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Dioxouraniun(VI) Complexes of Schiff Bases Obtained from Substituted Salicylaldehydes and Alkyl Amines[1]

Shoichiro YAMADA and Akira TAKEUCHI

Institute of Chemistry, College of General Education, Osaka University, Toyonaka, Osaka

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Dioxouranium(VI) complexes have been examined with Schiff bases obtained from substituted salicylaldehydes and alkyl amines. Many new complexes of the type abbreviated as $UO_2(NO_3)_2$(X-SAL·R·H)$_2$ have been prepared as orange-red crystals. The notation X denotes H, 5,6-benzo and 3-CH_3O, and R represents alkyl groups. Infrared spectra indicate that there is no uncoordinated nitrate ion, and that the nitrate ions are coordinated with the uranium(VI) ion as unidentate ligands in these complexes. It is to be noted that the molecules, and not anions, of the Schiff bases are coordinated with the metal ions, as in many other dioxouranium(VI) complexes.

A number of studies have been carried out on the Schiff base complexes of various metal ions.[2-4] These studies, however, were mainly concerned with the 3*d* transition elements, and comparatively little has been reported on the corresponding complexes of the heavier transition elements.

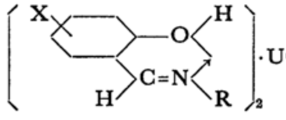

Fig. 1. $UO_2(NO_3)_2$(X-SAL·R·H)$_2$.

In the present work, dioxouranium(VI) ion has been taken up, and its complexes (Fig. 1) with Schiff bases[*1] obtained from substituted salicylaldehydes have been examined. The dioxouranium(VI) complexes are interesting, particularly in that the coordination number exceeding six may normally be expected for the uranium(VI) ion. Only a few papers[2,3,5] have so far been published about dioxouranium(VI) complexes with the Schiff bases, and systematic studies were thought to be desirable.

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[1] Presented, in part, at the 18th Symposium on Coordination Chemistry, September, 1968, Kyoto.

[2] P. Pfeiffer, E. Breith, E. Lübbe and T. Tsumaki, *Ann. Chem.*, **503**, 84 (1933).

[3] R. H. Holm, G. W. Everett, Jr., and A. Chakravorty, "Progress in Inroganic Chemistry," Vol. VII, ed. by F. A. Cotton, Interscience Publishers, New York, N. Y. (1966), p. 83.

[4] S. Yamada, *Coordin. Chem. Revs.*, **1**, 415 (1966).

[*1] These Schiff bases are abbreviated as X-SAL·R·H in the present paper.

[5] I. A. Savich, A. K. Pikaev, V. G. Lebedov and V. I. Spitsyn, *Zh. Neorg. Khim.*, **1**, 2736 (1956).

TABLE 1. ELEMENTAL ANALYSES OF THE DIOXOURANIUM (VI) COMPLEXES OF THE TYPE $UO_2(NO_3)_2(X\text{-}SAL\cdot R\cdot H)_2$

X	R	Calcd, %			Found, %			Method of prepara.
		C	H	N	C	H	N	
H	CH_3	28.92	2.73	8.43	28.67	2.54	8.11	(a)
	C_2H_5	31.22	3.20	8.09	31.93	3.18	7.64	(a)
	n-C_3H_7	33.34	3.63	7.76	33.10	3.39	7.84	(a)
	i-C_3H_7				32.80	3.65	7.51	(a), (b)
	n-C_4H_9	35.30	4.04	7.48	35.00	3.88	7·82	(b)
	t-C_4H_9				34.51	3.87	7.13	(a), (b)
5,6-Benzo	CH_3	37.70	2.90	7.33	38.01	2.62	6.68	(b)
	C_2H_5	39.40	3.31	7.07	39.49	2.98	7.43	(a), (b)
	n-C_3H_7	40.98	3.69	6.83	41.20	3.61	7.13	(b)
	i-C_3H_7				40.73	3.58	6.45	(b)
	n-C_4H_9	42.44	4.04	6.60	42.28	3.92	6.63	(b)
	t-C_4H_9				42.05	3.80	6.61	(a)
3-CH_3O	CH_3	29.84	3.06	7.73	29.91	2.97	7.47	(b)

Experimental

Materials. Dinitratobis(N-alkyl-salicylideneimine)-, dinitratobis(N-alkyl-5,6-benzosalicylideneimine)- and dinitratobis(N-alkyl-3-methoxysalicylideneimine)-dioxouranium(VI) complexes of the general formula $UO_2(NO_3)_2(X\text{-}SAL\cdot R\cdot H)_2$ were prepared according to the methods (a) and/or (b) given below. The notation X denotes H, 5,6-benzo and 3-CH_3O, and R represents alkyl groups. The elemental analyses of these complexes are given in Table 1.

