VIP **Actinides**

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A *cis*-Dioxido Uranyl: Fluxional Carboxylate Activation from a Reversible Coordination Polymer**

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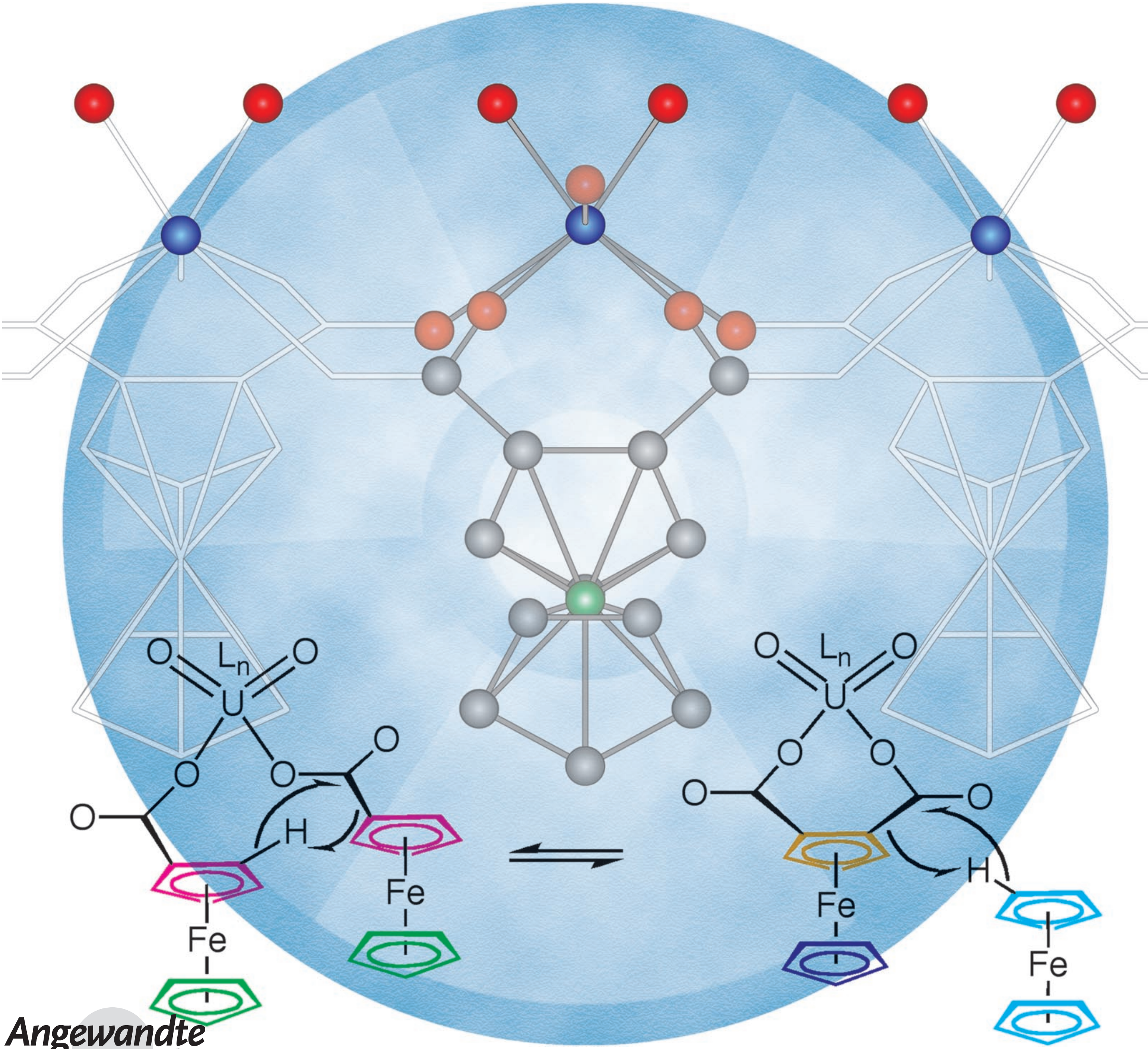

