New Preparative Methods for Oxopentachlororhenates(V) & Their Isolation in Two Magnetic Forms

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Oxopentachlororhenates(V) have been prepared by new methods involving (a) reduction of $[Re^{VI}OCl_5]^-$ in acetic acid with hydroquinone and (b) reduction of $[ReO_4]^-$ in conc. HCl with hydroquinone and of $[Re^{VI}OCl_5]^-$ in acetic acid with halides. Those obtained by method (a) show high magnetic moments of ~ 2 B.M. (α-form) and those obtained by method (b) show low magnetic moments of ~ 0.6 B.M. (β-form). Different cations cause only a slight variation in magnetic moment values for salts prepared by a given method. Reflectance spectra in the UV-visible region, IR and far IR spectra, powder X-ray diffraction patterns and thermal analysis show that the two forms are structurally different; the $[Re^{V}OCl_5]^{2-}$ ion has different site symmetries in the two cases. The upper energy levels of the ion have lower values in the α-form than those in the β-form. This leads to spin-free configuration and thus the higher magnetic moment in the case of the α-form. The present study seems to be the first to report two magnetic forms in oxohalocomplexes.

Oxopentachlororhenates(V) obtained by earlier methods have been reported to show magnetic moments varying widely from 0.4 to 2.85 B.M.[1 -6]

In view of the importance of oxopentachlororhenates(V) in the chemistry of Re(V) ($5 d^2$ system) we thought it worthwhile to prepare these salts using some new preparative methods. The methods used in the present study allow the preparation of oxopentachlororhenate(V) salts with various cations in two forms with high and low magnetic moments but for an expected small variation due to the cation.

Materials and Methods

All the solvents and other chemicals used were of high purities and were dried thoroughly by suitable methods. As oxopentachlororhenates(V) are highly susceptible to decomposition by atmospheric moisture and oxygen, all the experiments were carried out in a glove box under dry nitrogen using appropriate techniques. Oxopentachlororhenate(VI) solution was prepared each time from potassium perrhenate by a method reported by us recently[7]. Conc. HCl was prepared by saturating 10 M HCl with HCl gas. All the preparations were carried out at room temperature. Preparation of oxopentachlororhenates(V) was carried out by two general methods: (A) in acetic acid medium and (B) in conc. HCl medium.

(A) Acetic acid medium: (i) Hydrogen chloride reduction of Re(VI)

Rubidium and caesium oxopentachlororhenates were prepared by this method. The rhenate(VI) solution was prepared from potassium perrhenate (1.5, 2.1 mmol) in acetic acid (50, 90 ml) and acetic

anhydride (2.0, 2.5 ml), passing HCl gas till a clear solution was obtained.

Rubidium chloride and caesium chloride (4.6, 5.0 mmol) were dissolved in acetic acid (30, 15 ml), acetic anhydride (2.5, 1.5 ml) and refluxed for 0.5 hr. They were added separately to rhenate(VI) solution prepared above and allowed to stand for a few days. After 14 and 6 days respectively, the rubidium and caesium salts were filtered on a glassfrit G4, washed several times with acetic acid and kept *in vacuo* over sodium hydroxide for 5 hr.

(ii) Hydroquinone reduction of Re(VI)

Potassium, caesium, rubidium, quinolium and *o*-phenanthrolinium oxopentachlororhenates(V) were prepared by this method. The rhenate(VI) solution was prepared as in (i) and mixed with an equal number of moles of hydroquinone in acetic acid. An yellow precipitate of potassium salt was formed in a few minutes. The mother liquor (yellow) in each case was transferred to another vessel through a G4 frit. From the yellow mother liquor caesium, rubidium, quinolinium and *o*-phenanthrolinium salts were precipitated immediately on adding a slight excess of CsCl, RbCl, quinoline and *o*-phenanthroline in a minimum volume of acetic acid containing 4-12% acetic anhydride. The above precipitates were filtered and processed as in (i) above.

(III) Potassium iodide reduction of Re(VI)

Potassium salt was prepared by this method. To the red rhenate (VI) solution obtained from 2.3 mol potassium perrhenate in 39 ml acetic acid and 23 ml acetic anhydride, were added 2.3 mmol potassium

iodide in 10 ml acetic acid and 3.5 ml acetic anhydride. An yellow precipitate of the potassium salt was immediately formed. It was filtered and processed as in (i) above.

