J. inorg. nucl. Chem., 1975, Vol. 37, pp. 739–742. Pergamon Press. Printed in Great Britain

ELECTRON SPIN RESONANCE OF URANIUM(IV) CHELATES WITH CUPFERRON AND NEOCUPFERRON

TETSUHIKO YOSHIMURA*, CHIE MIYAKE and SHOSUKE IMOTO
Department of Nuclear Engineering, Faculty of Engineering, Osaka University, Suita, Osaka

(*Received* 22 *April* 1974)

Abstract—ESR spectra were observed on tetrakis(cupferronato)uranium(IV) and tetrakis(neocupferronato) uranium(IV) at room temperature and 77 K with g-value of 4·27 and 4·50, respectively. In the solution of degassed tetrahydrofuran, the same signal was observed only at 77 K. Since these signals did not appear in the corresponding diamagnetic complexes with Th(IV), Ce(IV), Hf(IV), Zr(IV), and Ti(IV), the spectra were discussed from the point of the crystal field effect with the symmetry of D_{4d} on $^3H_4$ term of U(IV) with $(5f)^2$ electronic configuration. On the other hand, ESR spectra having g-values of 2·003 ~ 2·005 were also observed irrespectively to the kind of the central metal ion. As one of the possible causes of these signals, an unpaired electron produced by an N–N bond fission in the ligand after the formation of the complex seems to be considered.

INTRODUCTION

THE ESR of tetravalent uranium ion has been observed in uranium(IV) incorporated into single crystals of diamagnetic matrix such as CaF_2, SrF_2 and BaF_2[1] and the eigen state of the ground doublet was discussed from the shape and the g-value of the resonance line and the site symmetry around uranium(IV) ion. Ghosh *et al.* obtained the ESR spectra from powdered compounds UF_3 and UF_4, though the results have not been well interpreted[2]. In order to observe ESR in a discrete complex, molecular volume of the organic ligands should be large enough to avoid the dipole–dipole interaction between the neighbouring ions. The ammonium salts of *N*-nitroso-*N*-phenylhydroxylamine and *N*-nitroso-α-naphthylhydroxylamine, which are called cupferron and neocupferron respectively, are known as a useful analytical reagent and form less watersoluble chelates with uranium(IV) ion as well as many metal ions[3]. In these tetrakis(cupferronato)- and tetrakis(neocupferronato)uranium(IV), the uranium(IV) ion is considered to be magnetically enough diluted.

In this paper the ESR observation on these chelates is reported.

EXPERIMENTAL

Cupferron (GR grade) was obtained from Nakarai Chemicals, Ltd., Japan and neocupferron, from Fluka AG., Switzerland. Aqueous solutions of cupferron and neocupferron were filtered before used for the synthesis. The other reagents were of GR grade and used without further purification. The uranium(IV) hydrochloric acid solution (6N-HCl) containing about 302·8 g of natural uranium per liter was supplied by Power Reactor and Nuclear Fuel Corporation (Tokai works). Enriched uranium(IV) hydrochloric acid solution was obtained by dissolving U_3O_8 with the enrichment of 89·0 per cent U^{235} into hydrochloric acid solution. The uranium ion in the solution was completely reduced to uranium(IV) ion by the electrolytic reduction. Hereafter, Cupf and Ncupf represent the anions of cupferron and neocupferron, respectively.

Uranium(IV) hydrochloric acid solution diluted to 0·13 mole/l. was dropwisely added to the aqueous cupferron or neocupferron solution (U(IV):ligand = 1:5). The precipitate was filtered off, repeatedly washed with cold water, washed with small portions of cold methanol, and then dried *in vacuo* for a day. The brown colored crystals were recrystallized twice from chloroform-petroleum ether and dried *in vacuo*. Since uranium(IV) ion in solution is particularly sensitive to oxidation so that cupferron and neocupferron are gradually decomposed in air at room temperature, the synthesis as well as the purification was carried out under cooling with ice in a dry box filled with argon gas or nitrogen gas.

Anal. Calcd for: $U(Cupf)_4$; Found: C, 36·28; H, 2·75; N, 14·02; U, 30·47%. Calcd: C, 36·65; H, 2·56; N, 14·25; U, 30·27%. $U(Ncupf)_4$; Found: C, 48·92; H, 2·88; N, 10·83; U, 23·5%. Calcd: C, 48·69; H, 2·86; N, 11·36; U, 24·12%.

