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SYNTHESIS AND THERMAL BEHAVIOUR OF ADDUCTS OF $[Mo(CN)_8]^{3-}$ AND $[W(CN)_8]^{3-}$ WITH 8–HYDROXYQUINOLINE

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The adducts of $[Mo(CN)_8]^{3-}$ and $[W(CN)_8]^{3-}$ with 8-hydroxyquinoline (oxine) synthesized were of the type $K_3[Mo(CN)_8]\cdot(C_9H_7ON)_8\cdot4H_2O$ and $K_3[W(CN)_8]\cdot(C_9H_7ON)_6\cdot3H_2O$. The FTIR spectra show the presence of the (CN) and oxine group in the adduct compounds through the peaks in the range 2047–2108 cm^{-1} and 1015–1461 cm^{-1} respectively. The lower region of FTIR spectra show the M=O stretching while the higher range to ν(N–H) and ν(OH) modes. The uncoordinated water in these adducts was removed at around 110°C in a single step. The decomposition of adduct compounds starts from 125°C and continues to higher temperatures upto 850°C in different stages. The second stage of decomposition was predominant with the removal of oxine molecules with the formation of polymeric oxide of the type $K_2O\cdot M_2O_5$ (where M= Mo or W) obtained as the pyrolysis product.

Keywords: adducts, complexes, 8-hydroxyquinoline

Introduction

8–hydroxyquinoline (oxine) is widely used in the analysis to form insoluble, non-ionic complexes containing the bidentate ligand ox^- but the adducts containing the neutral ligand ox are not well known. 8–hydroxyquinoline behaves as a neutral ligand to form the covalent halide adduct [1–3] of the type $MCl_4\cdot n(ox)$ (where M=Sn or Ti). In these adducts ligand 8–hydroxyquinoline is probably unidentate [4]. The adducts of 8–hydroxyquinoline with complex compounds are very few. Recently Haider *et al.* [5] have synthesized the adduct of 8–hydroxy-

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quinoline with bis(8–hydroxyquinolinato) dioxouranium(VI). Crystallographic studies [6] indicated that extra molecule is directly bound to the metal through phenolate oxygen. This work was undertaken in continuation of our earlier study [7] relating to the adducts of this ligand with $Mo(CN)_8^{4-}$ and $W(CN)_8^{4-}$ for comparing the nature of the adducts in the two oxidation states of the metal and the difference in the pattern of their thermal dissociation.

In this paper we report the synthesis of adducts of 8-hydroxyquinoline with $[Mo(CN)_8]^{3-}$ and $[W(CN)_8]^{3-}$ and their characterization with the help of elemental analysis, Fourier transform infra-red spectroscopy and thermal studies.

Materials and methods

Potassium molybdate, potassium cyanide, potassium tungstate, potassium borohydride, 8–hydroxyquinoline and other chemicals of analytical grade were used as such as supplied from the firms. Potassium octacyano molybdate(IV) dihydrate $K_4[Wo(CN)_8]\cdot 2H_2O$ and – tungstate(IV) dihydrate $K_4[W(CN)_8]\cdot 2H_2O$ were prepared by the method of Leipold *et al.* [8]. The products were crystallized in ethanol-water mixture and dried on fused calcium chloride. The products were characterised by elemental analysis and FTIR spectroscopy. $K_3Mo(CN)_8$ and $K3W(CN)_8$ were obtained by the oxidation of $M(CN)_8^{4-}$ with MnO_4^-, precipitating the silver salt of the complex by adding silver nitrate and finally reacting $Ag_3M(CN)_8$ with minimum amount of KCl where-upon double decomposition reaction took place and $K_3M(CN)_8$ was formed in solution. Its strength was determined by titrating it potentiometrically against standard hexacyano ferrate(II) [9]. 0.1 *m* 8–hydroxyquinoline(oxine) was prepared by dissolving the compound in 0.1 *N* acetic acid which was neutralized by ammonia and then slightly acidified with a few drops of acetic acid [10].

