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Complexes of Nb(V) and Ta(V) with 8–Quinolinol and Tropolone

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The reactions of niobium or tantalum pentaalkoxides with 8–quinolinol (oxH) yielded the derivatives of the type $M(OR)_{5-n}(ox)_n$ *(M = Nb or Ta; R =* Pr^i *or Et; n = 1, 2 and 3). Niobium pentaethoxide with an excess of tropolone (tH) yielded Nb (OEt)*t_4*. Some physical and chemical studies of these compounds are reported.*

Introduction

The reactions between niobium and tantalum pentachlorides or pentabromides (MX_5) with 8–quinolinol (oxH) give derivatives of the type $MX_m(ox)_{5-m}$ (m = 1 to 4), which are insoluble in nondisruptive solvents. $NbBr(ox)_4$ and $TaBr(ox)_4$ were found to be 1:1 electrolytes, whereas other compounds are nonelectrolytes with the metal possessing co-ordination number 6–9. Even with large excess of 8–quinolinol $M(ox)_5$ could not be isolated. The only reported derivative of the type $M(ox)_5$ (M = Nb or Ta) is $Ta(ox)_5 \cdot 5HCl$ obtained by the reaction between $TaCl_5$ and excess of oxH [2]. Later on it was shown by Frazer and coworkers [1] to be in fact $TaCl_5 \cdot 5(oxH)$. Similarly in the reaction of tropolone (tH) with niobium and tantalum pentahalides, it was not possible to replace the fifth halogen atom of pentahalide by tropolone [3, 4]. Brown and Rickard [5] while studying the reaction of $PaCl_5$ or $PaBr_5$ with tropolone in nonaqueous solvents observed that $PaXt_4$ (X = Cl or Br) is the final product. However, Bagnall and coworkers [6] in their recent communication reported the preparation of pentakistropolonates of protactinium(V) or uranium(V) by the reaction of $Pa(OEt)_5$ or $U(OEt)_5$ with an excess of tropolone in benzene at room temperature.

Deutscher and Kepert [7, 8] have obtained the complexes of the type $Nb^{IV}t_4$ and $Nb^{IV}(ox)_4$ having co-ordination number eight, by the reaction of $NbCl_4$ with tropolone (tH) and 8–quinolinol (oxH). $Ta(NMe_2)_5$ reacts with CS_2 to form $Ta(S_2CNMe_2)_5$ in which the metal atom attains the co-ordination number ten [9].

A literature survey reveals that no work has been done with alkoxides of Nb or Ta with tropolone and 8–quinolinol. In view of the interesting results obtained by Bagnall and coworkers [6] in the case of Ut_5 and Pat_5 and Bradley and coworkers [9] in the case of $Ta(S_2CNMe_2)_5$ it was considered worthwhile to investigate reactions of Nb/Ta pentaalkoxides with tH and oxH to attempt the preparation of Mt_5 or $M(ox)_5$ (M = Nb or Ta).

Experimental

The metal alkoxides were prepared according to the literature [10–12]. Benzene (BDH) was dried over sodium wire followed by azeotropic fractionation in presence of ethanol. Tropolone (tH) (Aldrich Chemicals) was recrystallised several times from isopentane, m.p. 48–50 °C. 8–quinolinol (oxH) (E. Merck) was distilled (100–110 °C/5 mm) before use, m.p. = 75 °C. All the reactions were carried out under anhydrous conditions.

Niobium and tantalum were analysed as metal pentoxides by direct ignition of the compounds after digestion with ammonia and nitric acid. Nitrogen was estimated by the Kjeldahl method. Carbon and hydrogen analyses were done at the University of Jammu, Jammu. Alcohol was estimated by oxidation with normal dichromate solution in 12.5% sulfuric acid [13].

Molecular weights were determined in a semimicro ebulliometer (Gallenkamp) using a thermistor sensing. Infra-red spectra were recorded on a Perkin–Elmer 621 using KBr pellets. X-ray powder photograph was obtained using a Debye Scherrer camera of diameter 57.3 mm (Nickel filtered and CuK α radiation).

