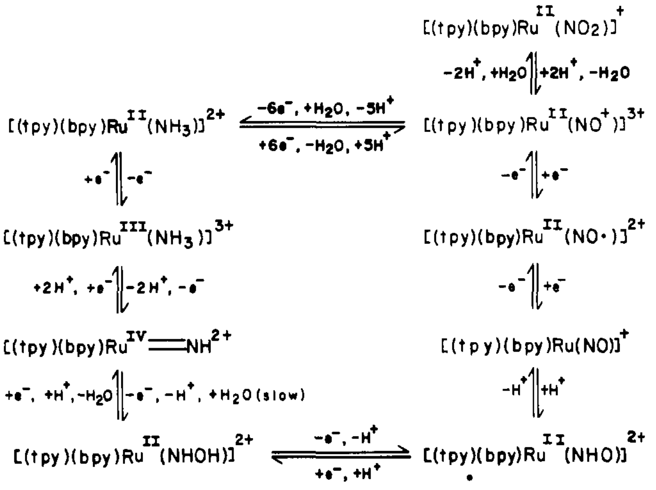
Scheme II



lations of the intermediates proposed here which differ with regard to water content, e.g., $[(tpy)(bpy)Ru^{II}(NH_2O)]^{2+}$ vs. $[(tpy)(bpy)Os^V{\equiv}N]^{2+}$, may be profound with regard to both electronic structure and reactivity characteristics. For example, the spectral properties of $[(tpy)(bpy)Ru^{IV}{=}NH]^{2+}$ are essentially those of the high-oxidation-state oxo complex $[(tpy)(bpy)Ru^{IV}{=}O]^{2+}$, which features an absence of visible absorption bands.[11b] The "reductive hydration" reaction

$$[(tpy)(bpy)Ru^{IV}{=}NH]^{2+} + H_2O \rightarrow [(tpy)(bpy)Ru^{II}(NH_2OH)]^{2+}$$

produces a typical complex of Ru(II) having intense metal to ligand charge-transfer (MLCT) absorption bands (π^*(bpy) ← $d\pi$(Ru^{II})) at nearly the same energy as for the ammine complex $[(tpy)(bpy)Ru(NH_3)]^{2+}$.[11] The presence or absence of hydrated–dehydrated pairs like $M^{IV}{=}NH^{2+}/M^{II}{-}NH_2OH^{2+}$, $M^V{\equiv}N^{2+}/M^{II}{-}NH_2O^{2+}$, and $M^{IV}{=}N^+/M^{II}{-}NHO^{2+}$ may depend on the pH, the metal, and the ligand environment involved, and we hope to learn how to control this chemistry in a systematic way.

In Schemes I and II an attempt has been made to summarize our best guesses as to the mechanistic details for the nitro–ammine interconversion for the Ru and Os complexes in the pH range 2–6.

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Structures and Energies of B_2H_4

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Optimized structures and energies have been determined at the HF/6-31G and MP2/6-31G** levels for B_2H_4. At the MP2/6-31G** level the optimized BB distances are 1.653 Å for the orthogonal 0012 D_{2d} structure, 1.537 Å for the 1011 C_s structure (BH_2 perpendicular to BHBH plane), and 1.462 Å for the doubly bridged 2010 C_{2v} structure. The C_s and C_{2v} structures are less stable than the D_{2d} structure by 9.6 and 1.5 kcal/mol, respectively. The barrier for rotation of the D_{2d} form through the planar 0012 D_{2h} form (BB, 1.742 Å) is 12.6 kcal/mol, while the barrier for inversion of the 2010 C_{2v} form through the planar 2010 D_{2h} form (BB, 1.493 Å) is 19.0 kcal/mol.

Although B_2H_4 is unknown, it is of theoretical interest[1-8] and has been proposed in interconversion reactions of boranes.[9] It is among the simplest models of a classical to nonclassical transformation in which terminal hydrogens could potentially become bridge hydrogens, thus using the vacant orbital on each BH_2 group of the classical structure. Here we show that, although the classical H_2BBH_2 (D_{2d}) structure is more stable than the nonplanar doubly bridged structure, only 1.5 kcal/mol separates these two structures (Figure 1).