Tetrakis cupferronate of enriched uranium(IV) was prepared and purified by the same procedure as that described above. Moreover, tetrakis cupferronates and neocupferronates of thorium(IV), cerium(IV), hafnium(IV), zirconium(IV) and titanium(IV) of stoichiometric composition were also synthesized by the similar methods, which are described elsewhere[4].

The ESR measurements were carried out using a JES-ME-2X type spectrometer at X-band microwave frequencies with 100 Hz field modulation at room temperature, 77 K and 4·2 K, and also at K-band microwave frequencies with 80 Hz field modulation at room temperature and 77 K. Quartz tubes which had been checked so as not to give any ESR signal in the magnetic field region lower than 10 kG at X-band, were used. As the standard material POA radical ($g_2 = 2{\cdot}00537$, $a_N = 13$ G) was used at room temperature, and MgO powder doped with Mn^{2+} ($g_s = 2{\cdot}034$, $a = 86{\cdot}9$ G), at 77 K.

---

*Present address: The Environmental Science Institute of Hyogo Prefecture, Hyogo-ku, Kobe.

RESULTS

Two ESR signals were observed on cupferronates and neocupferronates of uranium(IV) each at about 1500 G and at 3200 G. In Fig. 1 are shown the spectra of ESR on $U(Cupf)_4$ and $U(Ncupf)_4$ observed at 77 K near the magnetic field of 1500 G. The spectra were not observed at room temperature. The g values calculated from the magnetic field at the points where the derivative curve intersects with the base line, were 4·27 and 4·50 for $U(Cupf)_4$ and $U(Ncupf)_4$, respectively. The spectrum with uranium enriched to 89·9 per cent U^{235} at 77 K showed the same shape and g values as that for $U(Cupf)_4$ with natural uranium. In the solution of degassed tetrahydrofuran, the signal was not observed at room temperature but the same signal as appeared in the powder state was observed at 77 K, at which temperature the solution was frozen. For the tetrakis-cupferronates and neocupferronates of the tetravalent metal ion having closed shell structure, such as Th(IV), Ce(IV), Hf(IV), Zr(IV) and Ti(IV), this kind of signal was not observed.

The other signal observed at about 3200 G had the half width of 25 G (Fig. 2). This rather sharp signal both observed at room temperature and 77 K appeared irrespectively of the kind of the central metal ion. In Table 3 are presented the g values obtained. These values of 2·003 ~ 2·005 seem to suggest that an unpaired electron localizing about nitrogen atom is responsible for ESR signal. It has been known that the N–N bond in *N*-nitroso-*N*-phenylhydroxylamine is weak and breaks into nitrobenzene at temperature slightly above ambient [5, 6]. Even after the formation of cupferronates and neocupferronates, an N–N bond fission in ligand seems to occur with leaving an unpaired electron at a nitrogen atom. However, the origin of the signal at 3200 G is not yet obvious at this stage.

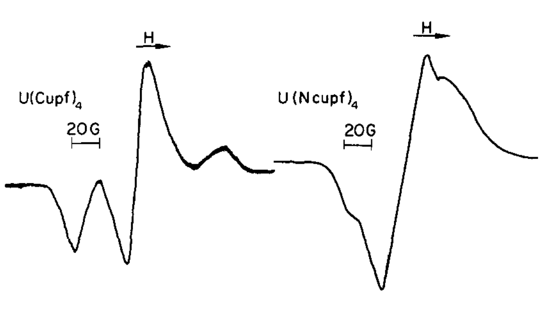

Fig. 1. ESR spectra of $U(Cupf)_4$ and $U(Ncupf)_4$ at about 1500 G.

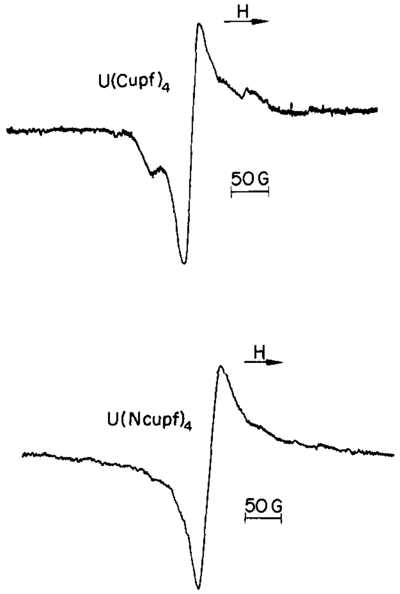

Fig. 2. ESR spectra of $U(Cupf)_4$ and $U(Ncupf)_4$ at 3200 G.

