

Table I. Structural Data for the Bridging Groups and Magnetic Properties

| | 1 ^a | 2 ^a | μ -MeO ^b |
|-----------------------------------|----------------|----------------|-------------------------|
| Cr-O, Å ^c | 1.992 (2) | 1.980 (4) | 1.962 (9) ^d |
| Cr-O*, Å ^c | 1.974 (2) | 1.977 (5) | |
| Cr-Cr*, Å ^c | 3.087 (1) | 3.088 (3) | 3.028 (2) |
| Cr-O-Cr*, deg ^c | 102.24 (9) | 102.6 (2) | 101.0 (3) ^d |
| θ , deg ^e | 4.99 | 0.134 | 29.75 ^d |
| ϕ , deg ^e | 64.32 | 59.63 | |
| 2J, cm ⁻¹ ^f | -19.0 | -16.9 | -9.8 |

^aThis work. ^bReference 5. ^cFor complexes **1** and **2**, unasterisked atoms are related to asterisked atoms by the C₂ axis. ^dThese values are averaged. ^eSee text. ^f2J refers to the coupling constant determined from the observed susceptibility data.

complexes **1** and **2**⁸ substantiate the binuclear structure, where two octahedral six-coordinated chromium(III) ions are symmetrically bridged by two phenoxo ligands as shown in Figure 1. Both of the complexes are racemic isomers with respect to two configurational chiralities due to three chelating ligands in a chromium(III) ion. Such a racemic form is a rare one found only for a few complexes such as the corresponding μ -methoxo complex,⁵ whereas most binuclear Cr(III) complexes of this type generally adopt the meso structure as for the μ -alkoxo 3-halogenoacetylacetonato complexes.³ The structural data are summarized in Table I. The Cr-O and Cr-Cr distances and the Cr-O-Cr angles of the bridging moiety in both complexes are almost the same, but the former distances and the latter angles are a little longer and larger, respectively, than those of the μ -methoxo homologue. The phenyl planes and the Cr₂O₂ bridging plane are twisted with the angles ϕ ca. 60°. The dihedral angles between the C-O bond vectors of the phenoxo ligands (θ) for the present complexes are much smaller than those of the μ -methoxo homologue, implying the predominant sp² hybridization at the bridging phenoxo oxygen ligands.

The UV-vis absorption spectra show no significant difference between these complexes⁹ in spite of the large variation of pK_a values for the bridging ligands. The temperature-dependent magnetic susceptibility measurements for the complexes **1** and **2** reveal antiferromagnetic exchange interactions. As expected from the Gerup-Hodgson-Pedersen (GHP) model,¹⁰ the coupling constants (2J) for the phenoxo complexes with smaller θ angles become larger than those for the alkoxo ones as shown in Table I. A change from **2** to **1** with a very small increase in θ angles brings about an increase in the coupling constants, contrary to the expected decrease with an increase in the θ angles in terms of the GHP model.¹⁰ The preliminary results for all the present μ -(4-X-phenoxo) complexes with almost constant geometry in the bridging moieties demonstrate that the magnetic interactions in these phenoxo complexes tend to increase with increasing pK_a values of 4-X-phenols or the electron density at the bridging oxygen ligands. This observation is in accordance with the analogous one for Cu(II) complexes.¹¹ The present correlation will provide a suitable criterion to evaluate the electronic contribution to the magnetic interaction by varying the para substituents of the bridging 4-X-phenols.

- (8) The X-ray crystal structure analyses were carried out at the X-ray Diffraction Service of our Department of Chemistry. The intensity data were collected by a Rigaku AFC-5R diffractometer with use of Mo K α radiation ($\lambda = 0.71069$ Å). The program TEXSAN was used for the calculations. Crystallographic data: **1**, Cr₂C₁₄H₁₂O₁₀, C2/c, $a = 13.214$ (2) Å, $b = 16.438$ (3) Å, $c = 16.869$ (2) Å, $\beta = 101.773$ (9)°, $V = 3587.2$ (8) Å³, $Z = 4$, $R = 0.043$, $R_w = 0.047$ for 5428 independent reflections; **2**, acetone, Cr₂C₁₅H₁₄O₁₁, P2/c, $a = 10.568$ (3) Å, $b = 11.564$ (3) Å, $c = 16.485$ (3) Å, $\beta = 105.93$ (2)°, $V = 1937.3$ (8) Å³, $Z = 2$, $R = 0.065$, $R_w = 0.068$ for 5933 independent reflections.
- (9) Selected UV-vis data: [$\sigma_{\text{max}}/10^3$ cm⁻¹ (log (ε/dm³ mol⁻¹ cm⁻¹))]: **1**, 16.9 (2.08), 25.6 (2.60); **2**, 16.8 (2.08), 25.5 (2.64); **3**, 16.8 (2.09), 25.6 (2.64); **4**, 17.0 (2.16); **5**, 16.9 (2.13), 25.6 (2.66).
- (10) Gerup, J.; Hodgson, D. J.; Pedersen, E. *Acta Chem. Scand., Ser. A* **1983**, *37*, 161.
- (11) LeMay, H. E., Jr.; Hodgson, D. J.; Pruettingkura, P.; Theriot, L. J. *J. Chem. Soc., Dalton Trans.* **1979**, 781.