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Although situated beneath the lanthanides within the f block of the periodic table, the lighter members of the actinide series (that is, Th–Am) retain a closer affinity with early transition metals of the d block in the ability to access higher formal oxidation states and engage in metal–ligand multiple bonding.[1] These chemical properties are perhaps best exemplified by the dioxido cations MO_2^{n+} ($n = 1, 2$), which represent a group of considerable environmental importance for the actinides.[2] However, while the geometry of the dioxido unit (Figure 1) in transition-metal complexes is highly dependent on the valence-electron count, this electronic distinction is not observed with the actinides, where, regardless of oxidation state or valence-electron count, the dioxido group always adopts a linear (*trans*) geometry, which imparts unique chemical behavior. Herein we describe the structural and spectroscopic characterization of a carboxylate-bridged uranium(VI) coordination polymer that possesses a bent (*cis*) dioxido unit with an extraordinarily acute (70°) O=U=O bond angle.

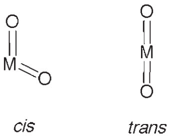
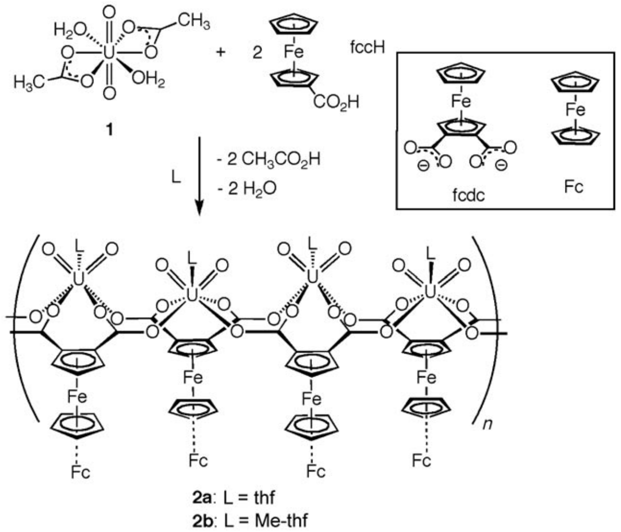


Figure 1. Dioxido geometries of MO_2^{n+} complexes.

When uranyl acetate dihydrate (**1**) was combined with two equivalents of ferrocenecarboxylic acid (fccH) in dichloromethane, acetic acid was eliminated, whereupon the addition of tetrahydrofuran slowly deposited the red coordination polymer $[UO_2(fcdc)(thf){\cdot}(Fc)]_n$ (**2a**, Scheme 1; fcdc = 1,2-ferrocenedicarboxylate, Fc = ferrocene) in 80–83 % yield. When the same reaction was performed with 2-methyltetrahydrofuran (2-Me-thf), the polymer $[UO_2(fcdc)(2\text{-Me-thf}){\cdot}(Fc)]_n$ (**2b**) was yielded. The generation of fcdc and Fc from these reactions is further discussed below. The mild conditions described here contrast with the elevated temperatures and/or pressures (that is, hydrothermal reactions) employed to synthesize many uranyl(VI) polymers,[3,4] including carboxylate derivatives.[5] Also, despite reports of the light sensitivity of ferrocene derivatives that possess electron-withdrawing (that is, carboxylate) substituents,[6] **2** is obtained reproducibly, regardless of whether or not the reaction mixture is shielded from light. The formation of **2** does not require rigorous exclusion of air or predried solvents, remains air stable in the solid state, but slowly decomposes to an uncharacterized brown material upon immersion in water.



Scheme 1. Formation of the coordination polymers **2**.

