σ- vs. π-Bonded Organoactinides. The Synthesis and Structural Analysis of Tris(η^5-cyclopentadienyl)-η^1-2-methylallyluranium(IV)

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Abstract: The synthesis, characterization, and structural analysis of the title compound, $(C_5H_5)_3[CH_3C(CH_2)_2]U^{IV}$, is reported. The reaction of $U(C_5H_5)_3Cl$ with $Mg[CH_3C(CH_2)_2]Cl$ under inert atmosphere conditions at −78° in THF gives a high yield of the uranium allyl. Slow recrystallization gives dark red-brown crystals. The structure has been determined from three-dimensional X-ray diffraction data collected by counter methods. Three π-bonded η^5-cyclopentadienide rings are bonded to the uranium atom with an average bond distance of 2.74(1) Å. A σ-bonded η^1-2-methylallyl group completes the coordination sphere with a U–C bond length of 2.48(3) Å. The coordination geometry is a distorted tetrahedron with approximate C_{3v} symmetry. The average (center of cyclopentadienide ring)–U–(allyl carbon) bond angle is 100°. A σ-bonded ground state geometry vs. the π-bonded geometry observed in $(C_5H_5)_4U$ is explained by the competition between the reorganization energy and the increase in coordinate bonds on going from the σ- to π-bonded complexes. The crystals conform to space group $P2_12_12_1$ with $a = 10.240$ (4), $b = 8.747$ (4), $c = 18.198$ (4) Å, $Z = 4$, and $\rho_{calcd} = 1.99$ g/cm^3. A total of 3470 reflections were collected of which 1698 independent reflections with $F^2 \geq 3\sigma(F^2)$ were used in the final refinement by full-matrix least-squares methods to give weighted and and unweighted R factors of 6.4 and 6.5%, respectively.

Transition metal σ-bonded complexes play a crucial role in several catalytic processes. (The coenzyme vitamin B_{12} is an example in biology, and the Wacker process, Ziegler–Natta, and Phillips catalysts are corresponding industrial examples.) These catalytic processes require that the metal-to-carbon bond be unstable or, more accurately, that it be labile. The reasons for this characteristic instability recently have been reviewed.[2]

Our interest in the structure and bonding of π complexes of the lanthanides and actinides[3] has recently focused on actinide allyl complexes. The low-temperature NMR spectra of $U[HC(CH_2)_2]_4$, $Th[HC(CH_2)_2]_4$, and $U[CH_3C(CH_2)_2]_4$ have been interpreted as suggesting a π-bonded structure.[4-6] Unfortunately, crystallographic investigations of these compounds have been prevented by their thermal instability. However, the coordinatively saturated actinide alkyls of the type $U(C_5H_5)_3R$[7-9] or $Th(C_5H_5)_3R$[10] are stable, and the σ-bonded nature of the alkyl or aryl R groups has been confirmed by at least one study.[11] For the case where R = allyl, NMR studies of $U(C_5H_5)_3[HC(CH_2)_2]$ have shown that the bonding to the allyl group is fluxional, with the spectra interpreted as a $\sigma \rightleftharpoons \pi \rightleftharpoons \sigma$ interconversion through a π-bonded intermediate which lies 8–9 kcal/mol higher in energy.[9] Attempts to obtain suitable crystalline samples of the simple allyl complex $U(C_5H_5)_3[HC(CH_2)_2]$ were unsuccessful, and this prompted us to undertake the synthesis and characterization of the methyl derivative. We report here the preparation and structural characterization of the new actinide allyl complex, tris(η^5-cyclopentadienyl)-η^1-2-methylallyluranium(IV). This is the first structural example of a simple σ-bonded allyl group in an organometallic complex.[12]

Experimental Section

All reactions were carried out under an inert atmosphere of high-purity nitrogen or argon on a vacuum line. Transfer and handling of the organometallic complexes were facilitated by the use of Schlenk techniques or a Vacuum Atmospheres HE 93-A inert-atmosphere glove box having an oxygen- and moisture-free nitrogen atmosphere.

Samples for elemental uranium analyses were weighed on a Cahn Model 4400 electrobalance in the glove box. Infrared spectra were measured with a Perkin-Elmer Model 337 spectrophotometer; an AEI-MS12 mass spectrometer was used to record mass spectral data.

