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ELECTROCHEMICAL REDUCTION OF DINUCLEAR COPPER(I) MIXED LIGAND COMPLEXES WITH TRI-*m*-TOLYLPHOSPHINE AND HETEROCYCLIC THIONES

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Abstract—Electrochemical studies on a glassy carbon electrode in acetonitrile solutions of dinuclear copper(I) complexes with the general formula $[Cu(tmtp)(L)Br]_2$, where tmtp = tri-*m*-tolylphosphine and L = pyridine-2-thione (py2SH), 1,3-thiazolidine-2-thione (tzdtH), benz-1,3-imidazoline-2-thione ($bzimtH_2$) and quinoline-2-thione (quintH) have been carried out. The monitoring of the peak position versus scan rate combined with semi-empirical calculations on model compounds provide a suitable method for the characterization of the nature of the bridge formed between the two copper atoms, which may be either sulphur or halogen.

Copper(I) complexes possess structures dictated by the ligand's steric and electronic effects.[1] We have recently reported on a series of mixed-ligand copper(I) complexes with thiones and tertiary phosphines as ligands,[2] which have been found to be dimeric with tetrahedral geometries around the copper atoms. A case of bond isomerism may be present in such complexes, concerning the nature of the atom bridging the two copper centres, thus giving rise to different physicochemical properties due to the existence of a Cu_2A_2 core (A = halogen or sulphur atom); X-ray structural studies confirmed the existence of both μ-S and μ-X species. In a recent study[3] of bromo derivatives we observed that the relative softness between bromine and sulphur atoms is a significant factor in the choice of the bridge between copper atoms of $[Cu(tmtp)(L)Br]_2$ dimer complexes. The use of aromatic and saturated heterocyclic thiones has been explored in order to establish the extent to which this difference in softness is decisive in the formation of μ-S or μ-Br complexes. The purpose of the present study is to ascertain the relationship between geometry and electrochemical behaviour of this and analogous groups of complexes.

EXPERIMENTAL

All solvents used were of reagent grade. Copper bromide and tri-*m*-tolylphosphine (Merck) were used as obtained, while the thiones (Merck or Aldrich) were recrystallized from hot ethanol prior to use. IR spectra were obtained as KBr disks with a Perkin–Elmer 1430 spectrometer, while a Shimadzu UV-160A spectrophotometer was used to obtain the electronic absorption spectra. ^1H NMR spectra were recorded on a Bruker AW 80 spectrometer.

Cyclic voltammetric experiments were carried out on a PAR electrochemistry system consisting

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of a 170 polarographic analyser and a single-compartment cell. Solutions of copper(I) complexes (10^{-3} mol dm^{-3}) in acetonitrile were used. Cyclic voltammetric experiments were conducted in acetonitrile with 0.1 M tetrabutylammonium tetrafluoroborate as supporting electrolyte at scan rates from 0.5 to 2 Vs^{-1}. The working electrode was a glassy carbon electrode, the auxiliary electrode was a platinum wire and the reference electrode was a saturated calomel electrode (S.C.E.). The current was recorded on a Nicolet model 310 digital oscilloscope. All potentials are reported relative to S.C.E. All the experiments were performed at room temperature, under dry nitrogen.

RESULTS AND DISCUSSION

The complexes were prepared according to the literature procedure[2a,b] by heating methanolic solutions of $[Cu_2Br_2(tmtp)_3]$ with stoichiometric amounts of the desired thiones at 50–70°C, for approximately 30 min. Structure determination by X-ray methods have proved that complexes have dinuclear structures with copper(I) atoms presenting tetrahedral coordination, surrounded by phosphorus, bromine and sulphur atoms. All of the copper(I) complexes studied have 1 : 1 : 1 metal-to-thione-to-phosphine ratio with the general composition as shown in Fig. 1. When aromatic heterocyclic thiones were used the exocyclic sulphur atom acted as the bridge between the two copper centres, while in the case of saturated thiones, bromine atoms have been observed to act as such.

