

FIG. 3. Diurnal variation of percentage duty cycle averaged over eleven months.

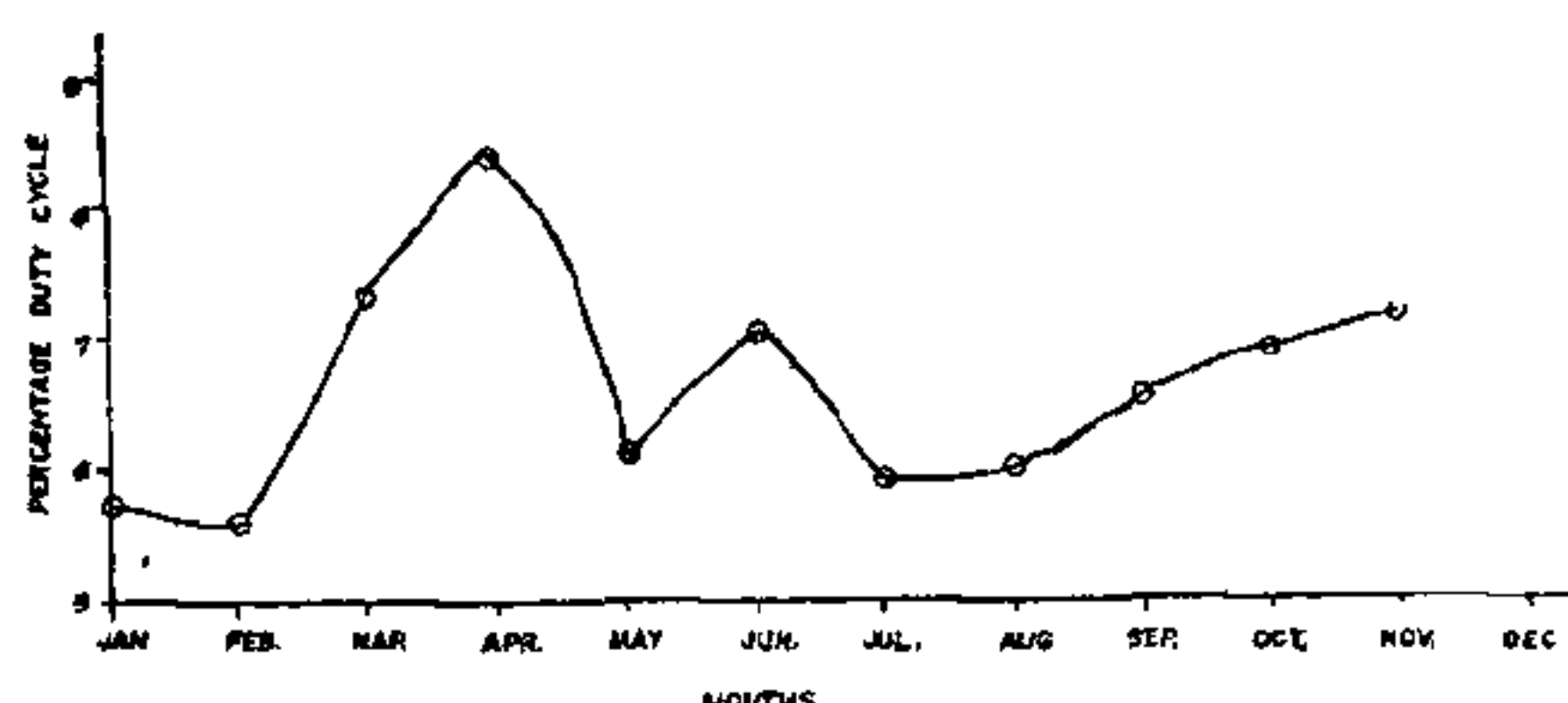


FIG. 4. Annual variation of percentage duty cycle.