(B) Conc. HCl medium: (i) Hydroquinone reduction of Re(VII) in conc. HCl

Caesium and *o*-phenanthrolinium salts were prepared by this method. Potssium perrhenate (2.0, 1.0 mmol) was suspended in conc. HCl (30, 15 ml) and vigorously shaken. Then hydroquinone (2.0, 1.0 mmol) in conc. HCl (20, 10 ml) was added. An yellow solution was obtained in each case. Addition of caesium chloride (4.9 mmol) and *o*-phenanthroline (2.6 mmol) in conc. HCl (10, 5 ml) gave immediately yellow and orange precipitates of the caesium and *o*-phenanthrolinium oxochlororhenates(V) respectively. They were filtered and processed as in (i) above.

The ultraviolet and visible spectra of solutions were recorded on a Beckman DU-2 spectrophotometer using 1 cm silica cells. IR spectra were recorded in the region 4000-400 cm^{-1} on a Beckman IR-20 spectrophotometer in nujol and in the region 400-30 cm^{-1} on a Polytech FIR 30 or Brucker IFS 113 instrument, as polyethylene discs. Diffuse reflectance spectra were recorded with Zeiss scanning reflection spectrophotometer. Magnetic susceptibilities were measured at room temperature by the Gouy method, using $Hg[Co(SCN)_4]$ as the calibrant. The Gouy tubes were packed under dry nitrogen in a glove box. Densities were determined by the pycnometric method[8] using toluene. The electrical conductivities were measured at $10^{-3} M$ concentration in nitromethane solution at room temperature on a Philips conductivity bridge PR 9500/90. The X-ray powder patterns were recorded with a Philips Camera 2PA using nickel filtered CuK_α radiation. Thermal studies were carried out using a Stanton Redcroft DTA instrument with 10 mg sample heated in air at 10 C/min from 20° to 1200°C and a Perkin-Elmer DSC-1B instrument with 31 mg sample heated at 16 /min from room temperature to 772°K.

After decomposition of the samples, rhenium was determined as tetraphenyl arsonium perrhenate and chloride as silver chloride using standard methods. The oxidation state was determined by the dichromate method[9].

Results and Discussion

The preparative methods using acetic acid as well as conc. HCl medium start from potassium perrhenate. Though a preliminary conversion to $KRe^{VI}OCl_5$ in the former case is necessary, it is easily done[7]. In acetic acid medium, hydrogen chloride, hydroquinone and iodide reduce Re(VI) to Re(V) and the $[Re^VOCl_5]^{2-}$ ion precipitates as the salt of the cation present. The reduction with hydrogen chloride is slow and takes a few days. It is assisted by the cation; the larger the size of the cation the shorter is the time for complete precipitation. With hydroquinone, the precipitation is completed in a few minutes. With potassium iodide also, the precipitation of K_2ReOCl_5 is immediate. It should be possible to prepare salts of other cations, using the corresponding perrhenate and iodide. In conc. HCl medium, hydroquinone reduces $[ReO_4]^-$ to $[ReOCl_5]^{2-}$ immediately and it has been used in the present work, but ascorbic acid also is equally useful. Only after several hours of standing, changes become evident in the electronic spectrum. By adding suitable cations, insoluble oxopentachlororhenates(V) can be precipitated immediately.

All the salts analyse to oxopentachlororhenate(V) of the respective cation (Table 1). The conductivities of quinolinium and *o*-phenanthrolinium salts confirm their formulation as 2:1 and 1:1 electrolytes[10] respectively. The salts are free of contamination from $[ReO_4]^-$ and $[ReCl_6]^{2-}$. All of them are obtained in almost quantitative yields. However, the salts show differences in magnetic moments, densities, X-ray diffraction patterns and thermal behaviour depending on the preparative method used. All of them are sensitive to moisture and oxygen. The alkali metal salts are insoluble in the common organic solvents, but are quite soluble in conc. HCl, the solubility decreasing with increase in size of the cation.

Magnetic moments

The magnetic moments of different oxopentachlororhenates(V) prepared by a given method are nearly the same but for a slight decrease with increasing cation size (Table 1). However, irrespective of the cation, the hydrogen chloride A(i) and iodide A(iii) reduction methods in acetic acid and the hydroquinone reduction in conc. HCl B(i) give salts with low magnetic moments (0.6-0.8 B.M.). The hydroquinone reduction in acetic acid A(ii) gives compounds with high magnetic moments (1.7-2.1 B.M.). Thus, oxopentachlororhenate(V) salts with the alkali metal and *o*-phenanthrolinium cations have been prepared with the high magnetic moment as well as with low magnetic moment values. Both the forms show almost no difference in solution absorption spectra (Table 2) which agree generally with the published spectral data on this anion.

