.1445(4)	0.00083(6)	0.0108(7)	0.0043(3)	0.0013(4)	0.0015(2)	0.0021(8)
C2	0.1918(2)	0.0965(6)	0.0991(4)	0.00114(7)	0.0100(7)	0.0040(3)	0.0025(4)	0.0015(2)	0.0019(7)
C3	0.1662(2)	0.0588(6)	0.1438(4)	0.00119(7)	0.0073(6)	0.0068(3)	0.0006(4)	0.0018(2)	0.0040(8)
C4	0.1749(2)	0.1453(7)	-0.2157(4)	0.00115(6)	0.0118(7)	0.0047(3)	0.0017(4)	0.0021(2)	0.0036(9)
C5	0.2065(2)	0.2377(7)	0.2149(4)	0.00112(7)	0.0105(7)	0.0040(3)	0.0009(4)	0.0010(2)	0.0007(8)
C6	0.2523(2)	0.2739(8)	0.1269(5)	0.00126(7)	0.0165(10)	0.0084(3)	0.0004(5)	0.0039(2)	0.0050(11)
C7	0.1941(2)	0.0264(8)	0.0229(4)	0.00190(9)	0.0156(10)	0.0055(3)	0.0042(5)	0.0027(2)	-0.0018(10)
C8	0.1393(3)	-0.0640(8)	0.1272(6)	0.00217(11)	0.0095(8)	0.0092(5)	-0.0020(5)	0.0026(4)	0.0020(12)
C9	0.1628(2)	0.1232(9)	0.2938(4)	0.00201(8)	0.0213(13)	0.0068(3)	0.0028(6)	0.0048(2)	0.0080(11)
C10	0.2259(2)	0.3482(8)	0.2821(4)	0.00160(9)	0.0142(9)	0.0048(3)	0.0001(6)	0.0005(3)	-0.0034(11)
C11	0.0845(2)	0.4716(8)	0.1044(5)	0.00154(8)	0.0123(9)	0.0106(4)	0.0018(4)	0.0044(3)	-0.0062(10)
C12	0.0668(2)	0.4794(8)	0.0150(5)	0.00150(7)	0.0137(9)	0.0084(4)	0.0041(4)	0.0042(2)	0.0073(10)
C13	0.0417(2)	0.3742(10)	-0.0229(5)	0.00078(7)	0.0275(13)	0.0066(4)	0.0035(5)	0.0002(3)	-0.0107(12)
C14	0.0453(2)	0.2931(7)	0.0511(7)	0.00142(6)	0.0092(8)	0.0210(6)	-0.0006(4)	0.0086(3)	-0.0067(12)
C15	0.0724(2)	0.3621(10)	0.1296(5)	0.00287(8)	0.0213(12)	0.0089(3)	0.0057(5)	0.0061(2)	0.0042(12)
C16	0.1134(3)	0.5738(11)	0.1762(7)	0.00241(14)	0.0271(14)	0.0178(7)	-0.0003(8)	0.0047(5)	-0.0273(15)
C17	0.0712(3)	0.5965(10)	-0.0339(7)	0.00470(14)	0.0230(12)	0.0246(7)	0.0148(7)	0.0159(4)	0.0325(16)
C18	0.0119(3)	0.3494(15)	-0.1230(7)	0.00232(14)	0.0661(25)	0.0093(6)	0.0154(9)	-0.0016(5)	-0.0241(19)
C19	0.0282(3)	0.1650(12)	0.0404(11)	0.00393(11)	0.0137(12)	0.0633(13)	-0.0034(7)	0.0276(4)	-0.0069(26)
C20	0.0793(3)	0.3277(14)	0.2280(6)	0.00491(14)	0.0471(23)	0.0124(4)	0.0180(9)	0.0125(3)	0.0202(18)
C21	0.1991(2)	0.5822(8)	0.0981(5)	0.00164(8)	0.0117(8)	0.0091(4)	-0.0018(5)	0.0039(3)	0.0032(11)
C22	0.2038(2)	0.6108(7)	0.0200(5)	0.00213(9)	0.0113(9)	0.0099(4)	-0.0015(5)	0.0049(3)	0.0032(11)
C23	0.1798(2)	0.5153(8)	-0.0408(5)	0.00195(9)	0.0152(10)	0.0074(4)	-0.0013(5)	0.0035(3)	0.0057(11)
C24	0.0891(3)	0.1670(9)	-0.1766(5)	0.00263(12)	0.0166(11)	0.0048(3)	0.0021(6)	0.0027(3)	-0.0029(11)
C25	0.0653(2)	0.0531(9)	-0.1914(5)	0.00176(10)	0.0206(12)	0.0076(4)	0.0021(6)	0.0017(3)	-0.0182(12)
C26	0.0654(2)	0.0253(9)	-0.1103(6)	0.00154(10)	0.0175(11)	0.0182(5)	-0.0021(6)	0.0021(4)	-0.0115(13)

