

However, the ^{11}B spectrum at twice the magnetic field strength remains unchanged, proving that the additional multiplicity is a result of long-range coupling and not two separate boron resonances.

Long-range P-H spin-spin coupling in the 40.5-MHz ^{31}P NMR spectrum is also observed in $\text{B}_4\text{H}_8\cdot\text{PF}_2\text{H}$ while none of the other PF_2X adducts exhibit this behavior. The proton-coupled 80-MHz ^{31}P NMR spectrum of $\text{B}_4\text{H}_8\cdot\text{PF}_2\text{H}$ was identical with that obtained at 40.5 MHz, again indicating that long-range spin-spin coupling is involved rather than nonequivalent ^{31}P resonances. A 200-MHz ^1H NMR spectrum was of no assistance in resolving the ambiguities associated with this compound.

As stated above, PF_2H is known to have unusual base properties toward BH_3 .¹² Recently on the basis of the reaction of PF_2H with nickel and the instability of the resulting compound, it has been concluded that the stability of $\text{PF}_2\text{H}\cdot\text{BH}_3$ results from specific hydride-proton interactions involving BH_3 rather than PF_2H being an unusually strong base.¹³ This type of interaction could also occur in $\text{B}_4\text{H}_8\cdot\text{PF}_2\text{H}$ and, indeed, on

the basis of our data it seems probable that the bonding and structural parameters in $\text{B}_4\text{H}_8\cdot\text{PF}_2\text{H}$ are different from those of the other PF_2X complexes studied. A single-crystal X-ray diffraction study of this molecule is clearly needed.

While this work has contributed significantly to the understanding of the $\text{B}_4\text{H}_8\text{L}$ complexes, several interesting factors are still not well understood. The anomalous properties of $\text{B}_4\text{H}_8\cdot\text{PF}_2\text{H}$, the factors which stabilize the endo isomer relative to the exo isomer, and the importance of the electronic and steric requirements of the ligand in determining the relative stability of the two isomers deserve further study.

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Registry No. $\text{B}_4\text{H}_8\cdot\text{PF}_2\text{N}(\text{CH}_3)_2$, 60930-18-9; $\text{B}_4\text{H}_8\cdot\text{PF}_3$, 60930-19-0; $\text{B}_4\text{H}_8\cdot\text{PF}_2\text{Cl}$, 36907-24-1; $\text{B}_4\text{H}_8\cdot\text{PF}_2\text{Br}$, 36907-25-2; $\text{B}_4\text{H}_8\cdot\text{PF}_2\text{I}$, 36907-26-3; $\text{B}_4\text{H}_8\cdot\text{PF}_2\text{H}$, 24189-89-7.

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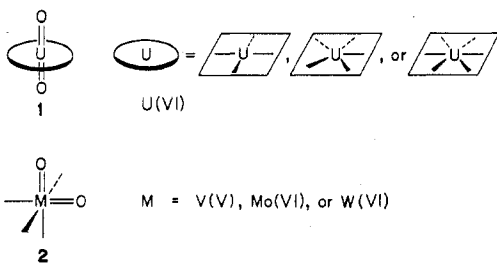
Bent Cis d^0 MoO_2^{2+} vs. Linear Trans d^0f^0 UO_2^{2+} : A Significant Role for Nonvalence 6p Orbitals in Uranyl

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The marked preference of uranyl, UO_2^{2+} , d^0f^0 , for linear geometries, while MoO_2^{2+} and isoelectronic d^0 molecules are bent, is not due to oxygen 2p-actinide 5f π bonding. Instead we trace the geometrical effect to a substantial involvement of formally inner-shell 6p orbitals of σ symmetry on uranium which interact significantly with oxygen p σ orbitals and "activate" these for σ bonding with U 5f.

Enigmatic is the contrast between the ubiquitous *linear* uranyl ion UO_2^{2+} and the common *bent* transition metal dioxo ions such as VO_2^+ , MoO_2^{2+} , and WO_2^{2+} . UO_2^{2+} , **1**, in which uranium has a formal 5f 0 6d 0 valence configuration, always occurs in crystals or in complexes with trans geometry, having four, five, or six secondary coordinations in an equatorial plane perpendicular to the main O-U-O axis.¹ In contrast, the VO_2^+ , MoO_2^{2+} , and WO_2^{2+} ions, **2**, which have a related d^0 valence configuration, occur, mostly in octahedral ligand sets, with exclusive cis geometry (O-M-O angle = 102-114°).²



An obvious difference in electronic structure between the *trans*- UO_2^{2+} and *cis*- VO_2^+ , MoO_2^{2+} , or WO_2^{2+} is that the uranium has f orbitals in the valence orbital set while the other

metals do not have them. So are the f orbitals in UO_2^{2+} really important in describing its geometrical preference of trans over cis? The numerous theoretical studies on uranyl certainly involve the f orbitals in bonding³ but do not address themselves to the choice among alternative geometries. We now hypothesize that the answer is *both no and yes* and that nonvalence 6p orbitals on U play a previously unappreciated role in determining the trans geometry.