(a) To a luke-warm solution of dioxouranium(VI) nitrate hexahydrate (0.01 mol) in ethanol (200 ml) was added a solution of a substituted salicylaldehyde (0.02 mol) in ethanol (100 ml). The solution immediately changed colour from orange-yellow to red. To this solution was added with stirring drop by drop a solution of an appropriate amine (0.02 mol) in ethanol (50 ml). The resulting red solution was allowed to stand for a few hours at about 30°C to 40°C. The orange-red crystals, which separated out, were collected by filtration and washed with ethanol.

(b) To a solution of dioxouranium(VI) nitrate hexahydrate (0.01 mol) in ether-ethanol (1 : 1, 300 ml) was added a solution of an appropriate Schiff base (0.02 mol) in ethanol (150 ml) with stirring at room temperature. The resulting solution was allowed to stand at about 5°C for a few hours. The orange-red crystals, which separated out, were collected by filtration, and washed with ethanol.

These dioxouranium(VI) complexes, the elemental analyses of which are given in Table 1, are slightly soluble in methanol, ethanol, chloroform and benzene, and a little more soluble in pyridine. Recrystallization from methanol, ethanol or chloroform was sometimes successful, but some of these complexes were so unstable against heat that they often underwent thermal decomposition during the process of recrystallization.

Measurements. The electronic absorption spectra of these complexes in solution were determined with a Shimadzu QR-50 spectrophotometer and a Shimadzu MPS-50 spectrophotometer. The infrared spectra in the region from 700 to 4000 cm^{-1} were measured with a Hitachi-EPI-2 infrared spectrophotometer using the Nujol mull technique.

The diamagnetism of the dioxouranium(VI) complexes in the solid state was detected by the Gouy method at room temperature.

Results and Discussion

Many new complexes of the type $UO_2(NO_3)_2(X\text{-}SAL\cdot R\cdot H)_2$, as shown in Table 1, have been prepared in the present work. They are stable against light and atmosphere in a solid state, and are all diamagnetic.

The infrared spectra of these complexes show no absorption band near about 1380 cm^{-1}, where the free nitrate ion is known to absorb. It is concluded, therefore, that there is no nitrate ion which is not bound with the uranium(VI) ion. Since these complexes show absorption peaks at about 1480 cm^{-1} and 1280 cm^{-1}, which are assigned to the ν_1 (NO stretching) and ν_4 (NO_2 asymmetric stretching) vibration, respectively,[6] it is presumed that in these complexes the nitrate ions are coordinated with the metal ion as unidentate ligands. It is thus found that the uranium(VI) ion takes an eight-coordination. A considerable number of dioxouranium(VI) complexes were previously reported which have nitrate ions coordinated with the uranium(VI) ion.[7] It is also to be noted that in the complexes of the type $UO_2(NO_3)_2(X\text{-}SAL\cdot$

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[6] E. P. Bertin, R. B. Penland, S. Mizushima, C. Curran and J. V. Quagliano, *J. Am. Chem. Soc.*, **81**, 3818 (1959); J. E. Fleming and H. Lynton, *Chem. Ind.* (*London*), **1963**, 1416; C. C. Addison and W. B. Simpson, *J. Chem. Soc.*, **1965**, 598; A. B. Lever, *Inorg. Chem.*, **4**, 1042 (1965).

[7] L. Sacconi and G. Giannoni, *J. Chem. Soc.*, **1954**, 2751; F. J. Frere, *J. Am. Chem. Soc.*, **55**, 4362 (1933).

$R\cdot H)_2$ the *neurtal molecules*, and not anions, of the Schiff bases are considered to be coordinated with the metal ion. Such was the case previously reported with dioxouranium(VI) complexes of 8-hydroxyquinoline, *β*-diketones and so on, in which the ligand *molecules* were considered to be bound with the metal ion.[7]

The electronic spectra of these dioxouranium(VI) complexes in the same solvent are all alike, independent of the nature of R, if comparison is made for the complexes with the same substituent X. The spectra of the complexes in chloroform are quite similar to those of the benzene solutions. In these solvents, Beer's law is found to hold, and it is most likely that these complexes may exist as eight-coordinated molecules, no decomposition or dissociation taking place. Since their solubility in organic solvents was considerably low, the absorption curves for the lower molar extinction coefficient was not very accurate. The absorption curves in Figs. 2 and 3 are regarded as superposition of the absorption due to the dioxouranium(VI) group[8] and that mainly due to the Schiff base molecules bound with the metal ion. The absorption of the former type is much stronger than that of the latter type, which is considered to be hidden by the former. Precise assignment of the absorption bands of these complexes is not possible at the present stage.

