Trapping of an Inner-sphere Charge-transfer Triplet State in a Single Crystal of a Uranyl Complex

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Summary Irradiation of a single crystal of $UO_2(NO_3)_2 \cdot 2OP(OEt)_3$ at 4·2 K produces a metastable triplet state whose e.s.r. characteristics indicate a localized electron transfer from an NO_3^- ion to the excited UO_2^{2+} ion.

We report here results from a continuation of our earlier investigations on uranyl photochemistry.[1] A single crystal of the complex $UO_2(NO_3)_2 \cdot 2OP(OEt)_3$ was irradiated with the light from an Osram HBO 500 W mercury lamp, filtered through aqueous $CuSO_4$ contained in a Pyrex cuvette. The irradiation was performed within the cavity of an e.s.r.

spectrometer maintained at 4·2 K. After 10–15 min of irradiation signals appeared (Figure), readily assignable to a species whose spin Hamiltonian is given by equation (1), with $S = 1$ and $I = 1$. Above 10 K the signals decay

$$\mathscr{H} = \beta H\mathbf{g}S + S\mathbf{D}S + S\mathbf{A}I \qquad (1)$$

extremely rapidly while at the lower temperature they are indefinitely stable.

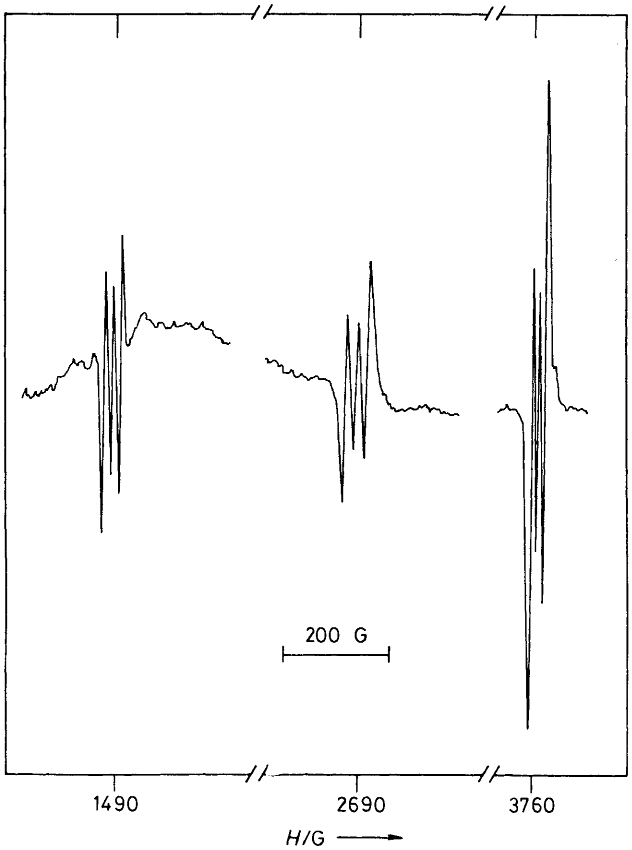

FIGURE. E.s.r. spectrum of a crystal of $UO_2(NO_3)_2{\cdot}2OP(OEt)_3$ irradiated at 4·2 K. The magnetic field direction is parallel to the *b* crystal axis.

The unit cell of the crystal is triclinic, space group $P1$, and contains one molecule of the complex, which has a local inversion centre of symmetry and six oxygen atoms (two from the phosphate and four from the nitrate groups) co-ordinated very nearly in a plane perpendicular to the axis of the uranyl unit. The co-ordinated nitrate oxygen atoms are at unequal distances from the uranium atom (2.62 and 2·48 Å respectively).[2] A single magnetic site is understandable under these circumstances.

A preliminary analysis of the **g** and **D** magnetic tensors has been performed. The **g** tensor is clearly very anisotropic with principal values from 1·996 to 1·871. The maximum principal value of the **D** tensor (870 G) corresponds to an interaction between point dipoles at a distance of 2·8 Å which is slightly larger than the distance between the uranium atom and the more distant of the two oxygen atoms of the nitrate ion in the complex. This is an indication of the origin of the **D** tensor even if the large anisotropy of the **g** tensor makes possible large spin–orbit coupling contributions to the **D** tensor magnitude. The **g** tensor anisotropy is also a clear indication of the involvement of the uranium atom in the species. The **A** tensor is more difficult to analyse owing to the low resolution under most crystal orientations and to strong second-order effects. The hyperfine multiplet however, when resolved as in the $\Delta m = 2$ transition (see Figure), shows unequivocally the interaction of the electron system with a single spin 1 nucleus.

It seems reasonable to assume that we are observing a triplet state corresponding to 'inner-sphere' electron transfer from one NO_3^- ion to the photoexcited UO_2^{2+} ion as in equation (2). Back reaction to the initial ground state of the complex may occur *via* a thermally activated back electron transfer or *via* a new photoexcitation of the triplet.

$$UO_2^{2+}-NO_3^- \xrightarrow{h\nu} UO_2^{2+}{*}-NO_3^- \rightarrow UO_2^{\cdot+}-NO_3{\cdot}\ (^3CT) \qquad (2)$$

The thermal barrier to the back electron transfer must be of the order of only 100 cm^{-1}, corresponding to a flat minimum along the co-ordinate of a low-frequency metal–ligand vibration.

The question is raised about the conditions which have to be met for the observation of such states in a metastable situation. A thermal barrier to the back reaction is essential, but this may be quite rare since its realization presumes a very large displacement of the minimum of the energy surface of the charge transfer state with respect to the complex ground state. The evidence in the present case is that the structural distortion is localized in one of the two NO_3^- groups of the complex and possibly along a particular one of the two non-equivalent U–O bonds.

A second important question is raised, namely if charge-transfer triplet states are necessary intermediates in uranyl photochemistry. The common idea that the photochemistry active state coincides with the emitting uranyl localized state may have to be modified.

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[2] J. E. Fleming and M. Lynton, *Chem. Ind. (London)*, 1960, 1415.

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