It is reported[1-6] that the magnetic moments of the oxopentachlororhenate(V) salts differ widely; depending upon the method of preparation, values in the range 0.6-2.0 B.M. have been observed. Further, salts

Table 1—Analysis and Some Physical Properties of Oxopentachlororhenates(V)

Preparative method	Compounds (Colour)	Yield (%)	Oxidation state	Found (Calc), %		$\mu_{eff.}$ (B.M.)	Molar conductivity (ohm^{-1} cm^2 mol^{-1})
				Re	Cl		
A(i)	Rb_2ReOCl_5 (Yellow)	95	4.95	33.67 (33.82)	32.60 (32.20)	0.58	—
	Cs_2ReOCl_5 (Yellow)	97	4.87	29.00 (28.85)	27.65 (27.50)	0.63	—
(ii)	K_2ReOCl_5 (Yellow)	100	5.00	40.10 (40.60)	39.00 (38.65)	2.14	—
	Rb_2ReOCl_5 (Yellow)	98	5.10	32.96 (33.82)	32.50 (32.20)	1.90	—
	Cs_2ReOCl_5 (Yellow)	99	5.00	28.20 (28.85)	27.70 (27.50)	2.00	—
	$(QuH)_2ReOCl_5$ (Yellow)	94	5.08	28.80 (29.10)	28.10 (27.71)	1.63	105.9
	o-phenH$_2$ReOCl$_5$ (Orange yellow)	100	5.13	32.61 (33.14)	32.00 (31.56)	1.60	71.3
(iii)	K_2ReOCl_5 (Yellow)	90	5.00	39.96 (40.60)	38.20 (38.65)	0.88	—
B(i)	Cs_2ReOCl_5 (Yellow)	87	5.00	28.60 (28.85)	27.70 (27.50)	0.68	—
	o-phenH$_2$ReOCl$_5$(O) (Orange)	100	4.97	32.50 (33.14)	31.77 (31.56)	0.62	65.1

Table 2—UV and Visible Spectra of Oxopentachlororhenates(V) in Solution and Solid State

Compound	Magnetic form	Medium	λ_{max}(nm)[a]
K_2ReOCl_5	α	Conc. HCl	210, 250, 410, 485, 800, 1100
		Solid state	260, 290, 380sh, 510sh
	β	Conc. HCl	210, 240, 405, 480, 800, 1100
		Solid state	245, 270, 370, 490
Rb_2ReOCl_5	α	Conc. HCl	— — — —
		Solid state	260, 290
	β	Conc. HCl	212(4580), 240(6016), 415(29.1), 482(29.6), 800(25.3), 1110(26.4)
		Solid state	245, 270, 370, 370, 490
$Cs_2ReOCl_5^b$	α	Conc. HCl	210, 240, 410, 480, 800, 1100
		Solid state	290, 365sh, 480sh
	β	Conc. HCl	212(4200), 240(6068), 405(29.8), 482(25.0), 800(24.6), 1110(27.7)
		Solid state	240, 275, 300, 320, 350, 375, 475sh
$H_2ReOCl_5^c$		Conc. HCl	412(27.3), 483(27.4), 800(22.1), 1110(24.0)
$H_2ReOCl_5^d$		Conc. HCl	412(25.7), 480(26.2), 800(21.9), 1110(23.4)

(a) Transmission spectra in conc. HCl in the region 190-1200 nm, solid state diffuse reflectance spectra in the region 220-650 nm using NaCl standard, and using silica gel standard for α, β-forms of Cs_2ReOCl_5, ε values in parentheses.

(b) The bands are broad and asymmetric.

(c) By hydroquinone reduction.

(d) By ascorbic acid reduction.

prepared by the same method give different values[3] (0.6 to 2.0 B.M.) for different cations. This difference is too large to be explained on the basis of variation in the size of the cation. However, it may also be observed that the hydrogen chloride reduction of Re(VI) oxytetrachloride[6] and the iodide reduction of perrhenate[2] at $-10°$ gave magnetic moments near the lower limit of ~0.6 B.M. The same results are obtained also with the present methods [A(i), A(iii)] by the action of these two reductants on Re(VI) in acetic acid. Further, the rhenium pentachloride method, where no reduction of rhenium is involved, gave higher values of ~2.0 B.M. Both the solid rhenium pentachloride, which has rhenium octahedrally surrounded[11a] by chloride ions, and its solution in conc. HCl show magnetic moments of ~2 B.M. Among the present methods, only hydroquinone reduction of $[ReOCl_5]^-$ in acetic acid gives the salts with high magnetic moments of ~2B.M. irrespective of the cation.

