

## STUDY OF THE PHOTOREDUCTION OF URANYL IONS BY TRIPHENYLPHOSPHINE, TRIPHENYLARSINE, TRI-*p*-TOLYLPHOSPHINE AND TRI-*p*-TOLYLARSINE IN ACETONE

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### Summary

The photochemical reduction of uranyl ions by triphenylphosphine, tri-*p*-tolylphosphine, triphenylarsine and tri-*p*-tolylarsine in a dry acetone medium in the presence of trimethylacetic acid, using radiation in the visible region ( $\lambda > 365$  nm), was investigated. The electron spin resonance and electronic spectral data supported the proposal that uranium(V) was formed. The quantum yields and Stern-Volmer quenching constants were also calculated for all four types of substrate. Keeping in view the available evidence, an electron transfer mechanism was postulated for the formation of uranium(V) which disproportionates into uranium(IV) and uranium(VI) in aqueous acidic media.

### 1. Introduction

The photo-oxidation of a variety of organic and inorganic substrates with uranyl ions has been studied [1 - 3]. Both intermolecular and intramolecular mechanisms have been proposed to explain the photochemical redox reaction. However, in the intermolecular mechanism either hydrogen atom abstraction or electron abstraction by the excited uranyl ions has been proposed to take place [3]. In earlier communications describing the photochemical reduction of uranyl ion with triphenylphosphine [4], triphenylarsine [5], triphenylantimony [6], triphenylbismuth [7] and dialkylsulfides [8] in aqueous acidic media, an oxygen atom transfer mechanism has been suggested. Uranium(V) as an intermediate in the electrolytic reduction of the uranyl ion has been reported in dimethyl sulphoxide media [9].

In the present investigation, dry acetone was used for the photochemical reduction of uranyl ions with triphenylphosphine, tri-*p*-tolylphosphine, triphenylarsine and tri-*p*-tolylarsine, since this aprotic solvent is expected to increase the lifetime of the uranium(V) species making its detection convenient using electronic absorption spectroscopy and electron spin resonance (ESR) spectroscopy.

## 2. Results

The electronic absorption spectrum of the uranyl ion is highly dependent on the nature of its environment [10 - 12], and the changes with time in electronic absorption spectra of uranyl ions and triphenylphosphine (molar ratio, 4:1) on irradiation in dry acetone in the presence of trimethylacetic acid, under an atmosphere of oxygen-free nitrogen, are given in Fig. 1. The peaks at 618 nm and 652 nm are attributed to uranium(V) complexed with the substrate or oxidized substrate [13]. Both peaks are quite stable but the intensity of the peaks in the dark in the presence of air starts falling rapidly (Fig. 2(a)) compared with the fall in intensity of the peaks in the dark in the presence of oxygen-free nitrogen (Fig. 2(b)). This may be due to the reoxidation of uranium(V) by oxygen and the oxidized substrate in the former case, and to the reoxidation of uranium(V) by the oxidized substrate alone in the latter case. With a 1:1 molar ratio of uranyl ions to triphenylphosphine under similar conditions of irradiation, the appearance of new bands for uranium(IV) along with bands for uranium(V) should be noted (Fig. 3). In the photochemical reduction of uranium(VI) to uranium(IV), uranium(V) has been proposed as an intermediate [14 - 16].

On the addition of 9 M hydrochloric acid to the irradiated reaction mixture (1:100 v/v) of uranyl ions and triphenylphosphine (4:1), peaks characteristic of uranium(V) (attributed to the  $\text{UO}_2^+$  species) in the solution