Acknowledgment. We thank Drs. W. Mori and H. Nakayama of the College of General Education, Osaka University, for constructing a Faraday apparatus for the magnetic susceptibility measurements. We gratefully acknowledge support of this research by a Grant-in-Aid for Scientific Research (No. 02453040) from the Ministry of Education, Science and Culture and also by the Yamada Science Foundation.

Supplementary Material Available: For **1** and **2**, complete tables of crystal data, positional and anisotropic thermal parameters, bond distances, and bond angles and ORTEP diagrams (8 pages); listings of observed and calculated structural factors (7 pages). Ordering information is given on any current masthead page.

Department of Chemistry
Faculty of Science
Osaka University
Toyonaka, Osaka 560, Japan

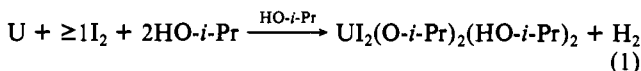
Manabu Nakahanada
Takashi Fujihara
Akira Fuyuhiro
Sumio Kaizaki*

Received September 24, 1991

Dissolution of Uranium Metal Using Iodine and 2-Propanol. Synthesis and X-ray Crystal Structure of Tetraiodotetraisopropoxybis(2-propanol)diuranium

Direct oxidation of reactive metals with alcohols has been used to prepare a range of metal alkoxide compounds.¹⁻⁴ In some systems, small amounts of mercuric halides are added to assist the oxidation and thus formation of the metal alkoxides. Despite the high reactivity of uranium metal, attempts in our laboratories to cleanly prepare uranium alkoxides by direct reaction of the metal with alcohols have not been entirely successful. Reaction of uranium metal in refluxing ethanol or 2-propanol does initially give small amounts of a green, presumably U(IV) alkoxide; however, the metal surface is eventually passivated, and the reaction stops. In contrast, direct oxidation of actinide metals to the metal halides has been reported using a number of halogen transfer agents.⁵⁻⁷ Clark and Sattelberger found that reaction of uranium metal with 3/2 equiv of I₂ in coordinating solvents leads to the formation of UI₃L₄ species (L = solvent molecule) of significant synthetic utility.⁵ Karraker reported the formation of similar actinide complexes, AnI₃(THF)_x (An = Pu, $x = 5$; An = Np, $x = 4$) by reaction of the metals with C₂H₄I₂ in THF solutions.⁶ We sought to extend this chemistry to the preparation of uranium alkoxides through simultaneous iodine and alcohol oxidation of uranium metal. This type of oxidation has been reported for cerium metal using 2-methylpropan-2-ol as the solvent.⁸ The product of the reaction, a presumed cerium-iodo-alkoxide catalyst for oxidation of alcohols, was never isolated and characterized.

Reaction of cleaned uranium metal turnings⁵ with I₂ in 2-propanol under anaerobic conditions results in complete dissolution of the metal in a matter of hours (eq 1). A light purple solution

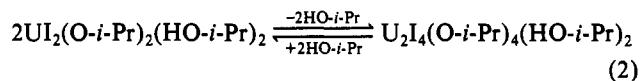


results from which lavender crystals of a compound formulated as UI₂(O-*i*-Pr)₂(HO-*i*-Pr)₂ (**1**) can be isolated by reducing the volume of the solution and cooling to -35 °C.⁹ In this reaction,

