

## Preparation and structural studies of a new series of bimetallic complexes

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**Abstract.** A new series of bimetallic Lewis acid,  $\text{Cu}(\text{NCO})_2(\text{NCS})_2\text{Hg}$ , and its complexes,  $\text{L}_2\text{Cu}(\text{NCO})_2(\text{NCS})_2\text{Hg}$  ( $\text{L} = \text{THF}$ ,  $\text{DMSO}$ ,  $\text{pyridine}$ ,  $\text{nicotinamide}$  and  $\text{Ph}_3\text{P}$ ) are prepared and studied by physical and spectroscopic methods.

**Keywords.** Bimetallic; thiocyanate; cyanate; magnetic moment; tetragonal; bridged; softness values; symmetry; Jahn-Teller distortion.

### 1. Introduction

There has been much interest (Bailey *et al* 1971) in the bonding capabilities of ambidentate ligands,  $\text{NCS}^-$ ,  $\text{NCSe}^-$  and  $\text{NCO}^-$ . Makhija *et al* 1973 prepared and studied some bimetallic tetrathiocyanate complexes,  $\text{MM}'(\text{NCS})_4$  and  $\text{L}_2\text{MM}'(\text{NCS})_4$  and the coordination behaviour of the thiocyanate ion,  $\text{NCS}^-$ . Singh *et al* (1980) extended this work to include the corresponding tetraseselenocyanate  $\text{MM}'(\text{NCSe})_4$  and mixed dithiocyanato-diselenocyanates,  $\text{MM}'(\text{NCSe})_2(\text{NCS})_2$ . The effect of the various ligands on the bonding modes adopted by  $\text{NCSe}^-$  and  $\text{NCS}^-$  ions is further discussed. Since the cyanate ion,  $\text{NCO}^-$ , also possesses two potential donor sites, it was thought worthwhile to study the coordination behaviour of this and the thiocyanate ions together in a mixed-metal system as there appears no such report in literature.

### 2. Experimental

#### 2.1 Synthesis of the Lewis acid

An aqueous solution of  $\text{Cu}(\text{NCO})_2$  was prepared by stirring hydrated  $\text{Cu}(\text{II})$  nitrate (40 mmol) with  $\text{KNCO}$  ( $> 80$  mmol) for 6 hr. To this, 35 mmol of  $\text{Hg}(\text{SCN})_2$  was added and the whole content was stirred for 3 days. A light green product formed which was suction-filtered, washed, *inter alia*, with water and acetone and dried over dehydrated silica gel. The compound, m.p.  $283^\circ\text{C}$ ,  $\mu_{\text{eff}} = 1.96$  B.M., was analysed for  $\text{CuHg}(\text{NCO})_2(\text{NCS})_2$ . Found: C, 10.88%; N, 11.97%; S, 13.78%; Cu, 13.52%; requires for  $\text{CuHg}(\text{NCO})_2(\text{NCS})_2$ : C, 10.34%; N, 12.07%; S, 13.79%; Cu, 13.68%.

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## 2.2 Synthesis of the complexes ( $L = \text{THF}$ , $\text{DMSO}$ , $\text{py}$ , $\text{nia}$ or $\text{Ph}_3\text{P}$ )

The THF and DMSO complexes were synthesised by stirring a small amount of the Lewis acid with an excess of the required ligand for 12 hr. For the synthesis of the remaining complexes, > 4 mmol of the ligand dissolved in acetone was stirred with 1 mmol of the Lewis acid followed by usual working of the products. In all the examples, complexes analysing for  $\text{L}_2\text{CuHg}(\text{SCN})_2(\text{OCN})_2$  were obtained. The bis-pyridine and bis-nicotinamide complexes could also be synthesised by an alternative procedure. First,  $\text{CuL}_4(\text{NCO})_2$  was prepared by the reaction between an aqueous solution of  $\text{Cu}(\text{NCO})_2$  and an excess of py (or nia) dissolved in alcohol. Further, 1 mmol of this was suspended in acetone-alcohol mixture and stirred with 1 mmol of  $\text{Hg}(\text{SCN})_2$  for 3 days. Complexes of the composition  $\text{L}_2\text{CuHg}(\text{SCN})_2(\text{OCN})_2$  were obtained.

## 2.3 Analysis of the complexes

Cu was estimated as its salicylaloximate, Hg as HgS, S as  $\text{BaSO}_4$  and C and N were analysed at CDRI, Lucknow.

## 2.4 Physical measurements

Magnetic moments were measured on a Gouy balance using  $\text{CoHg}(\text{SCN})_4$  as calibrant. Molar conductance of the complexes was measured in purified DMF using a Philip PR 9500 conductivity bridge. Electronic spectra were recorded on a DMR-21 uv-vis spectrophotometer. IR spectra were measured on a Perkin-Elmer-621 spectrophotometer ( $4000\text{--}200\text{ cm}^{-1}$ ) and on a FIR-30 spectrophotometer ( $650\text{--}100\text{ cm}^{-1}$ ).