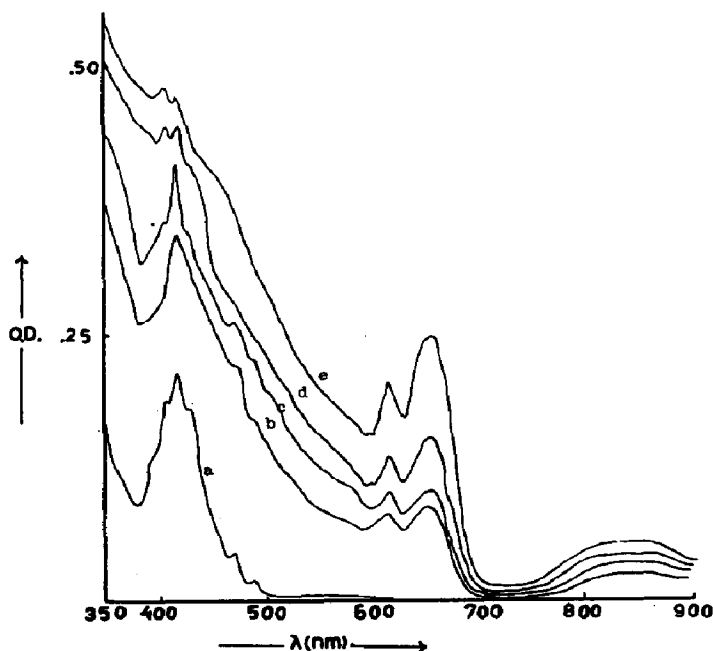


Fig. 1. Changes in the absorption spectra on irradiation of the reaction mixture of uranyl ions (0.02 M), triphenylphosphine (0.005 M) and trimethylacetic acid (0.1 M): curve a, before irradiation; curve b, after irradiating for 5 min; curve c, after irradiating for 10 min; curve d, after irradiating for 15 min; curve e, after irradiating for 20 min.

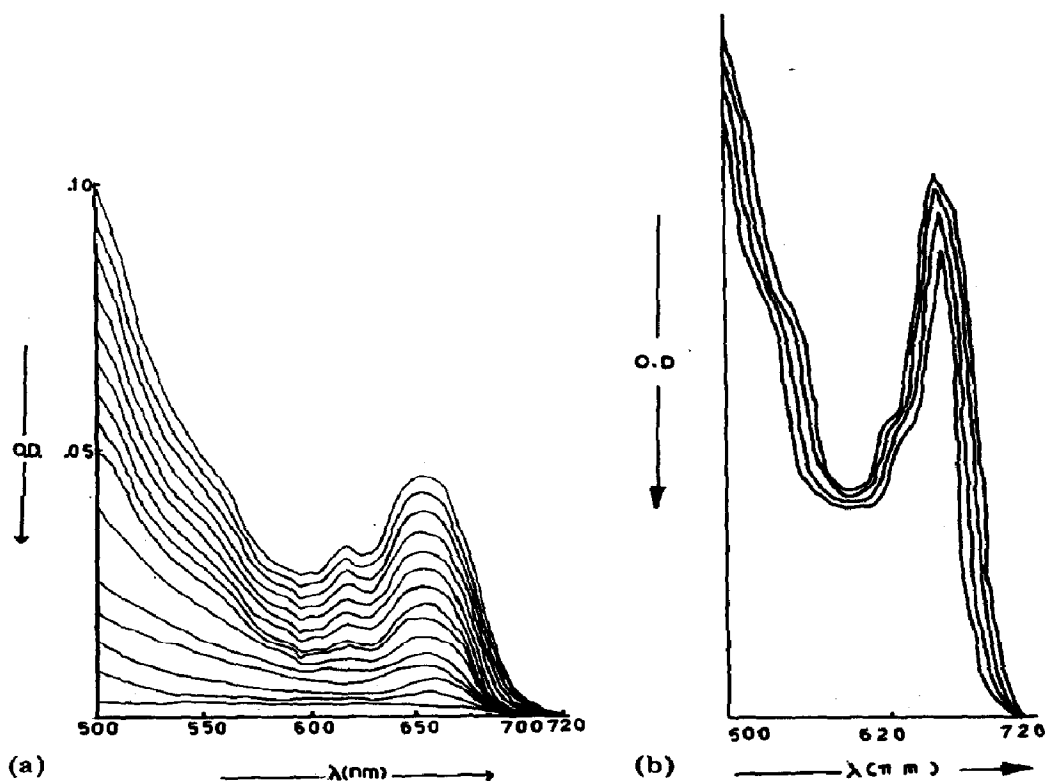


Fig. 2. The decrease in intensity of the uranium(V) band with regular intervals of time owing to the reoxidation of uranium(V) (a) in air and (b) in oxygen-free nitrogen.

