

Note

Synthesis and spectroscopic studies of a mixed metal 7,7',8,8'-tetracyanoquinodimethane (TCNQ) derivative—A novel example

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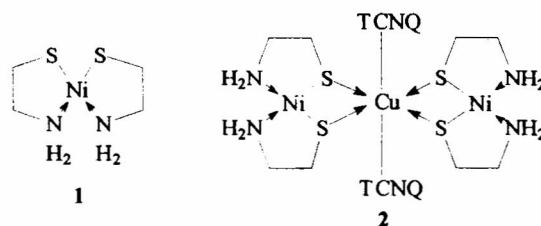
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Reaction of the diamagnetic tetrakis(β -mercaptoethylamine)nickel (II)-copper (I) chloride, $\{Cu[Ni(NH_2CH_2CH_2S)_2]_2\}Cl$, with lithium salt of LiTCNQ, LiTCNQ, furnishes a paramagnetic bis(7,7',8,8'-tetracyanoquinodimethanato) - tetrakis(β -mercaptoethylamine)dinickel (II)-copper(II), $\{Cu[Ni(NH_2CH_2CH_2S)_2]_2(TCNQ)_2\}$, a unique mixed metal TCNQ complex with a distorted octahedral (Oh) geometry around Cu (II) with four positions being occupied by the sulfur atoms from the two nickel chelate complexes and the two positions being occupied by the σ -monodentate TCNQ⁻ species. The magnetic moment and the EPR studies indicate the presence of TCNQ⁻ species as diamagnetic dimeric units and the existence of some magnetic interaction between copper ions. The EPR spectrum is different from the one expected for a normal 'Oh' environment in Cu (II) complexes and suggests an axially elongated system.

In the past few years there has been an increased interest in the complexes of TCNQ transition metal chelates due to their interesting conducting properties¹. A few nickel and copper complexes with TCNQ have been reported² and it has been proved that due to the high thermodynamic stability of the metal chelate, only the anionic ligand has been replaced by the TCNQ⁻. The ability of the metal centre in the chelate to extend its coordination sphere provides the way to TCNQ species to bind as σ -monodentate ligand. Though a number of mono metal complexes with TCNQ have been reported, but there seems to be no report on the mixed metal complexes of TCNQ. Here in this note the synthesis and characterisation of the complex, $\{Cu[Ni(NH_2CH_2CH_2S)_2]_2(TCNQ)_2\}$, have been reported.

Experimental

Physical measurements. IR spectra were recorded using KBr pellets of the powdered sam-



ples on a Shimadzu FT IR 8000 spectrometer ($4000-400\text{ cm}^{-1}$) and UV-VIS spectra on Shimadzu Graphicord 240 UV-VISIBLE spectrophotometer. Magnetic moments were measured using digital Gouy method at room temperature. The X-band EPR (9.44 GHz) spectra were recorded on a JEOL JES-FE 3xG ESR spectrometer (Field range $3000 \pm 2500\text{ G}$).

Preparation of complexes. All the reactions were carried out under inert atmosphere and degassed solvents were used. The complexes; $[Ni(NH_2CH_2CH_2S)_2]$, $\{Cu[Ni(NH_2CH_2CH_2S)_2]_2\}Cl$ and LiTCNQ were prepared by the reported methods^{3,4}. In a typical preparation a solution of LiTCNQ (0.76 g) in H_2O (20 mL) was added to $\{Cu[Ni(NH_2CH_2CH_2S)_2]_2\}Cl$ (1.0 g) in a mixture of CH_3OH and H_2O (20 mL 1:1, v/v). The mixture was stirred at room temperature for 2-3 hr. The dark coloured product was separated by filtration and washed with a mixture of CH_3OH and H_2O and was dried under vacuum.

