Nitric oxide has been used previously for ortho–para conversion of hydrogen.[22]   Of the lowest states of NO the $^2\Pi_{3/2}$ state is 345 cal. above the $^2\Pi_{1/2}$ ground state.  The upper state is paramagnetic, whereas the lower state is not.  Therefore, at room temperature a high percentage of the NO is paramagnetic while at liquid neon temperatures it is not only frozen out, but over 99% of the NO will be in the lower diamagnetic state.

The observed half lifetime for paratritium of 17 min. for a partial pressure of 100 mm. of NO was within 10% in agreement with the prediction of Wigner's formula[12]; thus, this result adds support to the validity of this equation for gas phase conversion, where the interacting distance is assumed unchanged.

## Conclusions

In the preceding paper[7] we have shown that it is possible to convert normal tritium to paratritium on charcoal in the temperature region of liquid neon and liquid helium.  Hydrogen and tritium have the spin $^1/_2$ and follow therefore the same statistics.  In addition they have almost the same nuclear magnetic moment.  It is therefore of major interest to compare the kinetic data of the ortho–para conversion of these two hydrogen species.  From the results obtained, we have been able to show that: (1) On a coconut charcoal under the same conditions the ortho–para transformation of tritium was 27 times faster than that of hydrogen.  (2) In the solid phase the ortho–paratritium conversion has a half lifetime of 17 min. which corresponds to a rate 210 times as fast as the rate of conversion of hydrogen.  (3) Concerning the occurrence of conversion reactions by ions the following conclusions could be drawn: (a) During the conversion experiments in the gas phase the heat conductivity cell remained always cooled with liquid neon; therefore the tritium gas was extremely pure.  It seems that under these conditions the ortho–para conversion occurs over an ion mechanism with practically zero heat of activation. (b) Metal surfaces enhanced the ion recombination process and thereby decreased the rate of conversion. (c) The application of an electric field to part of the cooled experimental arrangement removed some of the ions and decreased the rate of conversion.  (d) In the adsorbed phase on semiconducting charcoal, ions do not seem to play a role in the catalysis.

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# The Infrared Spectra of Some Alkyl-Substituted Pentavalent Antimony Compounds

BY G. GILBERT LONG, G. O. DOAK, AND LEON D. FREEDMAN

A number of antimony compounds of the type $R_3SbX_2$, where R is methyl or ethyl and X is a halogen, $NO_3$, OH, or $0.5SO_4$ have been prepared.  Attempts to prepare compounds of the type $R_3SbXOH$ have failed, and the existence of such compounds is doubtful.  However, compounds of the type $[R_3SbX]_2O$ are readily prepared.  The infrared spectra of these compounds have been determined.  The spectra of the dihalides are consistent with the trigonal bipyramid structure, suggested by other workers.  Trimethylantimony dinitrate contains the $Me_3Sb^{++}$ ion.  In trimethyl- and triethylantimony sulfates the sulfate groups are covalently bonded, but the exact structure is uncertain.  Oxybis-[trimethylantimony] diperchlorate and dichloride are clearly ionic and contain the $[(Me_3Sb)_2O]^{++}$ ion.

The structure of trialkyl- and triarylantimony dihalides has been established by the work of several investigators.  Wells, on the basis of X-ray diffraction studies, demonstrated that trimethylantimony dihalides exist as trigonal bipyramids with the methyl groups in the plane of the antimony atom and the halogens at the apices.[1]  The antimony–halogen distance is somewhat longer than expected for covalent bonds; this finding led Wells to suggest that the halogen–antimony bonds might be intermediate in character between covalent and ionic bonds.  Jensen obtained zero dipole moment values for triphenylantimony dichloride and dihydroxide and assigned the trigonal bipyramid structure to these compounds.[2]  This structure was recently confirmed for triphenylantimony dichloride by means of X-ray diffraction studies.[3]  It has also been demonstrated that triphenyl- and tribenzylantimony dichlorides do not conduct an electric current in acetonitrile solution.[4]  It has thus been quite clearly established that both triaryl- and trialkylantimony dihalides contain a pentacovalent antimony atom.

In addition to the dihalides, a number of similar antimony compounds have been reported.  These include such compounds as trialkyl- and triarylantimony sulfates, dinitrates, hydroxychlorides, hydroxynitrates, etc.  It is by no means clear that all or any of such compounds contain a pentacovalent antimony atom.  In fact a trialkyl- or triarylantimony sulfate with a trigonal bipyramid structure, in which a sulfato group is bonded to any two corner positions of the bipyramid, would involve a highly strained structure.  For this reason we have prepared a series of trialkylantimony compounds and examined their infrared spectra in the hope of elucidating the structure of such compounds.  The compounds prepared, together with the analytical results, are given in Table I.  The results of the spectral studies are reported later in this paper.