Reaction of Niobium Pentaethoxide with 8–quinolinol (oxH) (1:5 Molar Ratio)

To niobium pentaethoxide (1.20 g) in benzene was added the calculated quantity of 8–quinolinol (2.72 g). The contents were refluxed and alcohol liberated in the reaction was collected azeotropically. The progress of the reaction was ascertained by estimating the amount of alcohol in the azeotrope. Excess solvent was removed at room temperature and a yellowish brown solid was obtained. It was washed with hot benzene (3 X 10 ml) and recrystallized from CCl_4. Finally the product was dried at 40–50 ℃/0.5 mm for 3–4 hours and analysed:

	Nb	C	H	N	Amount of ethanol in azeotrope
Found:	15.2%	60.6%	4.3%	6.6%	0.50 g
Calc. for $Nb(OEt)_2(ox)_3$	15.1%	60.5%	4.6%	6.8%	0.52 g

The details of synthesis of different metal derivatives are recorded in Table I.

Discussion

A systematic study of the reactions of $Ta(OPr^i)_5$ with 8–quinolinol (oxH) in different stoichiometric ratios in refluxing benzene yield products of the type $Ta(OPr^i)_4(ox)$, $Ta(OPr^i)_3(ox)_2$ and $Ta(OPr^i)_2(ox)_3$, which are yellow to brown solids. Refluxing a mixture of $Ta(OEt)_5$ and oxH (in 1:3 molar ratio) in benzene for long period (24 hr) gave $Ta(OEt)_2(ox)_3$. Reaction of $Nb(OEt)_5$ with fivefold excess of oxH gave $Nb(OEt)_2(ox)_3$ as the final product.

With increasing number of 8–quinolinolate ligand (ox^-) attached to Nb or Ta in $M(OR)_{5-x}(ox)_x$ (x = 1, 2 and 3), these derivatives became insoluble in benzene. The failure to get products beyond trisubstitution appears presumably due to increased insolubility of $M(OR)_2(ox)_3$. The increased insolubility of the trisubstituted product may in turn be due to the polymerisation which is normally expected in such derivatives and consequent saturation in the co-ordination sphere of the central metal atom. Except $Ta(OPr^i)_4(ox)$, all the derivatives obtained during this work are insoluble in benzene. Molecular weight determination of this derivative indicated it to be monomeric in boiling benzene. All the solid complexes did not melt up to 250 ℃.

Failure to get $M(ox)_5$ or Mt_5 (M = Nb or Ta) indicate that Nb(V) and Ta(V) (ionic radii 0.67 Å) are too small to accommodate five molecules of tropolone or 8–quinolinol, whereas U(V) and Pa(V) give derivatives of the type Mt_5 (M = U(V) or Pa(V)) due to higher ionic radii [6]. The higher substituted derivatives of the type $M(OR)(ox)_4$ or $(M(ox)_5$ (M = Nb or Ta) could not be prepared, maybe due to steric hindrance. The structure of $M(OR)_2(ox)_3$ is probably similar to those of $M(OR)_2(dbm)_3$ (M = Nb or Ta, dbm = anion derived from dibenzoylmethane) [14].

The reactions of Nb/Ta pentaalkoxides with 8–quinolinol (oxH) could be represented by

$$M(OR)_5 + n\,oxH \xrightarrow[\text{reflux}]{\text{Benzene}} M(OR)_{5-n}(ox)_n + nROH$$

$$(n = 1, 2 \text{ and } 3)$$

With excess of 8–quinolinol (*i.e.* 4 to 5 mol) the end product was always the same as in the case of n = 3.

The observations of Frazer and coworkers [1] that the earlier reported tantalum compound $Ta(ox)_5 \cdot 5HCl$ is $TaCl_5 \cdot 5oxH$, is also supported by results of our studies.

