The effect produced by the solvent was studied on $Re(CO)_5Br$. Specific rate constants decreased with increasing solvent dielectric constant values; E_a values varied in the inverse order.

These results can be explained by suggesting a decrease in polarity in going from $Re(CO)_5X$ to the activated complex. Similar behavior has been reported for dissociative substitution reactions involving $Mn(CO)_5X$.[4]

Table II gives the energy and entropy of activation values and these are typical of the mechanism suggested. E_a values are compared with those obtained in the (also dissociative) substitution reactions of $Re(CO)_5X$ and $Mn(CO)_5X$. It will be noted that our $Re(CO)_5X$ exchange values vary inversely with those reported by other writers[11] for substitution reactions with these complexes but follow the same order (*i.e.*, $Cl < Br < I$) as those reported for $Mn(CO)_5X$ substitution reactions.[10]

Table II also shows lower E_a values for the manganese complex, but it must be pointed out that direct comparison is, in fact, unfeasible since the reactions were carried out in different solvents. However, reduction of the solvent dielectric constant is known to lead for these compounds to decreased E_a values and it may thus be deduced that the values for $Mn(CO)_5X$, as reported for chloroform, would have been lower had toluene been used and that the difference already apparent in Table II would in fact have been greater.

We can, therefore, claim lower reactivity for rhenium as opposed to manganese derivatives. This can be attributed to the greater ability of rhenium to form a π bond by the coupling of d_π electrons with carbon antibonding orbitals, a phenomenon generally observed in going from 3d to 5d metal complexes. For this reason, greater energy is needed to obtain the rhenium five-coordinated complex.

Experimental Section

Already reported techniques and treatment of data[13] were used for the exchange reactions.

In the case of high CO pressure reactions, we used a steel line equipped with a pressure gauge calibrated up to 25 atm. For reaction containers, we employed small steel bottles controlled by a needle valve. These were connected to the line by means of metal joints.

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Magnetic Susceptibility of Cubic Uranium Tungsten Bronzes between 4.2 and 560°K[1]

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The magnetic susceptibility of three uranium tungsten bronzes U_xWO_3 ($x = 0.08, 0.10, 0.12$) and of a mixed uranium–thorium tungsten bronze $U_{0.033}Th_{0.067}WO_3$ has been measured between 4.2 and 560°K. The bronzes were prepared as powders by allowing UO_2 (ThO_2), WO_2, and WO_3 to react in the proper molar ratio. The carefully ground reagents were enclosed in an evacuated, sealed silica capsule and heated for at least 100 hr at 1000° from which temperature they were rapidly cooled. Reaction products were studied by X-ray powder diffraction photography for homogeneity. The lattice parameters of the bronzes are listed in Table I.

TABLE I

CRYSTALLOGRAPHIC AND MAGNETIC DATA OF CUBIC URANIUM TUNGSTEN BRONZES

M in M_xWO_3	Lattice parameter a_0, Å	Δ distance U–U, Å	$10^6\chi_g$ at 4.2°K, cgsu	μ_{eff} of U,[a] μ_B
$U_{0.08}$	3.805_2	9.10	0.008	3.1_2
$U_{0.10}$	3.809_6	8.35	0.006	3.1_0
$U_{0.12}$	3.813_3	7.75	0.005	3.1_1
$U_{0.033}Th_{0.067}$	3.825_5	11.60	0.006	3.1_2

[a] In the computation of μ_{eff} of uranium, corrections were made by use of experimentally determined χ values of Th_xWO_3 ($x = 0.08, 0.10, 0.12$).

Magnetic susceptibility measurements were made by the Gouy method. The magnetic instrument consisted of a RH Cahn electrobalance with vacuum attachment, a 6-in. Varian electromagnet carrying tapered pole caps, and a Moseley X-Y recorder. The field was calibrated with $CoHg(SCN)_4$;[2] between 1 and 14 kG, field calibration was reproducible better than 0.2%. Temperature readings were accurate to ±1°. Force measurements were made at various temperatures and fields using ~4-g heavy, ~25-cm long specimens. A very slight field dependence of the susceptibilities was corrected for by extrapolating the χ values to zero reciprocal field.

Figure 1 shows $1/\chi$–T plots for the four compounds investigated. It can be seen that all curves are linear above roughly 60°K, and their linear portions extrapolate to a common value of -170 ± 5°K. At lower temperatures, susceptibilities pass through a maximum at 30°K and then drop rapidly toward zero. Table I lists the χ_g values of the various uranium bronzes observed at 4.2°K. Field dependence of the susceptibility maxima was not observed.

Data suggest that antiferromagnetic exchange interactions are the cause of the χ–T behavior of U_xWO_3 (Curie–Weiss type, $\Theta = -170 \pm 5°$). This permits evaluation of the effective moment of uranium on the basis of $\mu_{eff} = 2.84[\chi_{U^{4+}}(T - \Theta)]^{1/2}$. Table I lists the moments of uranium for each of the bronzes as calculated from this equation.

There are three possible mechanisms to be considered to explain the presence of exchange interactions in cubic uranium tungsten bronzes: the first involves direct U–U interactions; the second, coupling by bridging through an intervening oxygen atom (U–O–U superexchange); and the third, indirect coupling

[1] This work is dedicated to Professor Dr. W. Rüdorff, University of Tübingen, Germany, in honor of his 60th birthday.

[2] B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 4190 (1958).

