

by ferriyanide reduction activity of the chloroplasts. The inhibition of the phenyl urea compound was always greater than other nonphenyl urea compounds.

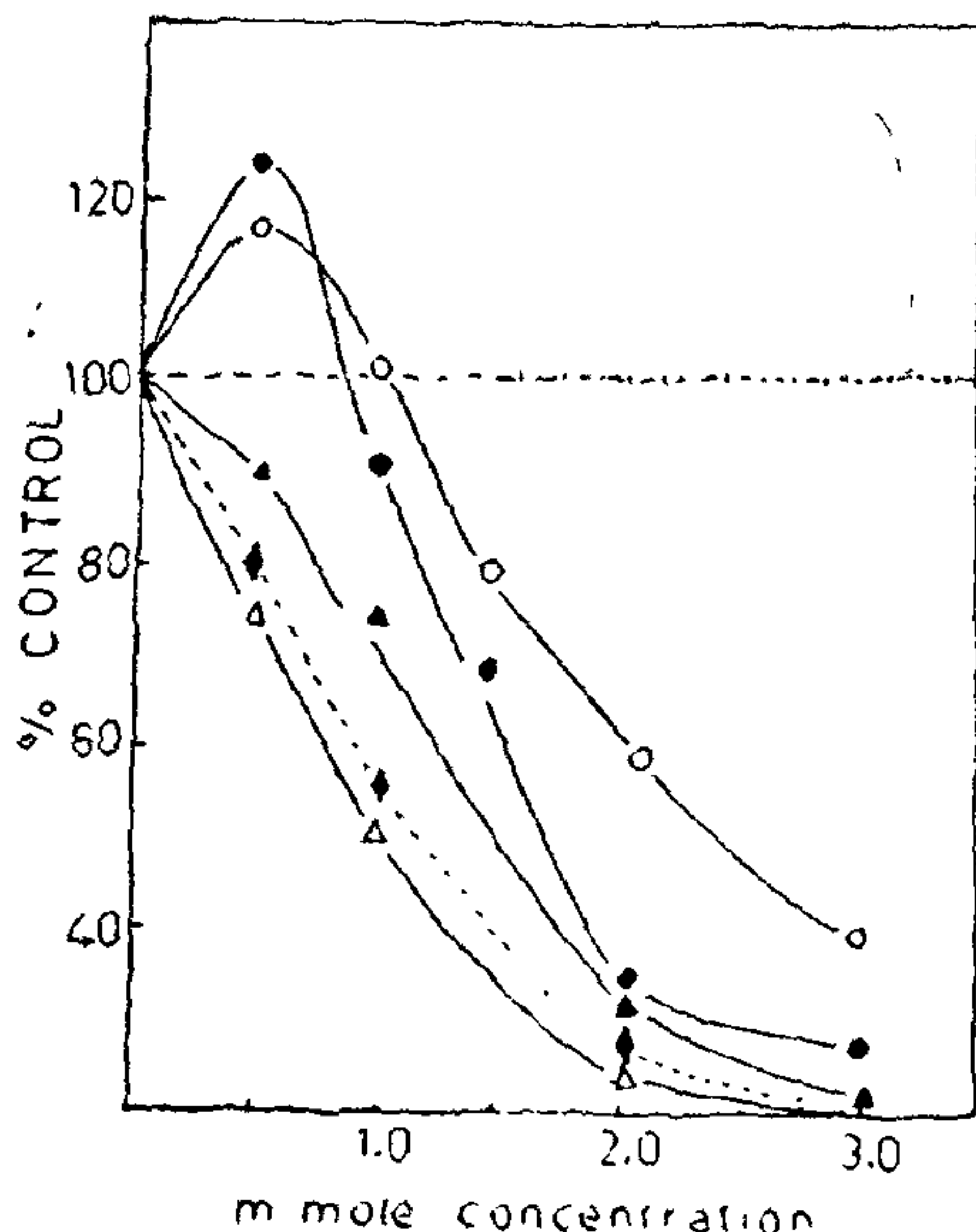


FIG. 3. Effect of growth regulators and herbicides on Hill reaction.

The various growth regulators and herbicides were used at concentrations indicated in the reaction mixture and incubated for 5 min prior to illumination.

- IAA
- 2,4-D
- △—△ DCMU
- ▲—▲ Amitrol
- ◆—◆ Simizine

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VIBRATIONAL SPECTRA OF BROMOANTIMONATES (III)

IN continuation of our work on bromoantimonate^S (III)¹⁻³ we report here the results of Raman and far i.r. spectral studies on these compounds.

The preparation of these compounds has been described earlier¹. The Raman and far i.r. data were recorded on solid samples at the Chemistry Department, University of Leicester, U.K. The spectral data are shown in Table I.

Hexabromoantimonates (III): The hexabromoantimonate (III) ion has a non-bonded pair of electrons in addition to the six bonded pairs. The interest in this ion and its analogues has been due to the nature of the non-bonded pair and attempts have been made to ascertain whether the lone pair of electrons is stereochemically active or not. A few X-ray studies have shown that these ions have nearly undistorted octahedral shapes^{4,5} consequent to the stereochemical inactivity of the non-bonded pair. Hooper and James⁶ have interpreted the spectra of $(Et_2NH_2)_3SbBr_6$ in terms of the presence of undistorted octahedral $SbBr_6^{3-}$.

