

any effect upon absorbance values. High absorbances are mainly due to the liberation of iodine which by virtue of being bonded to the iodide ions to give polyiodide ions, usually I_3^- , form ion-pair with the reagent in the form of a brown precipitate soluble in 1,2-dichloroethane. The extract has considerable absorption at 490 nm. If no reducing agent is used in the determination, the upper limit of acidity of the aqueous layer is restricted to 0.25N only.

Concentration of the potassium iodide solution has to be maintained in between 1% and 3% in case sodium hypophosphite is not used. Allowance upto a concentration of 20% could be provided by employing 1 ml. of a 20% solution of the hypophosphite. The use of a 20% solution of sodium hypophosphite was preferred to avoid interference due to a number of oxidizing ions.

The effect of varying reagent concentrations on extraction of bismuth was studied. A 0.24% solution of benzyldimethylphenylammonium chloride was preferred, since concentrations below 0.15% gave low values of absorbance, while increased reagent concentration produced no significant effect.

The effect of foreign ions was studied by adding different amounts of foreign ions to 50 μ g of bismuth (III) and determining the bismuth following the recommended procedure. It was found that Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Ag^+ , Au^{3+} , Zn^{2+} , Cd^{2+} , Hg^{2+} , Cr^{3+} , Mn^{2+} , Mn^{7+} , V^{5+} , As^{3+} , Sb^{3+} , Mo^{5+} , W^{6+} , Pb^{2+} , F^- , Cl^- , Br^- , $S_4O_8^{2-}$, SO_3^{2-} , NO_3^- , CNS^- , $S_2O_3^{2-}$, ClO_4^- , $C_2O_4^{2-}$, citrate, tartrate and acetate ions even in amounts five times that of bismuth did not interfere, and a good recovery of bismuth (within 4% error in microgram level) was achieved. Equal amounts of Pt^{4+} , Pd^{2+} and Cr^{6+} , however, interfered. Interference due to Cr^{6+} (upto a five fold excess) could be avoided by making the aqueous layer more acidic (eg., 2N).

The method thus proved to be simple and rapid, and yet provided a good recovery of bismuth in trace concentrations in presence of most of the common ions. When compared with the existing standard spectrophotometric method for the determination of bismuth using potassium iodide alone, the present method is found to be far more superior in selectivity and accuracy. The present method will be very helpful in estimating bismuth in trace concentrations from ores and minerals when interfering ions, viz Pt^{4+} and Pd^{2+} are absent.

The authors express their sincere thanks to Professor N. N. Siddhanta for having accorded permission to work in the Chemistry Department of

Gauhati University, and Dr N. K. Baishya for his help in carrying out this work.

8 February 1983; Revised 31 May 1983

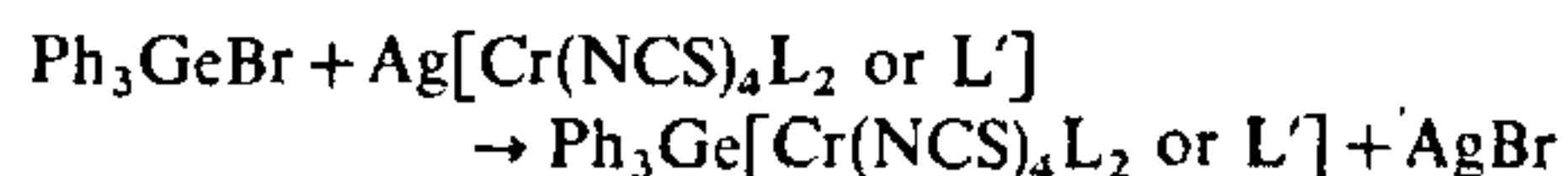
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SOME TRIPHENYLGERMANIUM DERIVATIVES OF MIXED LIGAND THIOCYANATOCHROMATE (III)

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IN continuation of our studies^{1,2} on $(R_3M)_3 [Cr(NCS)_6]$ or $R_3M[Cr(NCS)_4L_2]$ type of compounds, some triphenylgermanium derivatives have been prepared and characterized. Triphenylgermanium bromide and $Ag [Cr(NCS)_4L_2]$ or $Ag [Cr(NCS)_4L']$ were prepared by reported method¹⁻³. Triphenylgermanium complexes were prepared according to the following reaction -



L = aniline, urea, dimethylformamide, ammonia or pyridine.

L' = 1, 10-phenanthroline or ethylenediamine.