Therefore, it seems that the salts of $[Re^VOCl_5]^{2-}$ anion can exist in two different magnetic forms: (i) with a high moment of ~ 2 B.M. (α-form) and (ii) with a low moment of ~ 0.6 B.M. (β-form); the magnetic moment values do not depend so much on the cation. The intermediate values of the magnetic moments of the salts of oxopentachlororhenate(V) anion with the same cation prepared by different methods and of salts with different cations prepared by the same method of previous workers, are then possibly due to a mixture of these two magnetic forms (α and β) in varying proportions according to the experimental conditions used. Grove and Wilkinson[5] also observed that the magnetic moments of alkali salts of $[ReOCl_5]^{2-}$ depended on the preparative method without apparent differences in other properties.

The existence of two different magnetic forms of the same compound is not new in transition metal chemistry[11b]. Magnetic moments seem to be more sensitive to slight structural changes than are the X-ray diffraction and infrared absorption techniques.[12]

Spectral studies

The solution spectra of the alkali metal salts in both the forms are almost identical (Table 2) in the UV and visible region. The λ_{max} and ε values are in close agreement with those reported by Jezowska *et al.*[13] and Pavlova[14], but we observe an additional band at 210 nm with $\varepsilon = 4580$. Ferguson[2] also observed a band at 220 nm with $\varepsilon = 4580$. Ferguson[2] also observed a band at 220 nm. Our data generally agree also with those of Grove and Wilkinson[5]. The two magnetic forms are, however, expected to differ most in the solid state properties.

The diffuse reflectance spectra of the potassium and rubidium salts show that the λ_{max} values in the α-form are shifted to lower energies relative to those in the β-form. The peaks corresponding to 370(sh) and 490 nm of the β-form are absent (in Rb-salt) or not prominent

(in K-salt) in the α-form. A comparison of the reflectance spectra of Cs_α and Cs_β compounds shows that the bands of the Cs_α are not resolved, but similar relative shifts are evident. These facts point to energy differences in the unoccupied higher levels of the two forms, and a contraction of the levels in the α-form of the $[ReOCl_5]^{2-}$ salt.

The IR and far IR data of both the forms of oxopentachlororhenates(V) are shown in Table 3 with their assignments. The $\nu Re=O$ frequencies, while generally agreeing with those reported[5,6] earlier, differ in the two forms except in the case of the caesium salt. The frequency of the α-form is lower than that of the β-form of potassium salt indicating a weakening of the $Re=O$ bond. It is interesting to note that the modes $\delta Cl-Re-Cl$ at 169, 164 cm^{-1} in the β-forms of potassium and rubidium salts shift to 173 and 170 cm^{-1} respectively in their α-forms. Thus, the latter frequency is not due to the presence of $[ReCl_6]^{2-}$ only, as has been supposed[2]. The same mode is observed at 161 cm^{-1} in Cs_β form and is similarly shifted to a slightly higher frequency (165 cm^{-1}) in Cs_α form. The bands are sharper in the α-form than in the β-form of Cs_2ReOCl_5. Further, the lattice mode region in the α-form is significantly different from that in the β-form and there are more lattice modes in the former. Only the stronger modes are given in Table 3. Such small differences in IR spectra are observed when the same compound e.g. $CaCO_3$, $Pb_3(PO_4)_2$, U_3O_8 crystallises in different lattice symmetries[15]. Edwards and Ward also have argued for different site symmetry orientations of $[ReOCl_5]^{2-}$ ion in the lattice[16] on the basis of X-ray diffraction results.

The α-forms of $(K, Rb, Cs)_2ReOCl_5$ have definitely lower densities (2.849, 3.160, 3.280) at $35.4° \pm 0.2°$ than the corresponding β-forms (3.665, 3.563, 3.720) respectively. In the X-ray powder photographs of the potassium and rubidium salts taken under identical exposure times, the β-forms show many more lines

Table 3 — IR and Far IR Spectra of Oxopentachlororhenates(V)[a]