The excess of tropolone (>5 mol) reacts with $Nb(OEt)_5$ in benzene to yield $Nb(OEt)t_4$ (dark brown solid) at room temperature. Refluxing a mixture of $Nb(OEt)_5$ and tH (in 1:5 molar ratio) in benzene for 3–4 hr yielded the same derivative $Nb(OEt)t_4$. In contrast $Pa(OEt)_5$ and $U(OEt)_5$ react with excess tropolone in benzene to yield Pat_5 or Ut_5 at room temperature [6]. The structure of $Nb(OEt)t_4$ is to be compared with metal tropolonates $(MT_4)Y$ [M = Nb or Ta; T = the tropolonate anion, $C_7H_5O_2^-$; Y = Cl or PF_6] [3].

I.R. Spectra

I.R. spectra of some of the derivatives are recorded in Table I. Free tropolone in the solid state gives two strong bands appearing at 1613 cm^{-1} and 1548 cm^{-1}, the former attributed to C=O stretch while the latter is due to C=C stretch. C=O and C=C stretches in the complex $Nb(OEt)t_4$ appeared at lower frequencies (C=O at 1587 cm^{-1}(s) and C=C at 1525 cm^{-1}(s)) in our studies. The similar type of lowering in C=O and C=C stretch was noticed in the case of Ut_4Cl (C=O 1588 cm^{-1}(s), C=C 1522 cm^{-1}(s)). The decrease in carbonyl frequency in the complexes on replacement of the hydrogen atom by the heavy metal atoms probably indicates the increasing involvement of the oxygen atoms in the covalent bonding to the metal atoms, as suggested by Selbin *et al.* [16] in the case of tetrakis(tropolonato) actinides(IV).

The spectra of Nb and Ta complexes with 8–quinolinol were found to be different from that of the ligand. However, spectra of all the complexes of Nb as well as Ta were quite similar, as was also observed by Charles *et al.* [18] and Stone [17] in the case of complexes of Mg and Bi with 8–quinolinol.

C=C and C=N stretching vibrations of 8–quinolinol are observed at 1577 (m) and 1495 cm^{-1} (s) [19]. Due to complex formation the band at 1577 cm^{-1}(m) is lowered to 1570 cm^{-1}, while that at 1495 cm^{-1} remains unchanged.

8–quinolinol gives a band at ~3400 cm^{-1}(wb) due to OH group. In the spectra of Nb and Ta complexes this band (~3400 cm^{-1}(wb)) due to OH group disappears indicating the complex formation. The appearance of a band at 507 cm^{-1}(m) in Nb and Ta

TABLE I. Reactions of Nb and Ta Alkoxides with 8–quinolinol (oxH) and Tropolone (tH).