appear at 595 nm and 770 nm (Fig. 4). However, in the case of a molar ratio of 1:1 for uranium(VI) to the substrate, the addition of 9 M hydrochloric acid to the reaction mixture (1:100 v/v) leads to the appearance of two new peaks at 550 nm and 660 nm assignable to the uranium(IV) species, in addition to the peaks for uranium(V) already present. In this situation all three oxidation states, uranium(IV), uranium(V) and uranium(VI), are present together in the reaction mixture (Fig. 4). The addition of 1 M hydrochloric acid (1:1 v/v) gives the spectrum indicating complete disproportionation of uranium(V) to uranium(IV) and uranium(VI) (Fig. 5). A steady increase in the concentration of uranium(V) in the reaction mixture is observed during irradiation (Fig. 6). The stability of uranium(V) is enhanced by using a molar ratio of uranium(VI) to the substrate of 4:1; this is perhaps dictated by the law of mass action as disproportionation of uranium(V) to uranium(IV) and uranium(VI) is retarded by the presence of a higher concentration of uranium(VI) in the reaction mixture.

Quantum yields for the formation of uranium(V) with the tertiary phosphines and arsines have been calculated by employing  $\epsilon_{\max} = 591 \text{ mol}^{-1} \text{ cm}^{-1}$  at  $\lambda_{\max} = 652 \text{ nm}$  and are reported in Table 1. The value of  $\epsilon_{\max}$  was obtained by dividing the optical density of uranium(V) at  $\lambda_{\max} = 652 \text{ nm}$  by the concentration of uranium(VI) consumed in the redox reaction on irradiation.

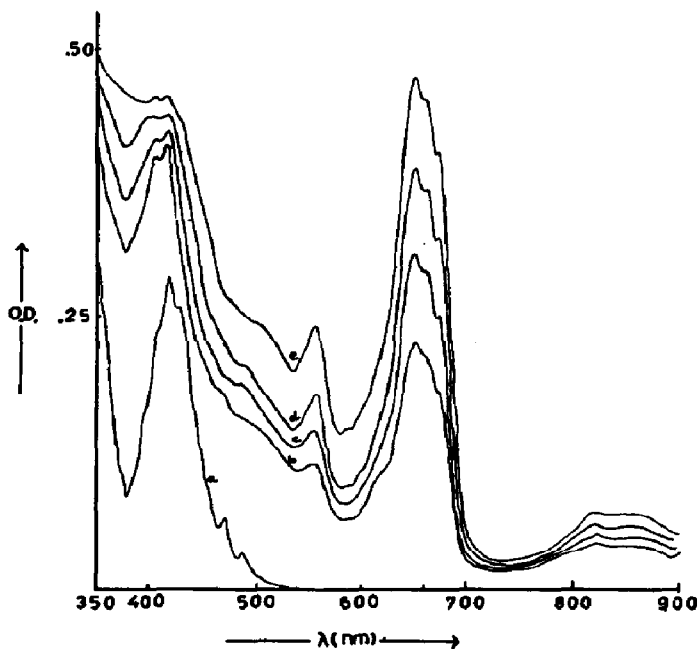


Fig. 3. Changes in the absorption spectra on irradiation of the reaction mixture of uranyl ions (0.005 M), trimethylphosphine (0.005 M) and trimethylacetic acid (0.1 M): curve a, before irradiation; curve b, after irradiating for 5 min; curve c, after irradiating for 10 min; curve d, after irradiating for 15 min; curve e, after irradiating for 20 min.

