1653	1600	*
	1607	1361
	1605	1375
	1653	1605 1607 1653 1600

Table 2. The stretching frequencies of carboxy group of dimethyltin dibenzoate (in cm<sup>-1</sup>)

\*Can not be observed by strong absorption of solvent.

formate in cyclohexane[10]. The i.r. spectra of dimethyltin dibenzoate in dimethylsulfoxide also suggests the existence of the configurations shown in Figs. 2 and 3 in basic solvents.

The results imply that the coordination of the carbonyl group in carboxylate to the tin atom is rather weak compared with that of nitrogen in oxinate or sulfur in N,N,dimethyldithiocarbamate. The fact that dimethyltin dibenzoate is very easily hydrolyzed by the water in solvents may be due to this weak co-ordination of the carbonyl groups.

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# Vanadium(IV) chloride in liquid sulphur dioxide

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IT HAS been stated that vanadium(IV) chloride is stable in liquid sulphur dioxide at room temperature but that it decomposes at 70° to give chlorine and vanadium(III) chloride[1]. We find that when vanadium(IV) chloride is sealed at room temperature in an excess of sulphur dioxide it dissolves to give a clear wine-red solution. After some time, purple crystals of vanadium(III) chloride precipitate out of solution and the supernatant liquid gradually turns yellow. The filtrate contains *only* excess SO<sub>2</sub>, unreacted VCl<sub>4</sub>, vanadium(V) oxychloride and thionyl chloride and all volatile materials were examined spectroscopically to confirm that neither chlorine nor sulphuryl chloride are liberated.

In the reaction of uranium(V) chloride with sulphur dioxide, uranium(IV) chloride and uranium(VI) oxychloride were formed. It was suggested that the first step of this reaction was the disproportionation of UCl<sub>5</sub> to UCl<sub>4</sub> and UCl<sub>6</sub> followed by the reaction of the hexachloride with the solvent to give  $UO_2Cl_2$  and  $SOCl_2[1]$ . There was no actual evidence for the formation of UCl<sub>6</sub> but the mechanism is consistent with the fact that the hexachloride can be prepared by the disproportionation of the pentachloride[2]. By contrast, vanadium(V) chloride has not been prepared and VCl<sub>4</sub> has been shown to decompose quantitatively to VCl<sub>3</sub> and Cl<sub>2</sub>[3].

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Thus it seems reasonable to assume that simple disproportionation is not an important step but that oxidation to  $V^{\nu}$  is assisted by solvation possibly as follows:

$$VCl_4 \longrightarrow VCl_3 + \frac{1}{2}Cl_2$$
$$VCl_4 + SO_2 + \frac{1}{2}Cl_2 \longrightarrow '[VOCl_5]^{2-'} + SO^{2+}$$
$$'[VOCl_5]^{2-'} + SO^{2+} \longrightarrow VOCl_3 + SOCl_2$$
$$2VCl_4 + SO_2 \longrightarrow VCl_3 + VOCl_3 + SOCl_2.$$

There is no evidence for the formation of  $VOCl_2$  as a stable intermediate and the absence of any sulphur containing compound other than  $SOCl_2$  indicates that the solvent is not taking part in any direct redox reactions. On the other hand,  $Cs_2 VOCl_5$  and  $Rb_2 VOCl_5$  may be obtained from the reaction of caesium or rubidium chloride with vanadium(V) oxychloride in sulphur dioxide [4], giving some support to the proposed mechanism.

## EXPERIMENTAL

Spectra were recorded in sealed glass tubes (5 mm o.d.) on a Cary 81 Raman spectrometer and on a Perkin-Elmer 337 spectrometer using a nujol mull between KBr discs.

### Materials

Vanadium(IV) chloride was obtained commercially in a "lecture bottle" (Anderson Chemical Co., Mich., U.S.A.). The microvalve was connected to the vacuum line with p.v.c. tubing and the system evacuated before the chloride was distilled into a trap surrounded by liquid nitrogen. A slush bath at  $-35^{\circ}$  was placed around the collection trap and the contents thoroughly de-gassed. The chlorine-free vanadium(IV) chloride was then analysed (Found: Cl, 73.55; V, 26.40 per cent. Calculated: Cl, 73.57; V, 26.43 per cent).

Sulphur dioxide (B.D.H. Poole) was distilled from the cylinder on to the vacuum line and dried by repeated distillations from phosphorus(V) oxide. The trap containing the liquid sulphur dioxide was always surrounded by an acetone/ $CO_2$  bath.

#### Analysis

Chloride was determined gravimetrically as silver chloride and vanadium volumetrically using N/10 potassium permanganate solution.

## Reaction of vanadium(IV) chloride with excess sulphur dioxide

In a typical experiment under strictly anhydrous conditions, chlorine-free vanadium(IV) chloride (approximately 0.02 mole) was distilled into a flask (100 ml capacity). Sulphur dioxide (approximately 1.2 mole) was distilled onto the chloride and the flask was sealed. On warming to room temperature, vanadium(IV) chloride dissolved to give a clear wine-red solution. Over a period of about two months a dark purple solid was formed and the supernatant liquid turned yellow. The flask was reopened onto the vacuum line and the excess of sulphur dioxide was filtered off and *all* the other volatile materials were distilled to another trap. During the course of this distillation, the solid was heated to 100° to ensure that all of the volatiles were removed.

The purple solid was then washed with *n*-pentane and pumped to dryness. Analysis confirmed that the solid was vanadium(III) chloride (Found: Cl, 67·3; V, 32·3 per cent. Calculated: Cl, 67·61; V, 32·39 per cent, approximately 0·008 mole). The i.r. spectrum in the region 400–4000 cm<sup>-1</sup> showed no bands attributable to other species and the magnetic moment at 22° of 2·69 B.M. was in good agreement with the literature value[5].

The volatile materials were partially separated by taking off fractions as the mixture was allowed to warm up. The most volatile fraction was sulphur dioxide as was confirmed by its Raman spectrum

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# Notes

which showed only the following bands: 524, 1174 and 1336 cm<sup>-1</sup> in good agreement with the literature[6]. The Raman spectrum of the second fraction showed a total of sixteen bands *all* of which were accounted for by the presence of vanadium(IV) chloride[7], vanadium(V) oxychloride[8], thionyl chloride[9] and traces of sulphur dioxide. The spectrum of the last fraction showed only the presence of the two vanadium compounds. In another experiment, the yellow liquid which contained mainly vanadium(V) oxychloride was redistilled several times before analysis (Found: Cl, 60.5; V, 28.9 per cent. Calculated for VOCl<sub>3</sub>: Cl, 61.39; V, 29.39 per cent).

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