- (1) Bradley, D. C. *Chem. Rev.* **1989**, *89*, 1317.
 (2) Bradley, D. C.; Mehrotra, R. C.; Gaur, D. F. *Metal Alkoxides*; Academic Press: London, 1978.
 (3) Mehrotra, R. C. *Adv. Inorg. Chem. Radiochem.* **1983**, *26*, 269.
 (4) Hubert-Pfalzgraf, L. G. *New J. Chem.* **1987**, *11*, 663.
 (5) Clark, D. L.; Bott, S.; Sattelberger, A. P. *Inorg. Chem.* **1989**, *28*, 1771.
 (6) Karraker, D. G. *Inorg. Chim. Acta* **1987**, *139*, 189.
 (7) Deacon, G. B.; Tuong, T. D. *Polyhedron* **1988**, *7*, 249.
 (8) Namy, J. L.; Souppé, J.; Collin, J.; Kagen, H. B. *J. Org. Chem.* **1984**, *49*, 2045.

the uranium center is oxidized by both the alcohol solvent (with the concomitant formation of hydrogen) and iodine to give a U(IV) species. This is in contrast to uranium oxidations with iodine done in aprotic solvents such as acetonitrile or THF,⁵ where U(III) species are obtained. We have not observed any intermediates such as $UI_4(\text{HO-}i\text{-Pr})_n$ or $U(\text{O-}i\text{-Pr})_4(\text{HO-}i\text{-Pr})_n$,¹⁰ thus, it seems unlikely that **1** is a result of ligand redistribution. In reaction with greater than 1 equiv of iodine, the excess I_2 could be recovered when the solvent was removed in vacuo. Studies into the formation of these mixed iodo-alkoxide complexes have been initiated.¹¹ There remains the possibility that an intermediate $UI_4(\text{HO-}i\text{-Pr})_n$ species undergoes alcoholysis, which would involve the production of catalytic amounts of HI. This has been observed in the alcoholysis of a number of transition-metal halides.^{2,12}

Compound **1** is moderately soluble in 2-propanol but readily turns green in noncoordinating solvents, e.g. toluene. Drying the lavender solid in vacuo (10^{-4} Torr, 24 h) removes coordinated 2-propanol and gives a light green solid $U_2I_4(\text{O-}i\text{-Pr})_4(\text{HO-}i\text{-Pr})_2$ (**2**) (eq 2). This light green compound is sparingly soluble in



toluene and insoluble in hexane. Toluene solutions of **2** vigorously react with KH, suggesting the presence of coordinated alcohols which are not labile in vacuo. This was confirmed by a broad OH stretch at 3200 cm^{-1} in the IR region, which was not removed even with sustained evacuation. Addition of 2-propanol to **2** and cooling to $-35\text{ }^\circ\text{C}$ again produces lavender crystals of **1**, which demonstrates that this monomer-dimer equilibrium is reversible. Attempts to obtain an X-ray structure of **1** have been unsuccessful because of this ready loss of solvent. Other coordinating solvents like pyridine or THF also displace the labile alcohol. A pale green THF adduct, $UI_2(\text{O-}i\text{-Pr})_2(\text{HO-}i\text{-Pr})(\text{THF})$ is formed by titration of **1** with stoichiometric amounts of THF. In neat THF, the coordinated alcohol is displaced over several hours to give light maroon $UI_2(\text{O-}i\text{-Pr})_2(\text{THF})_2$. These complexes also lose coordinated solvent. Attempts to prepare more stable monomeric species for X-ray diffraction studies are ongoing.

The formulation of **2** as $U_2I_4(\text{O-}i\text{-Pr})_4(\text{HO-}i\text{-Pr})_2$ is supported by elemental analysis and by ^1H NMR and IR spectroscopies.¹³ Peaks in the NMR spectrum are quite broad and paramagnetically shifted as is typical of U(IV) systems.^{14,15} The electronic absorption spectrum of **2** was also examined. The assignment of the $f \rightarrow f$ transitions to a U(IV) ($5f^2$) species is the result of the