Materials. Dried and degassed solvents were used in all syntheses and further characterizations. Toulene, benzene, and THF were dried by reflux over sodium–benzophenone ketyl while hexane was dried by distillation from phosphorus pentoxide. All solvents were degassed under vacuum prior to use.

Thallous cyclopentadienide was prepared by the method of Meister[13] and was purified by sublimation at 10^{-2} mm between 80 and 100°. Uranium tetrachloride was prepared from a published procedure.[14] The $U(C_5H_5)_3Cl$[15] was synthesized from UCl_4 and TlC_5H_5 and purified by recrystallization from a 1:1 mixture of THF–hexane. The 2-methylallyl magnesium chloride was prepared in a manner analogous to allyl magnesium chloride[16] with the following quantities: 26.8 g of Mg turnings and 97.8 ml of 3-chloro-2-methylpropene in 600 ml of THF. The concentration of the Grignard reagent (1.34 *M*) was determined by back-titration with standardized NaOH solution.

$U(C_5H_5)_3[CH_3C(CH_2)_2]$. To a rapidly stirred solution of 3.00 g (6.40 mmol) of $U(C_5H_5)_3Cl$ in 150 ml of THF at −78° was added under an argon flush in one portion 9.6 ml (12.8 mmol) of 1.34 *M* MgC_4H_7Cl in THF. The reaction mixture was stirred for 2 hr at −78° and then 12 hr at 0°. The solution was concentrated to dryness in vacuo, and ca. 100 ml of toluene was added to the residue to dissolve the desired product. The toluene slurry was filtered, and the filtrate was concentrated to dryness in vacuo. The product was then washed with three 15-ml portions of hexane. The yield of crude product[17] was quantitative. A modified version of the double dewar technique was used to recrystallize the complex. To a slurry of approximately 0.5 g of crude product in 30 ml of hexane was added small quantities of toluene until a saturated solution was obtained. This solution was filtered into Schlenk apparatus which was then enclosed in two inverted dewars separated by a styrofoam O-ring. The assembly was allowed to cool to −20° over 48 hr whereupon deep reddish brown crystals appeared: ir (Nujol, fluoro-mac), cm^{-1} (relative intensity), 3067 (m), 2899 (w), 1672 (w), 1580 (s), 1439 (vs), 1362 (s), 1271 (s), 1058 (m), 1005 (vs), 941 (s), 781 (vs, br), 683 (w). Anal. Calcd for $C_{19}H_{22}U$: U, 48.7. Found: U, 47.6.[18] No parent ion was observed in the mass spectrum; however, the fragmentation pattern was very similar to $U(C_5H_5)_3X$ (X = F, I).[19]

Data Collection. Suitable single-crystals for X-ray diffraction were grown as described above and were mounted with Corning high-vacuum silicone grease in thin-walled glass capillaries under a nitrogen atmosphere. A series of precession photographs exhibited Laue symmetry *mmm* and the systematic extinctions $h00$, $h \neq 2n$,

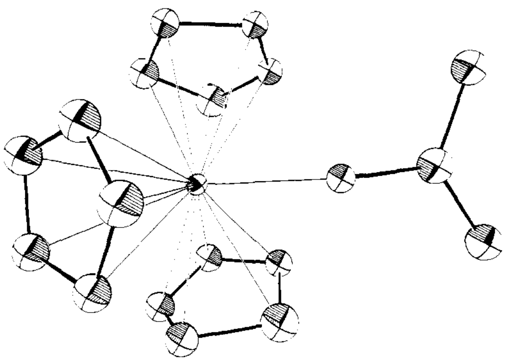

Figure 1. The $U(C_5H_5)_3[CH_3C(CH_2)_2]$ molecule viewed with the 2-methylallyl group in the plane of the paper. Atoms are drawn at the 40% probability contour scale.

Table I. Crystal Data

Molecular formula	$U(C_5H_5)_3[CH_3C(CH_2)_2]$
Molecular weight	488.42 g mol^{-1}
Space group	$P2_12_12_1$
Cell constants, *a*	10.240 (4) Å
b	8.747 (4) Å
c	18.198 (4) Å
Volume unit cell	1623.5 $Å^3$
Molecules/cell	4
Calcd density	1.99 g/cm^3
Obsd density	2.06 g/cm^3
μ (Mo Kα)	149 cm^{-1}

$0k0$, $k \neq 2n$, $00l$, $l \neq 2n$. The absences uniquely determine the space group $P2_12_12_1$ ($D_2{}^4$).