In earlier studies optimized geometries have been found by various methods: FSGO (floating spherical Gaussian orbitals),[1] PRDDO (partial retention of diatomic differential overlap),[2] single-ζ[3,4] and double-ζ[5-7] methods (Table I). The D_{2d} classical structure H_2BBH_2 is found in these studies to be more stable than the planar $HB(H_b)_2BH$ structure of symmetry D_{2h} (Table II). Experimentally, classical forms (D_{2d} or D_{2h}) are known[10] for B_2F_4, B_2Cl_4, and B_2Br_4. Perhaps for these reasons, the more extensive calculations on B_2H_4 have been concentrated on the D_{2d} and D_{2h} classical structures and on the rotational barrier. Polarization functions have been added for single geometry calculations[3] and double-ζ plus polarization basis sets including CI (configuration interaction) used in optimization of the preferred H_2BBH_2 (D_{2d}) isomer[7] (Table II). Comparisons have also been made of the planar 0012 (D_{2h}) and 2010 (D_{2h}) structures and of the barrier

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(10) Danielson, D. D.; Patton, J. V.; Hedberg, K. *J. Am. Chem. Soc.* **1977**, *99*, 6484. Trefonas, L.; Lipscomb, W. N. *J. Chem. Phys.* **1958**, *28*, 54. Jones, L. H.; Ryan, R. R. *J. Chem. Phys.* **1972**, *57*, 1012. Ryan, R. R.; Hedberg, K. *J. Chem. Phys.* **1969**, *50*, 4986. Atoji, M.; Wheatley, P. J.; Lipscomb, W. N. *J. Chem. Phys.* **1957**, *27*, 196. Danielson, D. D.; Hedberg, K. *J. Am. Chem. Soc.* **1979**, *101*, 3199.

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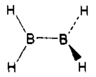
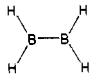
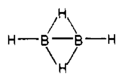
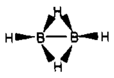
Table I. Optimized Geometries for Various Basis Sets[a]

	structure				
	 1A	 1B	 3B	 3A	ref
		FSGO			
r(BB)	1.7686	1.7820			1
$r(BH_t)$	1.2562	1.2541			
$r(BH_b)$	...	...			
$\angle(H_tBH)$	117.0	117.1			
$\angle$(dihedral)	90.00	0.00			
		PRDDO			
r(BB)	1.6189	1.6824	1.4306		2
$r(BH_t)$	1.1691	1.1691	1.1443		
$r(BH_b)$	...	...	1.3056		
$\angle(H_tBH)$	117.00	117.00	123.22		
$\angle$(dihedral)	90.00	0.00	180.00		
		STO-3G			
r(BB)	1.644	1.713	1.704[b]	1.651[b]	3,4[b]
$r(BH_t)$	1.162	1.162	1.137	1.150	
$r(BH_b)$	...	...	1.306	1.207	
$\angle(H_tBH)$	117.2	116.7	130.7	133.2	
$\angle$(dihedral)	90.0	0.0	180.0	?	
		HF/3-21G			
r(BB)	1.6618	1.7477	1.4939		5
$r(BH_t)$	1.1939	1.1921	1.1584		
$r(BH_b)$	...	...	1.2629		
$\angle(H_tBH)$	116.40	116.42	126.26		
$\angle$(dihedral)	90.00	0.00	180.00		
		double-ζ			
r(BB)	1.683	1.775	1.528		6
$r(BH_t)$	1.202	1.199	1.172		
$r(BH_b)$	...	...	1.296		
$\angle(H_tBH)$	116.2	116.2	126.1		
$\angle$(dihedral)	90.0	0.0	180.0		
		HF/DZ**			
r(BB)	1.684	1.762			7
$r(BH_t)$	1.196	1.196			
$r(BH_b)$	...	...			
$\angle(H_tBH)$	116.8	116.5			
$\angle$(dihedral)	90.0	0.0			
		CISD/DZ**			
r(BB)	1.669				7
$r(BH_t)$	1.195				
$r(BH_b)$	...				
$\angle(H_tBH)$	116.6				
$\angle$(dihedral)	90.0				
		MP2/6-31G**			
r(BB)	1.6534	1.7417	1.4928	1.4622	this work
$r(BH_t)$	1.1902	1.1888	1.1650	1.1690	
$r(BH_b)$	...	...	1.2557	1.3315	
$\angle(H_tBH)$	116.15	116.03	126.45	119.00	
$\angle$(dihedral)	90.00	0.0	180.00	107.34	

[a] r in Å and angles in deg. [b] See text.

to BH_2 rotation involving the classical H_2BBH_2 (0012) structures of symmetries D_{2d} and D_{2h}.[2,5]

Our objective is to examine and compare both classical and nonclassical structures by performing geometry optimizations at the double-ζ level including both polarization and correlation effects.