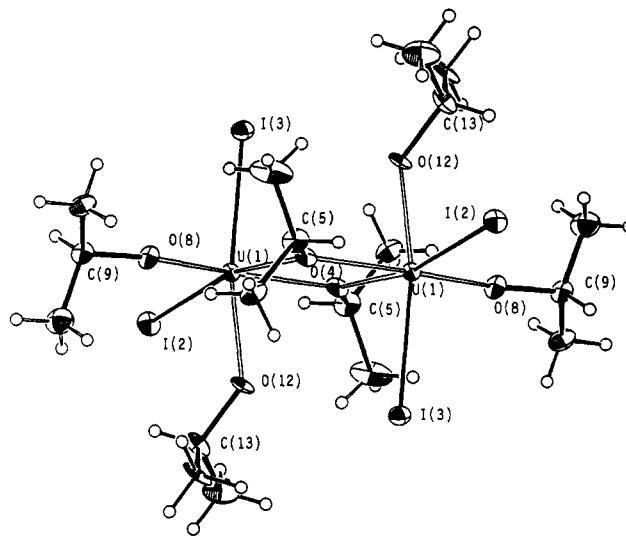


Figure 1. ORTEP view of **2**. Selected distances and angles: U(1)–U(1)' = 3.807 (1) Å; U(1)–O(4) = 2.27 (1) Å; U(1)–O(4)' = 2.32 (1) Å; U(1)–O(8) = 2.02 (1) Å; U(1)–O(12) = 2.40 (1) Å; U(1)–I(2) = 3.034 (3) Å; U(1)–I(3) = 3.050 (3) Å; I(3)–U(1)–O(12) = 170.0 (3)°; U(1)–O(4)–U(1)' = 112.4 (5)°; U(1)–O(8)–C(9) = 166.7 (10)°; U(1)–O(12)–C(13) = 134.4 (10)°.

unfavorable comparisons with U(III) or U(V) species and the favorable comparison with other U(IV) alkoxide complexes.¹⁶ In particular, the spectrum lacks the relatively intense (ϵ of ca. $10^3\text{ M}^{-1}\text{ cm}^{-1}$) $5f \rightarrow 6d$ transitions of a U(III) species usually found in the 400–700-nm region and the broad envelope of $f \rightarrow f$ transitions of a U(V) species.¹⁷ The absorption edge at 400 nm is tentatively assigned to an iodine-based ligand to metal charge transfer.

Single crystals of **2** were grown by slow evaporation (days) of a concentrated toluene solution at room temperature, and the structure was determined from diffraction data collected at $-182\text{ }^\circ\text{C}$.¹⁸ An ORTEP view of the centrosymmetric dinuclear structure can be seen in Figure 1. The overall geometry can be described as an edge-shared biotetrahedron held together by the asymmetrically bridging oxygen atoms of isopropoxide groups.^{15,19} The short bridging U(1)–O(4) distance is 2.27 (1) Å, and the longer U(1)–O(4)' distance is 2.32 (1) Å. The terminal isopropoxide ligands with a notably short U(1)–O(8) distance of 2.02 (1) Å are trans to the long bridging isopropoxide distance. There are two types of terminal iodide ligands, one set being trans to the bridging isopropoxide oxygens [U(1)–I(2) = 3.034 (3) Å] and another set trans to the 2-propanol ligand [U(1)–I(3) = 3.050 (3) Å]. Although we were unable to locate the proton of the 2-propanol ligand in the structure, its presence is inferred by the long U(1)–O(12) distance of 2.40 (1) Å and the clear presence of hydrogen bonding across the dinuclear unit with a I(3)–U(1)–O(12) angle of $170.0(3)^\circ$. In addition, the U(1)–O(12)–C(13) angle of $134.4(10)^\circ$ is very similar to the angle for the bridging alkoxide U(1)–O(4)'–C(5)' of $131.2(10)^\circ$. This structural feature is not unexpected; hydrogen bonding of coordinated alcohol ligands has been observed in a number of dimeric metal alkoxide compounds such as $M_2(\text{O-}i\text{-Pr})_8(\text{HO-}i\text{-Pr})_2$ (M

(9) (a) A small amount of an unidentified insoluble black material is also formed in this reaction. (b) We have been unable to obtain satisfactory analytical data for the complex we believe is best formulated as $UI_2(\text{O-}i\text{-Pr})_2(\text{HO-}i\text{-Pr})_2$ due to the fact that it readily loses coordinated isopropanol.

(10) A thorium complex formulated as $\text{Th}(\text{O-}i\text{-Pr})_4(\text{HO-}i\text{-Pr})$ has been proposed to be an intermediate in the preparation of $[\text{Th}(\text{O-}i\text{-Pr})_4]_n$. Bradley, D. C.; Saad, M. A.; Wardlaw, W. J. *Chem. Soc.* **1954**, 1091.