Results and Discussion

The number and intensity variations of the nitrile stretching bands in IR spectra indicate the coordination status of TCNQ⁴⁻⁸. The IR spectrum of the TCNQ complex (Figure 1) exhibits a weak band at 2218 cm^{-1} and a strong band at 2187 cm^{-1} attributed to Bu and Ag modes of TCNQ⁻. A strong band attributed to $\nu(C=C(CN)_2)$ of TCNQ⁻ appears at 1580 cm^{-1} . The two medium intensity bands at 1505 and 825 cm^{-1} are assigned as the $\nu(C=C)$ and $\delta(CH)$ of TCNQ⁻. These IR spectral data with the highest energy band being the weakest suggests the σ -monodentate nature of the TCNQ⁶⁻⁸. The strong absorption band at 825 cm^{-1} is a clear indication that solely TCNQ⁻ is present. Therefore, the IR data suggests that one of the metal atom has extended its coordination sphere from four to six. It has been reported³ earlier that due to the strong field strength of the ligand β -mercaptoethylamine

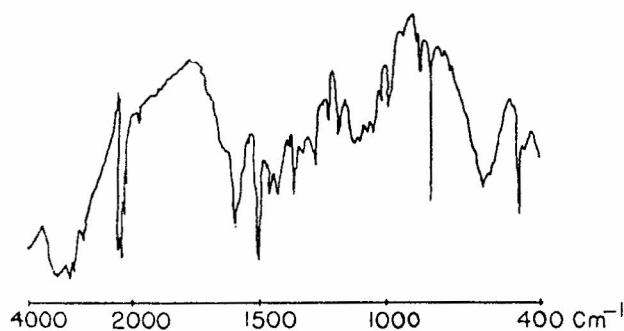


Figure 1—IR spectrum of the complex $\{Cu[Ni(NH_2CH_2CH_2S)_2]_2(TCNQ)_2\}$

the complex, $Ni(NH_2CH_2CH_2S)_2$, was found to be diamagnetic which is consistent with square planar configuration for Ni (II) (1).

It is well established that treatment with pyridine usually results in the expansion of coordination number of the planar four coordinate Ni (II) complexes to six. However the reaction of pyridine with $Ni(NH_2CH_2CH_2S)_2$ failed to produce such a derivative indicating the high stability of this planar system. On the basis of this we have suggested that $TCNQ^-$ is σ -coordinated to the Cu (II) which has thus attained the distorted 'Oh' geometry with four positions being occupied by four sulfur atoms from the two nickel chelate complexes and the two by nitrogen atoms from two $TCNQ$'s. $\nu(N-H)$ has been observed in the range of $3000-3250\text{ cm}^{-1}$.

Due to the insolubility of the complex in usual organic solvents the electronic spectrum was recorded in acetonitrile at lower concentrations. It has been reported that the absorption spectrum of $LiTCNQ$ shows generally three types of transitions in the visible and near IR regions^{9,10}. An electronic transition in the region 1110-830 nm results from a charge transfer between $TCNQ^-$ ions and is denoted as CT_1 transition. The lowest locally excited (LE_1) level of the $TCNQ$ anion is found between 625-555 nm. An absorption maximum in this region has been found for several dimerised $TCNQ$ complexes. The 2nd excited level LE_2 of the $TCNQ$ anions gives rise to maxima between 400-330 nm.

Apart from all of the bands that are characteristic of the $TCNQ^-$ (Figure 2), two bands at 395 and 840 nm with the intensity ratio ($\epsilon_{395}/\epsilon_{840}$) 0.45 confirm the presence of $TCNQ^-$ moiety in solution, since neutral $TCNQ$ only shows a band at 395 nm. Also the higher value of the intensity ratio would indicate the presence of a neu-

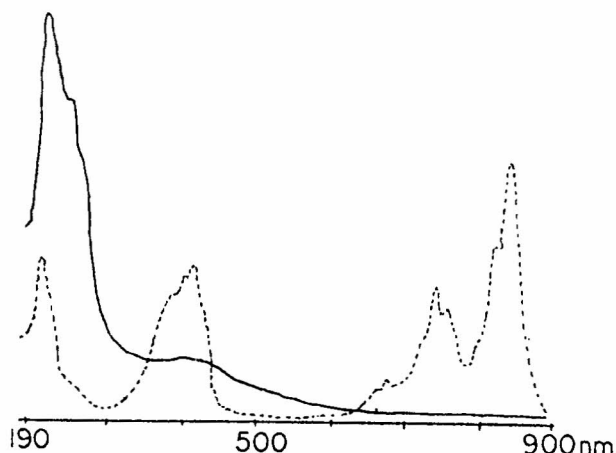


Figure 2— UV-VIS spectra of the complexes $\{Cu[Ni(NH_2CH_2CH_2S)_2]_2\}Cl$ (-) and $\{Cu[Ni(NH_2CH_2CH_2S)_2]_2(TCNQ)_2\}$ (---)