Theory and Calculations

Consistent with its nonexistence or possible transient existence, B_2H_4 has probable structures which violate the original *styx* rules[11] and associated topology.[11,12] Relaxation of the rules[2,13] for transient intermediates allows up to one vacant orbital per boron atom (e.g. in the 0012 H_2BBH_2 structures), and allows joining of two boron atoms by a single bond and one or more three-center BH_bB bonds (e.g. in the 1011 B_2H_4 and 2010 B_2H_4 structures). The number v of vacant orbitals is 2 for 0012, 1 for 1011, and 0 for 2010 structures. The symmetry restriction to at least a 2-fold element is no longer a requirement, even for stable boron hydrides.

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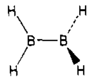
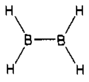
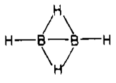
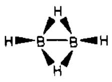
Table II. Relative Energies (kcal/mol)

	structure				
basis set[a]	 1A	 1B	 3B	 3A	ref
FSGO					1
FSGO	0	1.95			1
PRDDO					2
PRDDO	0	13.2	127.9		2
STO-3G	0	12.2	98.4		2
HF/4-31G	0	12.3	62.4		2
SCF	0	12.2	99.4		2
SCF-CI	0	12.9	73.1		2
HF/4-31G	0	12.2	62.3		8
STO-3G					3,4[b]
STO-3G	0	12.66			3
HF/6-31G*	0	10.49			3
STO-3G	0	12.66	127.11[b]	92.90[b]	4[b]
HF/4-31G	0	11.93	74.13[b]	39.93[b]	4[b]
STO-3G	0	12.66	94.55	46.66	this work
HF/4-31G	0	11.93	60.40	32.47	this work
HF/3-21G					5
HF/6-31G	0	11.71	58.12		5
HF/6-31G**	0	10.51	44.23		5
CID/6-31G	0	13.55	37.70		5
CID/6-31G**	0	12.00	25.17		5
double-ζ					6
double-ζ	0	11.91	68.97		6
HF/DZ**					7
HF/DZ**	0	10.86			7
CISD/DZ**	0	11.92			7
MP2/6-31G**					this work
HF/6-31G	0	11.68	58.20	32.59	this work
HF/6-31G**	0	10.45	44.10	19.49	this work
MP2/6-31G	0	13.87	36.23	16.18	this work
MP2/6-31G**	0	12.62	20.54	1.52	this work

[a] Geometries optimized at initial levels—see Table I. [b] See text.

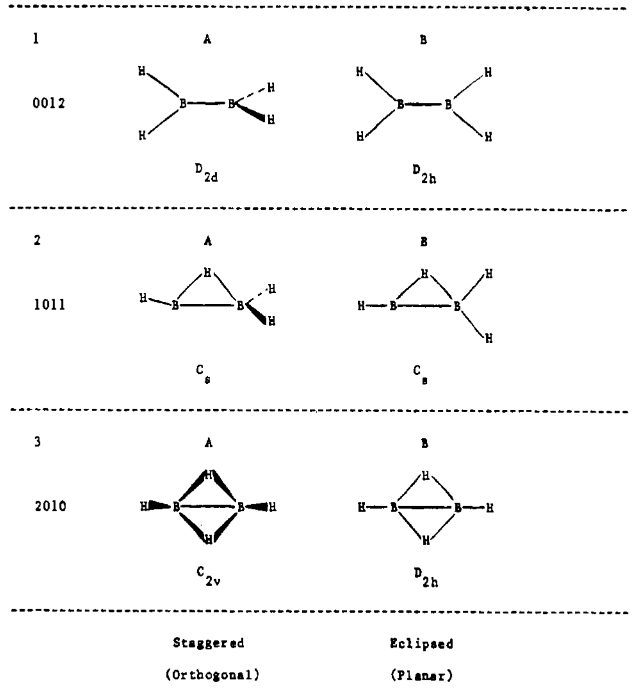


Figure 1. Structures for B_2H_4.