A feature characteristic of both MoO_2^{2+} and UO_2^{2+} complexes is a very short M-O distance (Mo-O \approx 1.67 Å, U-O \approx 1.76 Å) and labile coordination geometries. Thus, as a first approximation, we may consider that the geometrical preferences reside in the naked cations themselves, and not in the auxiliary ligands. We have carried out extended Hückel calculations for MoO_2^{2+} and UO_2^{2+} with a variety of basis sets:⁴ for Mo 4d, 5s, 5p separately (d or s or p) or all together

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(4) (a) Mo-O and U-O bond distances are assumed to be 1.67 and 1.76 Å, respectively. (b) Atomic parameters are as follows. H_{ii} : Mo 5s, -9.66 eV; Mo 5p, -6.36 eV; Mo 4d, -12.3 eV; U 7s, -5.50 eV; U 7p, -5.50 eV; U 6d, -5.09 eV; U 5f, -9.01 eV; U 6p, -30.03 eV. Orbital exponents: Mo 5s, 1.96; Mo 5p, 1.90; Mo 4d, 4.54 (0.5899) + 1.90 (0.5899); U 7s, 1.914; U 7p, 1.914; U 6d, 2.581 (0.7608) + 1.207 (0.4126); U 5f, 4.943 (0.7844) + 2.106 (0.3908); U 6p, 4.033. The parameters for U are estimated from the relativistic Dirac-Fock wave functions of Desclaux.⁵ Details will be given in a forthcoming paper.⁶

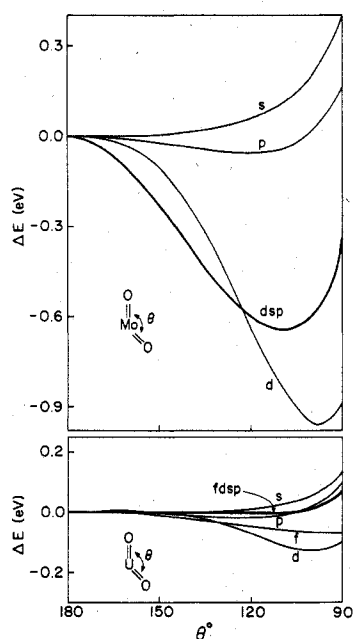
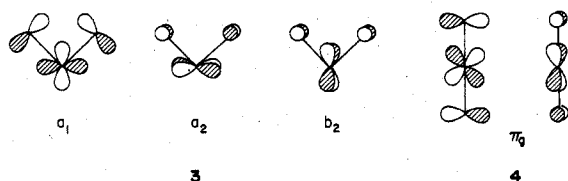


Figure 1. Relative total energy as a function of bond angle for Mo 4d, 5s, 5p (separately) and dsp (all together) basis sets in MoO_2^{2+} (top) and for U 5f, 6d, 7s, 7p (separately) and fdsp (all together) basis sets in UO_2^{2+} (bottom).

(dsp); for U 5f, 6d, 7s, 7p separately (f or d or s or p) or all together (fdsp).

Figure 1 shows the various calculated potential energy curves for bending MoO_2^{2+} or UO_2^{2+} . For MoO_2^{2+} the s and p curves lead to an angular differentiation, the d curve favors a strongly bent geometry, and the composite dsp surface has a minimum at an O–Mo–O angle of $\sim 110^\circ$, agreeing quite well with the observed structures.² It is evident that Mo 4d orbitals play a dominant role in stabilizing the bent MoO_2^{2+} . This may be explained simply in terms of maximum utilization of vacant d orbitals in π bonding with oxygen lone pairs.^{2d,7} There are four oxygen π -type lone pairs. In the cis geometry they can interact with three vacant d orbitals on the metal, **3**, whereas in the trans geometry they have to “share” two d orbitals, **4**.



In the case of the uranyl ion, the shapes of the energy curves for the d, s, and p basis sets bear a close resemblance to those

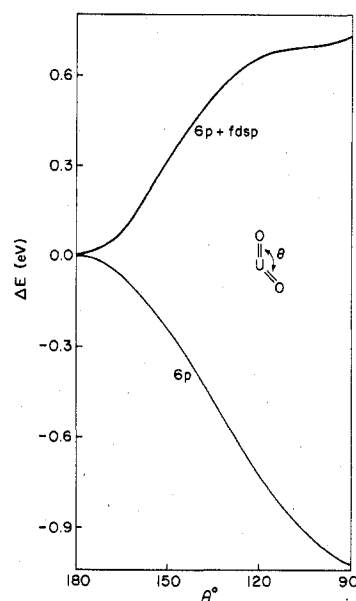


Figure 2. Relative total energy as a function of O–U–O bond angle for U 6p and 6p + 5f, 6d, 7s, 7p basis sets in UO_2^{2+} .