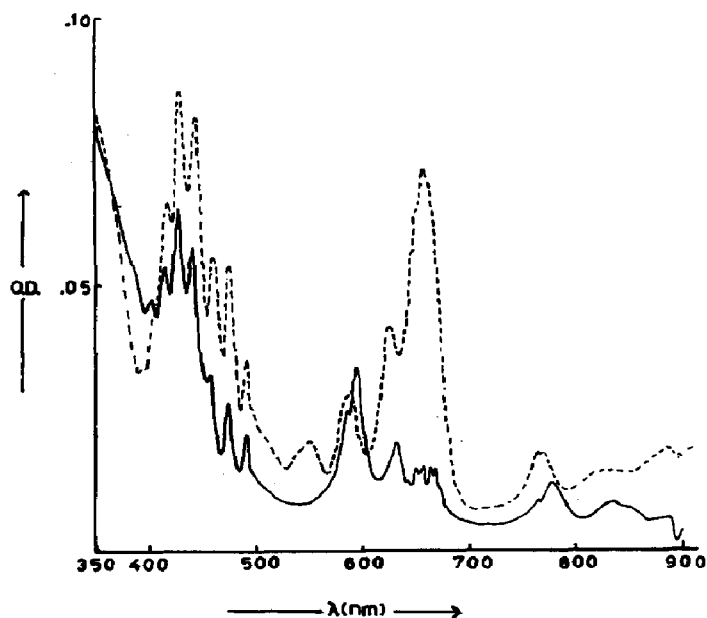


Fig. 4. Changes in the absorption spectra with the addition of 9 M hydrochloric acid (1:100 v/v) to the irradiated reaction mixtures: —, uranyl ions (0.02 M) and triphenylphosphine (0.005 M); ---, uranyl ions (0.005 M) and triphenylphosphine (0.005 M).

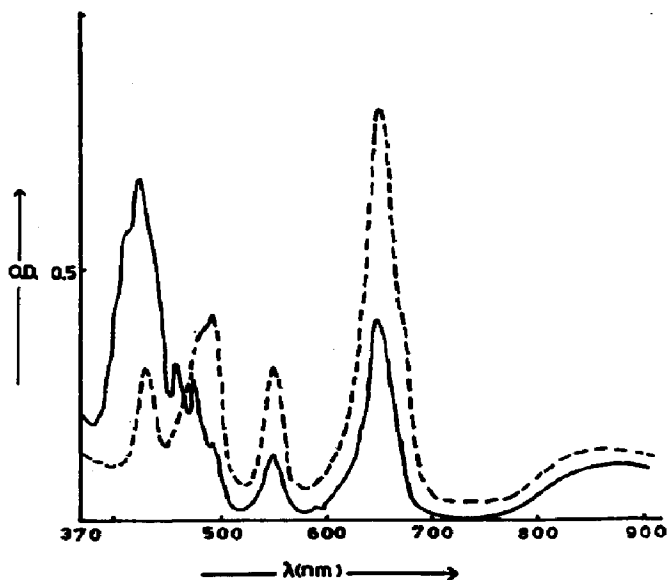


Fig. 5. Absorption spectra: —, showing the total disproportionation of uranium(V) to uranium(IV) and uranium(VI) with the addition of 1 M hydrochloric acid to the reaction mixture (1:1 v/v); ---, uranium(IV) in hydrochloric acid.

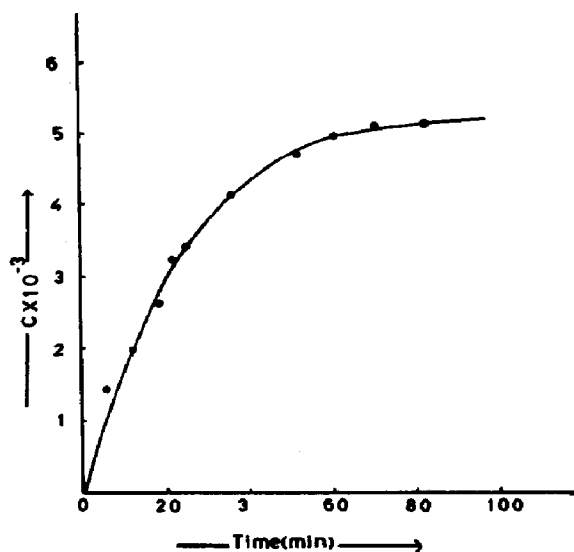


Fig. 6. Plot of uranium(V) concentration vs. the time of irradiation in the photochemical reduction of uranyl ions with triphenylphosphine.

tion and is comparable with the reported value [17]. The Stern-Volmer plots for the quenching of uranyl ion luminescence by tertiary phosphines and arsines are linear (Fig. 7). Quenching constants were calculated from the slopes of the plots and are given in Table 2.

