in our laboratories.

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(15) We have shown that the diastereomers **14a,b** are epimeric at the (*tert*-butyldimethylsilyl)oxy-bearing carbon, as opposed to endo/exo diastereomers, by obtaining the same diketone upon hydrolysis of **14a,b** (HF, CH_3CN) separation of the resulting keto alcohols, and subsequent oxidation (PCC). We have also shown that the diastereomers **16a** and **16b** are epimeric at the tertiary carbon bearing the methyl substituent by converting them to the cedranoids β- and α-pipitzol, respectively (unpublished results).

$Sm(\eta^6-C_6Me_6)(\eta^2-AlCl_4)_3$: The First Structure of a Rare Earth Complex with a Neutral π-Ligand

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The nature of the metal centers in most rare earth and actinide compounds has been recognized to approximate the ionic limit.[1a] An intriguing anomaly in this otherwise consistent behavior is the relative ease with which vapors of some f-block metal halides form intercalation phases with graphite.[1b,2] Clearly, a favorable interaction between the aromatic graphite layers and the metal halides must exist, viz., some form of π-bonding.

We and others have demonstrated before that one of these intercalators, UCl_4, can undergo arylation reactions to yield η^6-arene complexes and we have structurally characterized such compounds of U(IV)[3,4] and U(III).[5,6] In light of the fact that U arene complexes are the only examples of neutral π-ligands bonded to f-elements, we were wondering whether uranium constitutes a special case and whether an f-orbital contribution was instrumental in the bonding. It was therefore tempting to challenge our synthetic approach with lanthanide metals for which there is no structurally characterized complex with neutral π-ligands on record. We have chosen a known intercalator of graphite and wish to report here on the first arene complex of a rare earth element, $Sm(\eta^6-C_6Me_6)(AlCl_4)_3$-1.5toluene, (**1**).

The reaction of $SmCl_3$, $AlCl_3$ and hexamethylbenzene (hmb) in refluxing toluene in the presence of pieces of Al foil leads to a blood red solution (indicative of a Sm(II) compound) and complete dissolution of the salts within 20 min. The hot solution is filtered and very slowly cooled to room temperature. Yellow plates of the title compound deposit over a period of 2 days. Several batches were collected by filtration. The collection was discontinued when a tarry red residue started precipitating together with the title compound. This tar is insoluble in all solvents which are nondestructive for **1** and therefore impossible to separate. The total isolated yield of pure **1** was 14%. Addition of CH_2Cl_2 to the red solution results in a color change to yellow within 3 h but only impure products have so far been obtained. Although **1** formally was not involved in the reduction process attempts to prepare it directly have so far afforded only powders of erratic composition in very low yields. If, on the other hand, reflux is continued for longer time periods the yields of **1** decrease, probably in favor of the red compound which is presently under investigation.

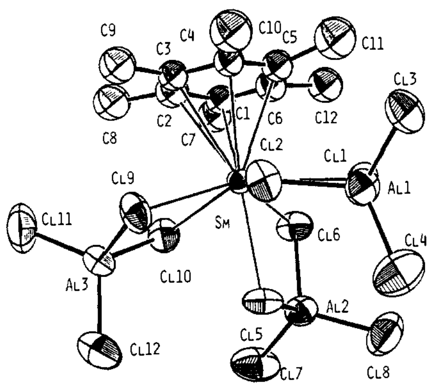

Figure 1. ORTEP drawing of $Sm(\eta^6-C_6Me_6)(AlCl_4)_3$. All atoms are represented by their ellipsoids of thermal vibration at the 40% probability level.