Structures were optimized at the HF/6-31G level and further optimized at the MP2/6-31G** level in order to include effects of correlation and polarization functions by using the GAUSSIAN 82 program.[14] No symmetry restrictions were imposed in the optimizations, except that for the 1011 structure the bridge hydrogen was constrained to a plane orthogonal to the BB axis and bisecting it. The results of the optimizations (Table III) show that the inclusion of correlation and polarization had little effect on the geometries, although the relative energies are strongly affected.

We now consider the three topologies (0012, 1011, and 2010) in either the planar (eclipsed) or nonplanar (staggered) form. Except for the relatively unstable planar 1011 form, which would not refine to a stable geometry, each of the other five structures (Table III) refined to a stable minimum as shown by the eigenvalues of the Hessian matrix.

0012 B_2H_4. As shown in Table III the staggered (D_{2d}) form is more stable than the eclipsed (D_{2h}) planar form by 12.6 kcal/mol. The relative stabilization is due to the electronic interactions, which overcome the increase in nuclear repulsion energy as D_{2h} transforms to D_{2d}. Much of this stabilization is due to back-bonding of the filled local π orbital of one BH_2 group into the adjacent vacant p orbital of the other boron atom in the staggered D_{2d} conformer. This is further indicated by the change in the BB distance from 1.742 Å in the D_{2h} form to 1.653 Å in the D_{2d} form. Such hyperconjugation is not available to the planar D_{2h} conformer. The distance of 1.653 Å is considerably shorter than that of 1.770 Å in B_2H_6[15] and suitably longer than that in

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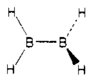
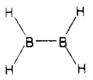
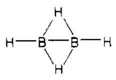
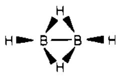
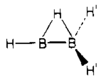
(14) Binkley, J. S.; Frisch, M.; Raghavachari, K.; Fluder, E.; Seeger, R.; Pople, J. A. "GAUSSIAN 82"; Carnegie-Mellon University: Pittsburgh, PA, 1982. Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257. Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213. Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618. Pople, J. A.; Binkley, J. S.: Seeger, R. *Int. J. Quantum Chem., Symp.* **1976**, *10*, 1.

(15) Kuchitsu, K. *J. Chem. Phys.* **1968**, *49*, 4456.

Table III. Optimized Geometries and Energies for HF/6-31G and MP2/6-31G** Levels

	structure				
	 1A	 1B	 3B	 3A	 2A
HF/6-31G^a					
r(BB)	1.6672	1.7490	1.4982	1.4671	1.5542
r(BH$_t$)	1.1926	1.1912	1.1588	1.1638	1.1702
r(BH$_b$)			1.2664	1.3789	1.4072
r(BH$_b$′)					1.1896
∠(H$_t$BH)	116.36	116.21	126.21	120.54	118.92
∠(dihedral)	90.00	0.00	180.00	104.65	90.00
∠(BBH$_t$′)					119.90
rel energy	0	11.71	58.11	31.51	23.83
MP2/6-31G**^{a}					
r(BB)	1.6534	1.7417	1.4928	1.4622	1.5366
r(BH$_t$)	1.1902	1.1888	1.1650	1.1690	1.1740
r(BH$_b$)			1.2557	1.3315	1.3650
r(BH$_t$′)					1.1882
∠(H$_t$BH)	116.15	116.03	126.45	119.00	115.47
∠(dihedral)	90.00	0.00	180.00	107.34	90.00
∠(BBH$_t$′)					119.48
Relative Energies^b					
HF/6-31G	0	11.68	58.20	32.59	24.35
HF/6-31G**	0	10.45	44.10	19.49	19.36
MP2/6-31G	0	13.87	36.33	16.18	15.64
MP2/6-31G**	0	12.62	20.54	1.52	9.57
Total Energies^c					
HF/6-31G	-51.61454	-51.59592	-51.52181	-51.56261	-51.57574
HF/6-31G**	-51.63833	-51.62129	-51.56807	-51.60728	-51.60748
MP2/6-31G	-51.71804	-51.69594	-51.66016	-51.69227	-51.69312
MP2/6-31G**	-51.81597	-51.79586	-51.78325	-51.81355	-51.80072
nuclear	22.30966	21.77568	25.20278	24.95724	23.74504
Populations^d					
B	4.868	4.837	5.127	5.032	4.788
B	4.868	4.837	5.127	5.032	5.062
H$_t$	1.066	1.081	0.958	0.971	1.002
H$_b$			0.915	0.998	1.057
H$_t$′					1.046
Overlap					
B-B	0.937	0.859	1.200	1.292	1.104
H$_t$-B	0.809	0.814	0.803	0.795	0.793
B-H$_b$			0.403	0.342	0.323
H$_b$-B					0.169
B-H$_t$′					0.814