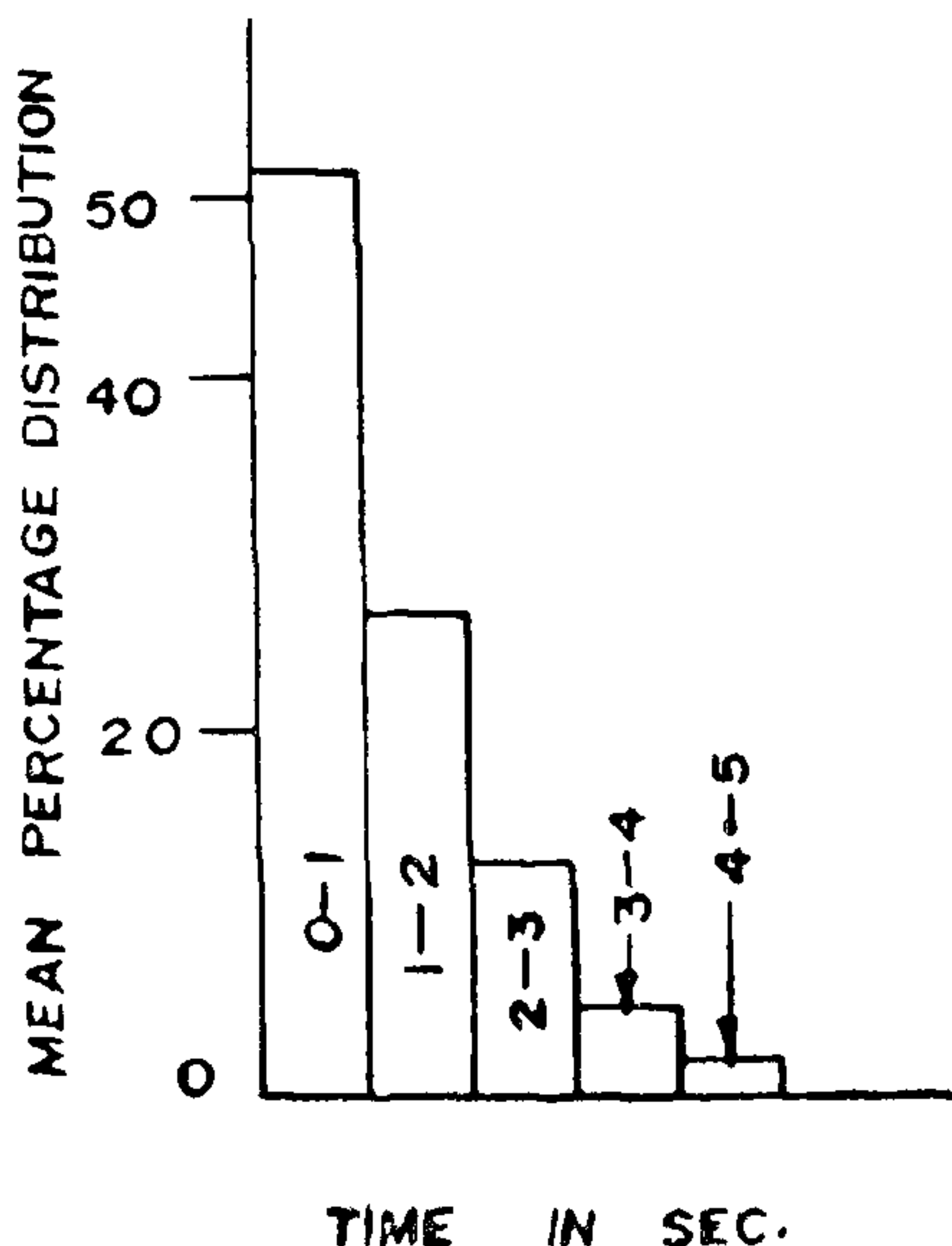


FIG. 5. Histogram of percentage distribution of meteor burst of different duration.

Duty Cycle

The fraction of time the echoes remain above a present value (Threshold) is defined as duty cycle. This varies with the threshold selected and also with days and months. In this experiment signals above 2 μ V were taken into consideration. The diurnal

variation of duty cycle over a period of eleven months is depicted in Fig. 3. This (like that of the bursts rate) clearly shows a maximum in the early morning and a minimum in the evening hours and is more or less sinusoidal in nature. The range of variation is from 2 to 8. The annual variation of duty cycle shows a maximum value near Mar.-Apr. and a minimum around February (Fig. 4). The range of variation is about 3-5%.

The duration of meter bursts varies from a fraction of a second to many seconds but more than 95% of bursts have duration less than 5 seconds. The distribution of duration of echoes of duration less than 5 seconds is shown in Fig. 5. All the above results were obtained by studying one second bursts only.

The results give a quantitative idea of the important characteristics of the meteor burst propagation which are essential for design of a meteor burst communication system.

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October 22, 1977.

