Caesium Tetrathiotungstate(VI). Matrix Isolation and Mass Spectrometric Studies of a Ternary Sulphide which is Stable in the Vapour†

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Cs_2WS_4 can be sublimed at approximately 800 °C *in vacuo* (*ca.* 10^{-5} Torr). The major species detected mass spectrometrically is the parent ion. Matrix-isolation i.r. studies suggest but do not prove that the molecule has a structure similar to that adopted by M_2XO_4 species (where M is an alkali-metal ion and X = S, Cr, Mo, or W). In argon and nitrogen matrices the symmetry appears to be lower than that in neon.

Many metal sulphides can undergo vapour transport in the presence of species such as halogens[1] or elemental sulphur.[2] However most binary metal sulphides decompose on heating *in vacuo*. Where the metal is in its maximum oxidation state the observed vapour species are usually S_n, the metal and the diatomic sulphide or its (small) oligomers.[3] Sodium tetrathioferrate(III) with discrete FeS_4 groups has recently been synthesised[4] at a temperature of approximately 700 °C suggesting an appreciable thermal stability for certain thiometalates. Further, by analogy with alkali-metal salts of oxoanions,[5] vapour transport of alkali-metal salts of thiometalates appeared possible. Such studies are not only of fundamental importance, they are also necessary in understanding corrosion in sulphur-rich combustion conditions, in crystal growth, and in vapour deposition for example.

The stability of higher oxidation states of the transition elements generally increases from the 3*d* to the 4*d* and 5*d* species. Assuming that a minimum of four ligands are required to 'coat' the transition element, a charge of not greater than 2− (with the corresponding number of alkali-metal cations) leads us to WS_4^{2-} and ReS_4^- as likely candidates. Previous work[5,6] suggested that caesium salts would be the most volatile. Data in the literature also suggested that alkali-metal thioperrhenates(VII),$MReS_4$, were unstable.[7] By contrast alkali-metal thiotungstates(VI) have been known for over one hundred years.[8] We therefore examined the species Cs_2WS_4.

Experimental

Cs_2WS_4 was prepared by a modification of the method used by Gattow and Franke.[9] WO_3 (5 g, 21.6 mmol) was added to aqueous ammonia (50 cm^3, *ca.* 25% w/w) and water (10 cm^3). The suspension was stirred for 18 h and the residue removed by filtration. The solution was saturated with H_2S until an orange solution was obtained (30—45 min) accompanied by the precipitation of a variable quantity of a citron yellow solid. (The solid which was removed by filtration gave a Raman spectrum corresponding[10] to that for $[NH_4]_2WO_2S_2$). An equal volume of ethanol was added to the filtrate to precipitate the $[NH_4]_2WS_4$. This was removed by filtration, washed with ethanol, dried, and dissolved in the minimum quantity of water. The required Cs_2WS_4 was precipitated from this solution by the addition of concentrated aqueous CsCl, followed by filtration, washing with ethanol, and drying *in vacuo*. In a few cases the product was heated at 650—700 °C in a stream of argon saturated with CS_2 (to remove any oxide contaminant). All samples when sublimed *in vacuo* gave a golden yellow solid with a Raman spectrum identical to that given[11] in the literature for Cs_2WS_4. Silica apparatus was used for the sublimations and no evidence of reaction with the container was observed. However there was invariably a small dark coloured residue left after the sublimation process. Isotopic enrichment was carried out by heating Cs_2WS_4 at 600 °C with elemental sulphur (90% ^{34}S) in a sealed evacuated silica tube having a cooler portion at 400 °C.