The morphology of the deep reddish brown data crystal was difficult to discern because the crystal was opaque and partially obscured by grease. It was approximated as a trapezoidal block bounded by the following six planes: 010, 0$\bar{1}$0, 001, 00$\bar{1}$, 100, $\bar{5}\bar{1}$0. The perpendicular distances to each of these planes from an arbitrary origin within the crystal were 0.0131, 0.0131, 0.0095, 0.0095, 0.00565, and 0.00870 cm, respectively. The crystal in its capillary was mounted on a eucentric goniometer head such that the 010 axis was nearly parallel to the ϕ axis of a Picker FACS-1 four-circle diffractometer. The lattice constants and orientation angles were determined from a least-squares refinement of the setting and 2θ angles of eight carefully centered reflections whose 2θ values ranged from 30 to 35°.[20] The crystal gave ω scan widths at half height of 0.05, 0.05, and 0.06° for the 002, 020, and 200 reflections, respectively. The density was determined by flotation in CH_2Br_2-CCl_4 solution. The refined cell parameters and other pertinent crystal data are given in Table I.[21]

Data reduction and processing were carried out as described elsewhere.[22] The intensities were corrected for Lorentz and polarization effects and converted to values of F^2. The calculated absorption coefficient, μ, is 149.0 cm^{-1}, and the maximum and minimum crystal thicknesses resulted in a range of μt from 2.59 to 3.90, so that an absorption correction was applied using an analytical integration method.[23,24] The correction factors ranged from 5.8 to 14.4 with an average value of 7.31. After this correction the data were averaged to give the 1698 independent reflections with $F^2 > 3\sigma(F^2)$ which were used in the final refinement. The R factor for averaging, based on F^2, was 5.6%.

Solution and Refinement of the Structure. The structure was solved by the application of Patterson, difference Fourier, and least-squares techniques. Full-matrix least-squares refinements on F were used in which the function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where F_o and F_c are the observed and calculated structure factors, respectively, and the weighting factor, w, is $4F_o{}^2/\sigma^2(F_o{}^2)$. The atomic scattering factors for neutral U and C were taken from the values tabulated by Cromer and Mann[25] and those for neutral hydrogen from Stewart, Davidson, and Simpson.[26] Corrections for anomalous dispersion effects of uranium using both $\Delta f'$ and $\Delta f''$ were included in the calculations.[27]

The hydrogen atom positions for the three cyclopentadienide rings and one of the carbon atoms (C_{41}) in the methylallyl group were calculated by assuming planar and tetrahedral geometry, respectively, and a C-H bond length of 1.0 Å. The terminal hydrogen atoms of the methylallyl group could not be satisfactorily located and consequently were not refined. Although the uranium atom dominates the scattering, the weighted R factor including *only* the uranium atom in the structure is 22.5%. Thus the fit to the model structure is sensitive to the light atoms. Subsequently, the uranium atom was refined anisotropically. Because the necessarily large and approximate absorption correction strongly affected the light atom thermal parameters, these were left isotropic. In the final refinement, the hydrogen atoms were fixed at their calculated positions, with a fixed isotropic temperature factor of 9.0 $Å^2$, and the overall temperature factor was varied. The model converged to give final weighted and unweighted R factors of 6.38 and 6.53%, respectively. The final error in an observation of unit weight is 1.62. Agreement of F_o with F_c did not vary systematically as a function of either $\sin\theta/\lambda$ or $|F_o|$. Refinement of the enantiomorphous structure gave weighted and unweighted R factors of 6.69 and 7.11%, respectively; thus the enantiomorphous structure can be rejected at the 0.05% significance level.[28] Examination of the final difference Fourier showed no peaks greater than 0.8 e/$Å^3$ or roughly 40% of a carbon atom other than noise peaks in the region of the uranium position. Table II gives the positional and thermal parameters for the non-hydrogen atoms. Positional parameters for the hydrogens included in the refinement are listed in Table III.[29]

Description of the Structure and Discussion.