TABLE 1

Quantum yields for uranium(V) formation during the photochemical reduction of uranyl ions with various substrates in dry acetone media at  $30 \pm 2^\circ\text{C}$

Sample	Substrate (0.005 - 0.01 M)	Quantum yield for uranium(V)
1	Triphenylphosphine	0.16 - 0.30
2	Tri- <i>p</i> -tolylphosphine	0.04 - 0.045
3	Triphenylarsine	0.003 - 0.0047
4	Tri- <i>p</i> -tolylarsine	0.007 - 0.010

$[\text{UO}_2(\text{tmac})_2 \cdot 2\text{H}_2\text{O}] = 0.02 \text{ M}$  (tmac, trimethyl acetate).

$[(\text{CH}_3)_3\text{CCOOH}] = 0.10 \text{ M}$ .

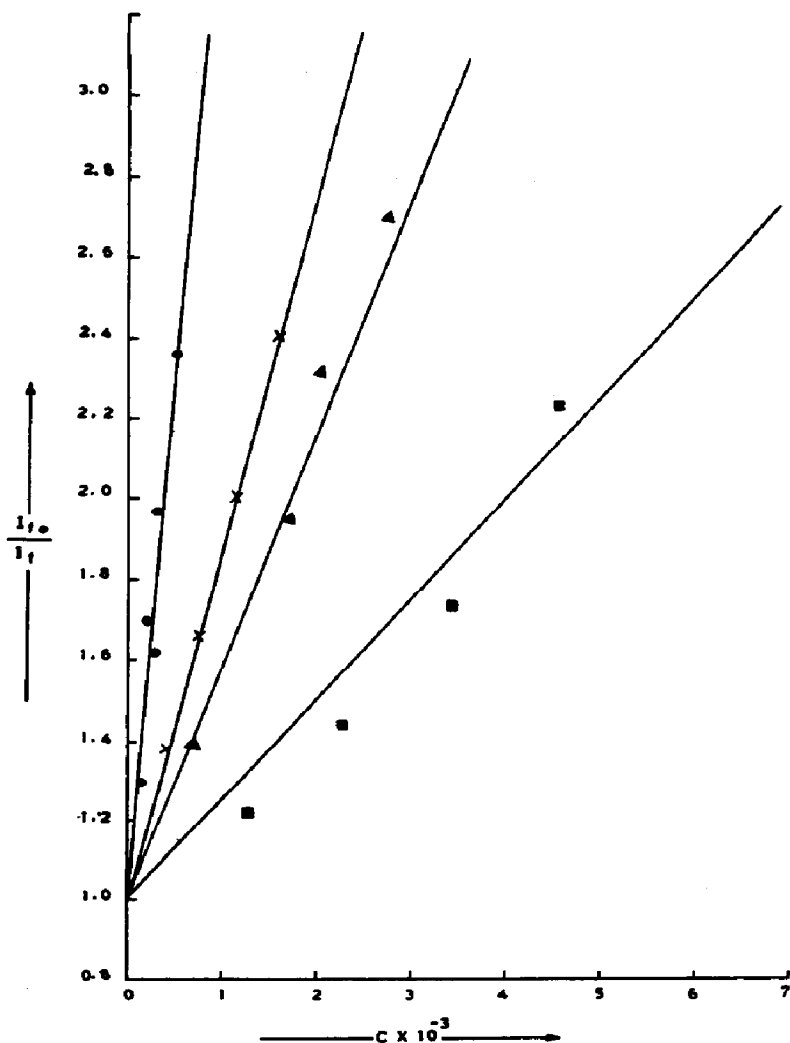


Fig. 7. Stern-Volmer plots for the quenching of uranyl ions (0.02 M) in trimethylacetic acid (0.1 M) in acetone media: ▲, triphenylphosphine; ■, tri-*p*-tolylphosphine; ×, triphenylarsine; ●, tri-*p*-tolylarsine.