The form of the anisotropic thermal parameter is: $\exp[-(\beta_{11}*H*H + \beta_{22}*K*K + \beta_{33}*L*L + \beta_{12}*H*K + \beta_{13}*H*L + \beta_{23}*K*L)]$.

Table VI. Bond Distances (A) and Angles (°)

for UCp''_2Cl_2(pyrazole)

U-Cl	2.696(2)	C(11)-C(12)	1.410(11)
U-C(11)	2.722(5)	C(11)-C(21)	1.422(7)
U-C(21)	2.737(5)	C(11)-C(41)	1.525(8)
U-C(31)	2.756(7)	C(21)-C(31)	1.396(7)
U-N(1)	2.607(8)	C(21)-C(51)	1.535(7)
C(31)-C(61)	1.525(12)	Cl-U-Cl	148.29(8)
N(1)-C(80)	1.327(14)	Cl-U-N(1)	74.14(4)
C(80)-C(71)	1.401(17)	Cl-U-Cp	95.73(1)
C(71)-C(72)	1.384(16)	Cp-U-N(1)	111.44(1)
U-C(ave)	2.74(2)	Cp-U-Cp	137.1

C(12)-C(11)-C(21)	108.0(3)
C(12)-C(11)-C(41)	123.9(4)
C(41)-C(11)-C(21)	127.8(6)
C(11)-C(21)-C(51)	126.6(6)
C(11)-C(21)-C(31)	107.0(5)
C(51)-C(21)-C(31)	125.9(6)
C(21)-C(31)-C(61)	124.5(3)
C(21)-C(31)-C(22)	110.1(7)
N(2)-N(1)-C(80)	106.(1)
N(1)-C(80)-C(71)	111.(1)
C(80)-C(71)-C(72)	105.4(6)

Table VIIa. Bond Distances (A) and

Angles (°) for UCp"$_2$Cl(pyrazolate)

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"(1)-U-Cl	102.5
Cp"(1)-U-(N-N)	104.6
Cp"(2)-U-Cl	98.4
Cp"(2)-U-(N-N)	107.4
Cl-U-(N-N)	103.2
N(1)-U-N(2)	33.3(2)

Table VIIb. Distances (A) and Angles (°)

for Cp"(1) and Cp"(1') in UCp"$_2$Cl(pyrazolate)

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(1)-C(2)-C(3)	108(1)	91(1)
C(2)-C(3)-C(4)	112(1)	106(2)
C(3)-C(4)-C(5)	106(1)	108(2)
C(4)-C(5)-C(1)	107(1)	108(2)
C(3)-C(4)-C(9)	140(2)	158(3)
C(5)-C(4)-C(9)	113(2)	94(3)
C(4)-C(5)-C(10)	136(2)	149(3)
C(5)-C(1)-C(6)	139(2)	130(2)
C(2)-C(1)-C(6)	114(2)	123(2)
C(1)-C(2)-C(7)	135(2)	133(3)
C(3)-C(2)-C(7)	116(2)	115(3)
C(2)-C(3)-C(8)	137(2)	160(3)
C(4)-C(3)-C(8)	111(1)	91(3)
C(1)-C(5)-C(10)	117(2)	102(2)