Table I. Geometric Properties of f-Element-Arene Complexes

compound	M-Cl, Å	M-C, Å	ionic radius	ref
$U(\eta^6-C_6H_6)(\eta^2-AlCl_4)_3$	2.88 [3][a]	2.91	1.025	5
$[U(C_6Me_6)Cl_2(\mu-Cl)_3-U(C_6Me_6)Cl_2]$	2.75 [5][b] 2.58 [1][c]	2.92 [4]	0.93	3
$(C_6Me_6)UCl_2(\mu-Cl)_3UCl_2-(\mu-Cl)_3UCl_2(C_6Me_6)$	2.78 [8][b] 2.53 [1][c]	2.94 [3]	0.93	4
$[U_3(\mu^3-Cl)_2(\mu^2-Cl)_3-(\mu^1,\eta^2-AlCl_4)(\eta^6-C_6Me_6)_3]$	2.78 [2][b] 2.99 [9][d] 2.94 [3][a]	2.92 [4]	1.025	6
$Sm(\eta^6-C_6Me_6)(AlCl_4)_3$	2.85 [2][a]	2.89 [5]	0.964	this work

[a] η^2-AlCl_4. [b] Bridging. [c] Terminal. [d] Capping.

$Sm(\eta^6-C_6Me_6)(AlCl_4)_3$ is a molecular complex (Figure 1).[7] The coordination polyhedron is a distorted pentagonal bipyramid with the arene in an apical position. The arrangement is similar to that reported for $U(C_6H_6)(AlCl_4)_3$.[5] The mean Sm-Cl and Sm-C distances are 2.85 [2] and 2.89 [5] Å, respectively. There is no statistically significant distortion of the hmb moiety.

Table I summarizes some metric properties of f-element-arene complexes. Although the differences in the lengths of comparable bonds are not significant in a statistical sense there are some interesting trends. In agreement with the difference of the ionic radii of Sm(III) and U(III), we find that the M-η^2-$AlCl_4$ and M-η^6-C_6Me_6 bonds are shorter in the Sm(III) compound, albeit by less than the differences in the ionic radii. The M-C mean distances in the U(IV) complexes, on the other hand, are systematically longer than those in either the Sm(III) or U(III) complexes. Not taking packing forces into account, this would indicate that the M-arene bonds are somewhat stronger in the trivalent compound.

Although arene bonding in actinides and lanthanides has not yet been rationalized by calculations supported by spectroscopy, we can now be confident that f-orbital contribution does not play an important role because the f-shells in lanthanide metals are efficiently screened by the closed $5s^2$ and $5p^6$ shells. Therefore, combinations of 5d, 6s, and 6p orbitals are assumed to be the

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(1) (a) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; Wiley: New York, 1980; pp 981-1046. (b) *Ibid.*; pp 359-361.

(2) *Gmelin Handbuch der anorganischen Chemie: Sc, Y, La-Lu*, 8th ed.; Springer Verlag: Berlin, 1982; Part C 4a.

(3) Cotton, F. A.; Schwotzer, W. *Organometallics* **1985**, *4*, 942.

(4) Campbell, G. C.; Cotton, F. A.; Haw, J. F.; Schwotzer, W. *Organometallics* **1986**, *5*, 274.

(5) Cesari, M.; Pedretti, U.; Zazetta, A.; Lugli, G.; Marconi, N. *Inorg. Chim. Acta* **1971**, *5*, 439.

(6) Cotton, F. A.; Schwotzer, W.; Simpson, C. Q. *Angew. Chem., Int. Ed. Engl.*, in press.

(7) Crystal data: $SmCl_{12}Al_3C_{12}H_{18}\cdot1.5C_7H_8$; monoclinic $P2_1/c$: a = 18.696 (4) Å, b = 16.906 (3) Å, c = 12.262 (2) Å, β = 100.81 (2)°, V = 3807 (2) $Å^3$, Z = 4; R = 5.2%, R_w = 6.1%. A table with information pertaining to data collection and refinement and a list of fractional coordinates are available as supplementary material.

acceptor orbitals in a fashion reminiscent of arene complexes of third-row transition and main-group 14 elements.[8]

Finally, there is an interesting side aspect to the arylation reaction in that it provides a means of rendering f-metal halides soluble in aromatic hydrocarbons. This drastic change in the solubility is undoubtedly due to arene substitution. Since the metal-arene interaction is a weak one which will be dependent on the nature of the metal as well as the nucleophilicity of the arene, one can envision new sequestering techniques for f-block elements based on extraction procedures involving arene complexes.