for corresponding basis sets on MoO_2^{2+} . For example, U 6d orbitals want UO_2^{2+} to bend, as 4d orbitals do for MoO_2^{2+} . However, the curvatures for UO_2^{2+} are all decreased compared to those for MoO_2^{2+} . Our orbital parameters^{4b} have U 6d, U 7s, and U 7p at much higher energies than Mo 4d, Mo 5s, and Mo 5p, respectively, causing smaller interactions between the vacant U orbitals and occupied O 2p orbitals in UO_2^{2+} . It is also apparent that f orbitals by themselves do not favor linearity, even though the surface computed is very soft. In bent UO_2^{2+} all four oxygen lone pairs are stabilized, not all equally, by four f orbitals. In the linear alternative only two f orbitals are available for the stabilization of two oxygen combinations. This picture is rather similar to that drawn for the role of d orbitals in favoring a cis geometry for MoO_2^{2+} . It is supported by angular overlap model calculations which show explicitly that d or f orbitals by themselves will always provide a better opportunity for π bonding in the bent cis geometry, no matter what the metal is.

This result may disappoint the chemist who wants to attribute the linearity of uranyl to f orbitals. But please do not come to a hasty pessimistic conclusion at this stage.

When 5f, 6d, 7s, and 7p orbitals are all used in the fdsp basis, the potential energy curve becomes very flat in the range of θ 110–180°. A complicated hybridization of the basis set is probably behind this, but we would like to bypass an explication here, for while the result is encouraging, it does not account for the experimental preponderance of strictly trans uranyl groupings.

Now we take into account the influence of the filled nonvalence, “inner-shell” 6p orbitals. There are several reasons for doing so. First, the weighted average 6p level, estimated from the relativistic Dirac–Fock wave functions of the U 6p_{3/2} and 6p_{1/2} orbitals,⁵ is at -30.0 eV in energy, with the maximal radial density at $R_{\text{max}} = 0.853$ Å. Considering the short U–O distance and the energy levels of O 2s (-32.3 eV) and O 2p (-14.8 eV), it is natural to expect substantial overlap interactions of a U 6p level with O 2s and O 2p. Note that the corresponding inner Mo 4p level is much more corelike, being at -48.5 eV with $R_{\text{max}} = 0.569$ Å. Second, XPS and ESCA spectra of uranyl compounds⁸ show a reorganization of U 6p_{3/2} and 6p_{1/2} and O 2s energy levels in the region between -12 and -32 eV, ascribable to the presence of a U 6p–O 2s covalent interaction. And third, both the MS–X α and DVM calculations^{3e,f} confirmed strong coupling between the O 2s and U