The unit cell consists of four discrete molecules of $U(C_5H_5)_3[CH_3C(CH_2)_2]$. No unusually short intermolecular nonbonded distances (less than 3.7 Å) are found, and interaction between individual molecules is minimal. A perspective drawing of the molecule is shown in Figure 1. Coordination about the uranium is a slightly distorted tetrahedron with three *π-bonded* η^5-cyclopentadienide rings pushed toward a *σ-bonded* η^1-2-methylallyl group to give C_{3v} coordination symmetry. The extent of the distortion from a tetrahedron is illustrated by the angles between vectors from the uranium atom to the first atom in the methylallyl group (C_{41}) and the uranium atom to the centers of individual cyclopentadienide rings. The average C_{41}-U-(center of the ring) angle of 100° is the same as the corresponding value of 100° reported for both $U(C_5H_4CH_2C_6H_5)_3Cl$[30] and $U(C_5H_5)_3(C_2C_6H_5)$.[11] The average center of ring-U-(center of ring) angle of 117° is also the same as reported for $U(C_5H_4CH_2C_6H_5)_3Cl$ and $U(C_5H_5)_3(C_2C_6H_5)$. The average uranium-carbon distance for all three rings is 2.74 (1) Å (Table IV). Similar averages for $U(C_5H_4CH_2C_6H_5)_3Cl$ and $U(C_5H_5)_3(C_2C_6H_5)$ are 2.733 (1) and 2.68 Å. The uranium-carbon σ-bond distance in the methylallyl group is 2.48 (3) Å, while that reported for the U-C σ-bond in $U(C_5H_5)_3(C_2C_6H_5)$ is 2.33 (2) Å,[11] and in $U(C_5H_5)_3$(*n*-butyl) the U-C distance is 2.43 (3) Å.[31] The allyl and *n*-butyl bond lengths (2.48 and 2.43 Å) should be equal since both involve U-C bonds from sp^3 hybridized carbon atoms. Within experimental error, the distances are comparable. In $U(C_5H_5)_3(C_2C_6H_5)$ the uranium-acetylide bond involves an sp hybridized carbon atom. For *single bond* covalent radii the difference between CH_3-C (sp^3) and CH_3-C (sp) is 0.08 Å.[32,22] The acetylide U-C distance of 2.33 Å is 0.10 and 0.15 Å less than the *n*-butyl and allyl bond lengths. Although marginally significant, this may indicate some multiple bonding is present in the acetylide U-C bond. The cyclopentadienide rings have an average C-C bond length of 1.43 (2) Å. The maximum range in C-C distance is 1.25-1.68 Å and is due to an anomalous refined position for atom C_{15}. The cyclopentadienyl C-C bond lengths are given in Table V.[29] The large individual standard deviations for the C-C distances (0.06 Å) are consequences of the librational thermal motion of the rings, the errors in the absorption correction, and the domi-

Table II. Positional[a,b] and Thermal[c] Parameters

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
U	0.19533 (12)	0.52198 (12)	0.59764 (6)	73.5 (13)	113.4 (17)	24.1 (4)	7.88 (2)	2.75 (10)	0.28 (10)

	x	y	z	B		x	y	z	B
C_{11}	0.233 (4)	0.661 (5)	0.461 (2)	7.4 (12)	C_{31}	0.162 (4)	0.257 (4)	0.513 (2)	6.3 (12)
C_{12}	0.265 (4)	0.777 (5)	0.516 (2)	7.3 (11)	C_{32}	0.047 (5)	0.356 (5)	0.498 (2)	7.4 (11)
C_{13}	0.382 (4)	0.723 (5)	0.554 (2)	6.4 (11)	C_{33}	−0.030 (5)	0.373 (5)	0.560 (2)	7.9 (11)
C_{14}	0.421 (5)	0.584 (6)	0.518 (3)	10.4 (12)	C_{34}	0.045 (5)	0.275 (5)	0.614 (2)	7.5 (12)
C_{15}	0.293 (4)	0.537 (5)	0.465 (2)	7.9 (12)	C_{35}	0.150 (5)	0.209 (5)	0.584 (2)	7.8 (11)
C_{21}	0.022 (4)	0.578 (4)	0.709 (2)	5.7 (11)	C_{41}	0.371 (3)	0.385 (4)	0.664 (2)	3.9 (11)
C_{22}	0.005 (5)	0.704 (5)	0.658 (2)	7.9 (12)	C_{42}	0.482 (4)	0.454 (5)	0.707 (2)	6.4 (11)
C_{23}	0.127 (5)	0.790 (6)	0.665 (3)	9.5 (12)	C_{43}	0.605 (4)	0.491 (5)	0.673 (2)	7.0 (12)
C_{24}	0.203 (4)	0.702 (4)	0.719 (2)	5.6 (11)	C_{44}	0.458 (3)	0.467 (4)	0.786 (2)	6.1 (11)
C_{25}	0.154 (3)	0.562 (4)	0.744 (2)	4.6 (11)					