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SYNTHESIS AND STRUCTURAL STUDIES OF TETRATHIOCYANATE COMPLEXES WITH FIVE MEMBERED RING MOLECULES AS LEWIS BASES

RECENTLY^{1,2}, we have studied the effect of six membered ring ligands towards the mode of thiocyanate bonding in tetrathiocyanate complexes. It has been pointed out that the mode of thiocyanate bonding depends upon the nature of the ligand and metal. In the present communication we are presenting the synthesis and structural studies of some new binuclear tetrathiocyanate complexes with five membered ring ligands having multisites of bonding.

Synthesis of the complexes and physical measurements were made as described earlier^{1,2}. These complexes have been characterized by elemental analysis, molar conductance, magnetic moment and infrared spectral studies. Elemental analyses indicate the complexes to be of the type $\text{CuM}(\text{NCS})_4 \times \text{L}$ [$\text{M} = \text{Cd}(\text{II}), \text{Hg}(\text{II})$ $x = 2, 4$ and $\text{L} = \text{Thiozolidine-thione (tzt)}, \text{thiohydantoin (thn)}$ and $\text{Ethylenethiourea (etu)}$]. To establish the structure of the complexes, group theoretical calculation have also been performed, treating ligands as points (3).

TABLE I
Analytical molar conductance and Magnetic Moment data

Complexes	Colour	M.P. (°C)	% Copper		% Metal (Hg/Cd)		% Nitrogen		% Sulphur		μ_{eff} (B.M.)	ΔM in ace- tone (cm ²) mho/mole)
			cal.	obs.	cal.	obs.	cal.	obs.	cal.	obs.		
(etu) ₂ Cu (NCS) ₂ Hg (SCN) ₂	Yellow	105	8.8	9.0	24.4	23.9	15.9	15.4	27.3	25.9	1.75	25.5
(etu) ₂ Cu (NCS) ₂ Cd (SCN) ₂	Yellow	120	10.3	9.7	18.1	17.7	18.1	18.0	31.2	30.8	1.78	24.8
(tzt) ₂ Cu (NCS) ₂ Hg (SCN) ₂	Green	220 (d)	8.5	8.0	27.2	26.9	11.4	11.0	34.9	24.3	1.87	..
[Cu (tzt) ₄] ⁺⁺ [Cd (NCS) ₄] ⁻⁻	Yellow	145 (d)	7.1	7.0	12.6	12.1	12.0	18.0	45.0	45.0	1.70	92.5 (1:1)
(SCN) ₂ Cu (NCS) ₂ Hg (thn) ₂	Yellow	170 (d)	8.9	8.6	27.4	27.2	15.4	14.9	26.4	26.3	1.74	30.0
[Cu (thn) ₄] ⁺⁺ [Cd (SCN) ₄] ⁻⁻	Yellow	120	7.2	7.1	12.8	12.3	19.2	18.8	29.3	28.9	1.80	88.5 (1:1)

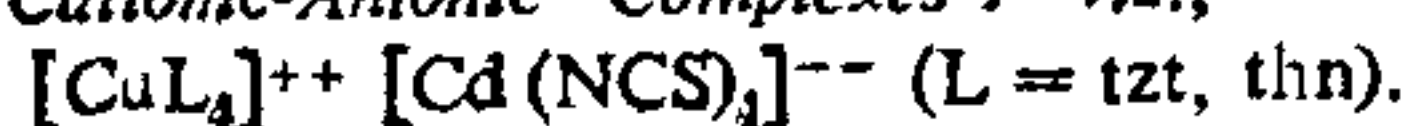
d = decomposes.

All the three ligands have several possible sites of bonding, viz., ring sulphur, thiocarbonyl sulphur, carbonyl oxygen and imino nitrogen. To decide the actual site of bonding, we have recorded the spectra of ligand in chloroform in order to eliminate the effect of hydrogen bonding.

In 'tzt' and 'etu', there is a negative shift of the order 90-135 cm⁻¹ in NH stretching frequency on complex formation, indicating that the imino nitrogen is the coordinating site in these ligands^{4,5}. There is no shift (or slight positive shift) in the bands of thiocarbonyl sulphur and ring sulphur vibrations which indicate that these sites are inert towards coordination. In the case of *thiohydantoin*, there is a negative shift of the order 25-30 cm⁻¹ in the bands of thiocarbonyl vibrations on complex formation, indicating thiocarbonyl sulphur as the donor site⁶. The bands due to imino nitrogen and carbonyl oxygen are either unaffected or shifted slightly towards higher frequency region which rules out the possibility of being imino nitrogen or carbonyl oxygen as the donor sites in 'thn' (Table II).