(11) We have attempted to prepare the analogous bromide compounds by the metathesis of $U\text{Br}_4(\text{THF})_3$ with 2 equiv of KO-*i*-Pr. Unfortunately, the uranium product of the reaction could not be cleanly separated from the byproduct salt, KBr, for full characterization. We were not able to conclusively demonstrate that the isolated product was $U_2\text{Br}_4(\text{OR})_4(\text{HOR})_2$. Recent work by Steven McKee at Los Alamos has shown that $UI_4(\text{CH}_3\text{CN})_3$ with KOR, where R = di-*tert*-butylphenoxide, gives the monomeric species $UI_2(\text{OR})_2(\text{THF})$.

(12) The reaction of chlorinated alcohols with TiCl_4 produces a mixed chloride-alkoxide-alcoholate species, which has been structurally characterized. See: Winter, C. H.; Sheridan, P. H.; Heeg, M. J. *Inorg. Chem.* **1991**, *30*, 1962.

(13) Anal. Calcd for green $U_2I_4O_8C_8H_{22}$: C, 16.14; H, 3.32; N, 0.00. Found: C, 17.15, 17.21; H, 3.27, 3.77; N, <0.30, <0.30. ^1H NMR (22 $^\circ\text{C}$, benzene- d_6): δ 32 (br, CHMe_2), -5 (vv br, CHMe_2). IR (cm^{-1}): 720 (w), 795 (s), 851 (m), 907 (s), 970 (vs), 1075 (s), 1089 (ms), 1101 (s), 1138 (m), 1159 (m), 1283 (w), 1300 (w), 1320 (w), 1336 (w), 3193 (br, m, OH).

(14) U(IV) is a f^2 ion having a paramagnetic ground state of 3H_4 . For a general discussion of the effects of paramagnetic species on NMR spectra, see: Becker, E. D. *High Resolution NMR, Theory and Chemical Applications*; Academic Press: New York, 1980.

(15) Cotton, F. A.; Marler, D. O.; Schwotzer, W. *Inorg. Chem.* **1984**, *23*, 4211.

(16) Van Der Sluys, W. G.; Sattelberger, A. P.; McElfresh, M. W. *Polyhedron* **1990**, *9*, 1843.

(17) Katz, J. J.; Seaborg, G. T.; Morss, L. R. *The Chemistry of the Actinide Elements*; Chapman and Hall: New York, 1986.

(18) Crystal data for **2** at $-182\text{ }^\circ\text{C}$: space group $P1$, $a = 9.643(7)\text{ \AA}$, $b = 11.283(8)\text{ \AA}$, $c = 9.598(7)\text{ \AA}$, $\alpha = 95.59(3)^\circ$, $\beta = 117.39(2)^\circ$, $\gamma = 108.59(3)^\circ$, $Z = 2$, $V = 841.13\text{ \AA}^3$, $d_{\text{calcd}} = 3.479\text{ g cm}^{-3}$. Diffraction data were not corrected for absorption. The structure was solved by a combination of direct methods and Fourier techniques and refined by full-matrix least-squares methods. Final discrepancy indices were $R_F = 0.0518$ and $R_{FW} = 0.0545$ for those reflections with $F_o \geq 2.33\sigma(F_o)$. The limits of the data collection were $6^\circ \leq 2\theta \leq 45^\circ$ (Mo K α).

(19) Vaartstra, B. A.; Huffman, J. C.; Gradoff, P. S.; Hubert-Pfalzgraf, L. G.; Daran, J. C.; Parraud, S.; Yunlu, K.; Caulton, K. G. *Inorg. Chem.* **1990**, *29*, 3126.

= Ce, Zr, Hf, U)¹⁹ and $\text{Ti}_2\text{Cl}_2(\text{OR})_2(\text{HOR})_2$ ($\text{R} = \text{CH}_2\text{CH}_2\text{Cl}$).¹² We also note that the longer U(1)-U(1) distance of 3.807 (1) Å and the U(1)-O(4)-U(1') angle of 112.4° are indicative of a net repulsive interaction of the two f² uranium atoms.

The iodine oxidation of uranium in 2-propanol has resulted in the synthesis and structural characterization of a new uranium-iodo-alkoxide dimer. We are currently investigating the extension of this chemistry to other actinide metals, to other alcohols, and to other oxidants.