Electrochemical study

As has been evidenced in spectroscopic[4] and cyclic voltammetric[3,5] studies in analogous systems, there exists, in acetonitrile solution, an equilibrium between the initial copper complexes and the ones resulting from the phosphine displacement by CH_3CN molecules. Our investigation, mainly based on the electronic spectral data, about the displacement of phosphine by CH_3CN shows that the reaction is considerably time consuming. A gradual enhancement of the phosphine absorptions observed in UV spectra over several hours indicates that the above equilibrium is reached very slowly. Moreover, electronic spectra, as well as molecular weight measurements recorded in acetonitrile, suggest that a further equilibrium exists between the dimeric complexes and their monomeric fragments in solution. These two equilibria, which take a considerable time to stabilize, depend upon the Cu_2A_2 core and may be presented by the following equations:

$$[Cu(tmtp)(L)Br]_2 \leftrightarrows 2[Cu(tmtp)(L)Br] \quad (1)$$

$$[Cu(tmtp)(L)Br]_2 + CH_3CN \leftrightarrows [Cu(L)(CH_3CN)Br]_2 + 2\,tmtp. \quad (2)$$

The Cu^{I} to Cu^{0} reduction takes place in three irreversible steps, the corresponding peaks being observed in the regions -0.75 to -1.00, -1.50 to -1.75 and -2.00 to -2.25 V, respectively, at 100 mVs^{-1} scan rate. This observation can be explained by copper reduction of the initial complexes, as

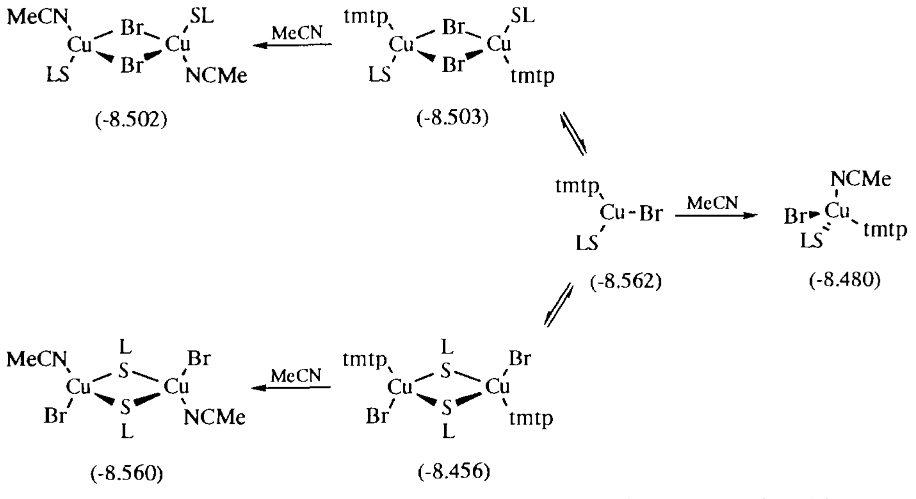

Fig. 1. Structure of the initial complexes studied and the assumed species produced in acetonitrile solution. Values in parentheses correspond to the LUMO energies (in eV) obtained from EHT calculations on model compounds, where tmtp has been substituted by PMe_3 and LS, in the figure denoting thione ligand by thioformaldehyde.

well as those derived via the above dissociation and ligand displacement reactions [eqs (1) and (2)]. Fortunately, tri-*m*-tolylphosphine is electrochemically inactive in the investigated range as a reference study indicated, in accordance with literature data.[6,7]

The observed reductions are indicative of a chemical–electrochemical mechanism. In the case of saturated thione ligands, i.e. for $Cu_2(\mu\text{-}Br)_2(tmtp)_2(tzdtH)_2$, no difference in cyclic voltamograms is observed with increasing scan rates. The rest of the complexes possess a double sulphur bridge between copper atoms and a dependence of the first peak's position on scan rate is apparent, which is shifted to more negative voltage values. Typical full scans at different scan rates vs. S.C.E. for the complexes $[Cu(tmtp)(py2SH)Br]_2$ and $[Cu(tmtp)(tzdtH)Br]_2$ are shown in Figs 2 and 3. This observation may be explained by the rearrangement of the Cu_2A_2 core that has to occur upon reduction. It therefore seems that a Cu_2Br_2 core bears closer resemblance to the resulting species than that of a Cu_2S_2 core. Extended Hückel[8] calculations on models designed to represent the species expected to occur in solution in their highest symmetry possible were carried out by substituting tmtp with PMe_3, thiones with thioformamide, using the mean values of experimental structural parameters and literature orbital parameters. Both μ-Br and μ-S initial complexes were considered, as well as the products of phosphine substitution by acetonitrile, along with the three-coordinate Cu(tmtp)(thione)Br fragment and its tetrahedral solvolysed counterpart $Cu(CH_3CN)(tmtp)(thione)Br$. Assuming that the above-mentioned reactions have been initiated in the samples following solution preparation, it is of interest to focus on the LUMO energies of the species of interest, since their values should reveal the tendency of each species for electron uptake. The most facile reduction is predicted for the "monomer fragment" Cu(thione)(tmtp)Br and the less facile one for $Cu(CH_3CN)(tmtp)(thione)Br$, the initial complexes in both cases being intermediate between the two extremes. Of interest is the observation that the bromo-bridged model possesses almost identical LUMO energies, even when the phosphine ligand has been substituted by acetonitrile, while for the sulphur-bridged model the acetonitrile-substituted species is almost as reducible as the monomeric fragment.