In addition to the structural problem discussed above, we have also attempted to clear up several rather puzzling findings reported in the literature dealing with the trialkylantimony dihalides.  Hantzsch and Hibbert were the first to demonstrate that compounds of the type $R_3MBr_2$ (where R is an alkyl group and M is P, As, or Sb) are extensively hydrolyzed in aqueous solution.[5]  This work was subsequently extended by Nylen, who made a detailed study of the hydrolysis of trialkylar-

(1) A. F. Wells, Z. Krist., **99**, 367 (1938).

(2) K. A. Jensen, Z. anorg. allgem. Chem., **250**, 268 (1943).

(3) T. N. Polynova and M. A. Porai-Koshits, J. Struct. Chem. (U.S.S.R.) (Engl. Transl.), **1**, 146 (1960).

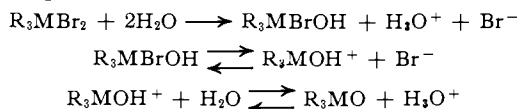(4) L. Kolditz, M. Gitter, and E. Rösel, Z. anorg. allgem. Chem., **316**, 270 (1962).

(5) A. Hantzsch and H. Hibbert, Ber., **40**, 1508 (1907).

Table I

The Antimony Compounds Prepared together with the
Analytical Results

| R$_3$SbX$_2$ R = Me, X = | Sb analyses, % Calcd. | Found |
|---|---|---|
| F$^a$ | | |
| Cl | 51.21 | 51.39 |
| Br | 37.27 | 37.21 |
| I | 28.95 | 29.31 |
| NO$_3$ | 41.86 | 42.19 |
| 0.5SO$_4$ | 46.31 | 46.83 |
| OH | 60.61 | 60.49 |
| 0.5O | 66.73 | 66.46 |
| R = Et, X = | | |
| 0.5SO$_4$ | 46.31 | 46.83 |
| [R$_3$SbX]$_2$O R = Me, X = | | |
| Cl | 57.90 | 57.33 |
| ClO$_4$ | 43.38 | 43.59 |

$^a$ Antimony analyses were unsatisfactory for this compound, possible due to loss of volatile SbF$_3$ during digestion. *Anal.* Calcd. for C$_3$H$_9$F$_2$Sb: C, 17.59; H, 4.43; F, 18.55. Found: C, 17.88; H, 4.40; F, 18.90.

senic and trialkylantimony dibromides.[6] Nylen concluded that these compounds are hydrolyzed according to the equations

$$R_3MBr_2 + 2H_2O \longrightarrow R_3MBrOH + H_3O^+ + Br^-$$

$$R_3MBrOH \rightleftharpoons R_3MOH^+ + Br^-$$

$$R_3MOH^+ + H_2O \rightleftharpoons R_3MO + H_3O^+$$

There can be no doubt that the trialkylantimony dihalides are extensively hydrolyzed in aqueous solution, and we have demonstrated that trimethylantimony dihalides can be converted to the corresponding dihydroxides by passing an aqueous solution of the dihalide through a column containing an anionic exchange resin (see Experimental). Nevertheless, contrary to Nylen's formulations, all of the hydrolysis equations must be reversible, since trialkylantimony dihalides can be recovered essentially quantitatively by recrystallization from water.

Morgan and Yarsley report that the addition of concentrated hydrochloric acid to an aqueous solution of trimethylantimony dihydroxide results in the precipitation of trimethylantimony hydroxychloride, Me$_3$SbClOH.[7] This result is difficult to explain since trimethylantimony dichloride (where the antimony–chloride ratio is 1:2) can be recrystallized from water. Accordingly, we have repeated some of the experimental work of Morgan and Yarsley and found that only trimethylantimony dichloride is obtained from trimethylantimony dihydroxide and concentrated hydrochloric acid. The dichloride is also the sole product when the dihydroxide is dissolved in 2 equivalents of 1 N hydrochloric acid and the solution evaporated to incipient crystallization.

We have also reinvestigated the work of Landholt[8] and of Hantzsch and Hibbert,[5] who obtained oxybis-[trimethylantimony]dihalides, (Me$_3$SbX)$_2$O, from the reaction between equimolar quantities of trimethyl antimony dihalide and trimethylantimony dihydroxide. From trimethylantimony dihydroxide and trimethylantimony dichloride we have indeed obtained a compound which, after recrystallization from alcohol, gave analytical values consistent with the formula (Me$_3$SbCl)$_2$O. The compound showed no hydroxyl band in the infrared. Its infrared spectrum was quite similar

to that of trimethylantimony dichloride but contained an additional band at 775 cm.$^{-1}$ which we have assigned to antimony–oxygen (see Results and Discussion).