Compound **2** was characterized by elemental analysis, spectroscopic methods, thermogravimetric analysis (TGA), and X-ray diffraction. Single crystals of **2a** and **2b**, suitable for X-ray crystallography, were obtained directly from the respective reaction mixtures. Bulk solid samples display the same powder diffraction pattern as calculated from single-crystal data. The solid-state structure of **2a** (and **2b**, although disorder of the capping Me-thf ligand precludes further data refinement beyond establishing connectivity) consists of uranium *cis*-dioxido units connected in a polymeric network of fcdc ligands and interstitial Fc molecules (Figure 2). Each uranium center is seven coordinate (Figure 2 A), and adopts a distorted monocapped trigonal prismatic geometry. While the short terminal U(1)–O(3) bond distance of 1.745(9) Å in **2a** is comparable to those found in many uranyl(VI) complexes,[1] the O(3)-U(1)-O(3A) bond angle of 69.5(6)° is considerably smaller than the range (95–105°) that is typically observed in transition-metal dioxido complexes.[7] This enormous angular discrepancy reflects a more crowded seven-coordinate geometry in **2** that is not observed in transition-metal derivatives for which coordination numbers greater than six are unknown (Scheme 1).[7]

In polymer **2**, each carboxylate group coordinates in a bridging bidentate fashion generating a zigzag chain that connects the uranium centers along the *a* axis (Figure 2 B). The carboxylate groups are nearly coplanar with the attached C_5H_3 ring, thus aligning fcdc units in an eclipsed conformation. This pattern is repeated by another row of fcdc ligands that is shifted along the chain by one unit. However, whereas in uranyl(VI) polymers the linear dioxido geometry often directs equatorial coordination into extended planar sheets,[8] in **2** the *cis*-dioxido unit tilts the staggered rows of fcdc units nearly perpendicular to one another in an *endo*/*endo* conformation, which positions these groups for an interpenetrating network of C-H···π interactions[9] with interstitial Fc molecules (Figure 2 C). Parallel chains aligned along the *a* axis are thus knitted together across the *b* axis to form 11 Å thick layers that stack along the *c* axis, separated by long-range C-H···O=U (3.5 Å) interactions[10] between a phalanx of *cis*-dioxido groups from one layer and a row of interstitial Fc molecules from the next layer.

The strength of the intermolecular C-H···π interactions is borne out from TGA analysis of a solid sample of **2a**, which

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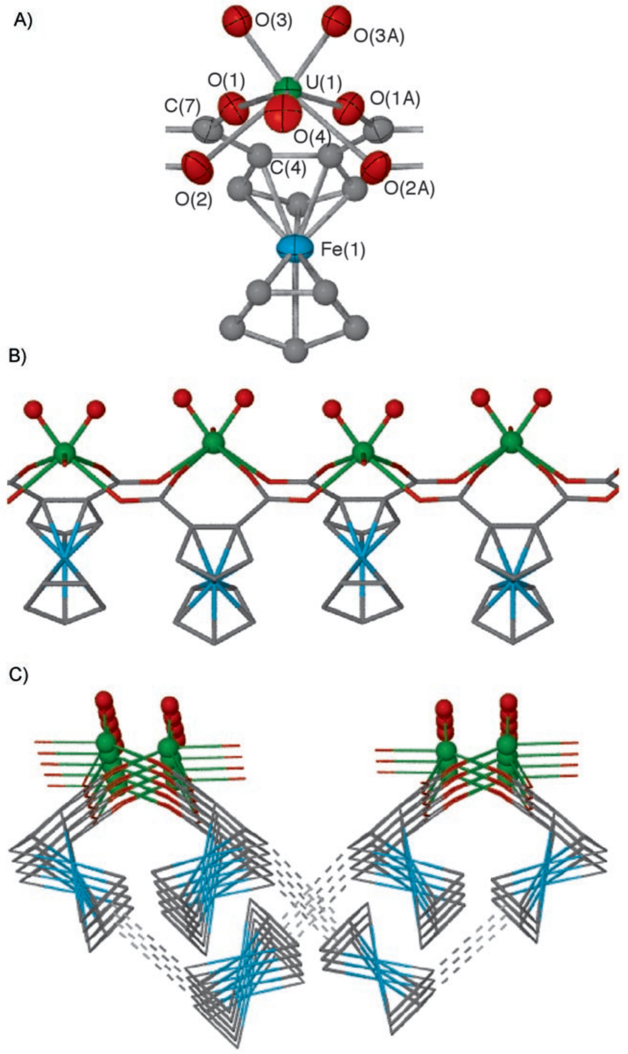