Table VIIc. Distances (A) and Angles (°)

for Cp"(2) and Cp"(2') of UCp"$_2$Cl(pyrazolate)

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(2);1.40(2)	C(15)-C(20)	1.53(3);1.55(3)

C(15)-C(11)-C(12)	104(1)	103(1)
C(11)-C(12)-C(13)	109(1)	110(1)
C(12)-C(13)-C(14)	106(1)	100(1)
C(13)-C(14)-C(15)	110(1)	116(2)
C(14)-C(15)-C(11)	112(1)	113(2)
C(13)-C(14)-C(19)	131(2)	121(2)
C(15)-C(14)-C(19)	119(2)	122(2)
C(14)-C(15)-C(20)	146(2)	132(2)
C(15)-C(11)-C(16)	146(2)	141(2)
C(12)-C(11)-C(16)	110(2)	116(2)
C(11)-C(12)-C(17)	140(2)	123(1)
C(13)-C(12)-C(17)	111(2)	127(1)
C(12)-C(13)-C(18)	136(2)	129(2)
C(14)-C(13)-C(18)	117(2)	129(2)
C(11)-C(15)-C(20)	103(2)	117(2)

Table VIII. Bond Distances (A) and Angles (°)

for UCp"$_2$(pyrazolate)$_2$

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)	1.31(8)

Angles of interest

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

Table IX. Comparisons Between UCp"$_2$Cl$_2$(pyrazole),

UCp"$_2$Cl(pyrazolate), and UCp"$_2$(pyrazolate)$_2$. a)

	HPYZ	1:1	1:2
coord. number	9	9	10
U-C(ave)(A)	2.74(2)	2.73(3)	2.75(2)
U-Cl(A)	2.696(2)	2.611(2)	---
U-N(A)	2.607(8)	2.351(5)	2.403(4)
		2.349(5)	2.360(5)
			2.363(5)
			2.405(5)
Cp"-U-Cp"(°)	137	136	137
Cp"-U-N(°)	111.4	---	---
Cp"-U-(N-N)(°)	---	107.4	101.2
		104.6	103.1
			100.9
			101.7
X-U-N(-N)(°)	X=Cl	X=Cl	X=(N-N)
	74.14	103.2	112.2
Cp"-U-Cl(°)	95.7	102.5	---
		98.4	

a) HPYZ is UCp"$_2$Cl$_2$(pyrazole), 1:1 is UCp"$_2$Cl(pyrazolate),

and 1:2 is UCp"$_2$(pyrazolate)$_2$.

Table X. Distances (A) and Angles (°)

from some reported structures

compound	Cp"-M-Cp"	M-C(ring) ave.	coord. number	ref.
$(ThCp"_2H_2)_2$	130	2.83(1)	9	20
$(ThCp"_2O_2C_2Me_2)_2$	129	2.83(6)	8	21
$ThCp"_2Cl(COCH_2CMe_3)$	138	2.80(3)	9	19
$ThCp"_2Cl(CONEt_2)$	138	2.78(4)	9	19
$UCp"_2(CONMe_2)_2$	138	2.79(4)	10	19

Figure Captions

Figure 1. Graph of $\dfrac{1}{\chi_M^{corr}}$ vs T for UCp"$_2$(pyrazolate)$_2$.

Figure 2. Stereoscopic drawing of the unit cell of UCp"$_2$Cl$_2$(pyrazole).

Figure 3. ORTEP drawing of the molecular unit of UCp"$_2$Cl$_2$(pyrazole).

Figure 4. Stereoscopic drawing of the unit cell of UCp"$_2$Cl(pyrazolate).

Figure 5. ORTEP drawing of the molecular unit of UCp"$_2$Cl(pyrazolate)$_2$.

Figure 6. Stereoscopic drawing of the unit cell of UCp"$_2$(pyrazolate)$_2$.

Figure 7. ORTEP drawing of the molecular unit of UCp"$_2$(pyrazolate)$_2$.

$1/X_M^{corr}$ vs. T for $UCp_2''(pyrazolate)_2$

XBL 811-7787

XBL 811-7789

XBL 811-7788

XBL 811-7794