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# Influence of arenechromium tricarbonyl on the redox behavior of copper in new heteropentanuclear complexes prepared from functionalized phenanthroline tweezer ligands

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## Abstract

Novel mixed $[Cu(\mathbf{4a}-\mathbf{c})_2]CF_3SO_3$ pentanuclear copper(I)/chromium(0) complexes containing tweezer ligands that contain, within the same molecule, a 2,9-disubstituted-1,10-phenanthroline and two arene-chromium subunits. The mononuclear copper(I) complexes $[Cu(\mathbf{5a}-\mathbf{c})_2]$ $CF_3SO_3$ have been prepared from the chromium free ligand species **5a–c**, obtained by quantitative photochemical decomplexation of the parent species **4a–c**. Cyclic voltammetry showed that in these complexes copper(I) can be reversibly oxidized to copper(II) in $CH_2Cl_2$. The $Cu^{II/I}$ couples are more positive in the presence of the four surrounding redox-active arenechromium subunits, revealing an electron-withdrawing effect. Complexes $[Cu(\mathbf{4c})_2]^+$, $[Cu(\mathbf{5c})_2]^+$ form new species (1:1 ligand copper stoichiometry) upon addition of excess $[Cu(CH_3CN)_4]^+$, which were identified electrochemically and by $FAB^+$ mass spectroscopy.

There has been much interest in the coordination chemistry, photophysical and redox properties of copper(I) phenanthroline and bipyridine complexes [1]. All such complexes had been found to display a ligand to copper stoichiometry of 2:1 in a pseudo-tetrahedral geometry until we recently discovered a new class of complexes with a ligand to copper stoichiometry of 2:2 and showing unusual geometry [2].

Heteropolynuclear copper(I)/transition metal complexes have not previously been prepared. Polynuclear metal complexes are of interest in view of metal–metal

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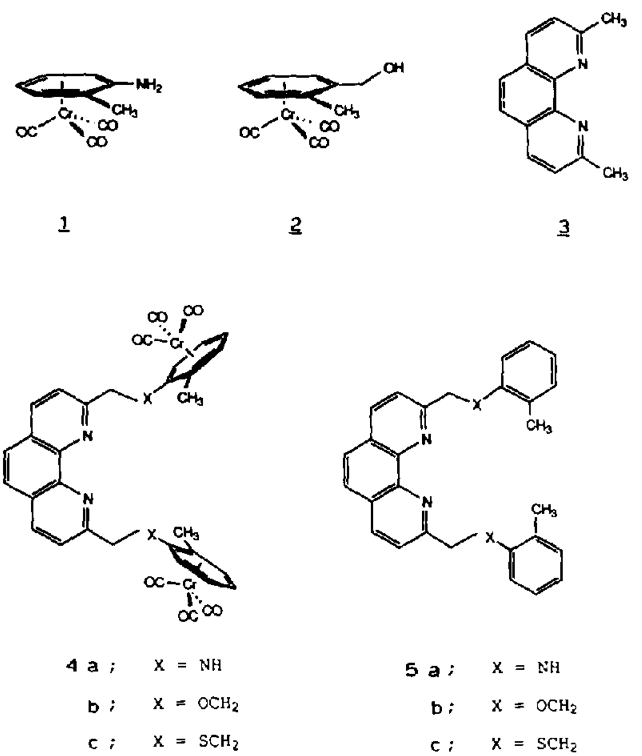
interactions and in respect of their electron or energy transfer properties. The rare examples include tetranuclear ruthenium-bipyridine complexes, which display efficient intramolecular energy quenching properties [3]. Di- [4] and tri-metallic [5] iron(I)/chromium(0) complexes have also been prepared and investigated electrochemically.

Our interest in this field involved synthesis of novel heteropolynuclear complexes [6], the central metal being copper, surrounded by additional, redox-active centers (arenechromium subunits) in order to study electronic interactions. We report here the synthesis and spectroscopic characterization of novel mixed pentanuclear copper(I)/chromium(0) complexes and describe our findings on the electronic influence of arenechromium tricarbonyl on the redox behavior of copper(I).