DISCUSSION

The signal shown in Fig. 1 was considered to be originated from the central uranium(IV) ion, because it was observed only in the paramagnetic uranium(IV) complexes and its spectrum was relatively broad with half width of about 40 G. Tetravalent uranium ion has $(5f)^2$ configuration with $^3H_4$ ground term; that is a non-Kramers ion. ESR for the compound with non-Kramers ion was theoretically investigated by Baker and Bleaney [7]. When the non-Kramers ion is placed in a crystal field with a symmetry higher than twofold, there are two possibilities to raise degeneracy of the accidental doublet so that the small zerofield splitting causes the ESR absorption in the ground state. One is the splitting of the doublet by the static Jahn–Teller distortion into two singlets energetically much closely spaced and the other is that of the time reversed doublet by a dynamic Jahn–Teller distortion. In the former the shape of the resonance line is symmetrical and in the latter, asymmetrical. As is shown in Fig. 1, the shape of the derivative curves is almost symmetrical and rather sharp, so the signal seems to be due to the transition between two singlets in the ground state of $^3H_4$ in uranium(IV) ion.

Tetrakis-bidentate chelate of $U(Cupf)_4$ and $U(Ncupf)_4$ has the coordination number of eight around the central metal ion with forming an octacoordination polyhedron. If only eight donor atoms in the bidentate ligands are taken into consideration, two structures with octacoordination polyhedron are possible, one of which is square antiprism with the symmetry around the uranium ion of D_{4d} and the other, dodecahedron with the symmetry of D_{2d}. Among the known tetrakis-bidentate chelates of uranium(IV) ion only two chelates have been elucidated to have such structures, that is tetrakis(acetylacetonato)uranium(IV) having square antiprism structure and tetrakis(dibenzoylmethanato) uranium(IV) having dodecahedron structure. It is known that the difference between the square antiprism and the dodecahedron configurations becomes less marked either when the square antiprism is twisted around one of the twofold axes or when the dodecahedron, around the rotatory reflection axis [8, 9]. The structure of $U(Cupf)_4$ and $U(Ncupf)_4$ has not yet been determined, but it is expected that the structure is either of dodecahedron, square antiprism or some intermediate between them.

The ninefold degeneracy of the $^3H_4$ ground term for uranium(IV) is split into a singlet and four doublets under the crystal field with D_{4d} symmetry, and into five singlets and two doublets under the D_{2d} crystal field, as shown in Table 1. Therefore, two singlets with very small separation at the ground state could either arise in pure D_{2d} crystal field or result from the static Jahn–Teller splitting of a doublet in the D_{2d} or D_{4d} crystal field.

The potential function of D_{2d}, tetragonal crystal field, is given by

$$V = B_2^0O_2^0 + B_4^0O_4^0 + B_4^4O_4^4 + B_6^0O_6^0 + B_6^4O_6^4 \tag{1}$$

where O_2^0, O_4^4, O_6^0 and O_6^4 are equivalent operators[10], and

$$B_2^0 = 0{\cdot}269(e^2/a^3)\alpha\langle r^2\rangle,\ B_4^0 = -0{\cdot}0425(e^2/a^5)\beta\langle r^4\rangle,$$

$$B_4^4 = 2{\cdot}066(e^2/a^5)\beta\langle r^4\rangle,\ B_6^0 = -0{\cdot}0745(e^2/a^7)\gamma(r^6\rangle,$$