In a typical reaction, triphenylgermanium bromide (5 mmol) in acetone (25 ml) was refluxed for 4 hr on a water bath with an acetonic suspension of the silver complex (6 mmol) in 25 ml. The precipitated silver bromide was rejected and the excess solvent was distilled off from the filtrate under reduced pressure. The treatment of the residual viscous mass with diethyl ether followed by petroleum ether (40-60°C) yielded a coloured pure crystalline complex. The product was washed with petroleum ether (40-60°C) and dried in vacuum. No further purification was needed.

Table 1 Analytical and infrared data for $Ph_3Ge [Cr(NCS)_4 2L \text{ or } L]$

L/L'	Colour	m.p. (°C)	Analyses Found/(calculated)			%SCN	Molar conductance ($cm^2 \text{ ohm}^{-1} \text{ mol}^{-1}$)	Infrared absorption (cm^{-1})		
			%C	%H	%Cr			ν_{CN}	ν_{CS}	δ_{NCS}
Aniline	grey	137	3.71 (3.75)	10.78 (10.85)	5.87 (6.71)	29.25 (30.00)	96.15	2062s	820w	458m
Ammonia	light pink	160	3.36 (3.38)	13.50 (13.50)	7.65 (8.36)	36.87 (37.34)	102.04	2072s	835w	456m
Pyridine	pink	167	3.29 (3.35)	11.06 (11.26)	6.28 (6.97)	30.28 (31.09)	89.28	2063s	823w	470m
Urea	green	93	3.30 (3.35)	11.78 (11.86)	6.86 (7.34)	31.69 (32.76)	104.16	2070s	840vw	460m
DMF	green	116	3.87 (3.95)	11.40 (11.44)	6.39 (7.09)	30.97 (31.64)	113.30	2068s	826w	476m
phen.	brick red	165	2.90 (2.99)	10.82 (10.94)	6.02 (6.77)	29.72 (30.20)	112.50	2073s	840br	465m
en.	pink	148	3.41 (3.55)	12.89 (12.96)	7.30 (8.02)	34.88 (35.80)	106.38	2065sh 2058sh 2072s 2068sh 2056s	830w	470m

s = strong, m = medium, br = broad, sh = shoulder, w = weak, vw = Very weak

Table 2 Electronic spectral and magnetic data of compounds of the formula $Ph_3Ge [Cr(NCS)_4L_2$ or $L']$

L/L'	${}^4A_{2g} \rightarrow {}^4T_{2g}$ (ν_2) (nm)	${}^4A_{2g} \rightarrow {}^4T_{1g}(F)$ (ν_1) (nm)	10 Dq (cm^{-1})	B (cm^{-1})	β	L.F.S.E. (k Cal/mol)	μ eff. (at 300 K°) B.M.
Aniline	575	404	17391	751	0.82	56.61	3.68
Ammonia	578	402	17301	784	0.86	59.30	3.51
Pyridine	572	398	17483	790	0.86	59.93	3.59
Urea	570	390	17544	859	0.94	60.14	3.62
DMF	565	392	17699	811	0.88	60.66	3.65
Phen.	565	390	17699	831	0.91	60.66	3.73
En.	575	402	17391	769	0.84	59.61	3.83

Analyses and physical measurements were done as reported earlier^{1,2}. The relevant experimental data are presented in tables 1 and 2.

The compounds reported are coloured crystalline solids, thermally stable and unaffected by atmospheric oxygen and moisture. They are soluble in common organic solvents such as methanol, ethanol, acetone and solvent ether. Conductance measurements indicate 1:1 electrolytic behaviour in solution. The magnetic moments lie between 3.51 to 3.83 B.M. at 300 K° indicating the presence of three unpaired electrons. In a few complexes the magnetic moment values are slightly lower than those expected for three unpaired electrons and this is attributed to orbital contributions. The electronic spectra of the complexes give rise to two broad bands in the region 17699–17301 cm^{-1} and 25641–25126 cm^{-1} assigned as ${}^4T_{2g} \leftarrow {}^4A_{2g}$ and ${}^4T_{1g}(F) \leftarrow {}^4A_{2g}$ respectively. 10 Dq (ligand field splitting parameter) values were calculated from the first spin allowed band (ν_1) following the procedure of Orgel⁴. The values of Racah parameter "B" and nephelauxetic ration (β) support the ionic character of the compounds. The calculated values of 10 Dq, "B", LFSE and β for the complexes agree with the data for octahedral chromium (III) complexes^{5,6}. The absence of splitted ${}^4T_{2g} \leftarrow {}^4A_{2g}$ transition band in all the complexes is in agreement with the proposed octahedral geometry of the complexes⁷.