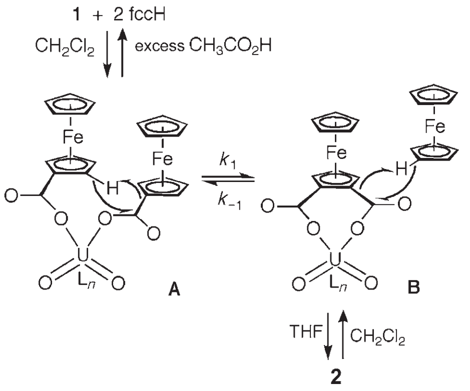
Figure 2. A) Thermal ellipsoid drawing (ellipsoids at the 50% probability level) of the monomeric unit of **2a** (carbon atoms of fcdc ligand represented by ball-and stick; disordered carbons atoms of thf ligand omitted for clarity). B) Ball-and-stick representation (*cis*-O=U=O groups highlighted) that shows the one-dimensional chain. C) two-dimensional network looking down the chain axis with dashed lines representing C–H···π bonds between fcdc ligands and interstitial ferrocene (Fc) molecules.

shows initial loss of coordinated thf prior to loss of the interstitial ferrocene (see the Supporting Information, Figure S1). At this point the sample turns black and all recognizable features of the IR spectrum disappear. The apparent lability of the capping thf ligand is further demonstrated by NMR spectroscopy, which shows dissociated thf even in a non-coordinating solvent such as dichloromethane.

The IR spectra show absorption peaks at 935 and 916 cm^{-1} for **2a** and 938 and 918 cm^{-1} for **2b** that correspond to the ν_1(symmetric) and ν_2(asymmetric) O=U=O stretches, respectively (see the Supporting Information, Figure S2). Both of these vibrational modes are typically observed in the IR spectra of transition-metal dioxido complexes that possess lower (that is, bent) symmetry,[11] whereas in linear actinide derivatives only the ν_2 stretch is IR active.[2] The absorption peaks for **2** are also present in IR spectra obtained in methanol, which suggests that the *cis*-dioxido geometry is retained in solution. Strong absorption bands at 1520 and 1470 cm^{-1} assigned to COO carboxylate modes are red-shifted within the normal range relative to uncoordinated carboxylate groups,[12] thus reflecting a lower bond order as a result of electron donation to the metal center.

Compound **2** is soluble in dichloromethane as well as coordinating solvents such as dimethylsulfoxide (DMSO), dimethylformamide, and methanol. However, **2** is only sparingly soluble in refluxing THF, from which a small amount of interstitial Fc can be extracted, as evidenced by NMR spectroscopy and X-ray crystallography. In fact, THF addition induces recrystallization of **2** from a dichloromethane solution, thus representing an example of a reversible coordination polymer that can be alternatively disassembled/reassembled.[13]

^{1}H NMR spectroscopy reveals solvent-dependent fluxional behavior for **2** based on line broadening, coalescence features, and changes in peak integration as a function of temperature, which represents an equilibrium process that interconverts fcc coordination (**A**, Scheme 2) with an environment that combines fcdc coordination and free Fc (**B**, Scheme 2) as is found in the solid state.[14] A reversible mechanism consistent with these observations involves a concerted abstraction of the α-hydrogen atom and reciprocal carboxylate migration that features activation of the C–C bond that connects a coordinated carboxylate group to the cyclopentadienyl ring, which is a particularly vulnerable site, noted independently in separate photochemical decomposition pathways that involve either substituted ferrocene derivatives[6] or uranyl carboxylate complexes.[15] In this context, the anomalously long C(4)–C(7) bond distance of 1.574(18) Å in the solid-state structure of **2a** is notable given the prominence of this bond in the reversible mechanism.