Synthesis of complexes

(i) Octacyano (8-hydroxyquinoline) Molybdenum(V): A 0.1 *m* 8–hydroxyquinoline solution was added into $[Mo(CN)_8]^{3-}$ solution dropwise with constant stirring in the ratio of 1:8 (M:L). Greenish yellow precipitates obtained were filtered off and washed with water-ethanol mixture. The product was dried in vacuum. The adduct compound was analysed for $K_3[Mo(CN)_8]\cdot(C_9H_7ON)_8\cdot 4H_2O$.

Found % C=59.15, H=4.1, N=15.46, Mo=5.80

Calculated % C=58.08, H=3.87, N=13.55, Mo=5.82

(ii) Octacyano (8–hydroxyquinoline) tungsten(V): A 0.1 *m* 8–hydroxyquinoline solution was added into $[W(CN)_8]^{3-}$ solution dropwise with constant stirring in the ratio of 1:6 (M:L). Dark red colour precipitates were formed. The precipitates were filtered and washed with water-ethanol mixture. The compound was dried in vacuum. The complex compound thus formed was analysed by Electron-photometer Esca–750 and micro-analysis for $K_3[W(CN)_8]\cdot(C_9H_7ON)_6\cdot 3H_2O$.

Found % C=51.23, H=3.63, N=15.49, W=12.81, O=12.42.
Required % C=51.92, H=3.35, N=13.68, W=12.84, O=12.28

Physical measurements

Fourier Transform Infra–red spectra were recorded in KBr pellet with BIO-RAD, Digilab FTS–40 Fourier Transform Michelson Interferrometer which was equipped with highly sensitive Hg-Cd. Te detectors and KBr beam splitter in the wavelength range 450–4000 cm^{-1}. Thermal studies of the complex compounds were carried out by 1090 Thermal Analyser with TG moduled 951 of DuPont Instruments at the heating rate 10 deg·min^{-1} and approximately 10 mg sample was used for this study. Insolubility of the complex compounds in most of the common organic solvents did not permit for conductance measurements.

Results and discussions

The elemental analysis shows the composition of adduct compounds of 8-hydroxyquinoline with $[Mo(CN)_8]^{3-}$ as $K_3[Mo(CN)_8]\cdot(C_9H_7ON)_8\cdot4H_2O$ (I) and with $[W(CN)_8]^{3-}$ as $K_3[W(CN)_8]\cdot(C_9H_7ON)_6\cdot3H_2O$ (II). FTIR spectra of adduct I and II (Table 1) show the presence of strong band at 2093 cm^{-1} and 2078 cm^{-1} in the range of 2047–2108 cm^{-1} which implies the presence of cyano group with the mode M–C≡N [11]. The ν(CN) in octacyano molybdate(IV) is 2078 cm^{-1} while in the adduct-I the ν(CN) is shifted by 15 cm^{-1}. The shift in ν(CN) in adduct(II) is not very prominent. The two strong and two weak peaks are present in FTIR spectra in the range of 2047–2108 cm^{-1}. The weak peaks at 2063 cm^{-1} in adduct I and 2047 cm^{-1} in adduct II are attributed to the presence of isotopes C^{13} which have approximately 9% intensity of the major band and the band due to N^{15} has about 3% intensity. The cyanide peaks in adduct I and II are closely packed similar to $K_3[Mo(CN)_8]\cdot6H_2O$ complex. The ν(CN) is decreased for $[W(CN)_8]^{3-}$ ion because of larger molecule of W(V). The presence of oxine in complexes is indicated by the strong peak at 1120 cm^{-1}, but the adduct compound I & II have oxine bands at around 1108 cm^{-1} which shows that adduct of oxine are formed through the mode (C–O). The free oxine ligand exhibits ν(NO) at 1050 cm^{-1} while in adduct I and II this peak due to ν(NO) is found at 1200 cm^{-1} and 1216 cm^{-1} (W) respectively. This shift is due to the fact that an increase in electron density at the Mo/W atom which leads to an increase in the repulsive forces with non-bonding elections. The region 450–1100 cm^{-1} is very significant in which band characteristics of M–O modes appear. The peaks at 843 cm^{-1} (*VS*) in adduct I and 835 cm^{-1} (*VS*) in adduct II in the region 800–870 cm^{-1} is assigned to

M–O stretching. A broad band at 764 cm^{-1} (*m*) is attributed to M–O stretch because of consistency with metal-oxygen stretch reported for the compounds $K_2[OsO_2(CN)_4]$ and $K_3[ReO_2(CN)_4]$, [12, 13]. The broad bands in the region 3100–3300 cm^{-1} indicate the presence of uncoordinated water in these adducts.