The infrared spectral data show all absorptions characteristic of the organo group. Thus ν_{C-H} , δ_{C-H} and ν_{C-C} are observed at their usual positions. Similarly CH in plane C-H out of plane and ring deformation modes also occur at the expected position⁸⁻¹⁰. In the infrared spectra the characteristic absorption attributed to $\nu_{C=N}$, $\nu_{C=S}$ and δ_{NCS} mode of vibration (table 1) lie in the ranges 2040–2100 cm^{-1} , 780–860 cm^{-1} and 450–490 cm^{-1} respectively characteristic of isothiocyanate bonding¹¹⁻¹³. In the spectra of all the

complexes containing unidentate ligand (L), the $\nu_{C=N}$ mode of vibration shows single band (except pyridine) while in the complexes of bidentate ligands (L') splitting occurs giving rise to two or three absorptions indicating *trans* and *cis* octahedral arrangement respectively¹⁴. A comparison of the spectra of the free donor bases with those of the corresponding complexes indicates a distinct shift in the characteristic absorption frequencies of the functional groups suggesting the presence of co-ordinated bases. The data are omitted for the sake of brevity.

The authors thank the Director, Central Drug Research Institute, Lucknow for facilities for spectroscopic measurements and Organisch Chemisch Institute, Holland, for a gift of tetraphenylgermanium. Financial assistance from CSIR (New Delhi) is also acknowledged.

28 June 1983; Revised 7 November 1983

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THE EFFECT OF DITHIOTHREITOL ON THE GROWTH HABIT OF COPPER ELECTRODEPOSITS ON COPPER (111) PLANE

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AN investigation of the anisotropy with respect to morphology and electrode kinetics of copper electrodeposit on the (111) plane of copper deposited from highly purified solution of acidified copper sulphate containing very small concentrations of dithiothreitol (DTE) was made for the first time. Pyramids observed on (111) plane of copper when deposited changed to layers, ridges and polycrystalline type of growth as the concentration of DTE was increased.

Studies of a number of organic sulphur compounds as addition agents in copper plating have been reported in literature¹. However the role of individual groups in the performance of an addition agent has been only meagerly studied. Such studies of addition agents are important in understanding the basic growth mechanism on a molecular level in plating baths.

Recently it was reported that the brightening effect of mercaptoethanol was due to the presence of -SH group in the molecule². In order to study the group effect systematically, investigation with DTE was undertaken since it contains two -SH groups

$$\begin{array}{cccc} \text{CH}_2 & -\text{CH} & -\text{CH} & -\text{CH}_2 \\ | & | & | & | \\ \text{SH} & \text{OH} & \text{OH} & \text{SH} \end{array}$$

In the present work the effect of dithiothreitol on the growth habit modification of copper electrodeposited on (111) plane of a copper single crystal from an acid copper sulphate bath was studied. The (111) face of the copper cathode was mechanically polished on an emery paper finishing with 4/0 and then electropolished in 1:1 H₃PO₄. The depositions were carried out at

2.5, 7.5, 10 and 12.5 mA/cm² to a thickness of 3.6 μ on the plane from a (0.25 M CuSO₄ + 0.1 M H₂SO₄) bath with a known amount of freshly prepared DTE. The overpotentials (η) were measured with respect to a freshly prepared copper electrode acting as a reference electrode. The deposit was examined under a metallogical microscope. The other experimental details have been described earlier⁴.

In pure solution at 2 mA/cm², characteristic triangular pyramids and at 5, 7.5, 10 and 12.5 mA/cm² hexagonal block type of growth were observed as noticed by earlier workers^{5,6} (figure 1). The triangular type of growth transformed into small layers in the presence of 10⁻¹⁶ M/l of DTE and the layers changed to ridges at 5 × 10⁻¹⁶ M/l of DTE, (figure 2). When the concentration of DTE was increased to 10⁻¹⁵ M/l, the deposit became polycrystalline in nature (figure 3). At higher current densities 5, 7.5, 10 and 12.5 mA/cm² the hexagonal block type of structure observed in pure solution changed to circular layers, dragged pyramids and then to polycrystalline deposit with increasing concentration of DTE in the bath. However the critical concentration of DTE for the above transitions depended upon the current density of deposition. Interestingly the presence of DTE in the electrolyte reduced the overpotential value at all current densities. The η - log i relationship was linear in pure solution with a slope of 120 ± 10 mv. In solutions with DTE η - log i relation was linear up to 10⁻¹⁵ M/l of DTE, but deviated at concentrations > 10⁻¹⁵ M/l. The presence of DTE in the electrolytic bath may stimulate the electro-chemical-discharge reaction through a complex formation due to the oxidation of dithiothreitol