Compound	Magnetic form	ν(Re=O)ν(Re−Cl)		ν(Re−Cl)		δ(Cl−Re−Cl) δ(O−Re−Cl)				Lattice modes				
K₂ReOCl₅	α	965s	323s	243sh	227m	186m	173m	141w	120sh	95m	91sh		56w	
	β	980s	321s	240sh	227s	188s	169s			103s	93s	66w	56w	42w
Rb₂ReOCl₅	α	970s 958s	318s	240sh	225m	187m	170m	133w		78m	70m	58sh	43w	
	β	970s	317s	238sh	226s	187s	165s	135w		82s	69m	62m	43w	
Cs₂ReOCl₅[b]	α	950s	314s	239m	224s	183w	165w	137w	129w	108m	100m	—		
	β	950s	316s	241s	224s	184s	161s	134s		80.6s				
(QuH)₂ReOCl₅	α	972w 943s	—	—	—	—				—				
o-phenH₂ReOCl₅	α	982s	—	—		—				—				
	β	980s 920w	—	—		—				—				

(a) according to ref. 2.
(b) only the stronger lattice modes are given.

than the α-forms. Also, lines in the α-forms are more diffuse. Grove and Wilkinson[5] found that samples of Cs_2ReOCl_5 with μ_{eff}. values 2.0 B.M. and 1.0 B.M. were only slightly different in their X-ray powder patterns. Edwards and Ward[16] have reported that Cs_2ReOCl_5 belongs to space group O_h^5 (or at least O^3). Their arguments indicate that the crystal is not completely ordered. The caesium salt prepared by the present methods also shows almost the same diffraction pattern in both α and β forms. However, their lattices might contain different degrees of disorder. It is probable that in the β-form either the molecular arrangement (and with it the packing in the unit cell) has changed or the unit cell dimension as well as the packing have been affected. This is supported by the fact that the β-form is distinctly of higher density than the α-form. The changes in packing are likely to affect the intramolecular and intermolecular interactions in these two forms and these would be reflected in the electronic, vibrational, thermal and magnetic properties of the two forms. These expectations are confirmed by our observations on the differences in their spectra and on their thermal behaviour.

Thermal behaviour

In the DTA operations no residue remained behind. The DTA curves of both the α and β forms of the three alkali metal salts show endothermic peaks. The α-form of the caesium salt shows a peak at 456°C which is broader and weaker than the peak of the β-form at 509°C. The peak of the α-form of rubidium salt is at 499°C, sharper and stronger than that of the β-form at 484°C. Besides the difference in transition temperatures of the two forms, there are differences in the base line variations on either side of the peaks of the α- and β-forms of these two alkali salts. The DTA scans of both α- and β-forms of the potassium salt show peaks at 494°C. But that of the former is sharper and strogner. In the latter there are probably endothermic transitions also at 796°C and 985°C, besides differences in variations of post transitional base line. The DSC scans of the α- and β-forms of the potassium salt show thermodynamically first order peaks respectively at 502 K and 508-511 K when heating, and at 472 K and 495-496 K when cooling, with very little or no loss of sample, under identical scanning conditions.

Thus, the α- and β-forms show a distinclty different thermal behaviour even in the case of the caesium salt where little difference is noticeable in the X-ray diffraction patterns.

It is thus evident that the difference in the magnetic moments of the α- and β-forms is due to differences in the crystal packing of the $[ReOCl_5]^{2-}$ ion in the two forms.

The spectral data of $[ReOCl_5]^-$, a d^1-system, have been interpreted on the basis of an energy diagram[13,17], with the energy levels in the following increasing order of energy $e^b_\pi < b_2 < e^*_\pi < b^*_1 < a^*_1$ and is modified for $[ReOCl_5]^{2-}$, d^2-system, to $e^b_\pi < b_2 < b^*_1 < e^*_\pi < a^*_1$. The e^*_π level (d_{xz}, d_{yz}) is sufficiently higher in energy than $b_2(d_{xy})$ level due to the tetragonal distortion of the C_{4v} ion and the metal-oxygen π-bonding. Also, the chloride π-bonding effects[18] are to be taken into consideration. Therefore, the d^2 electrons occupy b_2 level with pairing. The orbital momentum being quenched by the splitting of the T_{2g} level; this b_2^2 configuration of $[ReOCl_5]^{2-}$ is expected to be diamagnetic, as we find in the β-forms. The higher magnetic moment in the α-form is due to a different packing in the crystal lattice, as the above evidence shows, leading to a general lowering in energy of the higher levels. A lowering of b^*_1 level makes the energy gap between b^*_1 and b_2 of the same order as the pairing energy, resulting in some spin-free configuration and thus giving a higher magnetic moment in the α-form.

To the best of our knowledge, the oxopentachlororhenates(V) are the first instance of two magnetic forms in oxohalocomplexes.

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