[a] In fractional cell coordinates. [b] Carbon atom positional parameters are for the set bonded to the uranium listed in the table. [c] Anisotropic β values are multiplied by 10^4; the form of the thermal correction is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{44}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. Isotropic β values are of the form $\exp[-\beta(\sin^2\theta/\lambda^2)]$.

Table IV. Bond Lengths and Angles for the Uranium 2-Methylallyl Complex

Atoms	Distance, Å	Group	Distance, Å	Group	Angle, deg
U–C_{11}	2.80 (4)	U–1[b]	2.44	1–U–2	119
U–C_{12}	2.77 (4)	U–2	2.44	1–U–3	115
U–C_{13}	2.72 (4)	U–3	2.47	2–U–3	118
U–C_{14}	2.78 (5)			1–U–C_{41}	102
U–C_{15}	2.62 (4)			2–U–C_{41}	99.5
U–C_{21}	2.74 (4)			3–U–C_{41}	97.5
U–C_{22}	2.74 (4)	2-Methylallyl Group			
U–C_{23}	2.74 (5)				
U–C_{24}	2.71 (3)	Atoms		Atoms	
U–C_{25}	2.72 (3)	C_{41}–C_{42}	1.51 (4)	C_{43}–C_{42}–C_{44}	123 (3)
U–C_{31}	2.80 (4)	C_{42}–C_{43}	1.43 (4)	C_{43}–C_{42}–C_{41}	122 (3)
U–C_{32}	2.78 (4)	C_{42}–C_{44}	1.46 (4)	C_{44}–C_{42}–C_{41}	114 (3)
U–C_{33}	2.73 (4)	U–C_{41}	2.48 (3)	U–C_{41}–C_{42}	127 (4)
U–C_{34}	2.67 (4)	U–C_{42}	3.60 (4)		
U–C_{35}	2.79 (4)	U–C_{43}	4.42 (4)		
U–C_{41}	2.48 (3)	U–C_{44}	4.38 (3)		
U–C (cyclopentadienyl) (mean) bond length 2.74 (1) Å[a]					

[a] Standard deviations for the mean in this and subsequent tables were estimated from the variance using the equations $\sigma^2 = (\Sigma_{i=1}{}^n(x_i - \bar{x})^2)/n$ and $\sigma_{\bar{x}} = (1/(n-1)^{1/2}\sigma$. [b] Center of ring 1 designated as 1, etc.

nance of uranium atom scattering for all classes of reflections in this structure.

The most important feature of the structure is the σ-bonded 2-methylallyl group. The bond distances and angles for this group are given in Table IV. The structure clearly indicates the σ-bonded nature of the methylallyl group. However, the localized double and single bonds (expected in the C_{42}-C_{43} and C_{42}-C_{44} distances) are not observed since there is a crystallographic disorder between the methylene and methyl groups. The observed bond lengths, 1.43 (4) and 1.46 (4) Å, are therefore equal within experimental error and are an average of the expected C-C double- and single-bond distances. However, this disorder does not appreciably affect the rest of the structure.

