minimum and a very strong but asymmetrical hydrogen bond. Although hydrogen bonds between nitrogen atoms are normally rather weak, these acids seem to provide a favourable opportunity for strong hydrogen bonding. Symmetrical-type hydrogen bonding would result in reasonable structures for both compounds, that is, infinite chains for aurocyanic acid, and a three-dimensional lattice based on linked octahedra for cobalticyanic acid. Further work is in hand and it may be noted that preliminary infra-red data on a number of related anhydrous acids indicate that they fall into two classes which resemble ferrocyanic acid or cobalticyanic and aurocyanic acids, respectively.

Measurements were made using nujol and fluorolube mulls, a Perkin-Elmer model 21 spectrometer with calcium fluoride, sodium chloride and potassium bromide prisms, and Infracord and Unicam SP200 spectrometers.

The acids were prepared by standard procedures¹⁻³ and dried *in vacuo* at 80°–100° C. The deuterio acids were obtained either directly, using deuterium chloride and deuterium oxide, or by repeated exchange with deuterium oxide, and the extent of deuteration (> 90 per cent) was checked from examination of their proton resonance spectra in deuterium oxide solution.

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Far-infra-red Absorption Spectra of some Complex Halides of Molybdenum and Tungsten

In a previous publication¹ Adams and Gebbie reported the far-infra-red absorption spectra of some transition metal complex halides containing regular octahedral ions of the type MX_6^{2-} , X = halogen. We have now extended our observations to a series of halides of molybdenum and tungsten recently prepared by Edwards, Kennedy, Peacock and Said².

The spectra were obtained by means of a far-infra-red interferometer, the samples being in the form of 'Nujol' mulls sealed in polythene cells; details of techniques and procedure have already been published¹. The results are given in Table 1.

Table 1. FAR-INFRA-RED ABSORPTION FREQUENCIES (CM⁻¹) OF SOME COMPLEX HALIDES OF MO^{VI} AND W^{VI}

	ν_3	ν_4	Lattice mode (?)
K_2WCl_6	324	165	77
Rb_2WCl_6	306	160	66
Cs_2WCl_6	308	166	71
K_2MoCl_6	340	174	74
Rb_2MoCl_6	334	172	70
Cs_2MoCl_6	325	170	70
K_2WBr_6	229	74	—
Rb_2WBr_6	220	78	—
Cs_2WBr_6	214	60	—

Spectra of the halides $M'_2[MX_6]$, M = molybdenum or tungsten, are analogous to those found for compounds such as K_3PtCl_6 and K_2IrCl_6 , a three-band spectrum being observed¹. The spectra of the molybdenum chlorides all had absorption near 230 cm⁻¹; but as this increased if the sample was exposed to air, we consider it to be due to a breakdown product. Weak absorption was also found in

Rb_2WBr_6 and Cs_2WBr_6 at 116 and 114 cm⁻¹ respectively. Absorption in the range 308–340 cm⁻¹ is due to ν_3 (metal-chlorine stretching) and that at 160–174 to ν_4 (metal-chlorine bending). In the bromides, M_2WBr_6 , ν_3 and ν_4 are correspondingly lower and compare closely with those observed for K_2PtBr_6 , namely, 240 and 78 cm⁻¹. As expected ν_3 is lower for the tungsten than for the molybdenum compounds, and it is interesting to note that ν_4 follows this trend.

There is a marked dependence of ν_3 (and to a lesser extent, ν_4) on the nature of the cation. As the size of the cation is increased, cation-anion interactions decrease. The rise in ν_3 —and hence in the $M-X$ bond-strength—with increasing ionic interaction may be caused, at least in part, by varying amounts of $d\pi-d\pi$ bonding between metal and halogen in the anion. This dative π -bonding, which Woodward and Ware³ have shown to be present in $PtCl_6^{2-}$ and $PtBr_6^{2-}$, will be favoured by the proximity of a relatively small cation such as K^+ .

In $(NEt_4)WVCl_6$, ν_3 is at 329 cm⁻¹ (ref. 4); in Cs_2WIVCl_6 , ν_3 is at 308 cm⁻¹ and would presumably be a little lower in $(NEt_4)_2WIVCl_6$. Thus a drop of some 25 cm⁻¹ in ν_3 occurs as the oxidation state of tungsten is changed from +5 to +4, comparable with that of 37 cm⁻¹ for the +4 to +3 change in K_2IrCl_6 and K_3IrCl_6 (ref. 1).

The third, and lowest, frequency band found for the chlorides (Table 1) is in addition to the predicted infra-red-active internal modes of an isolated MX_6^{2-} ion. It was previously assigned to a lattice mode¹, largely on the basis of the large shift it suffered (45 cm⁻¹) in M'_2IrCl_6 when M' was changed from K^+ to $(NH_4)^+$. An alternative assignment is to ν_6 (f_{2u}), the inactive bending frequency, made active by the lower symmetry of the crystal lattice.

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Polymorphism in Silicon Carbide

SILICON carbide exists in two distinct crystalline polymorphs, the cubic or β -form, and the hexagonal or α -form¹⁻³. Although the crystal structure and related physical properties of the two forms of silicon carbide have been extensively investigated, the chemical relationship between the two silicon carbide polymorphs has apparently failed to receive equivalent attention. The problem was attacked by Baumann⁴, who investigated both the chemistry of silicon carbide formation, and the rate of conversion of β -silicon carbide to α -silicon carbide at several temperatures. Baumann observed that although β -silicon carbide began to transform to α -silicon carbide slowly at 2,100° C, the reaction was rapid at 2,300° C.

The suggestion that the transformation from the cubic form to the hexagonal form may proceed via the vapour phase has been made by Slack⁵. Thus, if a solid-phase transition occurs at all, it must be very slow as compared with the vapour phase process. Indeed, Kistler⁶ summarized the problem when he stated, "It is probable, although I believe the subject has not been sufficiently