On the basis of structure, complexes are divided into three groups :

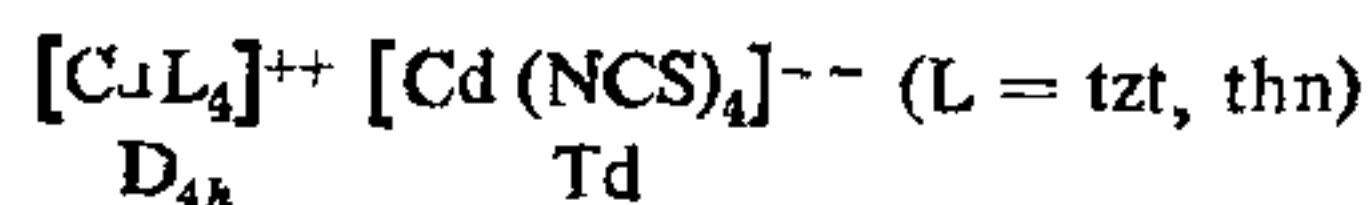
I. Cationic-Anionic Complexes : viz.,



The molar conductance data of these complexes in acetone are equivalent to 1:1 electrolyte. The posi-

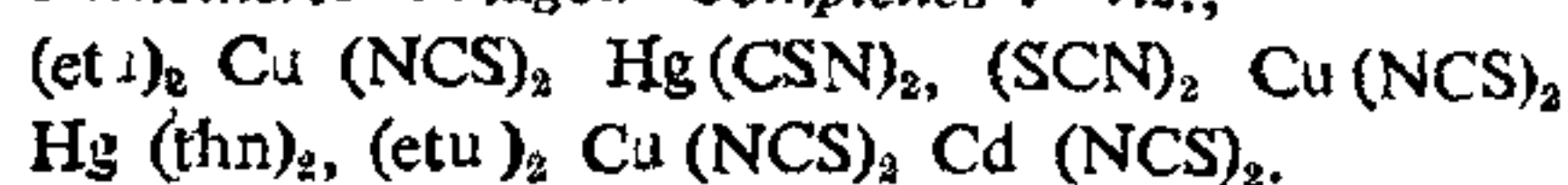
tion and nature of infrared spectral bands due to γCN , γCS and δNCS modes as presented in Table II clearly indicate that thiocyanates are N-bonded in 'tzt' and S-bonded in 'thn' complexes^{2,3,7-9}. These complexes are yellow in colour having magnetic moment values of about 1.75 B.M.

On the basis of these results, a cationic-anionic structure in which four ligands are attached to copper to form planar cation and thiocyanate to cadmium to give tetrahedral anion, may be proposed



If the proposed structure is true then cation will belong to D_{4h} and anion to Td point groups. Assuming these point groups we have made group theoretical calculations. The similarity in the observed and calculated bands favours the proposed structure³.

II. Monomeric Bridged Complexes : viz.,



The molar conductance of these complexes in acetone indicate that they are non-electrolyte. The position, nature and number of infrared spectral bands due to γCN , γCS and δNCS modes as presented in Table II clearly show the presence of both bridged and terminal thiocyanate groups^{2,3,7-9}. These complexes are yellow in colour having magnetic moment values of about

TABLE II
Assignments of infrared spectra of ligands and complexes (cm^{-1})