Since an aqueous solution of trimethylantimony dichloride is almost completely hydrolyzed to Me$_3$Sb-(OH)$_2$, it is necessary to explain why, in the presence of added Me$_3$Sb(OH)$_2$, we obtain the oxide rather than the dichloride. The formation of a trimethylantimony dihalide can be summarized by the equation

$$Me_3Sb(OH)_2 + 2X^- + 2H_3O^+ \rightleftharpoons Me_3SbX_2 + 4H_2O$$
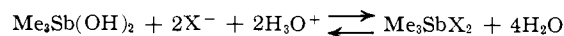
The formation of [Me$_3$SbX]$_2$O is similarly shown by the equation

$$Me_3Sb(OH)_2 + X^- + H_3O^+ \rightleftharpoons Me_3SbXOH + 2H_2O$$

$$\downarrow$$

$$1/2[Me_3SbX]_2O + 1/2H_2O$$
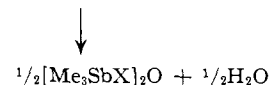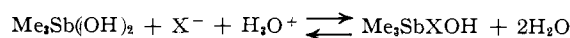
Obviously if Me$_3$SbX$_2$ and (Me$_3$SbX)$_2$O have about the same solubilities, the dihalide will separate from solution when the concentrations of halide and hydronium ion are large compared to the concentration of Me$_3$Sb(OH)$_2$. On the other hand, the anhydride will separate from solution if the concentrations of halide and hydronium ions are smaller.

Morgan and Yarsley also reported that the hydrolysis of trimethylantimony cyanobromide gives trimethylantimony hydroxybromide, which could be recrystallized from alcohol as lustrous needles. We have hydrolyzed trimethylantimony cyanobromide by the procedure of Morgan and Yarsley and obtained a compound which crystallized from alcohol in needles. This compound, however, contained no hydroxyl band in the infrared, and both analytical values and infrared spectra were in agreement with those found for trimethylantimony dibromide.

In view of our findings we doubt that alkyl compounds of the type R$_3$SbXOH have ever been prepared. It is interesting to note that Kolditz, Gitter, and Rösel[4] were unable to obtain triphenylantimony hydroxychloride by the procedure of Morgan, Micklethwait, and Whitby,[9] but rather obtained the anhydride [(C$_6$H$_5$)$_3$SbCl]$_2$O. Hartmann and Kühl have recently reported that tricyclohexylantimony dichloride yields tricyclohexylantimony hydroxychloride on hydrolysis.[10] They do not report an infrared spectrum and rely only on analysis for assigning the hydroxychloride structure to this compound. Actually there is an error in their calculations, and their analytical results are much closer to the theoretical values for the oxide [(C$_6$H$_{11}$)$_3$SbCl]$_2$O.

### Results and Discussion

**Trimethylantimony Dihalides and Trimethyl-$d_3$-antimony Dibromide.**—With the exception of the fluoride, the infrared spectrum of each of these compounds between 4000 and 300 cm.$^{-1}$ shows only one strong absorption band and one band of moderate intensity. However, closer inspection reveals a number of weak and very weak bands. Listed in Table II are all of the observed bands for trimethylantimony dibromide and for its deuterated analog. In addition to these bands, the fluoride shows complex bands in the 1120–1050, 730, and 540–450 cm.$^{-1}$ regions; the chloride shows a strong band at 277 cm.$^{-1}$; the bromides and iodide show increased absorption at 250 cm.$^{-1}$ which is probably indicative of an absorption band with a peak below 250 cm.$^{-1}$.

(6) P. Nylen, *Z. anorg. allgem. Chem.*, **246**, 227 (1941).

(7) G. T. Morgan and V. E. Yarsley, *Proc. Roy. Soc.* (London), **A110**, 534 (1926).

(8) H. Landholt, *J. prakt. Chem.*, **84**, 328 (1861).

(9) G. T. Morgan, F. M. G. Micklethwait, and G. S. Whitby, *J. Chem. Soc.*, **97**, 34 (1910).

(10) H. Hartmann and G. Kühl, *Z. anorg. allgem. Chem.*, **312**, 186 (1961).

