

(Acid)/(Cu⁺⁺) \simeq 400 and E_b is the extinction at the stoichiometric molar ratio of the complex. (iv) The extinction vs. λ for various 1:1 complexes are given in Fig. 1. (v) Log of formation constants (log K) for various 1:1 complexes are 2.0 (ligand formate, 28° C., $\mu = 0.5$); 2.3 (propionate, 30° C., $\mu = 0.1$); 2.55 (lactate, 31.5° C., $\mu = 0.1$); 2.05 (β -hydroxy propionate, 30° C., $\mu = 0.1$); 2.44 (isobutyrate, 30° C., $\mu = 0.1$); 5.00 (itaconate, 30° C., $\mu = 0.1$).

A detailed paper with experimental results and discussion will appear elsewhere.

Dept. of Physical Chemistry, V. P. DEVENDRAN.
University of Madras, M. SANTAPPA.
Madras-25, October 19, 1964.

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HOPPER GROWTH IN BISMUTH

AMELINCKX¹ has suggested a dislocation mechanism for the growth of hopper crystal faces and has observed them on salol and thymol. Hurle² has observed facets on decanting bismuth which are the {100} planes, frequently with a diagonal twin plane. Wagner and Brown³ have observed {111} facet planes also and have explained the morphology of the twinned crystals. We have been studying the effect of various parameters such as growth rate, temperature gradient and impurity concentration on the growth of bismuth single crystals and we thought of studying the facets of crystals obtained by decanting also. Bismuth of 99.9% purity was heated and brought to the molten state. This molten mass was allowed to cool for ninety seconds and then the contents of the crucible were suddenly decanted. Hopper type crystal faces were observed on the substrate sticking to the crucible. Figure 1 shows a hopper crystal face obtained in this way. This hopper crystal face is the {100} face and must have developed due to the large supercooling by the sudden decantation of the metal from the crucible and segregation of impurities at these points.

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FIG. 1

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Physics Department, B. S. SHAH.
M.S. University of Baroda,
Baroda, January 20, 1964.

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TRIPHENYL PHOSPHINE, CARBONYL, BROMO COMPLEXES OF RHODIUM

COMPOUNDS of the type $L_2 Rh(CO)Cl$ (L is a ligand of the type Ph_3P or Ph_3As) have been prepared by boiling rhodium trichloride with excess of the tertiary phosphine or arsine in high boiling alcoholic solvents like methoxy and ethoxy ethanol.^{1,2} Employing this elegant method two bromo complexes have been prepared for the first time using methoxy ethanol as the solvent.

Crystals of hydrated rhodium bromide were prepared by dissolving freshly precipitated rhodium hydroxide in warm hydrobromic acid (1:1) and evaporating the solution under vacuum. 0.75 gram of $RhBr_3 \cdot xH_2O$ was added to 130 ml. of methoxy ethanol containing 4 ml. of water and 4.5 grams of triphenyl phosphine. The contents were refluxed for two hours when yellow crystals appeared to separate. On cooling the solution to room temperature 1.2 gram of the crystals were isolated from the mother liquor. The compound was analysed by standard methods for both bromine³ and phosphorus.⁴ On the basis of analytical results the formula $[(C_6H_5)_3P]_2 Rh(CO)Br$ could be assigned to the compound [$C_{37}H_{30}OBrP_2Rh$ requires Br = 10.86, P = 8.43; found, Br = 10.43, P = 8.34%].

The infra-red spectrum of the compound taken in nujol shows a carbonyl peak at 1980 cm.^{-1} . The crystals were found to be soluble in chloroform and nitrobenzene but were insoluble in water and alcohol. The substance is a non-electrolyte in nitrobenzene.

The tribromo compound $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{Rh}(\text{CO})\text{Br}_3$ was prepared by treating the monobromo complex (0.24 gram) with the calculated quantity of bromine in chloroform at 0°C . The orange crystals (0.27 gram) could be isolated after evaporation under vacuum. Analysis of bromine and phosphorus gave a value of 26.41 and 6.73% respectively. Calculated values for the same in the tribromo complex require 26.78 and 6.92% respectively. The compound was soluble in chloroform and nitrobenzene and was a non-electrolyte in the latter.

The tribromo complex shows a carbonyl peak in the infra-red at 2110 cm.^{-1} . The occurrence of C=O stretch in the infra-red at 1980 cm.^{-1} for the Rh(I) compound as compared to 2110 cm.^{-1} for the Rh(III) compound is similar to the observation made in the case of the corresponding chloro compounds.⁵ This suggests that the metal carbon bond in the Rh(I) complex is stronger than the one in the Rh(III) complex.

It is of interest to mention that earlier attempts to prepare such bromo complexes starting from $\text{L}_2\text{Rh}(\text{CO})\text{Cl}$ were not successful.⁶

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Department of Chemistry, G. K. N. REDDY.
Central College, E. G. LEELAMANI.
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THE ELECTRON SPIN RESONANCE SPECTRUM OF GAMMA IRRADIATED SODIUM TETRATHIONATE

The authors have reported on the e.s.r. spectra of gamma irradiated thiosulphates.¹ It was

found to be of interest to record the electron resonance spectrum of sodium tetrathionate during a study of the effect of Co^{60} -gamma radiation on alkali tetrathionates.²

Sodium tetrathionate dihydrate, $\text{Na}_2\text{S}_4\text{O}_6 \cdot 2\text{H}_2\text{O}$, was prepared by mixing c.p. grade sodium thiosulphate and iodine by the method given in Abegg's *Handbuch der Anorganischen Chemie*.³ The salt was purified by repeated precipitation from aqueous solution with 95% ethanol. The purity and composition of the final sample was carefully checked by (i) obtaining its infra-red spectrum,⁴ (ii) analyzing for tetrathionate content by the method of Goehring *et al.*,⁵ (iii) dehydration and (iv) conversion to sodium sulphate on heating to 600°C .