Copper complexes of a family of functionalized tweezer ligands, which combine within the same molecule a 1,10-phenanthroline and two arenechromium subunits, were prepared by reaction of two equivalents of the pale yellow ligands **4a**, **4b** and **4c** with 0.5 equivalents of $[Cu(CF_3SO_3)]_2 \cdot C_6H_6$ [7] in dichloromethane, under argon. After purification by chromatography on alumina ($CH_3CN$/MeOH as eluent), the solids $[Cu(\mathbf{4a})_2]CF_3SO_3$, 78% yield ($m/z$ 1444.0 $[M]^+$, $\lambda = 448$ nm, $\epsilon = 6400$ $M^{-1}$ $cm^{-1}$), $[Cu(\mathbf{4b})_2]CF_3SO_3$, 81% ($m/z$ 1504.1 $[M]^+$, $\lambda = 445$ nm, $\epsilon = 5900$ $M^{-1}$ $cm^{-1}$) and $[Cu(\mathbf{4c})_2]CF_3SO_3$, 70% ($m/z$ 1568.8 $[M]^+$, $\lambda = 447$ nm, $\epsilon = 5500$ $M^{-1}$ $cm^{-1}$) were isolated as diastereoisomeric mixtures and gave satisfactory spectroscopic data ($^1H$, $^{13}C$-NMR, UV-Vis, IR and MS) in full agreement with their proposed structures. The chromium free ligands **5a** ($m/z$ 419.1 $[M + H]^+$), **5b** ($m/z$ 449.2 $[M + H]^+$) and **5c** ($m/z$ 481.1 $[M + H]^+$) were prepared by quantitative photochemical decomplexation of the parent **4a**, **4b** and **4c** species. Both series of copper(I) complexes display the expected pseudotetrahedral coordination geometry of Cu(I)-bis-phenanthroline complexes. The copper complexes used for cyclic voltammetry studies were either prepared as above or generated *in situ* by complexation of the ligands using copper(I) from $[Cu(CH_3CN)_4]ClO_4$ [8]. Cyclic voltammetric measurements were carried out in $CH_3CN$ and $CH_2Cl_2$ containing recrystallized tetraethylammonium perchlorate (TEAP) [9] and tetrabutylammonium perchlorate (TBAP) [10], respectively. The solvents were dried as previously described [11] and stored under argon.

The arenechromium tricarbonyl compounds are oxidized in two steps, but because of changes of the voltammetric response owing to strong electrode inhibition during oxidation we discuss here only the first oxidation step. In addition the electrode had to be cleaned between each potential scan. To compare our electrochemical results with those from previous studies [12–15], we also examined the "parent" compounds **1**, **2**, and the copper(I) complex of 2,9-dimethyl-1,10-phenanthroline **3**, which possess the same copper complexation site as our tweezers ligands **4a**, **4b** and **4c** (Scheme 1).

A comparison of peak heights with those of ferrocene under the same experimental conditions established that the first oxidation step of **1** and **2** involves the transfer of one electron. In cyclic voltammetry, this one-electron oxidation of **1** and **2** was reversible in $CH_2Cl_2$ (for sweep rates $v > 1$ V $s^{-1}$), whereas in $CH_3CN$ the oxidation was irreversible even at high sweep rates (Fig. 1a shows the absence of any reduction peak). The shape of the oxidation peak and the evolution of the peak parameters ($E_p$ and $I_p$) show clearly that the charge transfer in $CH_3CN$ occurs by an EC (Electrochemical Chemical) mechanism. Indeed $I_{p_a} v^{-1/2}$ is independent of $v$,



Scheme 1. Schematic representation of synthesized arenechromium tricarbonyls ligands. For clarity, only one enantiomer of the *d,l*-isomer mixture of ligands **4a–c** is shown.

and the $E_{p_a}$ (oxidation peak potential) is shifted to more positive potentials on increasing the sweep rate, with a slope of 55 mV/log unit, close to the theoretical value of 60 mV [16]. The chemical step involved was the reaction of the generated radical cation in $CH_3CN$ to give the $[Cr(CO)_3(CH_3CN)_3]\cdot^+$ species, identified by its reversible charge transfer at −0.07 V/SCE (Fig. 1a), as previously observed [12].

*Redox behavior of the **4a**, **4b** and **4c** ligands.* The first oxidation of ligands **4a**, **4b**, **4c** occurred on the arenechromium subunits as indicated by the absence of this wave in the chromium free ligands **5a**, **5b** and **5c**. The first oxidation in **4a–c** occurred in a single two-electron step despite the presence of two arenechromium tricarbonyl subunits. Analysis of the peak potential evolution and shape with sweep rate are typical of a one-electron step, as observed for **1** and **2**, but the peak currents are double that observed for a single arenechromium tricarbonyl subunit. This result indicates the involvement of two almost independent redox centers [17]. As in the case of **1** and **2**, the redox behaviour of **4a–c** is solvent dependent, irreversible in DMF (EC mechanism), and almost reversible in $CH_2Cl_2$ at high sweep rates with $\Delta E_p = E_{p_a} - E_{p_c}$ equal to 80 mV, and $I_{p_c}/I_{p_a}$ equal to 0.9 for **4a**, and to 0.6 for **4b** and **4c** at 10 V $s^{-1}$.

