rection for ion-pair formation between $(C_2H_5)_4N^+$ and anions by the use of $K_{(C_2H_5)_4N^+ClO_4^-} = 10^{1.05}$, $K_{(C_2H_5)_4N^+Cl^-} = 10^{1.54}$, and $K_{(C_2H_5)_4N^+Br^-} = 10^{1.35}$ changed the constant obtained by potentiometry for $AgCl_2^-$ from $10^{12.6}$ to $10^{13.6}$, and that for $AgBr_2^-$ changed from $10^{13.4}$ to $10^{14.1}$. The constants obtained by voltammetry were increased from $10^{13.6}$ to $10^{14.7}$ for $AgCl_2^-$ and from $10^{14.1}$ to $10^{14.8}$ for $AgBr_2^-$.

Acknowledgment.—Fellowship support from the National Institutes of Health is gratefully acknowledged by D. C. L.

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Far-Infrared Spectra of Oxochloro and Oxobromo Complexes of Nb(V), Mo(V), and W(V)

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Received August 4, 1965

The infrared spectra of the compounds $A_2[MOX_5]$, where A = Rb or Cs, M = Nb, Mo, or W, and X = Cl or Br, have been determined in the range 1000–80 cm.$^{-1}$. An assignment of the observed bands is presented.

Introduction

Although the far-infrared spectra of a number of metal halo complexes have been reported,[1-7] the study of oxohalo complexes has been limited to the M–O stretching vibration,[8] which occurs in the sodium chloride region. No Raman spectra of these ions have been reported in the literature. The present study extends the measure of the infrared spectrum down to 80 cm.$^{-1}$ and was undertaken in order to obtain more complete information about the vibrational spectra of the complex ions $[MOX_5]^{2-}$ where M = Nb, Mo, or W and X = Cl or Br.

Experimental Section

The compounds were prepared by standard methods[9] and were analyzed for halogen content. The spectra were recorded on Perkin-Elmer Model 337, 421, and 301 spectrophotometers. Mulls of the solids in Nujol were used to obtain spectra above 400 cm.$^{-1}$, whereas pressed polythene disks were used below this frequency. Spectra in the far-infrared region were recorded both at room temperature and at low temperature. The temperature of the disks, measured by means of a thermocouple in contact with it, varied between −150 and −160°.

Results

Figures 1 and 2 report two typical spectra of oxochloro and oxobromo complexes in the far-infrared region. Since some of the bands are rather diffuse at room temperature (A spectra in Figures 1 and 2), the spectra were also run at *ca.* −155° in the hope that overlapping bands might be resolved, but though a sharpening was clearly evident at the lower temperature (B spectra in Figures 1 and 2), the broad bands were only rarely resolved into more than one component. The frequencies of the absorption bands observed in the low-temperature spectra are given in Table I.

Discussion

The complex ions $[MOX_5]^{2-}$ belong to the point group C_{4v} in which the fifteen normal modes of vibration span the representations $4A_1 + 2B_1 + B_2 + 4E$. Only the species of A_1 and E symmetry are infrared active. The four A_1 species can be described approximately as a M–O stretching, two M–X stretching, and one X–M–X, O–M–X deformational mode; the four E species as one M–X stretching and three X–M–X, O–M–X bending modes. Taking into consideration the relative masses and bond strengths one of the degenerate modes can be approximately described as a M–O rocking mode.

Reported M–X stretching and X–M–X bending frequencies can be used as a guide to the assignment of these frequencies in the oxohalo complexes. Thus, the bands observed at *ca.* 320 cm.$^{-1}$ in the oxochloro complexes are assigned to the M–Cl stretching mode by comparison with the frequencies of 330 cm.$^{-1}$ in $M_2[MoCl_6]$ and 310 cm.$^{-1}$ in $M_2[WCl_6]$[4]; the bands at *ca.* 170 cm.$^{-1}$ are attributed to the Cl–M–Cl deformational modes ($[MoCl_6]^{2-}$ 170 cm.$^{-1}$, $[WCl_5]^{2-}$ 160 cm.$^{-1}$).