The vibration spectral data obtained for tris (*n*-dipropylammonium) hexabromoantimonate (III) are comparable to those obtained for tris (diethylammonium) hexabromoantimonate (III) by Hooper and James⁶. The band at 251 cm^{-1} (i.r.) may be assigned to the cation mode as this value is higher than that expected for Sb-Br vibration. Following Hooper and James⁶ the Raman bands at 181 and 151 cm^{-1} may be assigned to ν_1 and ν_2 modes and the i.r. band at 116 cm^{-1} to ν_4 mode. The bands at 165 , 150 , 140 and 125 cm^{-1} may arise due to the overlapping of symmetric and asymmetric stretches.

The spectra of tris (*n*-butylammonium) hexabromoantimonate (III) are markedly different from those of the dipropylammonium salt but they are similar to those of bis (piperidinium) pentabromoantimonate (III) (Table I). From this similarity, it appears that the butylammonium salt may, in fact, be a double salt, $(n-C_4H_9NH_3)_2SbBr_5 \cdot (n-C_4H_9NH_3Br)$. The situation

TABLE I

Spectral data (cm^{-1}) for bromoantimonates (III)

Tris (<i>n</i> -dipropylammonium) hexabromoantimonate (III)	Raman 181 w, 165 w, 151 w, 129 m, 100 wm, 94 w, 65 mw, 56 m. IR 251 m, 160 m, 140 w, 116 w, 70 m, 52 w.
Tris (<i>n</i> -butylammonium) hexabromoantimonate (III)	Raman 206 s, 187 s, 169 wm/sh, 105 vw, 69 w. IR 180 s, 108 m, 73 w, 58 w.
*Bis (piperidinium) pentabromoantimonate (III)	Raman 210 vs, 185 m, sh. IR 200 sh, 175 vs, 126 m, 104 s, 60 w.
Anilinium tetrabromoantimonate (III)	Raman 240 vs, 206 s, 164 w, 146 wm, 126 wm, 96 wm sh, 89 wm, 44 wm. IR 256 sh, 242 s, 202 m, 180 m, 146 m, 117 m, 90 w, 72 m.
Quinolinium tetrabromoantimonate (III)	Raman 203 wm, 193 w, 176 m, 170 m, 152 m, 126 m, 114 wm, 86 wm.
Tris (tri- <i>n</i> -propylammonium) nonabromodiantimonate (III)	Raman 212 s, 193 m, sh, 182 s, 107 w, 81 wm. IR 192 vs, 180 s, 140 w, 106 s, 72 w, 62 w.
Tris (methylammonium) nonabromodiantimonate (III)	Raman 220 m, 185 wm, 33 wm. IR 175 ms, 140 ms, 105 wm, 72 w, 50 w.

* Ref. 6.

is analogous to that in the case of $(n\text{-C}_4\text{H}_9\text{NH}_3)_3\text{SbCl}_6$ which has been formulated as $(n\text{-C}_4\text{H}_9\text{NH}_3)_2\text{SbCl}_5$. $(n\text{-C}_4\text{H}_9\text{NH}_3\text{Cl})$ on the basis of spectral studies by Walton *et al.*⁷. A similar double salt formulation is indicated for $(\text{C}_6\text{H}_5\text{NH}_3)_3\text{SbCl}_6$ by a partial crystallographic work⁸.

Tetrabromoantimonate (III): A simple consideration of the lone-pair bond-pair interaction shows that for ions like SbBr_4^- , C_{2v} symmetry (where the lone pair is in equatorial position) is the most probable⁹. Ahliah and Goldstein¹⁰ found a good similarity between the solid state and the solution spectra of $(n\text{-C}_4\text{H}_9\text{NH}_3)\text{SbBr}_4$ and they concluded that SbBr_4^- has C_{2v} symmetry in both the phases. Hooper and James⁶, on the other hand, found a good deal of difference between the solid state and solution spectra of (*α*-picolinium) SbBr_4 and also of (*α*-picolinium) SbI_4 . They concluded that in solution SbBr_4^- ions, with C_{2v} symmetry, exist but in solid state a bridged structure is present.

The spectra of (anilinium)—and (quinolinium) SbBr_4 (Table I) are comparable to those of (*α*-picolinium) SbBr_4 reported by Hooper and James⁶. The bands at 240 (Raman) and 256 and 242 cm^{-1} (i.r.) of $(\text{C}_6\text{H}_5\text{NH}_3)\text{SbBr}_4$ may be assigned to the anilinium cation as these positions are higher than those expected for Sb-Br vibrations. The main difference between the spectra of (anilinium) and (quinolinium) SbBr_4 on the one hand (Table I) and (*α*-picolinium) SbBr_4 ⁶ on the other is that the highest energy band is around 205 cm^{-1} in the former but around 220 cm^{-1} in the latter. This difference may be due to the difference in cations but it could also be due to the structural difference *e.g.*, difference in the mode of bridging.