*Copper complexes of ligands **4a**, **4a**, **4c*** (Scheme 2). in the heteropentanuclear complexes $[Cu(\mathbf{4a})_2]^+$, $[Cu(\mathbf{4b})_2]^+$ and $[Cu(\mathbf{4c})_2]^+$ the oxidation of arenechromium tricarbonyl occurred as for **4a–c**. The $Cu^{II/I}$ couple was only observed in dichloromethane for $[Cu(\mathbf{4b})_2]^+$ (Fig. 1b) and $[Cu(\mathbf{4c})_2]^+$, whereas for $[Cu(\mathbf{4a})_2]^+$ the redox

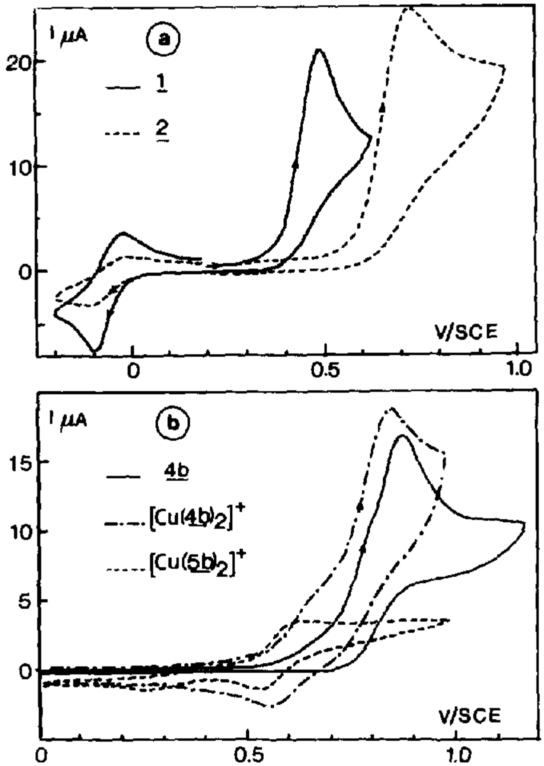
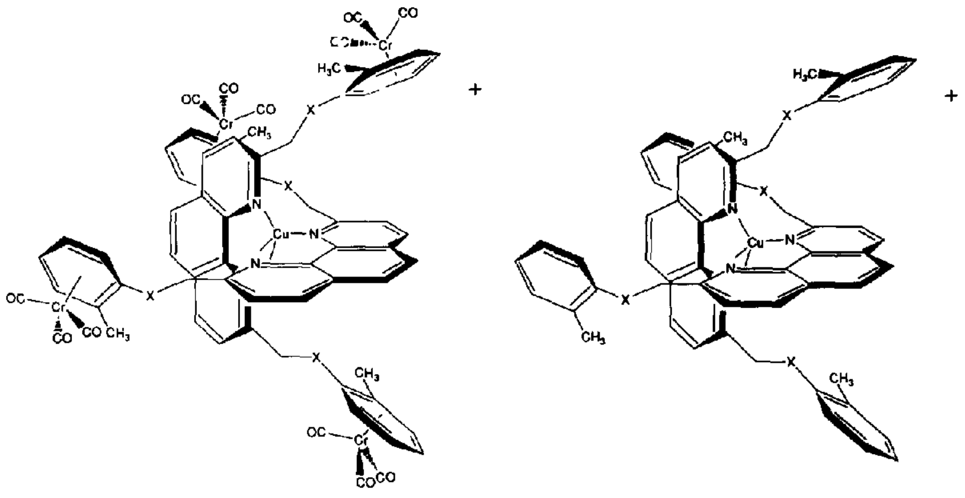


Fig. 1. Cyclic voltammograms of (a) **1** ($c = 6.8 \times 10^{-4}$ mol $l^{-1}$) and **2** ($c = 7.6 \times 10^{-4}$ mol $l^{-1}$) in $CH_3CN + 0.1$ *M* TEAP at $v = 0.5$ V $s^{-1}$; (b) **4b** ($c = 4.7 \times 10^{-4}$ mol $l^{-1}$), $[Cu(\mathbf{4b})_2]^+$ ($c = 2.3.10^{-4}$ mol $l^{-1}$) and $[Cu(\mathbf{5b})_2]^+$ ($c = 2.3.10^{-4}$ mol $l^{-1}$) in $CH_2Cl_2 + 0.1$ *M* TBAP at $v = 0.1$ V $s^{-1}$.

couple was probably located beyond the oxidation of the $Cr(CO)_3$ subunit (Table 1).