TABLE II

INFRARED ABSORPTION BANDS OF TRIMETHYLANTIMONY DIHALIDES AND TRIMETHYL-$d_3$-ANTIMONY DIBROMIDE

| $(CH_3)_3SbX_2^a$ | $(CH_3)_3SbBr_2$ | $(CD_3)_3SbBr_2$ | Ratio, $\dfrac{\text{cm.}^{-1} \text{ of } (CH_3)_3SbBr_2 \text{ band}}{\text{cm.}^{-1} \text{ of } (CD_3)_3SbBr_2 \text{ band}}$ | Assignment |
|---|---|---|---|---|
| 3020–3010 w | 3012 w | 2253 w | 1.34 | C–H asym. stretch |
| 2928–2920 w | 2927 w | 2112 vw | 1.38 | C–H sym. stretch |
| | 2410 vw | | | |
| | 1772 vw | | | |
| | 1723 vw | | | |
| | 1403 vw | 1408 vw | | |
| 1403–1387 s | 1387 w | 1021 w | 1.36 | C–H asym. bend |
| | 1332 vw | | | |
| | 1210 vw | 935 vw | 1.29 | C–H sym. bend (?) |
| 870–860 m | 870 s | 660 s | 1.32 | C–H rock |
| 587–554 m | 564 m | 547 m | 1.03 | C–Sb asym. stretch |

$^a$ X = F, Cl, Br, or I; s = strong, m = medium, w = weak, vw = very weak.

The carbon–hydrogen frequencies may be picked out unambiguously by comparison of the spectrum of $(CD_3)_3SbBr_2$ with that of $(CH_3)_3SbBr_2$. Considering the mass effect only, the carbon–hydrogen frequencies should be shifted upon deuteration to lower frequencies by a factor $1/\sqrt{2}$ or $1/1.41$. The actual shift is a little less than this, but four of the observed bands must be assigned to carbon–hydrogen. The band at 587 cm.$^{-1}$ in $(CH_3)_3SbBr_2$ is very little affected upon deuteration and therefore must be due to carbon–antimony stretching. These assignments are listed in Table II. Since only one carbon–antimony stretching frequency is observed, the antimony atom and the carbon atom must be arranged in the highly symmetric $D_{3h}$ point group in which the symmetric stretching frequency would be infrared inactive. Any other point group for the three carbon atoms and the antimony atom would give rise to both a symmetric and an asymmetric stretch. The 277 cm.$^{-1}$ band in trimethylantimony dichloride may be assigned to antimony–chlorine. Antimony–bromine and antimony–iodine bands would have to occur below 250 cm.$^{-1}$.

**Trimethylantimony Dinitrate, Trimethylantimony Sulfate, and Triethylantimony Sulfate.**—These compounds show C–H and C–Sb frequencies very similar to those found in the dihalides although the asymmetric C–H stretching frequency is high in both methyl compounds (3040 for the nitrate and 3030 for the sulfate). In addition, frequencies characteristic of the nitrate or sulfate group are observed. Determination of the symmetry of these anionic groups should tell something of the nature of their bonding to the antimony atom. A nitrate ion has $D_{3h}$ symmetry; a sulfate ion has $T_d$ symmetry. Covalent bonding in either case lowers the symmetry and thereby gives rise to additional infrared active frequencies.

The ionic nitrate, point group $D_{3h}$, gives rise to three infrared active absorption bands, $\nu_3$ (1380–1350 cm.$^{-1}$), $\nu_2$ (830 cm.$^{-1}$), and $\nu_4$ (about 730 cm.$^{-1}$).[11] Partial covalent bonding results in splitting of $\nu_3$ into two components, one of lower frequency and one of higher frequency. This difference, $\Delta$ in cm.$^{-1}$, has been suggested as a measure of the covalent character of the nitrate group.[12] As symmetry is further lowered to that of a covalent nitrate (point group $C_{2v}$), additional bands appear near 1030 and 830 cm.$^{-1}$. Frequencies of absorption bands arising from the nitrate group in trimethylantimony dinitrate are listed in Table III along with possible assignments. The splitting of $\nu_3$, along with the appearance of a very weak band at 1050 cm.$^{-1}$ and the appearance of a weak band at 834 cm.$^{-1}$, indicates essentially $D_{3h}$ symmetry with some distortion

toward $C_{2v}$ for the nitrate group. The bonding between the nitrate and the antimony atom in $(CH_3)_3Sb(NO_3)_2$ is very similar to that found in anhydrous calcium nitrate or anhydrous barium nitrate.[11]

TABLE III

INFRARED ABSORPTION FREQUENCIES OF THE NITRATE GROUP IN TRIMETHYLANTIMONY DINITRATE AND TENTATIVE ASSIGNMENTS

| Frequency, cm.$^{-1}$ | Assignment point group $D_{3h}{}^a$ | Frequency, cm.$^{-1}$ | Assignment point group $D_{3h}{}^a$ |
|---|---|---|---|
| 2758 | $2\nu_3$ | 1516 s ⎫ 1457 s ⎬ | $\nu_3$ |
| 2424 w ⎫ 2410 w ⎬ | $\nu_1 + \nu_3$ | 1050 vw | $\nu_1$ |
| 1763 w | $\nu_1 + \nu_4$ | 834 s | $\nu_2$ |
| | | 728 w | $\nu_4$ |

$^a$ Designations are those of G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1945, p. 178.