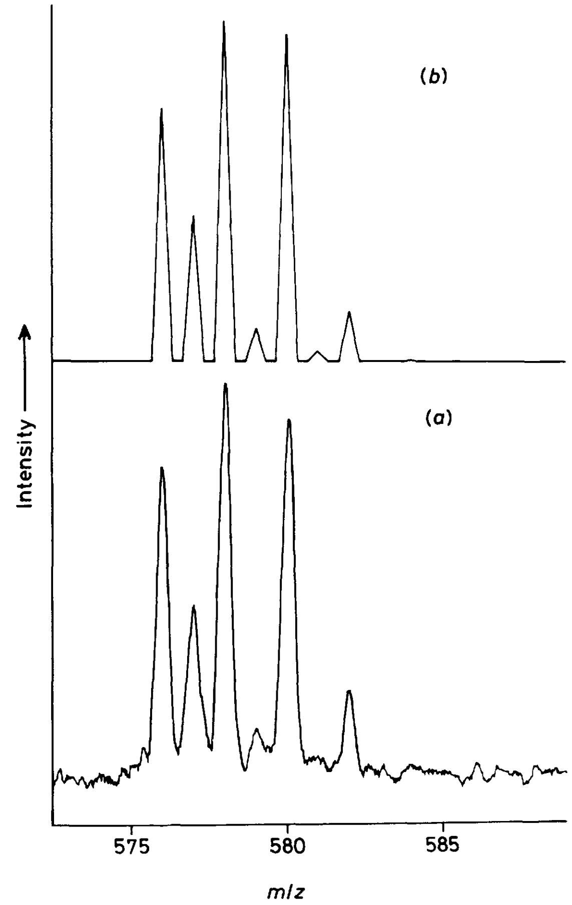

Figure 1. Mass spectrum of Cs_2WS_4 in the parent ion region: (*a*) observed, (*b*) calculated

The vapour above Cs_2WS_4 was examined using a quadrupole mass spectrometer (VG SXP600 interfaced to a Digital VT103 computer). The specially designed heated inlet source was similar to that used in the matrix-isolation studies.[12] Matrix isolation was carried out using a Displex CS202 cryostat or a

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† *Non-S.I. units employed:* eV ≈ 1.60 × 10^{-19} J, Torr = 133.322 Pa.

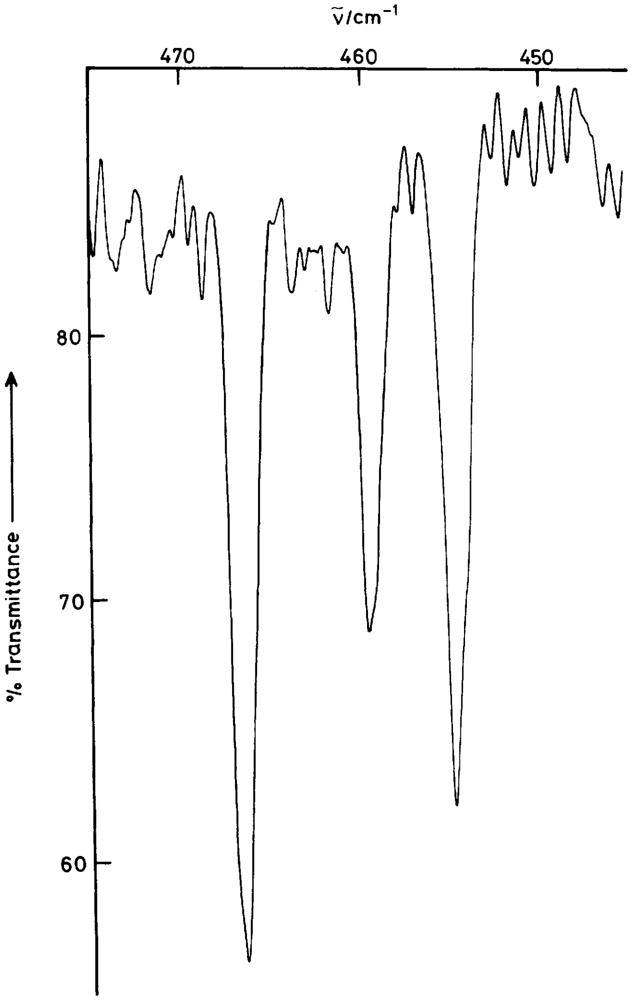


Figure 2. Matrix-isolation i.r. spectrum of Cs_2WS_4 in the 460 cm^{-1} region

modified DE204 SL cryopump, both manufactured by Air Products. The latter model was (just) capable of isolating samples in neon (*ca.* 8 K). Infrared spectra of matrix-isolated samples were obtained using a Perkin-Elmer 983 G spectrometer, at 0.9-cm^{-1} resolution. Research-grade matrix gases were obtained from BOC and used as supplied.