Nonabromodiantimonates (III): Little spectral work has been reported on the complexes of the type $\text{A}_3\text{M}_2\text{X}_9$ of group Vb elements. Hooper¹¹ has reported a study of $(\text{C}_6\text{H}_5\text{NH})_3\text{Bi}_3\text{Cl}_9$ in which bismuth is assumed to be octahedrally coordinated by three terminal and three bridging chlorine atoms. There is no report in literature on the spectra of $(\text{Sb}_2\text{Br}_9)^{3-}$.

The bands at 212, 193, 182 cm^{-1} (Raman) and 192 and 180 cm^{-1} (i.r.) for tris (tri-*n*-propylammonium) nonabromodiantimonate (III) and at 220 and 185 cm^{-1} (i.r.) for tris (methylammonium) nonabromodiantimonate (III) (Table I) may be assigned to the stretching modes of the terminal Sb-Br bonds. The band at 140 cm^{-1} (i.r.) in both the complexes can be assigned to the bridging bromines. Rest of the bands may be due to lattice modes and bending modes of (Br-Sb-Br).

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SPECTRAL STUDIES OF TRICHLOROACETATES OF LANTHANONS

THE halogen substituted acetates of *d*-transition elements have been extensively studied¹⁻². However, there has been only a very limited effort made in the study of halogen substituted acetates of lanthanons³⁻⁴. Trichloroacetates of lanthanons have been synthesized by Tilley *et al.*⁵ but no data have been reported on their spectral studies. The electronic and infrared spectra of these compounds are reported in this note.

Experimental

Trihydrated trichloroacetates were prepared by the method of Tilley *et al.*⁵. Electronic spectra were measured on Carl-Zeiss VSU-2 Spectrophotometer in water. IR spectra of the KBr pellets were run on Perkin-Elmer 621 Spectrophotometer. Magnetic properties of the compounds were measured by Gouy method at 295 K. The molar susceptibilities were corrected for the diamagnetism of the constituent atoms by means of Pascal's constant⁶.

Results and Discussion

COO⁻ stretching frequencies in acetates have been found to be sensitive to both coordination to a metal and substitution in the acetate group⁶⁻⁷. Comparing the values of ν_a COO⁻ in sodium trichloroacetate⁸, Cu(II) trichloroacetate² and lanthanon trichloroacetates we have observed that the value of ν_a COO⁻ changes considerably. Comparing the values of ν_a COO⁻ in sodium trichloroacetate and lanthanon analogue, there is sufficient change but its magnitude is less than that observed for copper analogue

indicating thereby that the lanthanon trichloroacetates form the bridge between highly ionic sodium trichloroacetate and covalent Cu(II) trichloroacetate. In lanthanon trichloroacetate themselves, the value of ν_a COO⁻ gradually increases which is in conformity of lanthanide contraction. In the lanthanon trichloroacetates the ν_a COO⁻ a strong band occurring at 1650–1655 cm⁻¹ shows a decrease while ν_s COO⁻ shows an increase as compared to sodium analogue, which can be interpreted in terms of bidentate structure for these trichloroacetates as suggested by Warriar *et al.*⁶⁻⁷ for Cu(II) trichloroacetates. Trichloroacetic acid and its anion show only high carbon halogen stretching frequencies⁸. Contrary to this the values for lanthanon trichloroacetates we find that the high carbon halogen frequencies are quite intense while lower are quite weak. This indicates that lanthanon trichloroacetates are most probably the mixtures of two conformations trans and gauche form on the same line suggested by Spinner⁸. Absorption between 500–400 cm⁻¹ in the spectra of lanthanon trichloroacetates probably arises from carbon halogen bending vibrations. Only two C–Cl₃ deformations are observed in Cu(II) trichloroacetate² while in lanthanon trichloroacetates four C–Cl₃ deformations are observed and the higher frequency bands are identified with asymmetric while those at lower frequencies are attributed to symmetric deformations.

TABLE I

Nephelauxetic ratio (β), covalency parameter (δ) and magnetic susceptibility data for trichloroacetates of lanthanons

Compound	β	δ (%)	Molar susceptibility $\chi_m^{\text{corr}} \times 10^6$ C.G.S. units	Magnetic moment μ_{eff} in B.M
Pr TCA	0.99447	+0.5560	5452	3.59
Nd TCA	1.00500	-0.4975	5288	3.54
Sm TCA	1.01165	-1.1516	1595	1.94

It has been shown by Karvaker⁹ that the band shape for hypersensitive transition can be correlated with the coordination number and ligand geometry on the lanthanide ion. The shape of the hypersensitive transition of Nd(III) trichloroacetate ($^4I_{9/2} \rightarrow ^4G_{5/2}, ^2G_{7/2}$) in water is quite identical with the bands of non-coordinated Nd (BrO₃)₃.9H₂O in water as well as in solid⁹ indicating thereby that these compounds are most likely non-coordinated.