FTIR spectroscopic studies of adduct compounds I and II indicate that 8-hydroxyquinoline forms the adduct with $[M(CN)_8]^{3-}$ of the type $K_3[Mo(CN)_8]\cdot(C_9H_7ON)_8\cdot4H_2O$ and $K_3[W(CN)_8]\cdot(C_9H_7ON)_6\cdot3H_2O$.

Thermal studies

The adduct $K_3[Mo(CN)_3]\cdot(C_9H_7ON)_8\cdot4H_2O$ (I) loses a molecules of water in the range 85.6°–143°C with the DTG peak at 102°C. The observed weight loss is 4.72% as against the calculated value 4.36%. The adduct compound $K_3[W(CN)_8]\cdot(C_9H_7ON)_6\cdot3H_2O$ (II) loses 3 molecules of water in the range of 93.6° to 148°C with DTG peak at 109.6°C for observed weight loss 3.87% as against the calculated value 3.77%. The adduct I splits off with 5 molecules of oxine and suffered a weight loss of 42.56% as against the calculated value 43.86% in the temperature range 142°–215° Cwith onset temperature 164.8°C and DTG peak at 182.8° ^{C} while adduct II loses 3 molecules of oxine in the range 148°–275°C with the observed weight loss of 29.10% as against the calculated value 30.36%. The adduct I further splits off with 2 molecules of oxine in the temperature range 215°–452°C for the observed weight loss 17.11% as against the calculated value 17.54%. It further suffered the weight loss of 13.69% as against the calculated value for the removal of 8 cyanide groups in temperature range 450°–800°C with DTG peak 679.8°C leaving behind the product which further changes to polymeric oxide $K_2O\cdot Mo_2O_5$. The adduct II suffered a loss of 3 molecules of oxine again for the weight loss 31.58% as against the calculated value 30.36% in the temperature range 270°–500°C with onset temperature 327.8°C and DTG peak at 358.5°C.

This adduct II again splits off with 8 cyanide groups for the weight loss of 13.80% as against the calculated value of 14.62%. The higher calculated value is due to the addition of atmospheric oxygen in the formation of polymeric oxide $K_2O\cdot W_2O_5$. The remaining polymeric oxides constitute the observed weight 21.72% as against the calculated value 21.56% for adduct I while for adduct II the observed weight was found 36.25% as against the calculated value of 36.77%.

The single step thermal dehydration indicates the removal of 4 molecules of water in adduct complex I and 3 molecules of water in adduct (II) respectively. The observed weight loss due to water is fairly close to the calculated amount. This further suggests that water molecules are equally bonded to the central Mo and W ions. Most important features of thermal curves is the higher degree of weight loss in stage II of the adduct compounds on the similar pattern of oxinates [14].

Table 1 FTIR spectra frequencies with their assignment for $K_3[Mo(CN)_8]\cdot(ox)_8\cdot4H_2O$ (I) and $K_3[W(CN)_8]\cdot(ox)_8\cdot3H_2O$ (II)