At first glance the monohapto coordination of the allyl group in this compound is surprising, since in $U(C_5H_5)_4$ all four rings are pentahapto.[34] As shown in Figure 2, the π-bonded structures of the allyl and cyclopentadienyl compounds are probably very similar since the allyl group requires nearly the same coordination geometry around the uranium when π-bonded as does cyclopentadienide. Yet the first is σ-bonded and the second is π-bonded. An explanation for this difference can be found in an examination of the differences in geometry for the σ- and π-bonded structures. The $(C_5H_5)_3UX$ structures (where X = halogens, alkyl, or aryl groups) all have the same basic geometry, characterized by U-C distances (for the cyclopentadienide rings) of 2.73 Å and ring-U-ring bond angles of 117°. When X = cyclopentadienyl the σ-bonded structure (shown in the top right of Figure 2) presumably has this same geometry. The conversion to the π-bonded form (top left of Figure 2) requires two changes in geometry to accommodate the greater coordination number. First, the cyclopentadienide rings move approximately 0.1 Å away from the metal ion to give U-C bond lengths of 2.81 Å. Second, the change to a tetrahedral geometry decreases the ring-U-ring angles from 117 to 109°. These rearrangements cost energy but this is apparently overcome by the energy released in forming what is formally two more coordinate bonds.

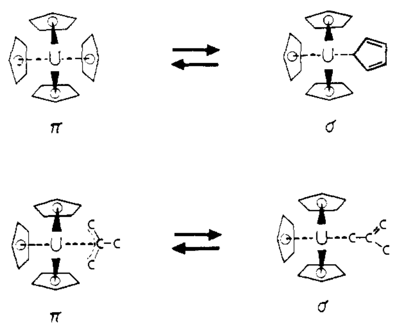

Figure 2. Interconversion of $(\eta^5\text{-}C_5H_5)_4U$ to $(\eta^5\text{-}C_5H_5)_3(\eta^1\text{-}C_5H_5)U$ and of $(\eta^5\text{-}C_5H_5)_3[\eta^3\text{-}CH_3C(CH_2)_2]U$ to $(\eta^5\text{-}C_5H_5)_3[\eta^1\text{-}CH_3\text{-}C(CH_2)_2]U$.

In the case of the allyl, the σ-bonded compound (lower right of Figure 2) also has the usual $(C_5H_5)_3UX$ structure. As mentioned earlier, the geometrical requirements of the π-bonded allyl group are approximately the same as cyclopentadienide in these compounds. Thus the π-bonded structure (lower left of Figure 2) can be assumed to have nearly the same geometry as the π-bonded cyclopentadienide. This means that the energy loss due to the change in geometry on going from the σ- to the π-bonded structure must be nearly the same as for the cyclopentadienide. However; in the case of the allyl only one additional coordinate bond is formed on this rearrangement. Since the stable form of the allyl is σ-bonded, *the energy loss due to the* π *to* π *rearrangement must lie between the energy released by one- vs. two-coordinate bonds.*

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Supplementary Material Available. A tabular listing of structure factor amplitudes, calculated coordinates of hydrogen atoms (Table III), and C–C bond lengths (Table V) will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 48 mm, 24× reduction, negatives) containing all the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th Street, N.W., Washington, D.C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number JACS-75-3049.

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(21) Intensity data were collected in the θ–2θ scan mode using monochromatic Mo Kα radiation and a scintillation counter. The Bragg 2θ angle for the highly oriented graphite monochromator crystal was 12.02°, and the X-ray tube takeoff angle was 1.9°. The pulse height analyzer was centered on the Mo Kα peak and set to admit approximately 90% of the maximum intensity at full window width. The detector was located 33 cm from the source with a 7 × 7 mm receiving aperature. The 2θ scans were from 0.65° below the Kα_1 peak to 0.65° above the Kα_2 with a scan rate of 1.0°/min. Copper foil attenuators were automatically inserted in the path of the diffracted beam to keep the count rate for a given reflection below 10^4 counts/sec. Stationary 10-sec background counts were taken at the start and finish of each scan. Throughout the data collection the intensities of three standard reflections (200, 020, and 002) were measured every 50 reflections as a check on the stability of the crystal and the instrument. A maximum variation in intensity of less than 5% was noted, and no decay correction was applied to the data. A total of 3470 reflections were collected including one unique form (h,k,l) out to $2\theta = 50°$ and three alternate forms $(\bar{h},k,l$; $h,\bar{k},l$; and $h,k,\bar{l})$ out to $2\theta = 30$, 30, and 40°, respectively.

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