$$B_6^4 = -0{\cdot}631(e^2/a^7)\gamma\langle r^6\rangle,$$

where α, β, and γ are the multiplying factors, $\langle r^n\rangle$ is the mean value of the *n*th power of the radial distance of the 5f-electron, and a is the U(IV)-oxygen distance. Assuming that the coordination polyhedron is the dodecahedron[11] with the U–O distance of 2·32 A which is determined for tetrakis(acetylacetonato)uranium(IV), and that $\langle r^2\rangle = 1{\cdot}68$, $\langle r^4\rangle = 5{\cdot}00$ and $\langle r^6\rangle = 24{\cdot}4$ atomic units for U(IV) ion[12], $\alpha = -2{\cdot}10\times10^{-2}$, $\beta = -7{\cdot}346\times10^{-3}$, and $\gamma = 6{\cdot}099\times10^{-5}$ for the $^3H_4$ term, the coefficients B_n^m are given in cm^{-1} as follows. $B_2^0 = -24{\cdot}75$, $B_4^0 = 2{\cdot}11\times10^{-2}$, $B_4^4 = -1{\cdot}029$, $B_6^0 = -7{\cdot}82\times10^{-4}$, and $B_6^4 = -6{\cdot}62\times10^{-3}$. The splitting scheme of the $^3H_4$ term calculated on the basis of the above potential function, in which the oxidation state of the oxygen is assumed to be −2, is shown in Table 2. As seen in Table 2, the ground state is the singlet $^1\Gamma_{t1}$ with the lowest excited state $^1\Gamma_{t2}$ located 49 cm^{-1} above. Although this scheme is supported by the measurement of magnetic susceptibility for $U(Cupf)_4$[13], the energy gap is too large to cause the resonance absorption.

Table 1. Eigen functions of $^3H_4$ term in D_{2d} and D_{4d} symmetry

Symmetry	irreducible representation: Eigen function
D_{2d}	$^1\Gamma_{t1}: (1/\sqrt{2})\cos\theta(\lvert+4\rangle + \lvert-4\rangle) - \sin\theta\lvert0\rangle$
	$^1\Gamma_{t3}: (1/\sqrt{2})(\lvert+2\rangle + \lvert-2\rangle)$
	$^1\Gamma_{t2}: (1/\sqrt{2})(\lvert+4\rangle - \lvert-4\rangle)$
	$^1\Gamma_{t1}: (1/\sqrt{2})\sin\theta(\lvert+4\rangle + \lvert-4\rangle) + \cos\theta\lvert0\rangle$
	$^1\Gamma_{t4}: (1/\sqrt{2})(\lvert+2\rangle - \lvert-2\rangle)$
	$^2\Gamma_{t5}: \cos\theta'\lvert\pm3\rangle + \sin\theta'\lvert\mp1\rangle$
	$^2\Gamma_{t5}: -\sin\theta'\lvert\pm3\rangle + \cos\theta'\lvert\mp1\rangle$
D_{4d}	$^1\Gamma_1: \lvert0\rangle$, $^1\Gamma_3 + {}^1\Gamma_4: \lvert\pm4\rangle$, $^2\Gamma_5: \lvert\pm1\rangle$, $^2\Gamma_6: \lvert\pm2\rangle$, $^2\Gamma_7: \lvert\pm3\rangle$

Table 2. Energy scheme of the ground term $^3H_4$ in the D_{2d} symmetry

Irreducible representation	energy (cm^{-1})
Γ_{t1}	1124
Γ_{t5}	934·2
Γ_{t4}	661·9
Γ_{t3}	−12·15
Γ_{t5}	−442·4
Γ_{t2}	−1357
Γ_{t1}	−1406

On the other hand, according to the splitting scheme of the $^3H_4$ term in the crystal field with D_{4d} symmetry calculated by Mulak and Czopnik[14], the ground state can be either of the doublet, $\lvert\pm1\rangle$, $\lvert\pm2\rangle$, $\lvert\pm3\rangle$, or $\lvert\pm4\rangle$, depending on the tetragonality of the coordination polyhedron. Therefore, it is possible that the signal should originate from the ground state doublet, if the crystal field with lower symmetry than D_{4d} operates to result in the static Jahn Teller splitting of the doublet. In this case $g_\perp$ is expected to be zero and only $g_\parallel$ has a non-zero value which is calculated from the eigenfunctions of the two singlets. As natural uranium is composed of 99·3 per cent U^{238} with a nuclear spin of $I = 0$, the term related to the nuclear spin will be neglected from the spin Hamiltonian, and the spin Hamiltonian with the effective spin of 1/2 is given by

$$\mathscr{H} = g_\parallel H_zS_z + \Delta_xS_x + \Delta_yS_y \tag{1}$$

where the first term is the Zeeman term and the second and third terms describe the zero-field splitting. When resonance occurs at the frequency ν, we obtain

$$h\nu = \{(g_\parallel\beta H\overline{\cos\theta})^2 + \Delta^2\}^{1/2}, \tag{2}$$