TABLE 2

Stern–Volmer quenching constants  $k_{SV}$  for uranyl ions with various substrates in dry acetone media

Sample	Substrate	$k_{SV}$ ( $M^{-1}$ )
1	Triphenylphosphine	688.00
2	Tri- <i>p</i> -tolylphosphine	113.34
3	Triphenylarsine	884.61
4	Tri- <i>p</i> -tolylarsine	2373.41

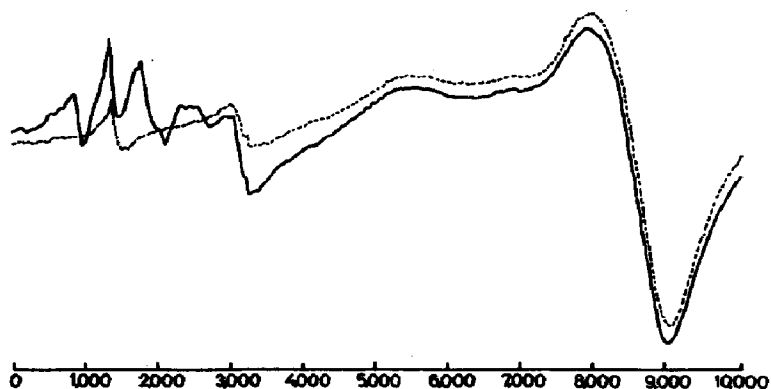


Fig. 8. ESR spectra of a uranyl trimethyl acetate dihydrate solution during photochemical reduction with triphenylphosphine: ....., before irradiation; —, after irradiation.

The ESR spectra for the irradiated solution show a new band at 2700 G with the broadening of the band at a field value of 3200 G (Fig. 8). The ESR spectrum for irradiated solutions with a signal at 2700 G assigned to uranium(V) has been reported in the literature [18].

### 3. Discussion

The lowest level of the excited uranyl ion to be quenched is in the range 49 - 61 kcal mol<sup>-1</sup> which is much lower than the lowest excited states of tertiary phosphines and arsines (120 kcal mol<sup>-1</sup>). Thus electronic energy transfer from the excited uranyl ion to the substrate is ruled out. Quenching by the external heavy atom effect or spin-catalysed deactivation is also unlikely owing to the presence of the heavy uranium atom itself. Thus electron transfer is the most plausible quenching mechanism supported by the formation of uranium(V). In the electron transfer mechanism, the formation of an intermediate complex in the excited state, usually called an exciplex, between the excited uranyl ion and the substrate is postulated.

For tertiary phosphines the trends in the values of quantum yields and Stern–Volmer quenching constants are the same and quenching seems to be mainly of a physical nature. The alkyl groups in tri-*p*-tolylphosphine contrib-

ute effectively towards increasing the steric hindrance around the phosphorus atom. In tertiary arsines the lone pair of electrons is more easily available with less steric hindrance due to the larger atomic size of the arsenic atom. With prolonged irradiation, oxides of tertiary phosphines and arsines complexed with uranium(IV) have been reported earlier in the photochemical reduction of uranyl ions in aqueous acidic media [4 - 7]. The formation of a complex between the excited uranyl ion and tertiary phosphines and arsines through oxygen to bring about an electron transfer supports the proposed mechanism. In the photochemical reduction of the uranyl ion, an oxygen atom of the uranyl ion is lost to the tertiary phosphine or arsine for the formation of an oxide.

Thus it can be concluded that the formation of uranium(V) through an electron transfer [19, 20] is the primary step in the photochemical reduction of uranyl ions with tertiary phosphines and arsines. This is supported by electronic absorption and ESR spectra of the species.