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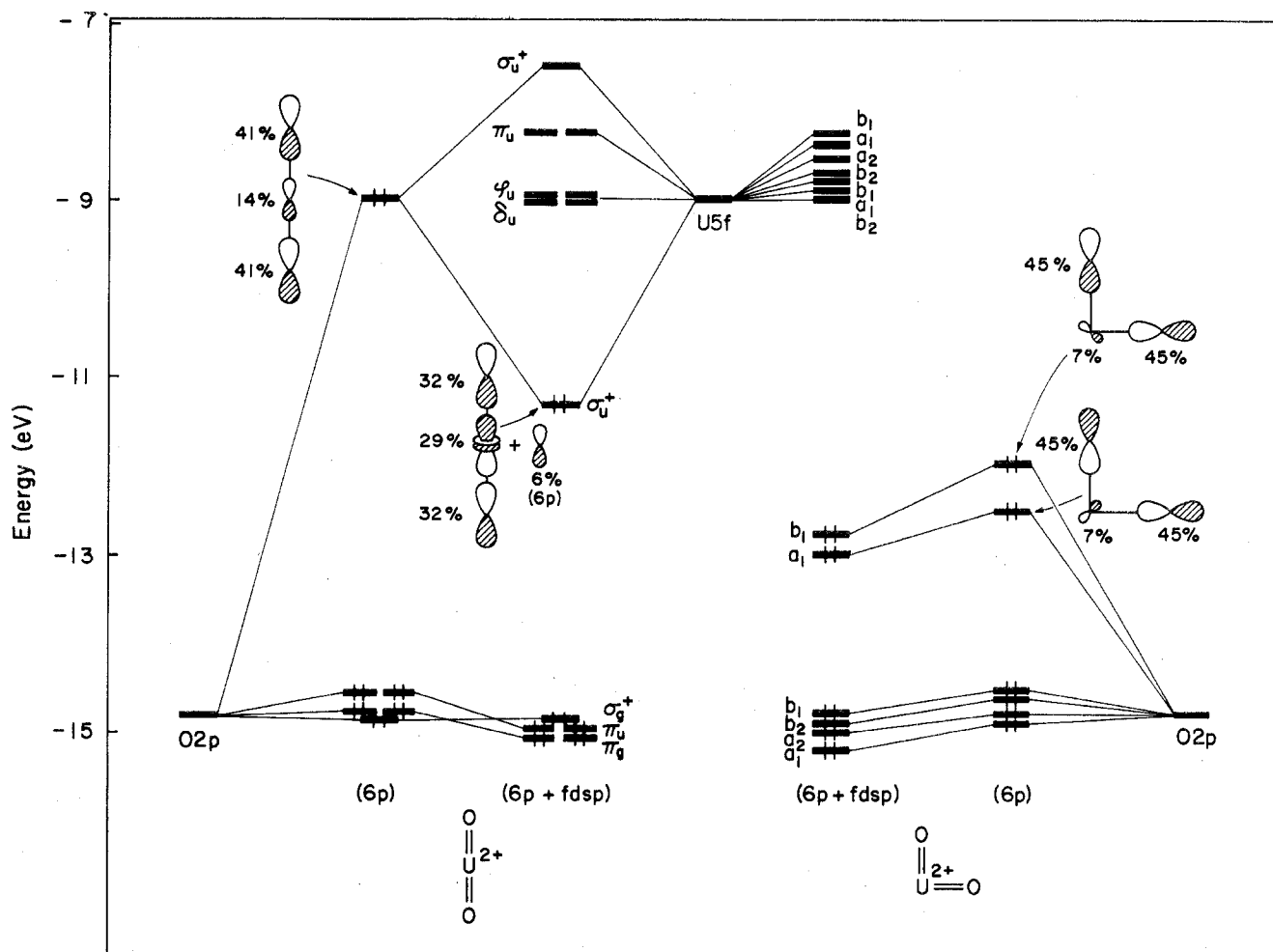


Figure 3. The valence orbitals of *trans*- UO_2^{2+} (at left) and *cis*- UO_2^{2+} (at right) calculated for U 6p and 6p + fdsp basis sets.

6p, especially the $6p_{3/2}$ level. The degree of admixture of O 2s in the 14 51_{1u} , which is formally identified as one of the U $6p_{3/2}$ states, amounts to $\sim 50\%$. Potential energy curves for the 6p and 6p + fdsp basis sets are in Figure 2.

Adding the 6p orbitals to the U fdsp valence set has a dramatic effect. The potential now clearly favors the linear form, while the 6p orbitals by themselves still want a bent UO_2^{2+} .

The way in which valence and "inner shells" operate to produce this effect is traced through Figure 3, which shows some of the frontier orbitals of *trans*- and *cis*- UO_2^{2+} . The six highest occupied orbitals are derived from the 2p orbitals of the two oxo ligands, in general destabilized by their mixing with occupied U 6p and stabilized primarily by unoccupied U 5f. Among these, the σ_u^+ orbital of the *trans* form is strongly pushed up (+5.8 eV) by $6p_z$ and is pushed back (-2.3 eV), mainly by $5f_{z^2}$.⁹ The two π_u orbitals are similarly affected by $6p_x$, $6p_y$, $5f_{xz}$, and $5f_{yz}$, but not so much. This is due to a relatively large O $2p_\sigma$ -U $6p_\sigma$ overlap integral (0.210) and a concomitant small O $2p_\pi$ -U $6p_\pi$ overlap integral (0.049). In the *cis* form, two orbitals, the highest occupied a_1 and b_1 , are pushed up by the sum of 5.1 eV and then pushed down by -1.2 eV. The σ_u^+ of the *trans* geometry is more destabilized by 6p, compared with a_1 and b_1 of *cis*, which in turn results in a more effective stabilization of σ_u^+ by 5f.

The considerations we present here are based on calculations without inclusion of spin-orbit interactions. The effects of

spin-orbit coupling are hardly negligible for uranium,^{10a} but we believe that trends in energy with angular deformation will carry over from calculations without spin-orbit interaction to those with such interaction,^{10b} especially for systems having f^0 electronic configurations.

We believe that we have found a reasonable explanation for the unique linear geometry of UO_2^{2+} . The nonvalence 6p and the valence 5f cooperate to determine the linear geometry—the repulsive 6p-oxygen interaction makes one oxygen p combination a superlative σ donor only in the linear form, for interaction with, stabilization by, an appropriate symmetry 5f combination.¹¹ We will also show⁶ that a similar cooperation of 6p and 5f orbitals accounts for the T shape of UO_3 .¹²

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Registry No. MoO_2^{2+} , 16984-32-0; UO_2^{2+} , 16637-16-4.

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(9) The z axis is along O-U-O.