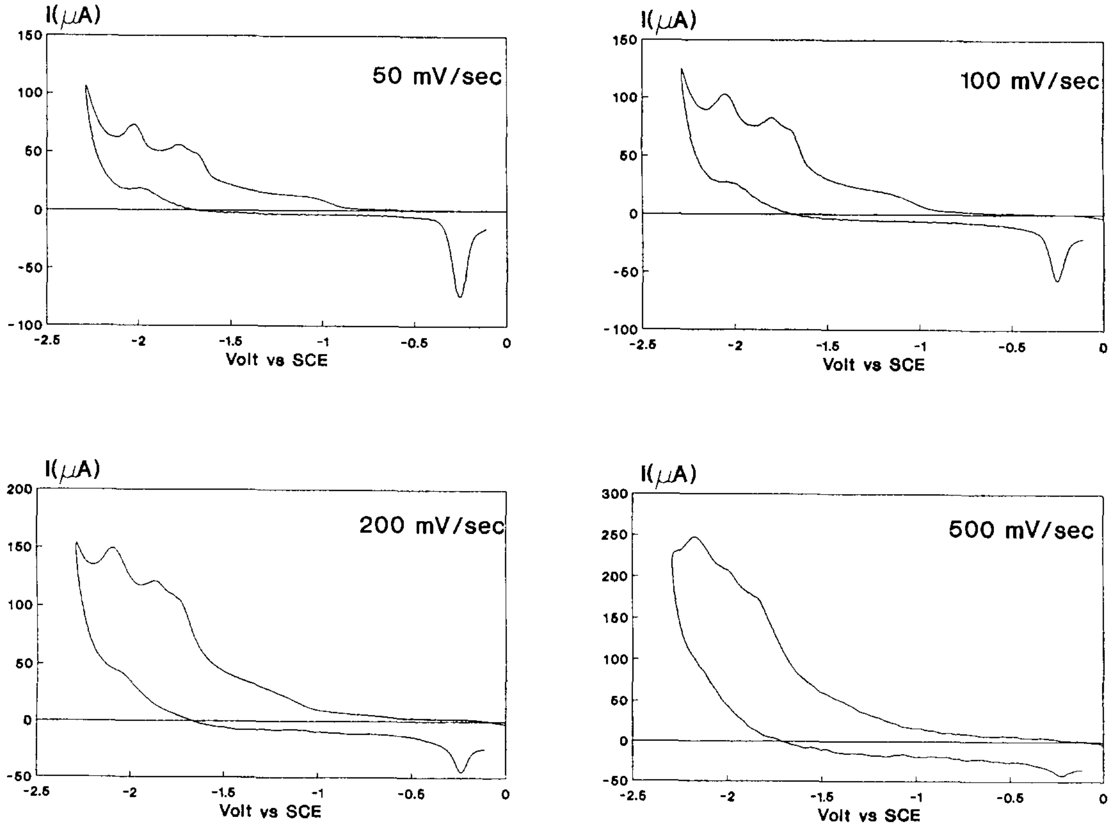

Fig. 2. Cyclic voltammogram of $[Cu(tmtp)(py2SH)Br]_2$ under N_2 (in acetonitrile, 0.1 M tetrabutylammonium tetrafluoroborate as supporting electrolyte; glassy carbon electrode; scan rate 50, 100, 200 and 500 mVs^{-1}; 25°C).