where $\Delta^2 = \Delta_x{}^2 + \Delta_y{}^2$ and θ is the angle between the applied magnetic field and the tetragonal axis. If the $\lvert\pm4\rangle$ doublet is the ground state and splits into two singlets, $1/\sqrt{2}\{\lvert+4\rangle + \lvert-4\rangle\}$ and $1/\sqrt{2}\{\lvert+4\rangle - \lvert-4\rangle\}$, one can obtain $g_\parallel = 8_{g_J} = 6{\cdot}4$, where g_J is Lande g-factor and equals to 4/5 for the $^3H_4$ term. Then Δ is calculated to be about 0·15 cm^{-1} both in $U(Cupf)_4$ and $U(Ncupf)_4$ from the Eqn (2).

Since the shape of the signal of cupferronate of enriched uranium with 89·9 per cent U^{235} having a nuclear spin of $I = 7/2$ was identical with that of cupferronate of natural uranium, the auxiliary splitting found in the spectra (Fig. 1) may not be attributed to the hyperfine interaction between the electron and the nuclei.

Concerning to the origin of the splitting of the doublet,

Table 3. g-values for cupferronates and neocupferronates

$U(Cupf)_4$	$2{\cdot}005_1$	$U(Ncupf)_4$	$2{\cdot}003_3$
Th	$2{\cdot}003_5$	Th	$2{\cdot}004_3$
Ce	$2{\cdot}004_6$	Ce	$2{\cdot}003_3$
Hf	2·003	Hf	$2{\cdot}002_5$
Zr	$2{\cdot}004_5$	Zr	$2{\cdot}003_4$
Ti	$2{\cdot}005_2$	Ti	$2{\cdot}004_3$

the effect of an unpaired electron which is a possible cause of ESR signal at 3200 G, seems to be responsible. As is mentioned before, there is a possibility that an N–N bond fission in the ligand often appearing after the formation of the complex may lead to an octacoordination structure of higher symmetry, that is D_{4d}, otherwise dodecahedron structure of $U(Cupf)_4$ and $U(Ncupf)_4$. Actually the signal originated from the uranium(IV) ion was only observed along with the appearance of the signal at 3200 G.

REFERENCES

1. (a) R. S. Title, P. P. Sorokin, M. J. Stevenson, G. D. Petit, J. E. Scardefield and J. R. Lenkard, *Phys. Rev.* **128**, 62 (1962); (b) A. Yariv, *Phys. Rev.* **128**, 1588 (1962); (c) S. D. McLaughlan, *Phys. Rev.* **150**, 118 (1966); (d) C. M. Bowden, H. C. Meyer, P. F. McDonald and J. D. Stettler, *J. Phys. Chem. Solids*, **30**, 1535 (1969).
2. S. N. Ghosh, W. Gordy and D. G. Hill, *Phys. Rev.* **96**, 36 (1954).
3. F. J. Welcher, *Organic Analytical Reagents*, p. 354, Vol. III, Chap. XIII (1955).
4. T. Yoshimura, C. Miyake and S. Imoto, *Technol. Rep. Osaka* **22**, 791 (1972).
5. T. Yoshimura, C. Miyake and S. Imoto, *Bull. chem. Soc. Japan*, **45**, 1424 (1972).
6. W. W. Wendlandt, S. I. Ali and C. H. Stembridge, *Analytica chim. Acta*, **31**, 501 (1964).
7. J. M. Baker and B. Bleaney, *Proc. Roy. Soc. Lond.* **A245**, 156 (1958).
8. R. V. Parish, *Coord. Chem. Rev.* **1**, 439 (1966).
9. S. J. Lippard and B. J. Russ, *Inorg. Chem.* **7**, 1686 (1968).
10. (a) K. W. H. Stevens, *Proc. Roy. Soc.* **A65**, 209 (1952); (b) R. J. Elliott and K. W. H. Stevens, *Proc. Roy. Soc.* **A215**, 437 (1952).
11. J. L. Hoard and J. V. Silverton, *Inorg. Chem.* **2**, 235 (1963).
12. C. J. Lenander, *Phys. Rev.* **130**, 1033 (1963).
13. T. Yoshimura, C. Miyake and S. Imoto, *Bull. chem. Soc. Japan*, **47**, 515 (1974).
14. J. Mulak and A. Czopnik, *Bull. Acad. pol. Sci. Sér. Sci. chim.* To be published.