The sulfate group may exist as the free ion ($T_d$ symmetry), as a monodentate group ($C_{3v}$ symmetry), or as a bidentate group ($C_{2v}$ symmetry). Characteristic frequencies have been reported for sulfate in each of these environments (Table IV).[13]

TABLE IV

INFRARED FREQUENCIES OF THE SULFATE GROUP[13]

| Symmetry | $\nu_1$ | $\nu_2$ | $\nu_3$ | $\nu_4$ | $\nu_5$ |
|---|---|---|---|---|---|
| $T_d$ | | | 1104 vs | 613 s | |
| $C_{3v}$ | 1038 s | 970 m | 645 s | 1130 s | 604 s |
| $C_{2v}$ | 1055 s | 995 m | 641 s | 462 m | |

| Symmetry | $\nu_6$ | $\nu_7$ | $\nu_8$ | $\nu_9$ |
|---|---|---|---|---|
| $T_d$ | | | | |
| $C_{3v}$ | 438 m | | | |
| $C_{2v}$ | 1105 s | 610 s | 1170 s | 571 s |

The spectra of trimethyl- and triethylantimony sulfates have been difficult to interpret. When the spectra of these compounds are determined in Nujol mulls, a number of bands are observed, which indicates that the symmetry of the sulfate is lower than $T_d$. In addition, the observed bands do not correspond well with those given for sulfates with $C_{3v}$ or $C_{2v}$ symmetry; there definitely is no strong absorption in the 1060–30 cm.$^{-1}$ region. Additional difficulties occur when the spectra are determined in KBr pellets. Pronounced changes occur rapidly when a pellet containing trimethylantimony sulfate is exposed to the atmosphere. Initially, the spectrum is essentially the same as that in the Nujol mull, but after several minutes a number of bands disappear, appear, or are shifted. Figure 1 shows these

(11) J. R. Ferraro, J. Mol. Spectry., 4, 99 (1960).
(12) J. R. Ferraro, J. Inorg. Nucl. Chem., 10, 319 (1959).
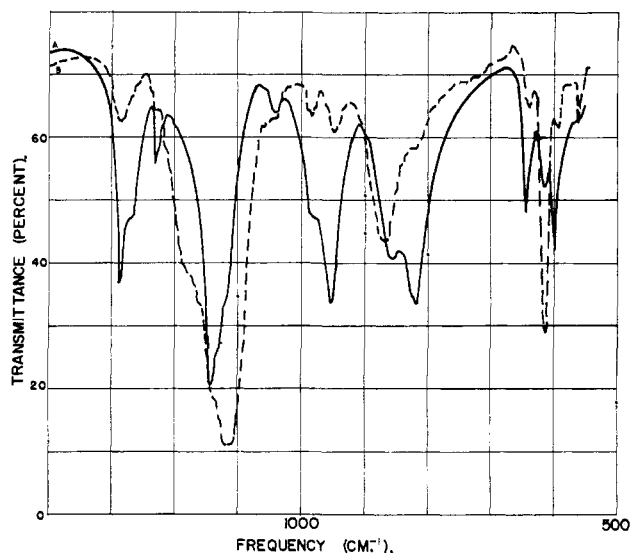(13) K. Nakamoto, J. Fujita, S. Tanaka, and M. Kobayashi, J. Am. Chem. Soc., 79, 4904 (1957).

Fig. 1.—Curve A (————), initial spectrum of 0.25% (CH₃)₃-SbSO₄ in KBr pellet; curve B (----------), spectrum of pellet A after 45-min. exposure to air at 40% relative humidity.

changes in the sulfate bands, the methyl rock at 870–860 cm.⁻¹, and in spectrum B, the carbon–antimony frequency at 562 cm.⁻¹. The initial spectrum, spectrum A, shows weak bands that are due to ionic sulfate, but the spectrum is predominantly that of a less symmetrical sulfate group. In the case of triethylantimony sulfate in a KBr pellet, the spectrum is always consistent with that of an ionic sulfate. These changes are probably due to exchange of sulfate for bromide in both of these compounds. Spectrum A shows weak bands that are due to ionic sulfate, but the spectrum is predominantly that of a less symmetrical sulfate group.