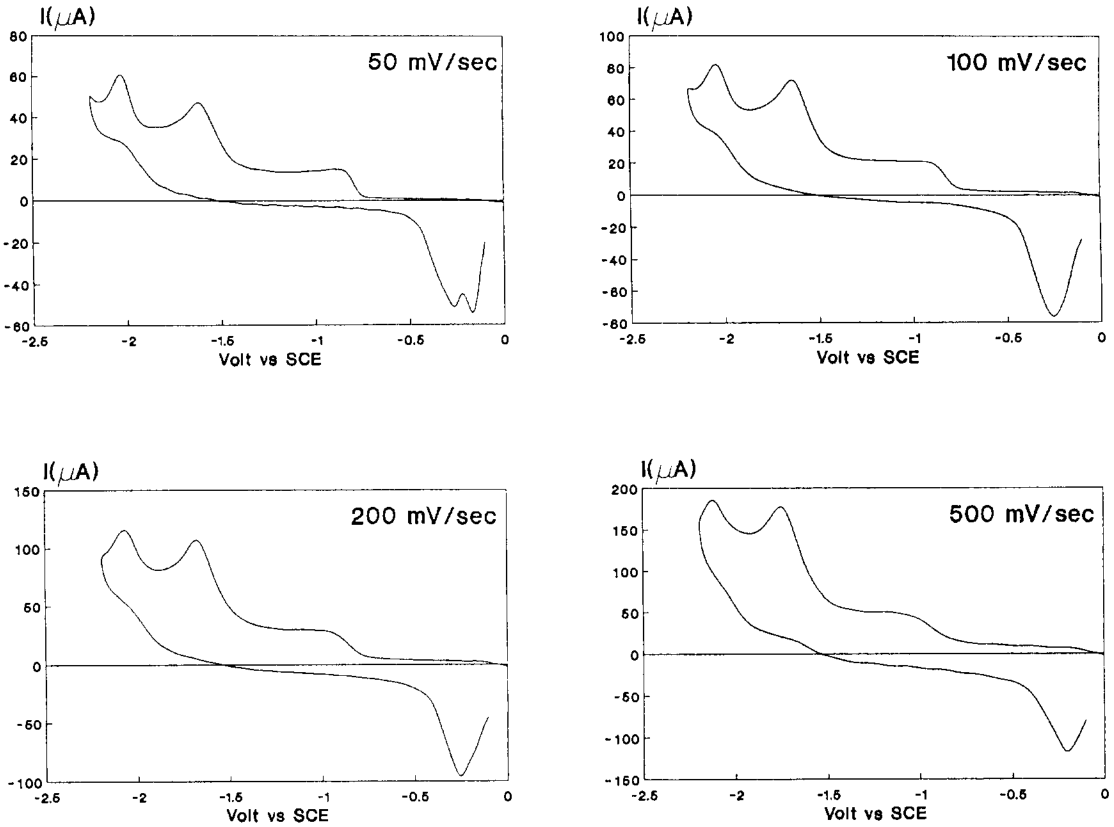

Fig. 3. Cyclic voltammogram of $[Cu(tmtp)(tzdtH)Br]_2$ under N_2 (in acetonitrile, 0.1 M tetrabutylammonium tetrafluoroborate as supporting electrolyte; glassy carbon electrode; scan rate 50, 100, 200 and 500 mVs^{-1}; 25°C).

In order to verify the role assumed for solvent molecules in producing new complex species *in situ*, cyclic voltamograms of $[Cu(tmtp)(tzdtH)Br]_2$ in acetone solution were recorded under identical conditions (Fig. 4) and revealed only two reduction peaks, attributed to the lack of processes identical to eq. (1). Since the missing peak is the one occurring at more negative voltages in acetonitrile solutions, it seems that the computationally derived argument about the existence of specific complexes in solution and their relative reducibility is justified.

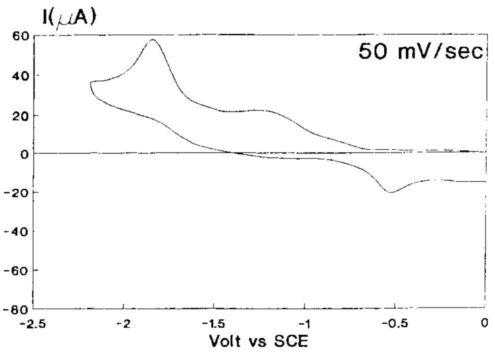

Fig. 4. Cyclic voltammogram of $[Cu(tmtp)(tzdtH)Br]_2$ under N_2 (in acetone, 0.1 M tetrabutylammonium tetrafluoroborate as supporting electrolyte; glassy carbon electrode; scan rate 50 mVs^{-1}; 25°C).

A fourth peak observed at more negative voltage (< -2.3 V) corresponds to free thione reduction and was confirmed by investigating the analogous binuclear chelate and mononuclear complexes which exhibit no reductions at potentials higher than -2.0 V under identical conditions. For these ligands only one irreversible peak appears in the range -2.1 to -2.3 V owing to the following reaction:[9]

$$2Ar\text{—}SH + 2e^- \rightarrow 2Ar\text{—}S^- + H_2.$$

Occurrence of free thione in solution is justified by the observation that in all model compounds the LUMO is clearly a thione-centred orbital, and in view of the irreversibility of the reaction it may be deduced that electron uptake of either of the species occurring in solution will lead to thione elimination.

Since the interest in the chemistry of monovalent copper complexes is growing, simple methods for the determination of the structural conformation adopted in every case will play a dominant role;

therefore, the present simple and straightforward application of cyclic voltammographic peak monitoring versus scan rate appears to be among the most promising methods.

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