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Supplementary Material Available: Table pertaining to data collection and refinement and a list of fractional coordinates (3 pages). Ordering information is given on any current masthead page.

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(8) Schmidbaur, H. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 893.

Fluorescence of Clay-Intercalated Methylviologen

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Methylviologen dichloride (MV) (1,1′-dimethyl-4,4′-dipyridinium dichloride or paraquat) is widely used as an effective electron relay in the process of sacrificial water photoreduction,[1] in conjunction with a variety of catalysts, such as colloidal platinum,[2] hydrogenase enzyme,[3] or ruthenium dioxide.[4] We have recently reported that a system consisting of tris(2,2′-bipyridyl)ruthenium(II) (Ru(bpy)$_3^{2+}$), MV, and a sacrificial electron donor, triethanolamine, in the presence of the clays, montmorillonite,[5,6] or hectorite,[7] when illuminated by visible light, produces hydrogen, albeit in low yield. It has been shown that MV intercalates into the sheets of these expandable smectites[6,8] with a basal spacing of 12.6 Å. Very recently, Ege et al.[9] have reported the catalytic hydrogen production in a clay/Pt/poly(vinyl acetate) film containing propylviologen sulfonate. The luminescence of colloidal suspensions of Ru(bpy)$_3^{2+}$ intercalated into these same smectites has been reported previously.[10-13] Its fluorescence is quenched by MV.[11] The elucidation of the effect of structure and composition of these complexes and of the function of each component on the photochemical processes may be assisted by a variety of spectroscopic studies. With this in mind we investigated the fluorescence behavior of MV. To the best of our knowledge fluorescence from MV at ambient temperatures has not been reported previously. However, fluorescence of MV^{2+} could be observed when it was incorporated into the lamellae of colloidal hectorite and montmorillonite suspensions. No fluorescence could be detected in the case of nontronite. Time-resolved fluorescence measurements as well as the fluorescence intensity variation with the ratio MV^{2+}/clay suggest different types of binding sites for MV^{2+} adsorbed on the clay colloidal particles.

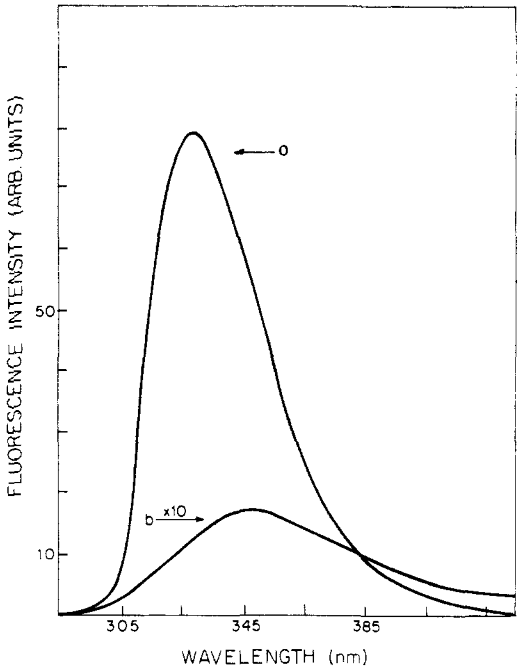

Figure 1. Corrected fluorescence spectra (λ_{ex} = 285 nm, excitation and emission band-pass, 3 nm) of methylviologen dication (MV^{2+}), 5 × 10^{-6} M, (a) in montmorillonite (0.25 g/L) and (b) in aqueous solution, pH 7. Spectra were measured on a Perkin-Elmer Model 44A spectrophotofluorimeter equipped with a DCSU-2 corrected spectral unit. The spectrum (b) in aqueous solution was recorded at a sensitivity which was 10× greater than that for spectrum a.