Complexes	Medium	Ligand Vibrations				Thiocyanate vibrations					
		γNH	δNH	Thio-carbonyl-vibration ($\gamma\text{CS} \pm \delta\text{NCS}$)	γCO	γCS (ring)	γCN	γCS	δNCS	$\gamma_{\text{Cu-NCS}}/\gamma_{\text{Hg-SCN}}/\gamma_{\text{Cd-SCN}}$	$\gamma_{\text{Cu-L}}$
$\cdot\text{-etu}$	CHCl_3	3425 (s)	1490 (s)	1265 (s)
$\cdot(\text{etu})_2, \text{Cu}(\text{NCS})_2, \text{Hg}(\text{SCN})_2$	Nujol	3330 (b)	1510 (s)	1270 (s)	2140 (s), 2085 (s), 2030 (s)	795 (s), 745 (s), 725 (s)	480 (s), 420 (s), 410 (m)	290 (sh), 240 (w)	205 (w)
$\cdot(\text{etu})_2, \text{Cu}(\text{NCS})_2, \text{Cd}(\text{NCS})_2$	Nujol	3335 (s)	1505 (s)	1270 (s)	2155 (s), 2105 (w), 2030 (s)	830 (sh), 800 (s), 710 (m)	475 (b), 430 (sh), 410 (m)	290 (m), 230 (sh)	200 (sh)
eti	CHCl_3	3425 (s)	1490 (s)	1295 (s)	..	652 (s)
$\cdot(\text{eti})_2, \text{Cu}(\text{NCS})_2, \text{Hg}(\text{SCN})_2$	Nujol	3250 (b)	1510 (s)	1510 (s)	..	660 (s)	2100 (s)	750 (m)	455 (m)
$\cdot[\text{Cu}(\text{eti})_4]^{++}$ $[\text{Cd}(\text{NCS})_4]^{--}$	Nujol	3290 (s)	1500 (s)	1315 (s)	..	670 (w)	2070 (s)	765 (s)	465 (m)
thn	CHCl_3	3400 (s)	1710 (s)	1535 (s)	1770 (s)
$\cdot(\text{SCN})_2, \text{Cu}(\text{NCS})_2, \text{Hg}(\text{thn})_2$	Nujol	3410 (b)	1710 (w)	1510 (m)	1800 (m)	..	2150 (s), 2110 (sh), 2050 (s)	760 (sh), 740 (m), 715 (w)	480 (m), 460 (m), 435 (sh)
$\cdot[\text{Cu}(\text{thn})_4]^{++} [\text{Cd}(\text{SCN})_4]^{--}$	Nujol	3420 (s)	1700 (sh)	1505 (s)	1770 (m)	..	2080 (s)	760 (s), 710 (s)	740 (m), 420 (m)

s = strong, m = medium w = weak, sh = shoulder, b = broad.