Two further bands were found in the spectra of the oxochloro complexes at *ca.* 230 cm.$^{-1}$. These are designated as the M–O rocking frequencies, no longer degenerate and separated by 11–14 cm.$^{-1}$, perhaps as a result of the low site symmetry of the complex ion in the

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TABLE I

INFRARED ABSORPTION FREQUENCIES (CM.$^{-1}$) OF MOX_5^{2-} IONS (WITH POSSIBLE ASSIGNMENT)[a]

	$Rb_2[NbOCl_5]$		
930 vs	M–O str.	180 m	Cl–M–Cl def.
339 sh	M–Cl str.	167 ms	Cl–M–Cl def.
327 s, b	M–Cl str.	125 (?) w	Cl–M–Cl def.
231 ms	M–O rock.	87 m	Cl–M–Cl def.
219 m, b	M–O rock.		
	$Cs_2[NbOCl_5]$		
928 vs	M–O str.	180 m	Cl–M–Cl def.
330 sh	M–Cl str.	168 m	Cl–M–Cl def.
320 s, b	M–Cl str.	87 w	Cl–M–Cl def.
231 ms	M–O rock.		
217 m, b	M–O rock.		
	$Rb_2[MoOCl_5]$		
967 vs	M–O str.	184 sh	Cl–M–Cl def.
339 sh	M–Cl str.	177 ms	Cl–M–Cl def.
327 s, b	M–Cl str.	88 m	Cl–M–Cl def.
230 ms	M–O rock.		
219 m	M–O rock.		
	$Cs_2[MoOCl_5]$		
952 vs	M–O str.	178 m	Cl–M–Cl def.
329 s	M–Cl str.	86 m	Cl–M–Cl def.
320 sh	M–Cl str.		
227 m	M–O rock.		
	$Rb_2[WOCl_5]$		
960 vs	M–O str.	177 m	Cl–M–Cl def.
339 sh	M–Cl str.	164 w	Cl–M–Cl def.
317 s	M–Cl str.	85 m	Cl–M–Cl def.
229 ms	M–O rock.		
	$Cs_2[WOCl_5]$		
957 vs	M–O str.	174 ms	Cl–M–Cl def.
333 w	M–Cl str.	164 mw	Cl–M–Cl def.
309 s, b	M–Cl str.	84 m	Cl–M–Cl def.
230 ms	M–O rock.		
	$Cs_2[NbOBr_5]$		
977 vs	M–O str.	140 w	Br–M–Br def.
241 s, vb	M–Br str.	111 mw	Br–M–Br def.
211 w	M–O rock.		
202 w	M–O rock.		
	$Rb_2[MoOBr_5]$		
972 sh	M–O str.	207 ms	M–O rock.
962 vs	M–O str.	187 m	M–O rock.
253 ms	M–Br str.	132 m	Br–M–Br def.
244 vs	M–Br str.	128 w	Br–M–Br def.
		119 m	Br–M–Br def.
	$Cs_2[MoOBr_5]$		
948 vs	M–O str.	136 w	Br–M–Br def.
246 vs, b	M–Br str.	125 w	Br–M–Br def.
209 mw	M–O rock.	118 w	Br–M–Br def.
195 m	M–O rock.		
	$Rb_2[WOBr_5]$		
968 vs	M–O str.	142 w	Br–M–Br def.
224 s	M–Br str.	120 m	Br–M–Br def.
203 s	M–O rock.		
	$Cs_2[WOBr_2]$		
960 vs	M–O str.	143 w	Br–M–Br def.
220 s	M–Br str.	119 m	Br–M–Br def.
202 s	M–O rock.		

[a] s, strong; m, medium; w, weak; v, very; sh, shoulder, b, broad.