Scheme 2. Solvent-dependent fluxional behavior for **2**.

At ambient temperature the fluxional process occurs near the fast exchange limit of the NMR timescale in dichloromethane and methanol but at the slow exchange limit in strong donor solvents such as DMSO; in the latter instance solvent coordination probably interferes with the exchange mechanism, which leads to a slower rate. Accordingly, at −70 °C the slow exchange limit is reached in methanol but exchange remains at the fast exchange limit in the non-coordinating solvent dichloromethane. These observations suggest that the equilibrium process involves considerable steric congestion around the uranium coordination sphere, and it seems plausible that this concerted mechanism may be more easily accommodated with a *cis*-dioxido geometry than the more restrictive equatorial coordination that is allowed by the corresponding *trans*-dioxido structure.

When **2** is dissolved in glacial acetic acid, **1** and two equivalents of fccH are quantitatively regenerated. Thus, depending on the conditions used, either **1** or **2** alternatively enters the equilibrium from one direction (thus generating the same equilibrium mixture) and the other separates as a kinetic product from the other side by precipitation, which drives the equilibrium towards near-quantitative product formation. A different perturbation of this equilibrium occurs from the addition of excess Fc, which prompts the conversion of B into A as revealed by NMR spectroscopy.

In regard to the *trans*/*cis*-dioxido isomerization, theoretical studies have examined the factors behind the structural preference for a linear dioxido geometry,[16–18] and some have predicted conditions under which a stable bent isomer may be viable.[19] It has been postulated that strong π-donor ligands, which are capable of competing effectively with the uranyl(VI) dioxido group for the same metal-based orbitals, could destabilize the linear geometry, thus rendering a bent structure more accessible.[19] However, the relatively weak-field carboxylate ligands in **2** undermine the importance of these electronic factors. Instead, unlike the numerous examples of sterically unhindered uranyl(VI) carboxylate derivatives for which the linear dioxido group remains unperturbed, the bulky ferrocenyl substituents in the fcc ligands (when rotation about the Cp–carboxylate C–C bond is considered), and especially the steric congestion associated with the anomalous fluxional exchange process, are probably responsible for causing the isomerization to the *cis*-dioxido geometry. Additional stability for the *cis*-dioxido geometry in the solid state is probably provided by the extensive C–H bonding between fcdc ligands and interstititial Fc.

These results offer a unique opportunity to acquire fundamental new insights into the electronic structure, bonding, and physicochemical properties of one of the most familiar and environmentally relevant units in actinide chemistry. Preliminary results indicate that the *cis*-dioxido geometry confers different electrochemical, photochemical, and solubility behavior (the latter is likely linked to a permanent dipole moment and may be exploited in new separations strategies) in comparison to well known *trans* uranyl(VI) analogues. Further investigations shall be directed towards spectroscopic and theoretical studies to assess the role of the valence 5f/6d orbitals in the O=U=O bonding within a *cis*-dioxido geometry.

Experimental Section

All experiments were conducted in a fume hood, and all reagents and solvents were used as received. ^{1}H NMR spectra (referenced to non-deuterated impurity in the solvent) were recorded on a Bruker AMX-250 or 300 spectrometer. Chemicals shifts are reported in ppm and all coupling constants are reported in Hz unless otherwise noted. Infrared spectra were obtained as a mull in a mixture of type-NVH and type-B immersion oil pressed between KBr plates on a Thermo Nicolet Nexus 670 FT-IR spectrometer. Thermal gravimetric analysis was performed using a Cahn TA-50 microbalance by heating the material at 5 °C min^{-1} in a flowing nitrogen atmosphere. Elemental analyses were performed by Desert Analytics.