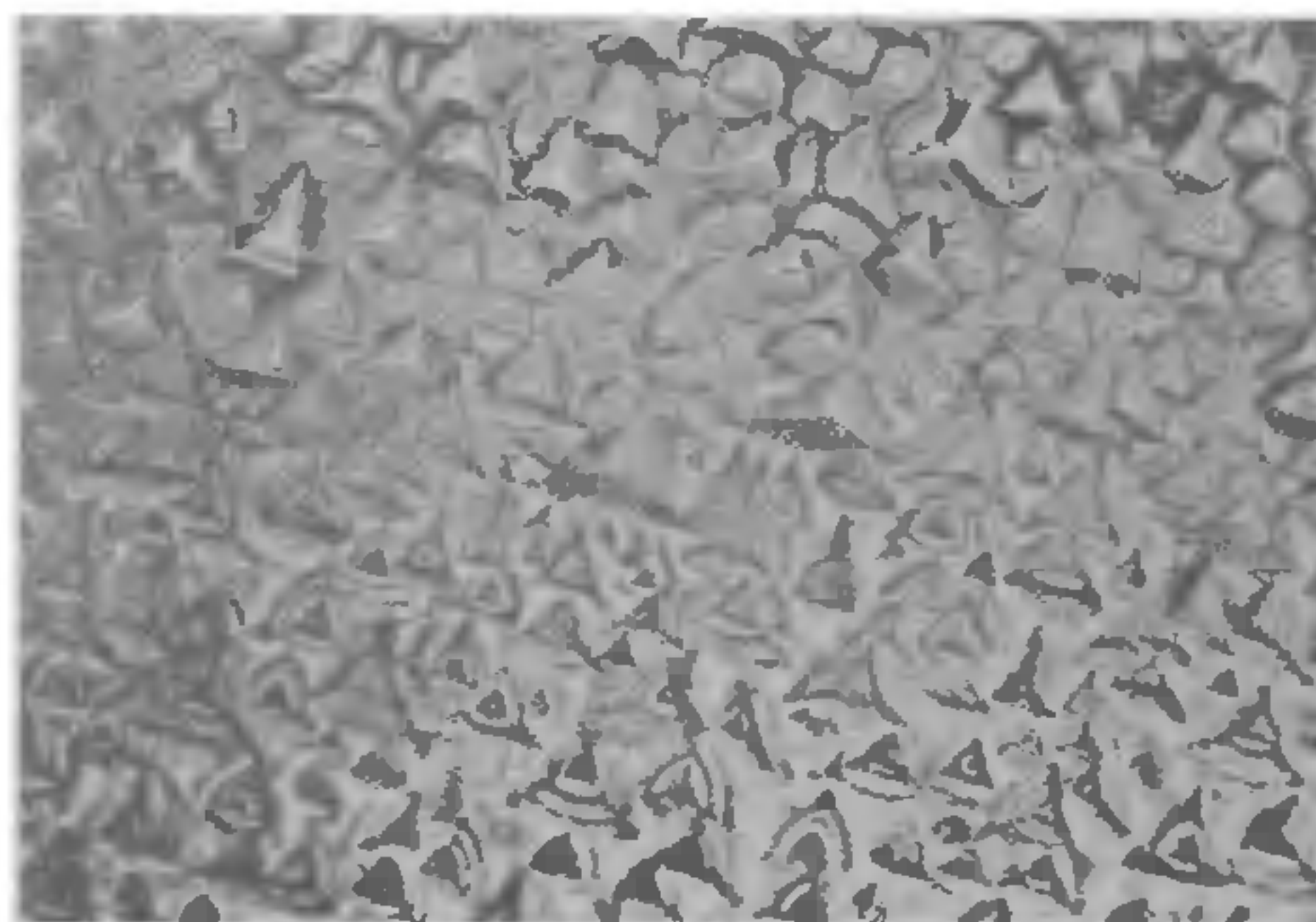


Figure 1. Triangular pyramids of copper deposited on copper (111) plane from pure copper sulphate bath at 2 mA/cm², × 625.