[a] r in Å, angles in deg, and relative energies in kcal/mol. [b] In kcal/mol. [c] In hartrees. [d] In electrons.

the ethylene-like $B_2H_4^{2-}$ ion, which has a BB distance optimized to 1.604 Å at the double-ζ level.[6]

2010 B_2H_4. Of the several previous studies of the eclipsed (planar) conformer of D_{2h} symmetry of 2010 topology, the STO-3G optimization yielded results[4] that differed from the others listed in Table I. Our repetition of this STO-3G optimization gave a BB distance of 1.428 Å and a relative energy in agreement with other values of Table II. At the MP2/6-31G** level the optimized BB distance is 1.493 Å.

Also, for the staggered (nonplanar) conformer of C_{2v} symmetry our optimized BB distance is 1.418 Å, in contrast to the value of 1.651 Å[4] in Table I and in reasonable agreement with our more reliable MP2/6-31G** distance of 1.462 Å. The staggered form is more stable than the eclipsed form by 19.0 kcal/mol (Table II), largely due to decreased nuclear repulsions, although both nuclear and electronic energies are decreased in absolute magnitude (Table III). The barrier for inversion of the staggered C_{2v} form is 19.0 kcal/mol, provided the symmetry of the transition state is indeed D_{2h}. In this process the BB distance increases from 1.462 Å in the C_{2v} form to 1.493 Å in the transition state (D_{2h}) at the MP2/6-31G** level. In the eclipsed form the bridge hydrogens are 2.02 Å apart, while they are 1.79 Å apart in the more stable staggered form.

1011 B_2H_4. The asymmetric structures (2A and 2B of Figure 1) have been considered previously.[4,8] The planar eclipsed conformer (2B) was found[8] to be some 158 kcal/mol less stable than the 0012 (D_{2d}) structure, in a single geometry calculation at the 4-31G level apparently based on the PRDDO geometry. The nonplanar staggered conformer (2A) was found[4] to be less stable than the 0012 (D_{2d}) structure by 43.5 kcal/mol at the optimized STO-3G level and by 29.4 kcal/mol at the 4-31G level using the STO-3G optimized geometry.

We have not listed our optimized results for the planar (2B) structure because the optimization was unstable: rearrangement occurred either to the 2010 structure when the single bridge hydrogen was constrained to lie in the median plane bisecting the BB axis or to the 0012 structure when this constraint was released.

On the other hand the nonplanar staggered conformer refined stably, and at the MP2/6-31G** level this 1011 (C_s) structure (2A) is less stable than the preferred 0012 (D_{2d}) structure by 9.6 kcal/mol.

The results (Table III) show that the most stable structure is, as expected, the nonplanar, staggered 0012 (D_{2d}) structure. However, it was a surprise to us that the nonplanar doubly bridged 2010 (C_{2v}) structure (3A) is, at the MP2/6-31G** level, within only 1.5 kcal/mol of the energy of the most stable structure. The balance[16] between strain and conversion of a terminal hydrogen to a bridge using an adjacent vacant orbital is apparently fairly even in B_2H_4. Both polarization functions and correlation corrections are usually required to exhibit the correct relative energies of isomers in this situation. When both of these effects are included, the instability of the nonclassical nonplanar 2010 (C_{2v}) structure over the classical nonplanar 0012 (D_{2d}) structure is reduced from 32.6 to 1.5 kcal/mol. The formation of the two hydrogen bridges does increase the BB overlap and population as compared with values for the 0012 (D_{2d}) isomer (Table III). However, the Mulliken charges of bridge and terminal hydrogen atoms are distorted by the change from one boron neighbor (terminal) to two boron neighbors (bridge). Hence, care must be used in relating these charges to the chemistry.

Because of the complexity of the potential energy surface we do not present a detailed reaction pathway between the two most stable isomers. Study of this pathway is left to the future.