Acknowledgment. We thank Drs. C. J. Burns, D. L. Clark, and A. P. Sattelberger for helpful discussions and the University of Montana, Office of Research Administration, for financial support for W.G.V.D.S.

Supplementary Material Available: Tables of crystal data, atomic positional parameters, anisotropic thermal parameters, and selected bond lengths and angles for 1 (6 pages). Ordering information is given on any current masthead page.

Department of Chemistry
University of Montana
Missoula, Montana 59812

William G. Van Der Sluys*

The Molecular Structure Center
Department of Chemistry
Indiana University
Bloomington, Indiana 47401

John C. Huffman

Inorganic and Structural
Chemistry Group
Isotope and Nuclear Chemistry
Division

Deborah S. Ehler
Nancy N. Sauer*

Los Alamos National Laboratory
Los Alamos, New Mexico 87545

Received October 25, 1991

Electronic Absorption and Resonance Raman Spectra of $[\text{Re}(\text{CO})_3(\text{pTol-DAB})\text{X}]$ (DAB = 1,4-Diaza-1,3-butadiene; X = Halide). Evidence for a Lowest Ligand to Ligand Charge-Transfer (LLCT) Transition

Although low-lying ligand to ligand charge-transfer (LLCT) transitions have been reported for many compounds containing both an oxidizing and reducing ligand, such transitions have only been observed for a few halide complexes¹ and not, e.g., for $[\text{Re}(\text{CO})_3(\text{bpy})\text{Br}]$, which is an efficient photosensitizer for energy- and electron-transfer processes. On the contrary, the lowest excited state of this complex has MLCT character.² This is rather surprising in view of the fact that MO calculations performed on complexes such as $[\text{Mn}(\text{CO})_5\text{I}]^3$ and $[\text{Re}(\text{CO})_3(\text{H}_2\text{DTO})\text{Br}]$ (DTO = dithiooxamide)⁴ have shown that their HOMO's have predominant halide character. Moreover, the preliminary results of our LCAO-X α calculations on $[\text{Mn}(\text{CO})_3(\text{bpy})\text{X}]$ (X = Cl, Br, I) show that also in this case the HOMO is mainly halide in character (85% X, 10% Mn for X = I; 60% X, 25% Mn for X = Cl).⁵ The LUMO of these complexes is the lowest π^* orbital of bpy. In the latter case the lowest excited state is therefore most likely a LLCT state.

This tentative conclusion is supported by our recent findings that these complexes produce the dimer $[\text{Mn}_2(\text{CO})_6(\text{bpy})_2]$ via the radicals $\text{Mn}(\text{CO})_3(\text{bpy})$, upon irradiation into their visible absorption band.⁶ LLCT excitation of $[\text{Mn}(\text{CO})_3(\text{bpy})\text{X}]$ is then

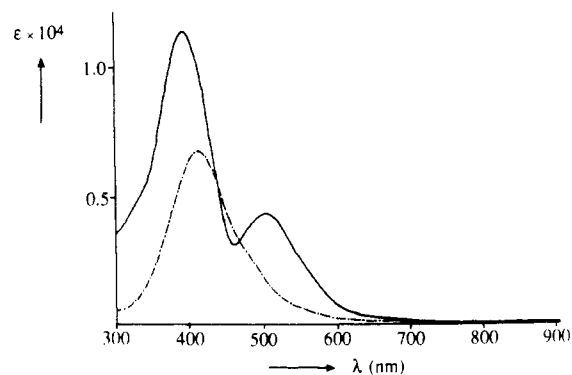


Figure 1. UV-vis spectra in CH_2Cl_2 of $[\text{Re}(\text{CO})_3(\text{pTol-DAB})\text{Br}]$ (—) and $[\text{Re}(\text{CO})_3(\text{pTol-DAB})]\text{OTf}$ (---).