Results and Conclusions

When Cs_2WS_4 was heated in the sample chamber of the mass spectrometer degassing started at 300—400 °C and the following species were present: H_2O^+, H_2S^+, $CO_2{}^+$, $CS_2{}^+$, $S_{2-6}{}^+$, and $S_8{}^+$. At 680 °C Cs^+ was detected and by 850 °C $Cs_2W_4{}^+$ was the principal species observed above m/z = 350. Figure 1 shows the mass spectrum of Cs_2WS_4 obtained in these experiments compared with that calculated on the basis of isotopic abundances. The maximum value of m/z for this mass spectrometer is *ca.* 700, so that the occurrence of polymers cannot be eliminated. However the mass spectrum did not change as a function of potential in the range 10—30 eV. Further, no fragments which could be directly attributed to polymers were observed.

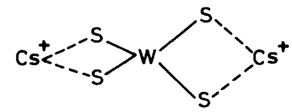
Figure 2 shows the i.r. spectrum of Cs_2WS_4 isolated in a nitrogen matrix in the region of 460 cm^{-1}. No other bands were observed in the range 1 100—200 cm^{-1} apart from some weak features of variable intensity between 800 and 900 cm^{-1}. (I.r. spectroscopy is a sensitive means of detecting tungsten oxide impurities, which have intense bands in the 800—900 cm^{-1} region.) Closely similar spectra were also obtained in argon matrices (see Table).

Table. Principal i.r. bands of Cs_2WS_4 in several matrix gases (1 100—200 cm^{-1})*

Matrix gas	Frequency (cm^{-1})		
Neon	485.9		474.5
Argon	469.2	462.4	457.9
Nitrogen	466.0	459.1	454.4

* Apart from bands due to oxide impurity, weak or variable intensity bands were found in Ar (*ca.* 473 cm^{-1}) and Ne (400—470 cm^{-1}).

Alkali-metal salts of *oxo*anions frequently show a bidentate interaction between the oxoanion and the alkali-metal ion,[5] a tridentate interaction occurring only rarely.[13] By analogy with K_2WO_4,[14] and also to minimise $M^+ \cdots M^+$ repulsions while maintaining bidentate interactions, we might expect a D_{2d} molecule of the form shown below.



For K_2WO_4 $^{16}O/^{18}O$ isotopic substitution enabled the nine observed bands to be fitted to a D_{2d} model. In the case of Cs_2WS_4 $^{32}S/^{34}S$ isotopic substitution gives a frequency spread roughly *half* that for the corresponding oxo species. Further, the separation between the upper and lower components of the triplet in Figure 2 is approximately equal to the predicted frequency shift between the all ^{32}S and all ^{34}S positions; the half-width of the bands is of the order of 1.5 cm^{-1}; ν_1 is above (but close to) ν_3 of the T_d ion so that in the $^{32}S/^{34}S$ matrix experiments components from ν_1 and ν_3 may interact if they are of the correct symmetry. In the event the individual bands in the experimental $^{32}S/^{34}S$ spectrum could not be satisfactorily resolved.

Because of the lack of detailed isotopic data it is not possible to give a rigorous discussion. The simpler, but broader * spectra in neon (a less strongly interacting matrix[15]) show splitting of the initial triply degenerate ν_3 into two bands (see Table). This implies the presence of *at least* a C_3 axis, and could be accommodated by the D_{2d} structure found for K_2WO_4. It could also be accommodated by a C_{3v} model with both tri- and uni-dentate co-ordination, although this seems less likely.

If we adopt the D_{2d} configuration for Cs_2WS_4 in neon, then the most likely distortion in nitrogen or argon is along the bidentate ••• tridentate (or edge ••• face) co-ordinate which is likely to be a very soft mode. This leads eventually to a C_{2v} facial model and formally any distortion along this mode fully resolves the degeneracy of ν_3.

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* A referee suggested to us that the broader spectra in neon imply polymerization. This could be true, but it would be unusual for the polymer bands to appear at higher frequency than monomer bands (the bands in neon are some 20 cm^{-1} higher than in argon).

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