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Notes

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Characterization and Structure of $[H_7O_3]^+[As(catecholate)_3]^- \cdot p$-Dioxane

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Although the "hydronium" salt of the catecholate (cat) complex of arsenic, $H[As(C_6H_4O_2)_3]\cdot nH_2O$, has been known since early in this century,[1] its structure has remained uncharacterized. It was originally assumed to be a bis chelate complex with a monodentate protonated-catechol ligand and a coordinated water ligand,[2] although a tris chelate structure was also considered. The latter formulation was strengthened when the complex anion was resolved into enantiomers with use of alkaloid bases.[3] The kinetics of the loss of optical rotation of acidic solutions of the complex were later studied,[4] and in the pH region below the acid dissociation constant for the complex ($pK_a = 2.75$) it was concluded that the apparent racemization was due to hydrolysis. Circular dichroism studies of the resolved complexes[5,6] supported the formulation as a tris chelate (at least for the potassium salt). Finally, the crystal structure of the resolved potassium salt $(-)_{585}$-$K[As(cat)_3]\cdot 1.5H_2O$ showed this structure to be a tris chelate complex in the Δ conformation.[7]

The nature of the "hydronium" salt has remained a mystery, particularly since the salt is a relatively weak acid that slowly hydrolyzes under acidic conditions. In principle, this interaction could range from a strong hydrogen bond, leaving the tris complex relatively undistorted, to actual protonation of a catechol oxygen, resulting in a phenolate mode of coordination for one of the catechol ligands, as has been observed in other catechol complexes.[8,9] We present here a structural characterization of the salt $[H_7O_3]^+[As(cat)_3]^- \cdot p$-diox ($p$-diox = p-dioxane), which clearly establishes the tris(catecholate) formulation as a hydronium tight ion pair.

Experimental Section

Arsenic was used in the form of $As_2O_5\cdot xH_2O$ (Mallinckrodt). It was analyzed for arsenic by the procedure of Vogel,[10] found to be 86.4% As_2O_5 by weight, and used as obtained. Catechol (Crown-Zellerbach) was recrystallized from benzene. Elemental analyses were performed by the Microanalytical Laboratory, Department of Chemistry, University of California, Berkeley, CA.

The complex was prepared with use of a scaled-down version of the procedure of Ryschkewitsch and Garret.[11] Crystallization was carried out by dissolving 200 mg of crude product in a solution of 10:1 p-dioxane/H_2O. Slow evaporation led to the formation of large platelike crystals of acceptable quality. Anal. Calcd for $[H_7O_3][As(C_6H_4O_2)_3]\cdot C_4H_8O_2$: C, 48.72; H, 5.02; As, 13.81. Found: C, 48.87; H, 4.99; As, 14.8.

Table I. Crystallographic Data

formula	$[H_7O_3][As(C_6H_4O_2)_3]\cdot C_4H_8O_2$	space group	$P2_1/c$
mol wt	542.2	Z	4
a, Å	16.299 (1)	ρ_{calcd}, g cm^{-3}	1.490
b, Å	14.457 (1)	ρ_{obsd}, g cm^{-3}	1.49 (1)
c, Å	10.320 (1)	radiation (λ, Å)	Mo Kα (0.71073)
β, deg	98.81 (1)	abs coeff, μ, cm^{-1}	14.55
V, Å^3	2410.0 (6)		
		cryst dimens, mm	0.45 × 0.25 × 0.21
Data Collection[a]			
h,k,l ranges			±19,±17,0–12
2θ range, deg			3–50
no. of reflecns			8829
no. of unique reflecns			4261
R for averaging intens, %			2.1
Refinement			
no. of reflecns with $F_o^2 > 3\sigma(F_o^2)$, n_{obsd}			2815
no. of variables, n_{var}			312
extinction coeff			2.8 (2) × 10^{-7}
R, %			2.94
R_w, %			3.75
goodness of fit (GOF)[b]			1.92

[a] At ambient temperature (23 °C); for details see ref 12. [b] GOF = $[\sum w(|F_o| - |F_c|)^2/(n_{obsd} - n_{var})]^{1/2}$.

X-ray Crystallography

Crystal fragments suitable for X-ray diffraction were cleaved from the large crystals and mounted on glass fibers with epoxy. A thin coating of epoxy was applied to the crystal to prevent its decomposition in air. Crystal density was measured by flotation in hexane/CCl_4. Crystal quality assessment and initial space group and lattice constant determinations were made from precession photographs. The cell volume and

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