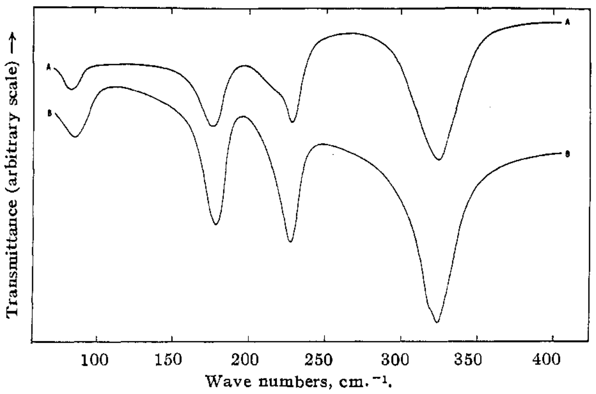

Figure 1.—Far-infrared spectra of $Cs_2[MoOCl_5]$: A, room temperature; B, low temperature (≈ −150°).

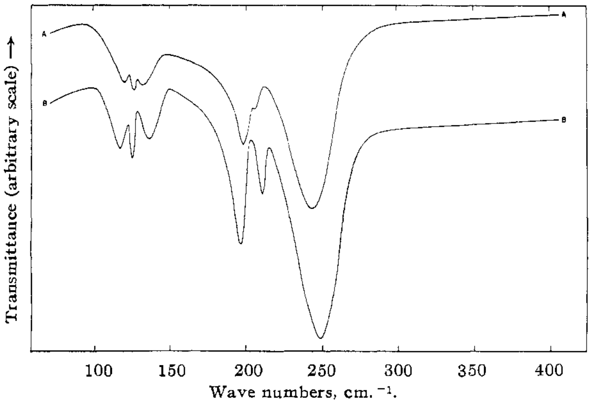

Figure 2.—Far-infrared spectra of $Cs_2[MoOBr_5]$: A, room temperature; B, low temperature (≈ −150°).

crystal lattice. No other data concerning a metal–oxygen rocking vibration appear to have been reported.

Lastly, an absorption band is observed at *ca.* 85 cm.$^{-1}$ in both rubidium and cesium salts of the oxochloro complexes. In view of its frequency, which is too high to be a rotation or a translation of the heavy anion, and of its insensitivity to the mass of the cation, the band may be assigned to a Cl–M–Cl deformational mode, rather than to a lattice vibration. In the hexachloro complexes of Mo(IV) and W(IV) a band was observed at *ca.* 70 cm.$^{-1}$ by Adams, *et al.*,[4] who noted that it could be assigned as the site symmetry activated vibration $\nu_6(F_{1u})$ rather than as a lattice mode. The presence of a band at about the same frequency in the oxochloro complexes lends support to the suggestion.

In the oxobromo complexes the bands found in the region 220–240 cm.$^{-1}$ are assigned to M–Br stretching modes by comparison with the frequency of 220 cm.$^{-1}$ found for $[WBr_6]^{2-}$. A further one or two bands are found at *ca.* 200 cm.$^{-1}$ which can be assigned either to M–Br stretching or M–O rocking modes. The latter alternative is preferred for the following reasons. If this band is attributed to the M–Br stretching mode no band attributable to the M–O rocking mode would be observed in the oxobromo complexes. Such a band is clearly observed in the oxochloro complexes. Secondly, one M–Cl stretching band was found in the oxochloro compounds and, analogously, one M–Br stretching is expected in the oxobromo complexes. Doubtless, these two modes, occurring so nearly at the same frequencies, will be strongly mixed.

Br–M–Br deformation frequencies are found at 110–140 cm.$^{-1}$ and are considerably higher than those observed in the few hexabromo complexes investigated.[3,4]

Of the three infrared-active M–Cl stretching modes expected, only a single broad band is observed, generally with one shoulder. It is likely that the three bands are contained within this envelope. The three M–Cl stretching frequencies of $[PtCl_6]^{2-}$ may be quoted for the sake of comparison: 320 cm.$^{-1}$ (E_g), 344 cm.$^{-1}$ (A_{1g}), and 340 cm.$^{-1}$ (F_{1u}).[10] The situation in the oxobromo complexes is not so clear. If the bands at *ca.* 200 cm.$^{-1}$ are assigned to the M–O rocking mode, a single M–Br stretching band without shoulders is found in all complexes except $Rb_2[MoOBr_5]$.