1.75 B.M. On the basis of these results a monomeric bridged structure as shown in Figs. 1 and 2 may be proposed.

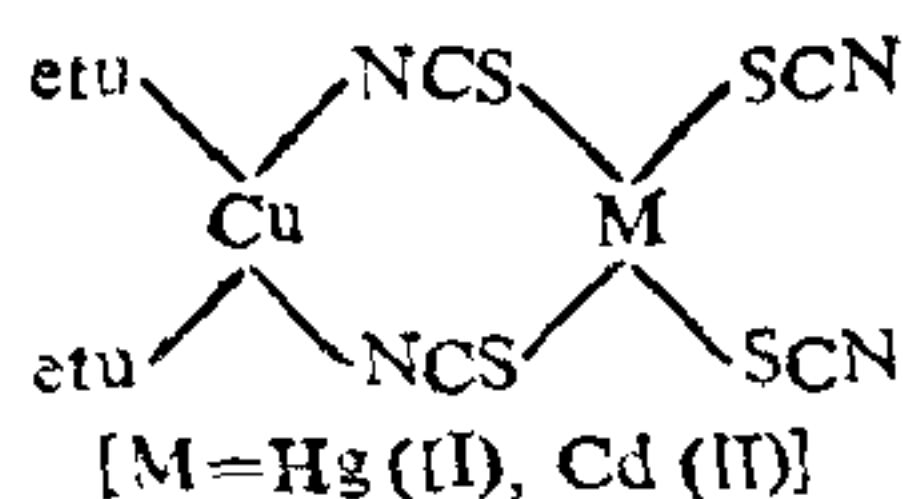


FIG. 1

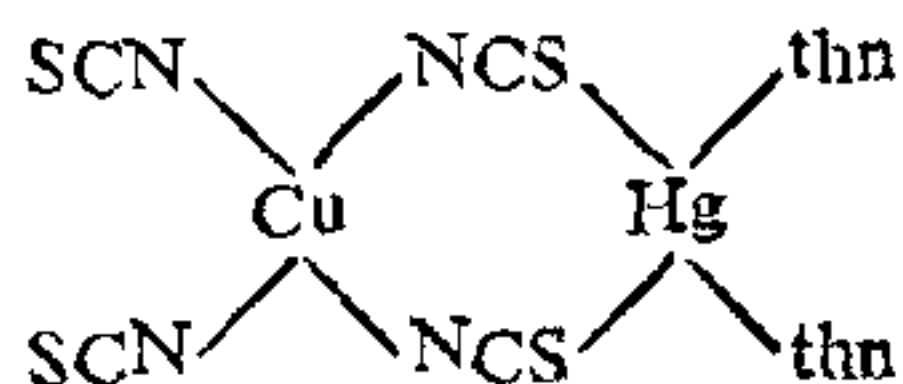


FIG. 2

Since in 'etu' 'N' is donor atom which is hard, will prefer to link with copper whereas in 'thn' in which 'S' is the donor atom which is soft will prefer to link with mercury according to HSAB theory¹⁰. If the proposed structures are true then they will belong to C_2 point group. Assuming this point group, we have calculated the infrared active modes and compared with the observed bands. This comparison again favours our proposed structures².

III. Polymeric bridged complexes: viz., $(\text{tzt})_2\text{Cu}(\text{NCS})_2\text{Hg}(\text{SCN})_2$

The position and the number of infrared spectral bands due to γCN , γCS and δNCS modes as presented in Table II clearly indicate the presence of only bridging thiocyanate groups in this complex^{2,3,7-9}. This complex is insoluble and decomposes at high temperatures. On the basis of these results a polymeric bridged structure in which the ligands are attached to copper may be suggested as shown in Fig. 3. Thus copper acquire distorted octahedral or tetragonal and mercury tetrahedral coordination geometry.

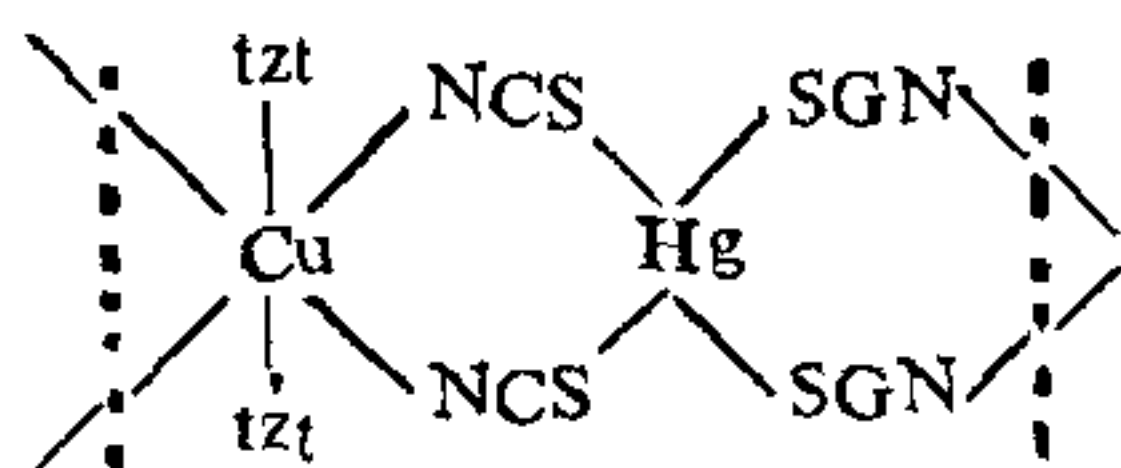


FIG. 3

This complex again belongs to C_{2v} point group for which the calculated and observed bands are compared. This comparison favours the proposed structure. The tentative assignments of $\gamma\text{M-NCS}$, $\gamma\text{M-L}$, $\gamma\text{Hg-SCN}$ and $\gamma\text{Hg-L}$ modes are also given in Table II in some complexes.

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HEAT OF FORMATION OF SOME ORGANIC COMPOUNDS USING IOC- ω -TECHNIQUE

HEAT of Formation of benzanthrone, acedanthrone, flavanthrone and some other organic compounds containing hetero-atoms have been calculated using IOC- ω -technique. The results obtained are in agreement with the experimental values, where ever available.

IOC- ω -technique has been widely used¹⁻⁵ to calculate the heat of formation of organic compounds. S. C. Tiwari⁶ has calculated the heat of formation of some cyclazines and some other organic compounds containing heteromolecules. The results obtained are in fairly good agreement with the available experimental results. In the present paper the method has been further used to calculate the heat of formation of benzanthrone, acedanthrone, flavanthrone and some other organic compounds containing heteromolecules.

Method of Calculation

The heat of formation of an organic compound is equal to the sum of the total π -bond and σ -bond energies (Eq. 1).

$$-\Delta H_f = E_{\pi b} + E_{\sigma b} \quad (1)$$