**Sb–O–Sb Group.**—Spectra were observed for oxybis-[trimethylantimony] diperchlorate and oxybis-[trimethylantimony] dichloride. The carbon–hydrogen and the carbon–antimony frequencies that appear in trimethylantimony dichloride also are found essentially at the same frequencies in these compounds. In addition, both of these compounds show a very strong band at 775 and a weak band at 528 cm.⁻¹. The former band must be associated with antimony–oxygen. The latter band may also be associated with antimony–oxygen or may represent distortion of the plane containing the carbon and antimony atoms so that the symmetric carbon–antimony stretching frequency now becomes infrared active. The oxybis-[trimethylantimony] dichloride shows an increase in absorption near 250 cm.⁻¹, but no antimony–chlorine band appears above this point as was the case with trimethylantimony dichloride. The perchlorate shows characteristic frequencies of this group which include a very strong absorption, partially resolved into three or four bands between 1150 and 1040 cm.⁻¹. This is ν₃ for T_d symmetry. The only other infrared active frequency, ν₄, is also split into peaks at 636 and 627 cm.⁻¹. These frequencies correspond to a slightly distorted perchlorate ion.[14,15]

**Carbon–Antimony Frequencies.**—With the exception of (CH₃)₃SbF₂ and (CH₃)₃SbSO₄ an absorption was observed near 570 cm.⁻¹ which may be ascribed to the carbon–antimony asymmetric stretch. Partial masking of this region occurs with the two compounds noted as exceptions, but the frequency can probably be picked out in the case of the trimethylantimony di-

fluoride. Table V lists this band for each of the compounds.

## Conclusions

The infrared spectra of the trialkylantimony dihalides are consistent with the trigonal bipyramid structure first suggested by Wells. Thus no bands were found which could be assigned to a carbon–antimony symmetric stretching vibration. Further, in trimethylantimony dichloride a band occurs at 277 cm.⁻¹ which is undoubtedly due to an antimony–chlorine stretch. By contrast, the spectrum of trimethylantimony dinitrate clearly suggests an ionic structure containing the doubly charged trimethylantimony ion. The spectra of trimethyl- and triethylantimony sulfates indicate covalent bonding of the sulfate group, but the exact structure of these compounds cannot be determined unequivocally on the basis of infrared spectra.

The spectra of oxybis-[trimethylantimony] diperchlorate and dichloride are remarkably similar; both compounds apparently contain the ion [(Me₃Sb)₂O]⁺⁺

**TABLE V**

CARBON–ANTIMONY ASYMMETRIC STRETCHING FREQUENCY

| Formula of compound | Frequency, cm.⁻¹ | Formula of compound | Frequency, cm.⁻¹ |
|---|---|---|---|
| (CH₃)₃Sb[a] | 591 | (C₂H₅)₃SbSO₄[c] | ∼585 |
| (CH₃)₃SbF₂[b] | 586 | [(CH₃)₃SbCl]₂O | 584 |
| (CH₃)₃SbCl₂ | 577 | [(CH₃)₃SbClO₄]₂O | 575 |
| (CH₃)₃SbBr₂ | 571 | (CH₃)₃SbSO₄[d] | 564 |
| (CH₃)₃SbI₂ | 554 | (CH₃)₃Sb(NO₃)₂ | 564 |
| (CH₃)₃Sb(OH)₂ | 566 | (CD₃)₃SbBr₂ | 523 |
| (C₂H₅)₃SbBr₂ | 534 | | |

[a] Not observed below 550 cm.⁻¹. [b] Partially masked. [c] Occurs as a shoulder. [d] Sample exposed to air; band may be masked by sulfate frequency in freshly prepared pellet.

## Experimental

**Determination of Spectra.**—Infrared spectra between 4000 and 550 cm.⁻¹ were made on a Perkin–Elmer 421 infrared spectrometer. Spectra below 550 cm.⁻¹ were made by using either the Perkin–Elmer MIR 421 interchange or MIR gratings.

The spectrum of trimethylstibine was determined over the 4000–550 cm.⁻¹ region in carbon tetrachloride solution and in carbon disulfide solution. Spectra in this region for all other compounds were determined on KBr pellets (1 mg. of sample/400 mg. of KBr). Spectra below 500 cm.⁻¹ are for the respective compounds mulled in Nujol. Spectra of the nitrates and perchlorates were also determined as Nujol mulls between 0.001-in. polyethylene films.[16] These spectra were very similar to those determined from KBr pellets, differing only in broadness of the peaks. Hence, the frequencies reported are for spectra determined from KBr pellets.

The spectra of trimethyl- and triethylantimony sulfates were also determined in Nujol mulls. As mentioned in the previous section, these spectra differed markedly from those done in KBr pellets.