All three expected Cl–M–Cl bending bands were found (except in $Cs_2[MoOCl_5]$). As one of these is at 85 cm.$^{-1}$, it is expected that one of the Br–M–Br deformation bands will be outside the range investigated. Indeed two bands were found for the niobium and tungsten bromo complexes, but with molybdenum three bands were observed.

It appears, therefore, that the observed spectra of the oxohalo complexes are never in complete agreement with what is expected for an ion of C_{4v} symmetry, even though this symmetry is beyond reasonable doubt. Site symmetry splitting, accidental degeneracy, or exceptionally weak band intensities may all operate to cause this discrepancy.

It is interesting to compare the frequencies of the oxohalo complexes with the analogous ones reported for other complexes. The M–Cl stretching frequencies in the oxochloro complexes are lower than those of the corresponding hexachloro complexes with the central metal ion in the same oxidation state. In fact M–Cl stretching bands are found at 309 and 320 cm.$^{-1}$ in $Cs_2[WOCl_5]$ and $Cs_2[NbOCl_5]$, respectively, while the same bands are at 329 and 333 cm.$^{-1}$ in $[(C_2H_5)_4N][WCl_6]$ and $[(C_2H_5)_4N][NbCl_6]$. On the other hand, these frequencies are close to the M–Cl stretching frequencies in the hexachloro complexes with the central metal ion in the oxidation state +4. The values are: 308 and 325 cm.$^{-1}$ for $Cs_2[WCl_6]$ and $Cs_2[MoCl_6]$, 309 and 329 cm.$^{-1}$ for $Cs_2[WOCl_5]$ and $Cs_2[MoOCl_5]$.

The Cl–M–Cl bending frequencies of the oxochloro complexes correspond to those found for the hexachloro complexes. The Br–M–Br bending frequencies are found between 110 and 140 cm.$^{-1}$, compared with the reported Br–M–Br bending frequencies of 60 cm.$^{-1}$ in $Cs_2[WBr_6]$ and 78 cm.$^{-1}$ in $K_2[PtBr_6]$. One might think that the bands found at about 130 cm.$^{-1}$ could correspond to the first overtones of the fundamentals located at 60–70 cm.$^{-1}$. We have then measured the spectra of $Rb_2[MoOBr_5]$ and $Cs_2[MoOBr_5]$ down to 70 cm.$^{-1}$. A rather broad band is observed at 72 cm.$^{-1}$ in $Rb_2[MoOBr_5]$. Since this band is less intense than those observed at 132 and 119 cm.$^{-1}$, these two bands cannot be overtones of the former one. Moreover, no absorption is observed in the range 100–70 cm.$^{-1}$ in the analogous cesium salt, while the absorption bands assigned as Br–M–Br bendings have the same frequencies in the two compounds. Probably the band at 72 cm.$^{-1}$ in $Rb_2[MoOBr_5]$ corresponds to a lattice vibration.

Acknowledgment.—Thanks are expressed to Professor L. Sacconi for having suggested this problem and for his interest. Acknowledgment is made to the Italian "Consiglio Nazionale delle Ricerche" for financial support.

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A Thiocyanate Complex of Iodine(I)[1,2]

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Received September 13, 1965

It has been shown that a complex having the probable formula $I(SCN)_2^-$ is formed by oxidation of iodide ion or elemental iodine in solutions containing potassium thiocyanate. Hydrogen peroxide or potassium iodate effect nearly quantitative conversion of the iodine to the complex form. The properties of solutions of $I(SCN)_2^-$ are described and values for the equilibrium quotient for the reaction $I(SCN)_2^- \rightleftharpoons I^- + (SCN)_2$ are reported at various temperatures.

In an earlier paper,[3] it was postulated that a rather stable complex, I_2SCN^-, is formed when iodine is dissolved in solutions of thiocyanate ion. This complex absorbs strongly in the ultraviolet region, having a typical charge-transfer band with a maximum at 303 mμ (ϵ_{max} 42,900). It was noted that exposure of solutions of this complex to bright sunlight resulted in a marked increase in the absorbance in the ultraviolet region,

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