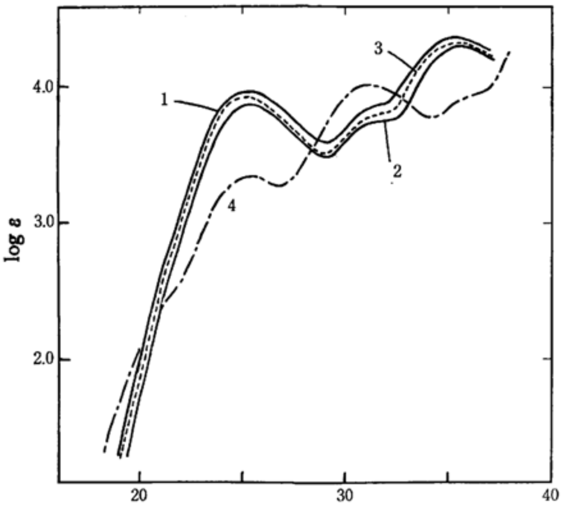

Fig. 2. Electronic absorption spectra of $UO_2(NO_3)_2$-$(H\text{-}SAL\cdot R\cdot H)_2$ in solution.
1, $R=C_2H_5$, in chloroform; 2, $R=t\text{-}C_4H_9$, in chloroform; 3, $R=n\text{-}C_4H_9$, in chloroform; 4, $R=n\text{-}C_4H_9$, in methanol

The electronic spectra of the methanol and the ethanol solution are different from those of the chloroform and the benzene solution. Some of the typical spectra in different solvents are also shown in Figs. 2 and 3. It is most likely that in methanol or in ethanol there occurs dissociation of the nitrate ions, and subsequent combination of the methanol or the ethanol molecule with the uranium(VI) ion. Incidentally, the combination of the methanol or the ethanol molecule with the uranium(VI) ion has often been observed, and indeed the alcohol adducts have been isolated as crystals, for example, with the dioxouranium(VI) complexes of the Schiff bases.[2,9]

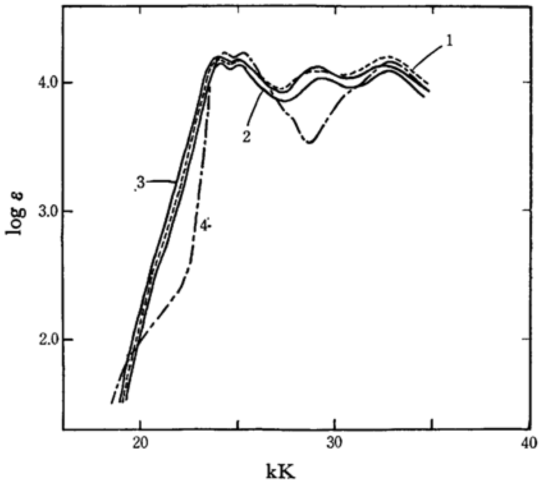

Fig. 3. Electronic absorption spectra of $UO_2(NO_3)$-$(5,6\text{-benzo-}SAL\cdot R\cdot H)_2$ in solution.
1, $R=C_2H_5$, in chloroform; 2, $R=t\text{-}C_4H_9$, in chloroform; 3, $R=n\text{-}C_4H_9$, in chloroform; 4, $R=n\text{-}C_4H_9$, in methanol

It is to be noted that the complexes of the type $UO_2(NO_3)_2(X\text{-}SAL\cdot t\text{-}C_4H_9\cdot H)_2$ were readily prepared and that their properties resemble those of the corresponding complexes with *n*-alkyl groups for R, all having an eight-coordinated configuration. This finding seems to be significant, particularly because it is known that the steric effect arising from the *t*-butyl group often favors the geometry which is different from that of the corresponding complex having an *n*-alkyl group instead of the *t*-butyl group.[10–12]

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[8] S. P. McGlynn and J. K. Smith, *J. Mol. Spectry.*, **6**, 164 (1961); C. K. Jϕrgensen, *Acta Chem. Scand.*, **11**, 166 (1957).

[9] S. Yamada and A. Takeuchi, unpublished.

[10] L. Sacconi "Essays in Coordination Chemistry," ed. by W. Schneider, G. Anderegg and R. Gut, Birkhäuser Verlag, Basel (1964), p. 148.

[11] S. Yamada and H. Nishikawa, This Bulletin, **36**, 755 (1963).

[12] S. Yamada and K. Yamanouchi, *ibid.*, **42**, 2543 (1969).