Adduct I frequency / cm^{-1}	Assignment	Adduct II frequency / cm^{-1}	Assignment
3270 (*m*)	$\nu(NH_2)$, $\nu(OH)$	3170 (*m*)	$\nu(NH_2)$, $\nu(OH)$
2108 (*sh*)	Mo–C≡N	2085 (*sh*)	W–C≡N
2093 (*s*)]	$\nu(CN)$	2078 (*m*)]	$\nu(CN)$
2063 (*m*)]	$\nu C^{13}N$	2047 (*w*)]	$\nu C^{13}N$
1631 (*w*)	$\nu(NH_2)$	1631 (*w*)	$\nu(NH_2)$
1601 (*s*)	$\nu(=N–H)$	1600 (*m*)	$\nu_a(=N–H)$
1554 (*s*)	$\nu(C'–N)$	1554 (*m*)	$\nu(C'N)$
1492 (*m*)		1508 (*w*)	
1462 (*m*)	$\nu_{sym}(C=O)$		
1401 (*m*)	$\nu(–N=H–)$	1401 (*m*)	$\nu(–N=N–)$
1308 (*w*)	$\nu_{sym}(C–O)$	1308 (*m*)	$\nu_{sym}(C–O)$
1262 (*vw*)]	$\nu(–N=O)$	1216 (*w*)	$\nu(–N=O)$
1200 (*w*)]			
1108 (*m*)	$\nu(C–O)$ of oxine	1108 (*m*)	$\nu(C–O)$ of oxine
1069 (*w*)	$\nu(N–O)$		
1015 (*w*)	$\nu(N–O)$		
905 (*w*)	Mo–O stretching+(C–C)	905 (*m*)	W–O stretching
843 (*vs*)	Mo–O stretching	835 (*vs*)	W–O stretching
795 (*w*)	$\delta_a(O–C–O)$		
764 (*m*)	$\delta_a(O–C–O)$	764 (*s*)	$\delta_a(O–C–O)$
709 (*w*)		733 (*w*)	W–O stretching
654 (*sh*)		638 (*w*)	$\nu(C–O–Mo–O)$
623 (*w*)	$\nu(C–O–Mo–O)$	591 (*s*)	ring vibration
576 (*m*)	Mo–O stretching	559 (*m*)	M–O stretching
544.2 (*w*)	$\delta_{sym}(C–C–O)$		
497.1	metal–ligand	497.1 (*s*)	metal–ligand

w (weak), *vw* (very weak), *m* (medium), *br* (broad), *s* (strong), *sh* (shoulder)

The TG and DTG thermograms of adduct I and adduct II (Figs 1 & 2) show that the rate of removal of different groups is fast in first stages and the rate decreases after 210°C. The rate of removal of the remaining ligand become slower after the expulsion of one or two ligands [15]. Moreover, in the present investigation the steric strain caused by bulky oxine ligand would further reduce the rate of decomposition in the last stages.

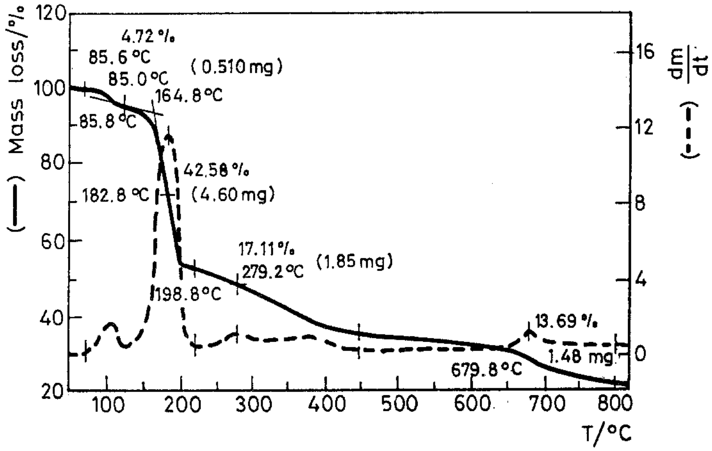

Fig. 1 The TG and DTG curves of adduct I

Scheme I

$$\mathrm{K_3Mo(CN)_8{\cdot}(C_9H_7ON)_8{\cdot}4H_2O} \xrightarrow[\substack{4.72\\(4.36)}]{-4\mathrm{H_2O}} \mathrm{K_3Mo(CN)_8{\cdot}(C_9H_7ON)_8}$$

$$\xrightarrow[\substack{42.56\\(43.86)}]{-5\,(\mathrm{C_9H_7ON})} \mathrm{K_3Mo(CN)_8{\cdot}(C_9H_7ON)_3} \xrightarrow[\substack{17.11\\(17.54)}]{-2\,(\mathrm{C_9H_7ON})}$$

$$\mathrm{K_3Mo(CN)_8(C_9H_7ON)} \xrightarrow[\substack{13.69\\(12.58)}]{-8\,(\mathrm{CN})} \mathrm{K_3Mo(C_9H_7ON)}$$