2a: Complex **1** (100 mg, 0.23 mmol) was added to a stirring suspension of fccH (108 mg, 0.47 mmol) in dichloromethane (5 mL). THF (5 mL) was added and the mixture stirred for 8 h. The resulting red solution was slowly evaporated to yield reddish-orange crystals (153 mg, 83 %). ^{1}H NMR (300 MHz, CD_2Cl_2, 23 °C, TMS): $\delta = 4.2$ (br s), 4.7(br s), 5.2 ppm (br s); IR: ν(U=O) 915 cm^{-1}, ν(U=O) 934 cm^{-1}, ν(C=O) 1472 cm^{-1}, ν(C=O) 1519 cm^{-1}; elemental analysis (%) calcd for $C_{26}H_{26}Fe_2O_7U$: C 39.03, H 3.27; found: C 38.46, H 3.32.

2b: The procedure followed was analogous to that for **2a** above, using MeTHF instead of THF, with similar yield. ^{1}H NMR (300 MHz, CD_3CN, 23 °C, TMS): same as for **2a** (both compounds generate dissociated capping ligand in solution along with the equilibrium mixture discussed in the Supporting Information); IR: ν(U=O) 918 cm^{-1}, ν(U=O) 938 cm^{-1}, ν(C=O) 1470 cm^{-1}, ν(C=O) 1520 cm^{-1}; elemental analysis (%) calcd for $C_{27}H_{28}Fe_2O_7U$: C 39.83, H 3.47; found: C 38.90, H 3.50.

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[1] F. A. Cotton, G. Wilkinson, C. A. Murrillo, M. Bochmann, *Advanced Inorganic Chemistry, 6th ed.*, Wiley, New York, **1999**.

[2] J. J. Katz, G. T. Seaborg, L. R. Morss, *The Chemistry of the Actinide Elements*, Chapman and Hall, London, **1986**.

[3] T. A. Sullens, R. A. Jensen, T. Y. Shvareva, T. E. Albrecht-Schmitt, *J. Am. Chem. Soc.* **2004**, *126*, 2676.

[4] M. B. Doran, A. J. Norquist, D. O'Hare, *Chem. Mater.* **2003**, *15*, 1449.

[5] L. A. Borkowski, C. L. Cahill, *Cryst. Growth Des.* **2006**, *6*, 2241.

[6] L. H. Ali, A. Cox, T. J. Kemp, *J. Chem. Soc. Dalton Trans.* **1973**, 1468.

[7] J. M. Mayer, *Inorg. Chem.* **1988**, *27*, 3899.

[8] J. Leciejewics, N. W. Alcock, T. J. Kemp, *Struct. Bonding* **1995**, *82*, 43.

[9] C. Janiak, *J. Chem. Soc. Dalton Trans.* **2000**, 3885.

[10] T. Steiner, *Chem. Commun.* **1997**, 727.

[11] Z. Xiao, R. W. Gable, A. G. Wedd, C. G. Young, *J. Am. Chem. Soc.* **1996**, *118*, 2912.

[12] M. Kakihana, T. Nagumo, M. Okamoto, H. Kakihana, *J. Phys. Chem.* **1987**, *91*, 6128.

[13] T. Vermonden, M. J. v. Steenbergen, N. A. M. Besseling, A. T. M. Marcelis, W. E. Hennink, E. J. R. Sudhölter, M. A. C. Stuart, *J. Am. Chem. Soc.* **2004**, *126*, 15802.

[14] Further details are provided in the Supporting Information.

[15] C. P. Baird, T. J. Kemp, *Prog. React. Kinet.* **1997**, *22*, 87.

[16] K. G. Dyall, *Mol. Phys.* **1999**, *96*, 511.

[17] K. Tatsumi, R. Hoffmann, *Inorg. Chem.* **1980**, *19*, 2656.

[18] R. B. King, *Inorg. Chem.* **1992**, *31*, 1978.

[19] G. Schreckenbach, P. J. Hay, R. L. Martin, *Inorg. Chem.* **1998**, *37*, 4442.