Alkoxide (gm)	Ligand (gm)	Molar ratio	Reflux time (hr)	Alcohol in Azeotrope (gm) (Calcd) found	Elemental Analysis %; (Calcd) Found				Compd. and Characteristics	Mol. Wt.	Observed Frequencies in the i.r. Spectra (in cm^{-1})
					M^a	C	H	N			
$Ta(OPr^i)_5$ 1.29	(oxH) 0.39	1:1	7	(0.16) 0.13	(32.2) 33.4	–	–	(2.5) 2.3	$Ta(OPr^i)_4(ox)$ Yellow viscous pasty compd. soluble in benzene	(561) 558	
$Ta(OPr^i)_5$ 0.64	(oxH) 0.39	1:2	15	(0.16) 0.14	(28.0) 29.1	(50.2) 50.0	(5.1) 4.8	(4.3) 4.2	$Ta(OPr^i)_3(ox)_2$ Yellow solid, sparingly. Soluble in benzene		1605(w), 1570(m), 1499(s), 1468(s), 1425(m), 1378(s), 1322(s), 1270(m), 1222(m), 1175(vw), 1110(s), 1000(m), 910(m), 825(m), 744(s), 603(m), 565(m), 507(m).
$Ta(OPr^i)_5$ 0.81	(oxH) 0.74	1:3	18	(0.30) 0.28	(24.8) 25.2	(54.2) 54.1	(4.4) 3.9	(5.7) 5.6	$Ta(OPr^i)_2(ox)_3$ Yellowish brown solid. Insoluble in benzene		
$Ta(OPr^i)_5$ 0.47	(oxH) 0.57	1:4	20	(0.18) 0.17	(24.8) 25.8	(54.2) 53.9	(4.4) 4.0	(5.7) 5.6	$Ta(OPr^i)_2(ox)_3$ Yellowish brown solid. Insoluble in benzene		1570(m), 1495(s), 1465(s), 1421(w), 1378(s), 1323(s), 1271(m), 1223(w), 1109(s), 905(w), 825(w), 743(s), 604(w), 506(m).
$Ta(OEt)_5$ 1.18	(oxH) 1.27	1:3	24	(0.40) 0.36	(25.7) 26.3	(52.9) 52.8	(4.0) 4.5	(6.0) 5.8	$Ta(OEt)_2(ox)_3$ Brown solid. Insoluble in benzene		1605(vw), 1585(w), 1570(m), 1493(s), 1468(s), 1421(w), 1222(m), 1173(vw), 1110(s), 1065(w), 912(m), 825(m), 803(w), 745(s), 609(m), 507(m).
$Nb(OEt)_5$ 1.20	(oxH) 2.72	1:5	7–8	(0.52) 0.50	(15.1) 15.2	(60.5) 60.6	(4.6) 4.3	(6.8) 6.6	$Nb(OEt)_2(ox)_3$ Yellowish brown solid. Insoluble in benzene		1589(m), 1570(m), 1498(s), 1470(vs), 1425(m), 1398(m), 1381(s), 1325(s), 1275(s), 1239(s), 1225(m), 1176(m), 1137(m), 1112(s), 920(s), 830(m), 822(s), 805(m), 785(s), 745(s), 610(s), 595(m), 557(m), 508(m).
$Nb(OEt)_5$ 0.62	(tH) 1.20	1:5	3–4	(0.35) 0.33	(15.0) 15.2	(57.9) 57.0	(4.0) 3.4	–	$Nb(OEt)t_4$ Dark brown crystalline solid. Insoluble in benzene		1587(s), 1525(s), 1425(s), 1368(s), 1330(s), 1260(s), 1222(s), 965(m), 910(s), 877(s), 735(s), 718(s), 685(m), 578(m), 533(s), 519(s), 421(s) 410(m).
$Nb(OEt)_5$ 0.41	(tH) 0.79	1:5	Room Temp.	–	(15.0) 15.2	(57.9) 57.2	(4.0) 3.6	–	$Nb(OEt)t_4$ Dark brown crystalline solid. Insoluble in benzene		

[a]The tantalum analysis is always found high (also corroborated by various workers [20, 21]). [b]s = strong, m = medium, w = weak, vs = very strong, vw = very weak.

complexes is probably due to formation of a metal oxygen bond.

Nb and Ta complexes of 8–quinolinol show a strong band near 1100 cm^{-1}, not found in the spectrum of free 8–quinolinol. A similar band was also observed by Stone [17] in the case of complexes of 8–quinolinol with magnesium and bismuth. The band near 1100 cm^{-1} in the spectra of certain metal complexes with 8–quinolinol was attributed to the C–O stretch by Charles *et al.* [18].

X-ray Diffraction Results

TABLE II. Partial X-ray Powder Diffraction Results for $Nb(OEt)t_4$.

$\sin^2\theta$	I (Intensity)[a]
0.0224	M+
0.0256	M+
0.0316	S
0.0407	S
0.0510	S
0.0622	W
0.0714	W
0.0835	W
0.1114	M
0.1273	W
0.1446	W
0.1545	W
0.1661	W

[a] Visually estimated; S = strong; M = medium; W = weak.

X-ray powder diffraction results for $Nb(OEt)t_4$ are given in the Table II, together with visually estimated intensities. No pentavalent Nb/Ta complexes are known for which X-ray data are available; however, X-ray data for some other pentavalent metal complexes like Pat_5, Pat_4Cl, $Pat_4(ClO_4)$ and Ut_5 are known.

Our compounds are not iso-structural with any of the above compounds, *e.g.*, $Nb(OEt)t_4$ is not isostructural with $Pat_4(OEt)$ [5], which was later proved to be Pat_5 [6], which is of low symmetry. However, our results have not been interpreted.

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