THE NATURE OF ACTINYL-LIGAND BINDING: AnX_2^{2+} IONS (X= S, Se, Te) VALENCE-ISOELECTRONIC WITH AnO_2^{2+}

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There is substancial current interest in theoretical studies of the actinides, which represent one of the main current challenges for computational chemistry. We have shown that 1-component pseudopotential methods are satisfactory for the uranyl ion; in particular, DFT methods are highly promising.

There does not appear to have been any previous work, either experimental or theoretical, on AnX_2^{2+} ions containing the heavier Group 16 elements (S, Se, Te). We find that their electronic and geometrical structures bear little resemblance to those of AnX_2^{2+}. They have quintet ground states for An=U, and are strongly bent, with X-U-X angles of around 50 degres and substantial X-X bonding. As a result of the differences beetween size and energy of the valence orbitals of S compared to those of O, the predominant bonding interactions in US_2^{2+} involve the 6d orbitals on U rather than 5f.

While the actinyls are all geometrically similar, the shapes of US_2^{2+} and PuS_2^{2+} differ appreciably. This observation, together with the novel bonding involved, suggests that these species may have applications as separation agents for the actinides.