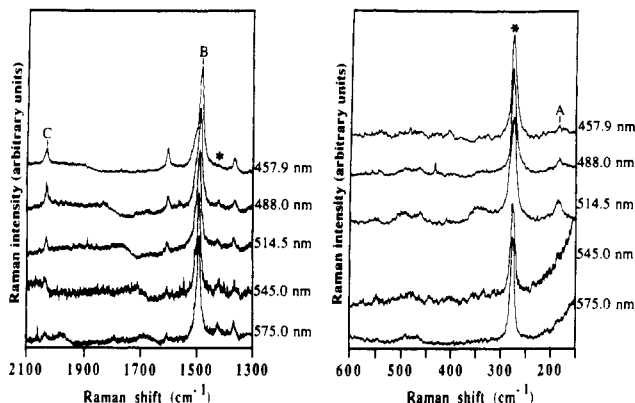


Figure 2. Resonance Raman spectra ($\lambda_{\text{exc}} = 457.9\text{--}575.0$ nm) of $[\text{Re}(\text{CO})_3(\text{pTol-DAB})\text{Br}]$ in CH_2Cl_2 in the wavenumber regions 150–600 cm^{-1} (right) and 1300–2100 cm^{-1} (left). A = $\nu(\text{Re-Br})$, B = $\nu_s(\text{CN})$, C = $\nu_s(\text{CO})$, and an asterisk = solvent band.

responsible for the formation of $\text{Mn}(\text{CO})_3(\text{bpy})$ and X radicals. The fate of the X radicals is not yet clear. The corresponding complex $[\text{Mn}(\text{CO})_3(\text{bpy})]\text{OTf}$ ($\text{OTf}^- = \text{trifluoromethanesulfonate}$) gave only rise to photodecomposition.

Further information about the character of the lowest-energy transitions of these complexes might in principle be obtained from their resonance Raman (rR) spectra. Unfortunately, the Mn complexes are too photolabile and rapidly decompose in the laser beam. We therefore focused on the photostable Re complexes since the characters of their lowest-energy electronic transitions are not expected to differ much from those of the Mn complexes. Attempts to record high-quality rR spectra of $[\text{Re}(\text{CO})_3(\text{bpy})\text{Br}]$ failed due to the disturbing luminescence of this complex. We therefore replaced the bpy ligand by pTol-DAB (=p-tolyl-1,4-diaza-1,3-butadiene; $\text{MeC}_6\text{H}_4\text{N}=\text{CH}-\text{CH}=\text{NC}_6\text{H}_4\text{Me}$) since the $[\text{Re}(\text{CO})_3(\text{pTol-DAB})\text{Br}]$ complex is not emissive at room temperature.

Its absorption spectrum in CH_2Cl_2 is shown in Figure 1. For comparison the figure also depicts the spectrum of the $[\text{Re}(\text{CO})_3(\text{pTol-DAB})]\text{OTf}$ complex. There is a clear difference between both spectra. The halide complex has two bands, at 505 and 400 nm, respectively; the spectrum of the OTf^- compound only shows the second band. On the basis of these observations,

- (1) Vogler, A.; Kunkely, H. *Comments Inorg. Chem.* 1990, 9, 201.
- (2) Lees, A. J. *Chem. Rev.* 1987, 87, 711.
- (3) Jolly, W. L. *J. Phys. Chem.* 1983, 87, 26.
- (4) Servaas, P. C.; Stufkens, D. J.; Oskam, A.; Vernooijs, P.; Baerends, E. J.; De Ridder, D. J. A.; Stam, C. H. *Inorg. Chem.* 1989, 28, 4104.
- (5) Stor, G. J.; Baerends, E. J.; Vernooijs, P.; Stufkens, D. J. Unpublished results.

- (6) $[\text{Mn}(\text{CO})_3(\text{bpy})\text{X}]$ (X = Cl, Br, I), dissolved in toluene or THF, was irradiated with 514.5-nm light into its visible absorption band ($\lambda_{\text{max}} = 425$ nm ($\epsilon = 2470$ mol^{-1} L cm^{-1}) for X = Br in THF). The formation of $\text{Mn}_2(\text{CO})_6(\text{bpy})_2$ was evident from the appearance of its characteristic absorption band ($\lambda_{\text{max}} = 840$ nm in THF) and IR CO bands (1980, 1963, 1936, 1886 and 1866 cm^{-1} in THF).⁷ The $\text{Mn}(\text{CO})_3(\text{bpy})$ radicals were trapped by tBu-NO giving rise to the characteristic ESR spectrum of the adduct.⁸ A detailed report of these experiments will be published elsewhere.
- (7) Kokkes, M. W.; Stufkens, D. J.; Oskam, A. *Inorg. Chem.* 1985, 24, 2934.
- (8) Andréa, R. R.; de Lange, W. G. J.; van der Graaf, T.; Rijkhoff, M.; Stufkens, D. J.; Oskam, A. *Organometallics* 1988, 7, 1100.