$$\rightarrow \mathrm{K_2O{\cdot}Mo_2O_5} \quad \substack{21.72\\(21.56\%)}$$

Scheme II

$$\mathrm{K_3W(CN)_8{\cdot}(C_9H_7ON)_6{\cdot}3H_2O} \xrightarrow[\substack{3.87\\(3.77)}]{-3\mathrm{H_2O}} \mathrm{K_3W(CN)_8{\cdot}(C_9H_7ON)_6}$$

$$\xrightarrow[\substack{29.10\\(30.36)}]{-3\,(\mathrm{C_9H_7OH})} \mathrm{K_3W(CN)_8{\cdot}(C_9H_7ON)_3} \xrightarrow[\substack{21.58\\(30.36)}]{-3\,(\mathrm{C_9H_7ON})} \mathrm{K_3W(CN)_8}$$

$$\xrightarrow[\substack{13.80\\(14.52)}]{-8(\mathrm{CN})} \mathrm{K_2O\cdot W_2O_5} \quad \substack{36.25\\(36.77)}$$

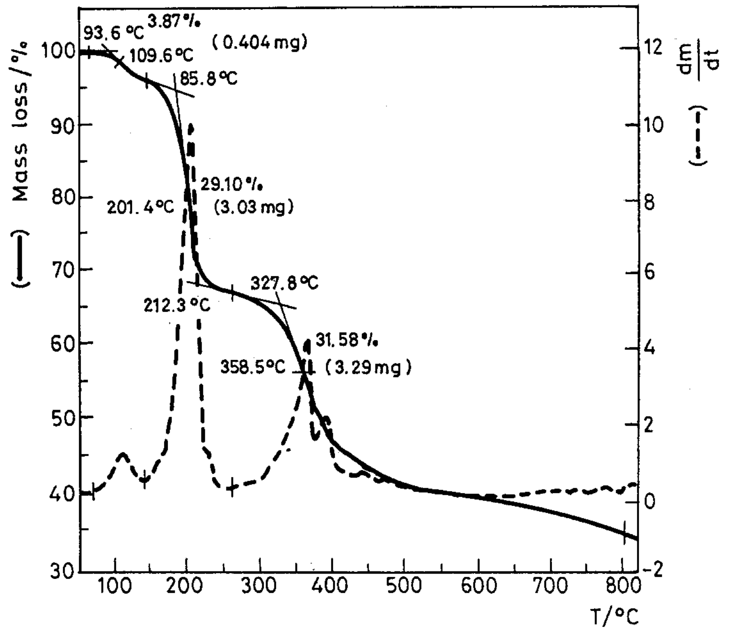

Fig. 2 The TG and DTG curves of adduct II

It may be concluded from the above mentioned studies that shining crystals formed when $M(CN)_8^{3-}$ where M = Mo or W interact with 8-hydroxyquinoline does not result in an increase in coordination number. The thermal decomposition of the adduct compounds is nearly of the similar pattern and calculated values are fairly close to the observed ones. Probably the end products of thermal decomposition are polymeric oxides of the type $\mathrm{K_2O\cdot M_2O_5}$ [16].

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Zusammenfassung — Die hergestellten Addukte von $[Mo(CN)_8]^{3-}$ und von $[W(CN)_8]^{3-}$ mit 8-Hydroxyquinolin (Oxin) haben die allgemeine Formel $K_3[Mo(CN)_8](C_9H_7ON)_8 \cdot 4H_2O$ bzw. $K_3[W(CN)_8](C_9H_7ON)_6 \cdot 3H_2O$. Die FTIR-Spektren beweisen die Gegenwart der (CN)- bzw. der Oxingruppen in den Adduktverbindungen durch die Peaks im Bereich 2047-2108 cm^{-1} bzw. 1015–1461 cm^{-1}. Die untere Region des FTIR-Spektrums zeigt die M=O Valenzschwingung, die obere Region (N–H) und (OH). Nichtkoordiniertes Wasser wird in diesen Addukten in einem einzigen Schritt bei 110°C abgegeben. Die Zersetzung der Adduktverbindungen beginnt bei 125°C und setzt sich in verschiedenen Schritten bis hin zu 850°C fort. Der zweite Schritt der Zersetzung wird durch die Abgabe von Oxinmolekülen beherrscht, wobei polymere Oxide der allgemeinen Formel $K_2OM_2O_5$ (mit M= Mo oder W) als Pyrolyseprodukte erhalten werden.