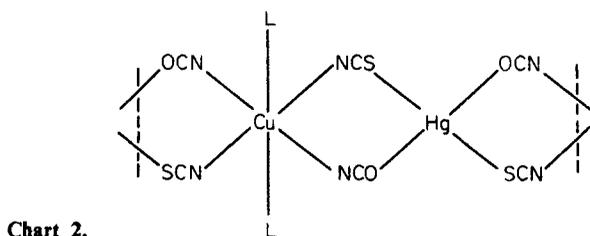
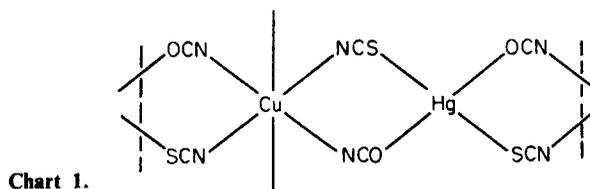
# 3. Results and discussion

## 3.1 Molar conductance, electronic spectra and magnetism

The calculated magnetic moment values ( $\sim 1.9$  B.M.) was greater than the theoretical value (1.73 B.M.) which was attributed to Jahn-Teller distortion effects. Electronic spectra exhibited a broad band (Forster and Goodgame 1965) around  $12840\text{--}15400\text{ cm}^{-1}$ , assignable to  ${}^2T_g \rightarrow {}^2E_g$  electronic transition. These features are consistent with a tetragonally distorted Cu(II) complex approximating to  $D_2$  symmetry. The molar conductance values for these complexes suggest their non-electrolytic nature (Geary 1971). This criterion indicates the polymeric nature of the complexes.

## 3.2 IR spectral studies

The IR spectra of all the complexes and the Lewis acid exhibited  $\nu_{\text{CN}}$ ,  $\nu_{\text{CS}}$  and  $\delta_{\text{NCS}}$  bands in the region assignable to the bridged NCS groups only (Makhija *et al* 1973; Singh 1980). The bands due to  $\nu_{\text{CN}}$  of the NCO groups appeared around  $2240\text{ cm}^{-1}$  which is a much higher value than expected for a N-terminal, O-terminal or > N-bridged cyanate group (Bailey *et al* 1971; Nelson and Shepherd 1965). X-ray crystal analysis and IR analysis of a Ni(II) cyanate complex (Hudson and Hendrickson 1973) has recently supported the existence of a three centre-NCO-bridges. Our IR data closely resemble IR data of this complex and based on this analogy, three-atom-NCO-bridges are proposed between Cu(II) and Hg(II) in our complexes.



Thus, all the NCO and NCS groups must be bridged between Cu(II) and Hg and a polymeric structure (chart 1) is proposed. In the Lewis acid, Cu(II) might acquire an octahedral coordination geometry through axial coordination of the adjacent NCS groups (chart 2). In the complexes, these weak axial bonds are replaced by the ligands.

The problem which now remains is the mode of coordination of the NCO and NCS groups between the two metal ions, Cu(II) and Hg(II). This could be overcome by calculating the Klopman's softness values (Klopman 1968) of the two coordinating sites of these ambidentate ligands. Using the procedure of Singh *et al* (1980), we have calculated the softness parameters ( $E_m^\ddagger$ ) of the NCO<sup>-</sup> and NCS<sup>-</sup> ions. For the O-end and the S-end of these ions, the values are  $-10.47$  and  $-7.71$  eV respectively. For the two metal ions (Lewis acids), Cu<sup>2+</sup> and Hg<sup>2+</sup>, the softness values ( $E_H^\ddagger$ ) are  $-0.73$  and  $-4.86$  eV respectively.

A higher negative value of softness of a base ( $E_m^\ddagger$ ) indicates a more hard (Klopman 1968; Singh *et al* 1980) character whereas this sequence is reversed for the acids ( $E_H^\ddagger$ ). Taking into account Pearson's (1968) HSAB theory which states that hard-hard (or soft-soft) interactions are more facile, it is proposed that Cu(II) must link to the N-ends of these ions whereas Hg(II) should link to the O-end (or S-end). Thus, the structure must consist of  $-(\text{NCS})_2\text{—Hg—(OCN)}_2\text{—Cu—(NCS)}_2\text{—}$  units. The larger number of bands observed each for  $\nu_{\text{CN}}$ ,  $\nu_{\text{CS}}$ ,  $\delta_{\text{NCO}}$  and  $\delta_{\text{NCS}}$  modes is on account of the presence of a symmetry of order lower than  $C_{2v}$ .

### 3.3 Structure of $(\text{Ph}_3\text{P})_2\text{CuHg}(\text{SCN})_2(\text{OCN})_2$

The IR spectra of the bis-triphenylphosphine complex indicates only bridged-thiocyanate groups and terminal cyanate groups. The cyanate groups are N-bonded. This is to be expected on account of increased negative charge density (Wagner 1965) ( $-0.7712$  eV) on the N-end than on the O-end ( $-0.1846$ ). It is suggested that the reaction of  $\text{Ph}_3\text{P}$  with the Lewis acid ruptures the cyanate bridges and thus, monomeric complexes are formed.

### 3.4 Effect of coordination on the IR spectra of ligands

The ligands, THF and DMSO are coordinated to the metal through their O-ends as is evident from the characteristic changes (Nakamoto 1963) in the IR spectra of these when in the coordinated form. The upward shifting in the lowest ring vibrations of py and nia (at 405 and 604  $\text{cm}^{-1}$  in uncomplexed molecules) indicates that these two ligands have coordinated through their ring nitrogen atoms.

### 3.5 Far-IR spectra

Absorption bands due to  $\nu_{MN}$ ,  $\nu_{ML}$ ,  $\nu_{HgS}$ ,  $\delta_{N-M-N}$  and  $\nu_{MP}$  modes were assigned by comparing with published data (Makhija *et al* 1973; Nakamoto 1963; Ferraro 1971). These support the assigned structures for the complexes.

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