Excitation at 285 nm of a sample of MV^{2+} (5.0 × 10^{-6} M) in a colloidal suspension of montmorillonite (0.25 g/L) resulted in the fluorescence spectrum shown in Figure 1a (maximum at 330 nm). The fluorescence spectrum of MV^{2+} in an aqueous solution of the same concentration could be observed but was barely detectable (Figure 1b), the maximum occurring at 345 nm.[14] On incorporation into clay, the absorption spectral maximum of MV was 280 nm, which was shifted from that found in water (257.5 nm). It is known that MV^{2+} is readily incorporated into the interlamellar space of swollen clays.[6,16] It has been shown by infrared spectroscopy that MV^{2+} adopts a planar conformation when incorporated into montmorillonite.[8] The interlamellar space was previously determined to be 2.95 Å,[6] a value corroborating previous work[16,17,23] and requiring MV^{2+} to adopt a planar

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[‡] National Research Council of Canada.

(1) Harriman, A., West, M. A. Eds. *Photogeneration of Hydrogen*; Academic Press: New York, 1982.

(2) (a) Moradpour, A.; Amouyal, E.; Keller, P.; Kagan, H. B. *Nouv. J. Chim.* **1978**, *2*, 547-549. (b) Kiwi, J.; Gratzel, M. *Nature (London)* **1979**, *281*, 657-658. (c) Kalyanasundaram, K.; Kiwi, J.; Gratzel, M. *Helv. Chim. Acta* **1978**, *61*, 2720-2730. (d) Lehn, J. M.; Sauvage, J. P. *Nouv. J. Chim.* **1977**, *1*, 449-451.

(3) (a) Okura, I.; Kim-Thuan, N. *J. Chem. Soc., Chem. Commun.* **1980**, 84-85; *J. Mol. Catal.* **1979**, *5*, 311-314.

(4) Amouyal, E.; Keller, P.; Moradpour, A. *J. Chem. Soc., Chem. Commun.* **1980**, 1019-1020.

(5) Detellier, C.; Villemure, G. *Inorg. Chim. Acta* **1984**, *86*, L19-L20.

(6) Villemure, G.; Kodama, H.; Detellier, C. *Can. J. Chem.* **1985**, *63*, 1139-1142.

(7) Villemure, G.; Bazan, G.; Detellier, C., unpublished results.

(8) Raupach, M.; Emerson, W. W.; Slade, P. G. *J. Colloid Interface Sci.* **1979**, *69*, 398-408.

(9) Ege, D.; Ghosh, P. K.; White, J. R.; Equey, J. F.; Bard, A. J. *J. Am. Chem. Soc.* **1985**, *107*, 5644-5652.

(10) Della Guardia, R. A.; Thomas, J. K. *J. Phys. Chem.* **1983**, *87*, 990-998.

(11) Ghosh, P. K.; Bard, A. J. *J. Phys. Chem.* **1984**, *88*, 5519-5526.

(12) Habti, A.; Keravis, D.; Levitz, P.; Van Damme, H. *J. Chem. Soc., Faraday Trans. 2* **1984**, *80*, 67-83.

(13) Nakamura, T.; Thomas, J. K. *Langmuir* **1985**, *1*, 568-573.

(14) That very small fluorescence was observed regardless of the history of the methylviologen: freshly twice recrystallized samples gave the same result as the commercial material. No fluorescence was detected in any sample above 450 nm.[15] Additionally, there was no absorbance above 330 nm as has been reported for charge-transfer complexes involving MV^{2+}.[15] Further, the excitation and the absorption spectra were virtually superimposable.

(15) Prasad, D. R.; Hoffman, M. Z. *J. Phys. Chem.* **1984**, *88*, 5660-5665.

(16) Weed, S. B.; Weber, J. B. *Am. Mineral.* **1968**, *53*, 478-490.

0002-7863/86/1508-4658$01.50/0