**Preparation of Compounds.**—Triethylantimony dichloride, dibromide and diiodide have been reported a number of times since their original preparation by Landholt in 1861.[8] We followed essentially the procedure of Morgan and Davies in which trimethylstibine was prepared from freshly distilled antimony-(III) chloride and the methyl Grignard reagent.[17] The trimethylstibine and ether were codistilled in a nitrogen atmosphere and the distillate treated with a carbon tetrachloride solution of the halogen to precipitate the desired dihalide. The dihalides were then recrystallized from water. The yields of pure products varied from 60 to 85%.

**Trimethyl-d₃-antimony dibromide** was made by the same procedure using 15 g. of CD₃I.[18] The resulting trimethyl-d₃-antimony dibromide was recrystallized from deuterium oxide. The yield was 2.3 g., 20%. The compound showed no bands in the infrared assignable to C–H bonds.

**Trimethylantimony Difluoride.**—To a solution of 10.21 g. of trimethylantimony dibromide in 200 ml. of hot water, an aqueous solution of silver fluoride (Aceto Chemical Co., 50% silver

(14) B. J. Hathaway and A. E. Underhill, *J. Chem. Soc.*, 3091 (1961).
(15) S. D. Ross, *Spectrochim. Acta*, **18**, 225 (1962).

(16) F. Vratny, *Appl. Spectry.*, **13**, 59 (1959).
(17) G. T. Morgan and G. R. Davies, *Proc. Roy. Soc.* (London) **A110**, 523 (1926).
(18) F. A. Cotton, J. H. Fassnacht, W. D. Horrocks, and N. A. Nelson, *J. Chem. Soc.*, 4138 (1959).

fluoride solution) containing 7.93 g. of AgF was added. After removal of the silver bromide the filtrate was evaporated to dryness and the product recrystallized from alcohol. The yield was 2.62 g., 42%.

**Trimethylantimony dinitrate and trimethylantimony sulfate** were prepared from trimethylantimony dibromide and silver nitrate or silver sulfate in aqueous solution by the same procedure as used for the difluoride.

**Trimethylantimony Dihydroxide.**—Although this compound has been prepared from moist silver oxide and trimethylantimony dihalides, solutions of trimethylantimony dihydroxide dissolve considerable amounts of silver ion, and it is difficult to prepare pure trimethylantimony dihydroxide by this procedure. We have found that when a hot aqueous solution of trimethylantimony dichloride (9.5 g. in 1 l. of water) was passed through a column of Amberlite IR4B and the resulting aqueous solution evaporated to dryness by means of a Rinco evaporator, trimethylantimony dihydroxide was obtained as a sirup which crystallized on scratching with a stirring rod. The compound was readily recrystallized from acetone; the yield was 85%. Trimethylantimony dihydroxide on heating *in vacuo* at 110° loses 1 mole of water to give the hygroscopic trimethylantimony oxide.

**Oxybis-[trimethylantimony] Diperchlorate.**—A solution of 3.26 g. of trimethylantimony dibromide in 165 ml. of hot water was mixed with a solution of 4.14 g. of silver perchlorate in 30 ml. of water. After removal of the silver bromide the filtrate was diluted to 200 ml. in a volumetric flask. Aliquots of this solution (20 ml.) were evaporated in desiccators over calcium chloride. After several days, white crystals and a sirupy liquid (probably perchloric acid) were obtained. In several cases explosions occurred during the final stages of the evaporation procedure, and preparation on a larger scale is extremely hazardous. The white crystals were very carefully removed by means of a rubber policeman, dried on a porous plate, washed with anhydrous ether, and dried over calcium chloride *in vacuo*. The resulting crystals proved to be quite insensitive to mechanical shock and decomposed on heating without exploding. Analysis of the compound corresponded to the formula $(Me_3SbClO_4)_2O$. The same analysis was obtained when the crystals were air dried; *i.e.*, there was no evidence that $Me_3Sb(OH)ClO_4$ separated from solution. We also performed the experiment with solutions of trimethylantimony dibromide and silver perchlorate in absolute alcohol. Again we obtained only $(Me_3SbClO_4)_2O$, and again there were several cases in which explosions occurred during the evaporation procedure.

**Oxybis-[trimethylantimony] dichloride** was prepared by mixing aqueous solutions of trimethylantimony dichloride (1.1883 g.) and trimethylantimony dihydroxide (1.0037 g.) and evaporating the resulting solution to a small volume. The white crystals which separated from solution were recrystallized from alcohol. The yield was 1.55 g., 71%.