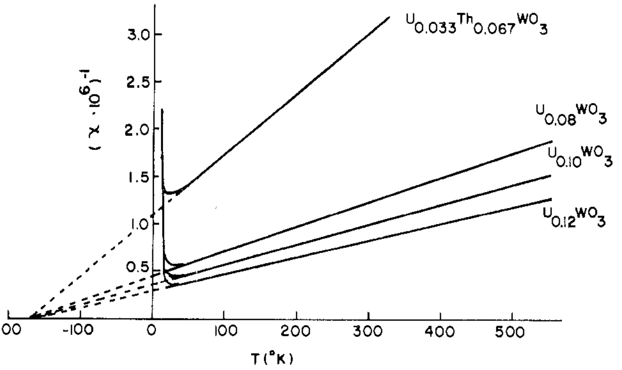

Figure 1.—The $1/\chi$ *vs.* T diagram of several cubic uranium tungsten bronzes.

through conduction electrons.[3] Direct U–U exchange interactions must be ruled out because of the large separation between the uranium atoms (average U–U distances for each compound are presented in Table I). The possibility of superexchange in U_xWO_3 can be excluded also, since reduction of the uranium concentration and substitution of uranium by "nonmagnetic" thorium do not affect the Θ value of the system. In terms of a U–O–U superexchange model, reduction of the uranium concentration and replacement of thorium for uranium should produce a "magnetic dilution" effect. This leaves the third mechanism in which conduction electrons are assumed to provide for an exchange interaction between the uranium atoms.

That conduction electrons do, in fact, play a role in the magnetic exchange interactions of U_xWO_3 could be shown by some orienting measurements on U_xWO_3 compounds which are semiconducting rather than metallic. Uranium tungsten bronzes for $x = 0.05$, 0.03, and 0.01 exhibit paramagnetic Curie temperatures, Θ, which decrease from -85 through -65 to $-45 \pm 5°$, respectively. This indicates clearly that the conductivity of the U_xWO_3 compounds influences the exchange interaction between the uranium atoms. The effective moment of uranium in all uranium tungsten bronzes studied is 3.1 μ_B.

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[3] Cubic uranium tungsten bronzes are metallic conductors: W. Ostertag and C. V. Collins, *Mater. Res. Bull.*, **2**, 217 (1967).

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The Preparation of Ethylenediaminediacetic-N,N'-di-α-propionic Acid and the Structure of Its Cobalt(III) Complex

BY DONALD H. WILLIAMS, JEANNE R. ANGUS, AND JACK STEELE

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It is well known that upon coordination to a metal ion like Co(III) the protons of ethylenediaminetetraacetic acid, EDTA, become quite dissimilar. Examination with pmr techniques[1,2] reveals a difference between the in-plane and out-of-plane methylene linkages (relative to the N–Co–N plane). These results are readily rationalized with reference to the X-ray crystal structure of the Co(EDTA)$^-$ anion provided by Weakleim and Hoard.[3] The explanations put forth involve either the observation that the out-of-plane glycinates are better bonded to the Co(III) *via* the Co–O bond[4] and/or the fact that the steric situation is quite different for the out-of-plane ring.[2]

The objective of this study was, first, to compare the steric requirements at the out-of-plane site with those of the in-plane linkage. To this end a ligand has been prepared, ethylenediaminediacetic-N,N'-di-α-propionic acid, H_4EDPA, which is like EDTA except that one of the two acetate groups attached to each nitrogen atom has a methyl group in place of one of the methylene protons.[5] Also, *via* pmr analysis of the complex formed with Co(III) the possibility of steric limitation has been tested. When EDPA coordinates, there may be three geometric isomers. With optically active EDPA the number of isomers possible is 20. The notion that upon coordination to a transition metal ion a hexadentate ligand might be subject to bonding in a specific fashion is not new. Dwyer[6] demonstrated the principle dramatically with the similar hexadentate, propylenediaminetetraacetic acid, PDTA.

Experimental Section

Materials.—Ethylenediaminediacetic acid and 2-bromopropionic acid were used as obtained, the former from K & K Laboratories and the latter from Aldrich Chemicals. All other materials were of reagent grade quality.

The pmr spectra were taken on a Varian HR-60 nmr spectrometer and given in ppm relative to TMS. Visible spectra were measured on a Cary Model 15 recording spectrophotometer. Elemental analyses were obtained with the use of an F & M Model 185 gas chromatograph. The ORD measurement was made on a Cary Model 60 ORD-CD.

Ethylenediaminediacetic-N,N'-di-α-propionic Acid.—This procedure is an adaption of Dwyer's preparation of PDTA.[7] We found this method to be much less difficult and much more successful than that of Majer.[5] To 50 ml of H_2O chilled in an ice bath of 10° was added 25 ml of 2-bromopropionic acid. A solution of 24 g of NaOH in 50 ml of H_2O was added slowly so as not to allow the temperature to rise above 20°. Ethylenediaminediacetic acid (10 g) was then added. The solvent had been degassed with N_2 and an atmosphere of N_2 was maintained to minimize oxidation of the amine. The mixture was allowed to stand at room temperature (20°) for 6 days at which time it was acidified with 6.5 ml of concentrated H_2SO_4. The solution was kept at 10° for 16 hr and the Na_2SO_4 was filtered off. The EDPA was precipitated from the cooled filtrate by the addition of a mixture of 50 ml of absolute ethanol and 100 ml of acetone. The product was filtered off and washed with 5-ml portions of cold H_2O, acetone, and ether. It was recrystallized twice from minimum amounts of ethanol–H_2O mixtures (25, 75%) using acetone addition to aid precipitation; yield 4.55 g (10.1%). *Anal.* Calcd

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