The irradiation source employed was a commercial unit "Gamma Cell 220 Co^{60} Irradiation Unit" manufactured by the Atomic Energy of Canada Ltd. The exposure dose was around 10^5 roentgens per hour. A Fricke dosimeter was used for measuring the dose absorbed by the samples.

A Varian Associates V-4500 E.P.R. Spectrometer was used for obtaining the e.s.r. spectrum of the irradiated samples. The unit is an X-band spectrometer with a nominal operating frequency of 9500 Mc./S. The experimental details are given elsewhere.¹ Electron spin concentrations were measured by graphical double integrations of the recorded spectra and comparison, through a substandard of gamma irradiated barium dichloroacetate, with solutions of D.P.P.H. in benzene.

The e.s.r. spectrum for the irradiated salt is shown in Fig. 1. The vertical line indicates the

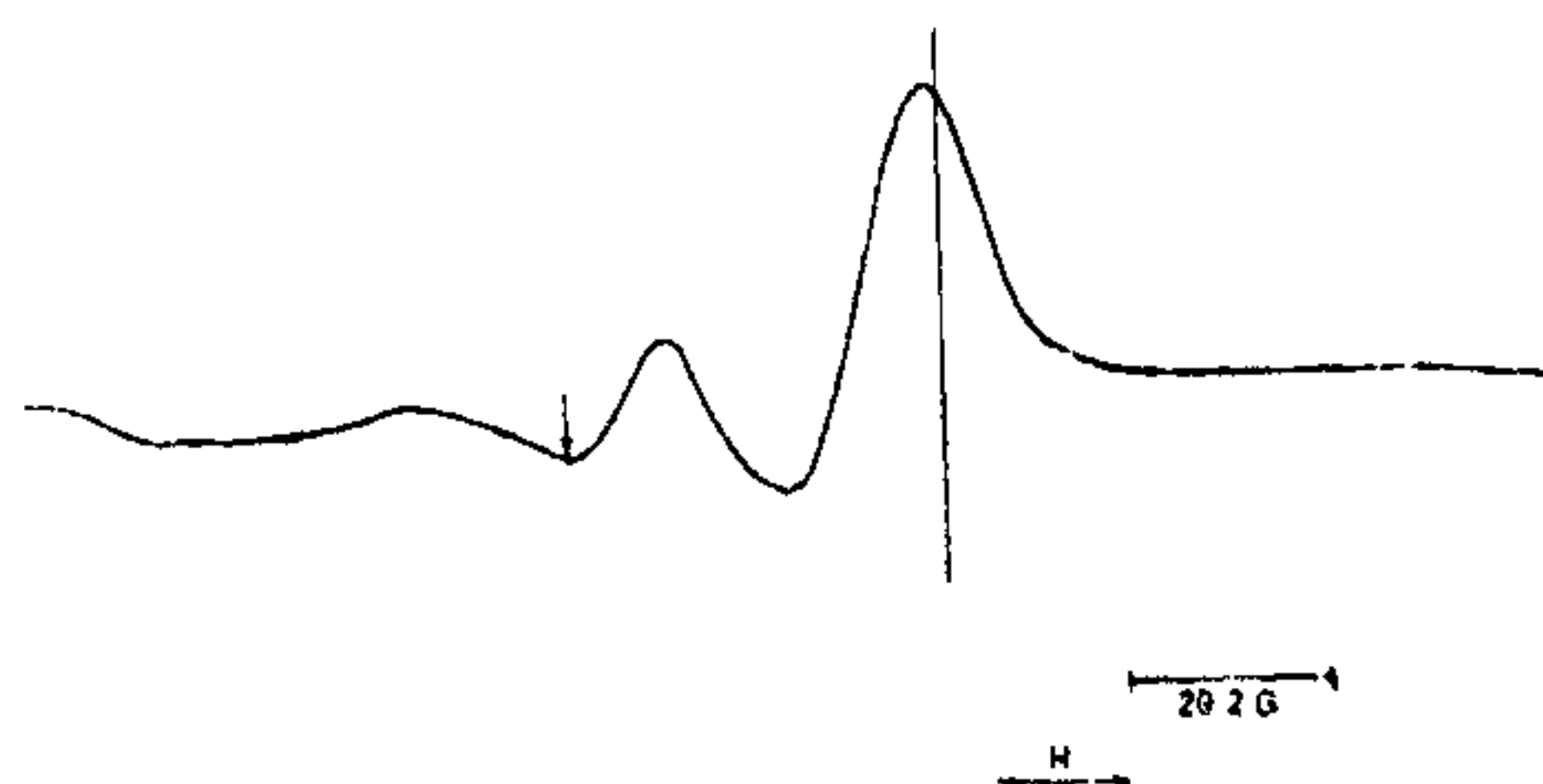


FIG. 1. Electron spin resonance spectrum of gamma-irradiated $\text{Na}_2\text{S}_4\text{O}_6 \cdot 2\text{H}_2\text{O}$ at room temperature. The vertical line indicates the position of the D.P.P.H. spectrum. The vertical arrow is at a g value of 2.024.

position of the D.P.P.H. spectrum. The magnetic field increases from left to right. The spectrum consists of a single absorption line with a low field structure and measures about 90 gauss. No hyperfine splitting was observed. The g value for the main cross-over point is 2.009. The