tral $TCNQ$ moiety¹¹. Similar observations have also been obtained for the other category of Ni (II), Cu (II) and Mn (II) complexes with $LiTCNQ^{2b}$. The expected shifts to higher energies for these band systems upon coordination are not observed again indicating that only free $TCNQ^-$ is present in solution. An intense band in the near ultraviolet region is attributable to the charge transfer transition¹². The d-d band observed at 400 nm in the non $TCNQ$ complex has been masked under the broad band and could not be assigned in the $TCNQ$ complex.

The $TCNQ$ complex has been found to be paramagnetic with magnetic moment 1.51 BM at room temperature and this paramagnetism is associated with the Cu (II) ions since it has been established earlier that Ni (II) is in the square planar geometry. However this low value of magnetic moment as compared with spin only value may be attributed to the magnetic interaction of the paramagnetic Cu(II) ions in the solid state which is however less as compared to copper acetate dimer. Moreover there is no significant contribution from the $TCNQ$ radicals suggesting that they are present as diamagnetic dimeric units resulting from intermolecular interactions between $TCNQ$ groups from adjacent molecules. This is possible due to the short $TCNQ-TCNQ$ distance that allows the electron pairing of the radical species. The EPR spectrum (Figure 3) was recorded at room temperature and compared with that of the starting complex $\{Cu[Ni(NH_2CH_2CH_2S)_2]_2\}Cl$ which was found to be EPR inactive confirming the oxidation state of copper. The EPR activity of $TCNQ$ complex shows that there is a change of Cu (I) \rightarrow Cu (II) which reflects acceptor propert-

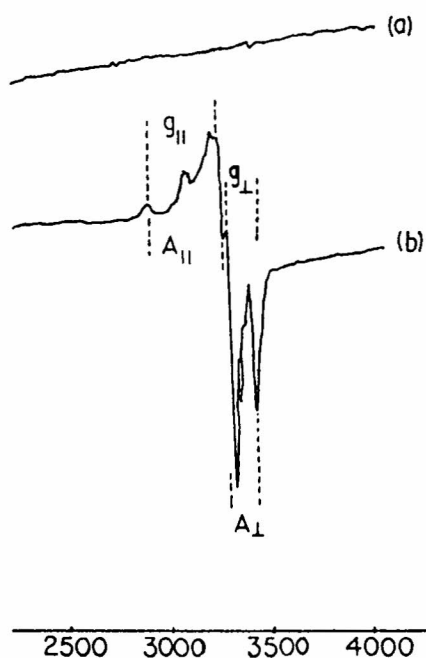


Figure 3—EPR spectra of the complexes (a) $[\text{Cu}[\text{Ni}(\text{NH}_2\text{CH}_2\text{CH}_2\text{S})_2]_2]\text{Cl}$, (b) $[\text{Cu}[\text{Ni}(\text{NH}_2\text{CH}_2\text{CH}_2\text{S})_2]_2(\text{TCNQ})_2]$

ies of TCNQ^1 . The spectrum shows the anisotropy with $g_{11} = 2.201$ & $g_{\perp} = 2.01$ indicating the distorted 'Oh' geometry around the Cu (II). Moreover the higher value of g_{11} than g_{\perp} suggests an axially elongated system. Furthermore, the g_{11} and g_{\perp} split up into four lines each with A_{11} greater than A_{\perp} further supporting the axially elongated geometry¹³. These EPR results are in contrast to those obtained for the Cu (II) tetraaza complexes with TCNQ (Cu (II) being surrounded by six nitrogen atoms) where an isotropic signal was obtained^{2b}. No signal for TCNQ radical is observed

further supporting their presence as diamagnetic dimeric units, $(\text{TCNQ})_2^{2-}$ in the solid state. On the basis of the above discussion we have assigned the structure (2) to this TCNQ complex.

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