**Triethylantimony dibromide** was originally reported by Löwig and Schweizer, who reported that the compound could not be distilled.[19] More recently Hartmann and Kühl reported that triethylantimony dibromide can be purified by distillation; b.p. 107° (90 mm.).[10] They do not report analyses on the distilled compound. We have been unable to distil triethylantimony dibromide even at 0.2 mm. without decomposition. Accordingly, we purified the dibromide (m.p. −10°) by recrystallization from alcohol at low temperatures and filtration through a cold funnel. We were unable, however, to obtain an analytically pure sample; the compound always contained slightly more than the theoretical antimony.

**Triethylantimony sulfate** was prepared from the dibromide and silver sulfate in 70% alcohol. It was recrystallized from alcohol; the yield was 45%.

**Trimethylstibine** was prepared from trimethylantimony dibromide and granulated zinc by the method of Morgan and Yarsley.[7] For the purpose of obtaining infrared spectra, the stibine was distilled into ampoules containing the necessary solvent ($CS_2$ or $CCl_4$) and the ampoules sealed at the conclusion of the distillation. The ampoules were opened and appropriate dilutions made in a drybox in a nitrogen atmosphere.

**The Reaction between Trimethylantimony Dihydroxide and Hydrochloric Acid.**—Trimethylantimony dihydroxide (1.6 g.) was dissolved in 10 ml. of water and 10 ml. of concentrated hydrochloric acid added. The dense white precipitate was removed by filtration, dried, and recrystallized from alcohol. The compound gave analytical values and an infrared spectrum identical with trimethylantimony dichloride. The recovery was 80%.

**The Hydrolysis of Trimethylantimony Cyanobromide.**—Trimethylstibine, prepared by reduction of the dibromide with zinc dust in a nitrogen atmosphere, was distilled into a solution of cyanogen bromide in petroleum ether. The precipitate was removed by filtration and dissolved in warm water. The clear solution was evaporated to a small volume, and the crystals that resulted were recrystallized twice from alcohol. The analysis and infrared spectrum of these were identical with the analysis and spectrum of trimethylantimony dibromide.

(19) C. Löwig and E. Schweizer, *Ann.*, **75**, 315 (1850).

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[Contribution from the Evans and McPherson Chemical Laboratories, The Ohio State University, Columbus 10, Ohio]

# Reactions of Coordinated Ligands. VI. Metal Ion Control in the Synthesis of Planar Nickel(II) Complexes of α-Diketo-bis-mercaptoimines

By Major C. Thompson and Daryle H. Busch

A series of nickel(II) complexes has been synthesized with the tetradentate Schiff base ligands formed between α-diketones and β-mercaptoethylamine. Although the formation of the α-diimine is strongly discriminated against under ordinary conditions, the reaction of the ligand components in the presence of nickel(II) ion results in high yields of the desired complexes. The α-diketones used were: biacetyl, 1,2-cyclohexanedione, 2,3-octanedione, 2,3-pentanedione, and 1-phenyl-1,2-propanedione. The planar complexes have been characterized by elemental analysis and through the determination of molecular weights, infrared spectra, solubilities, and magnetic moments. Two classes of template reaction have been defined.

## Introduction

Several investigators have worked with bidentate and tridentate ligands containing the amine group and the mercaptide group and found that these ligands form very stable chelate compounds.[1–7] It has been shown that mercaptoamines will produce diamagnetic square-planar structures with nickel(II).

In addition to intrinsic donor ability, it is to be anticipated that the stereochemical relationship of the ligand to the metal ion[5] will be of principal significance in determining the stability and nature of the metal complexes. The only tetradentate ligand containing nitrogen and mercapto donors, $N(CH_2CH_2SH)_3$, which has previously been prepared,[7] is incapable of occupying all four donor positions in a square-planar coordination sphere. Most of the remaining investigations involving tetradentate ligands, both planar and nonplanar, have concerned molecules containing nitrogen and oxygen as the relatively weak donors.

This study is concerned with a class of ligands specifically designed to provide square-planar, tetradentate coordination through nitrogen and mercapto donors.

(1) K. A. Jensen, *Z. anorg. allgem. Chem.*, **229**, 265 (1936).

(2) R. V. G. Ewens and C. S. Gibson, *J. Chem. Soc.*, 431 (1949).

(3) R. G. Charles and H. Freiser, *J. Am. Chem. Soc.*, **74**, 1385 (1952).

(4) S. E. Livingstone, *J. Chem. Soc.*, 1042 (1956).

(5) D. C. Jicha and D. H. Busch, *Inorg. Chem.*, **1**, 872, 878, 884 (1962).

(6) C. A. Root, Thesis, The Ohio State University, 1962.

(7) J. Harley-Mason, *J. Chem. Soc.*, 320 (1947).