#### 4. Experimental details

Standard uranyl ion solutions were prepared from uranyl trimethyl acetate dihydrate ( $\text{UO}_2(\text{tmac})_2 \cdot 2\text{H}_2\text{O}$ ), prepared and characterized in the laboratory. Glacial trimethylacetic acid was used in dry acetone as a solvent medium. Tertiary phosphines and arsines were recrystallized from ethyl alcohol. A medium pressure mercury lamp with a power of 125 W was used as the source of irradiation, the intensity of which was determined by using potassium ferrioxalate as an actinometer. The reaction mixture was deoxygenated in a Pyrex photochemical reactor with pure and oxygen-free nitrogen. The temperature of the reaction mixture was kept constant using an MK-70 cryostat. The relative intensities of the uranyl emissions were measured using a Perkin-Elmer MPF 448 fluorescence spectrophotometer with different concentrations of quenchers. Electronic absorption spectra were recorded with a UV-visible 240 Shimadzu spectrophotometer. The ESR spectra were recorded with a JES.FE3X6 spectrometer.

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#### References

- 1 E. Robinowitch and R. L. Belford, *Spectroscopy and Photochemistry of Uranyl Compounds*, Pergamon, Oxford, 1964.
- 2 V. Balzani and V. Carassiti, *Photochemistry of Co-ordination Compounds*, Academic Press, New York, 1970.



- 3 H. D. Burrows and T. J. Kemp, *Chem. Soc. Rev.*, 3 (1974) 139.
- 4 S. S. Sandhu, A. S. Brar and A. S. Sarpal, *Indian J. Chem., Sect. A*, 19 (1980) 413.
- 5 S. S. Sandhu, A. S. Brar and A. S. Sarpal, *Indian J. Chem., Sect. A*, 16 (1978) 587.
- 6 S. S. Sandhu, A. S. Brar and A. S. Sarpal, *Indian J. Chem., Sect. A*, 18 (1979) 19.
- 7 S. S. Sandhu, A. S. Brar and A. S. Sarpal, *Indian J. Chem., Sect. A*, 19 (1980) 902.
- 8 S. S. Sandhu, K. B. Kohli and A. S. Brar, *Inorg. Chem.*, 23 (1984) 3609.
- 9 G. Gritzner and J. Selbin, *J. Inorg. Nucl. Chem.*, 30 (1968) 1799.
- 10 G. H. Dieke and A. B. F. Duncan, *Spectroscopic Properties of Uranium Compounds*, McGraw-Hill, New York, 1949.
- 11 B. J. Trzebiatowska and A. Bartecki, *Spectrochim. Acta*, 18 (1962) 799, and references cited therein.
- 12 J. T. Bell and R. E. Biggers, *J. Mol. Spectrosc.*, 18 (1965) 247.
- 13 G. Cauzzo, G. Gennari, G. Giacometti, G. C. Agostini and A. Gambaro, *Inorg. Chim. Acta*, 32 (1979) 45.
- 14 R. Matsushima and S. Sakuraba, *J. Am. Chem. Soc.*, 93 (1971) 5421.
- 15 S. Sakuraba and R. Matsushima, *Bull. Chem. Soc. Jpn.*, 43 (1970) 2359.
- 16 C. K. Rofer-Depoorter and G. L. Depoorter, *J. Inorg. Nucl. Chem.*, 41 (1979) 215.
- 17 H. Fukutomi and T. Haranazo, *Abstr. XXIVth Int. Conf. on Co-ordination Compounds, Greece, August, 1986*, Association of Greek Chemists, Athens, p. 586.
- 18 C. Miyake, Y. Yamana, S. Imoto and H. Ohya-Nishiguchi, *Inorg. Chim. Acta*, 95 (1984) 17 - 21.
- 19 K. Ueno and A. Ohyoshi, *J. Inorg. Nucl. Chem.*, 36 (1974) 379.
- 20 S. Sakuraba, S. Mimura and R. Matsushima, *Bull. Chem. Soc. Jpn.*, 46 (1973) 2784.