*In situ* complexation of **4a**, **4b** and **4c** by copper(II) from $Cu(CF_3SO_3)_2$ gave a deep orange solution characteristic of copper(I) phenanthroline complexes. For example, the FAB$^+$ spectra of the solution in the case of **4a** showed the absence of mass peaks at *m/z* 1593 $[Cu^{II}(\mathbf{4a})_2, CF_3SO_3]^+$ and at *m/z* 1444 $[Cu^{I}(\mathbf{4a})_2]^+$, but the presence of a mixture of copper(I) complexes all obtained by the loss of one or more $Cr(CO)_3$ subunits. Copper(I) was produced in situ by a homogeneous redox process between the copper(II) and the arenechromium tricarbonyl. The generated $[Cr(CO)_3(CH_3CN)_3]^+$ cation was reduced reversibly in $CH_3CN$ as previously observed, at $-0.07$ V/SCE (Fig. 1a). Analogous redox processes have been observed during silver(I) complexation studies [18].

*Copper complexes of the chromium free ligands 5a, 5b, 5c (Scheme 2).* The *in situ* complexation of these ligands by copper(I) in a 2 : 1 ligand : metal ratio gave orange solutions whose FAB$^+$ spectra gave molecular peaks respectively at m/z 899.3 $[Cu(\mathbf{5a})_2]^+$ ($\lambda = 448$ nm, $\epsilon = 5300$ $M^{-1}$ $cm^{-1}$); *m/z* 959.4 $[Cu(\mathbf{5b})_2]^+$ ($\lambda = 447$ nm, $\epsilon = 5800$ $M^{-1}$ $cm^{-1}$); *m/z* 1023.3 $[Cu(\mathbf{5c})_2]^+$ ($\lambda = 455$ nm, $\epsilon = 4800$ $M^{-1}$ $cm^{-1}$). The copper(I) complexes were oxidized in a reversible one-electron step ($\Delta E_p = 60$ mV up to 1 V/s, $I_p$ versus $v^{1/2}$ linear and crossing the origin of the axis on the



$[Cu(4a\text{-}c)_2]^+$ $[Cu(5a\text{-}c)_2]^+$

Scheme 2. Schematic representation of synthesized pentanuclear $Cu^I/Cr^0$ (left-hand side) and mononuclear $Cu^I$ (right-hand side) complexes.

whole sweep rate range). At higher $L/Cu^I$ ratios the redox couple of $[Cu(CH_3CN)_4]^+$ in excess was also observed (Table 1) and the corresponding peak current increased with concentration. This behaviour indicates clearly that these copper(I) complexes have a stoichiometry of two ligands to one copper, as confirmed by $FAB^+$ in

Table 1

Cyclic voltammetry data

| Compound | $CH_3CN + 0.1$ *M* TEAP | | $CH_2Cl_2 + 0.1$ *M* TBAP | |
|---|---|---|---|---|
| | $E°$; $Cu^{II/I}$ (V) | $E_{p_{a1}}$ (0.1 V/s) [a] | $E°$, $Cu^{II/I}$ (V) | $E_1^{\circ}$ [b] (V) |
| $[Cu(CH_3CN)_4]^+$ | +0.98 | – | +0.84 | – |
| **1** | – | +0.47 | – | +0.58 |
| **2** | – | +0.70 | – | +0.77 |
| $[Cu(\mathbf{3})_2]^+$ | +0.65 | – | +0.83 | – |
| **4a** | – | +0.53 | – | +0.55 |
| **4b** | – | +0.75 | – | +0.81 |
| **4c** | – | +0.74 | – | +0.81 |
| $[Cu(\mathbf{4a})_2]^+$ | * [c] | +0.57 | * [c] | +0.57 |
| $[Cu(\mathbf{4b})_2]^+$ | * [d] | +0.75 | +0.62 [e] | +0.80 |
| $[Cu(\mathbf{4c})_2]^+$ | * [d] | +0.73 | +0.65 [e] | +0.79 |
| $[Cu(\mathbf{5a})_2]^+$ | +0.33 | – | +0.38 | – |
| $[Cu(\mathbf{5b})_2]^+$ | +0.42 | – | +0.59 | – |
| $[Cu(\mathbf{5c})_2]^+$ | +0.51 | – | +0.60 | – |

Data obtained at a platinum electrode Potentials vs. SCE. Ferrocene was used as an internal reference and was oxidized reversibly at +0.48 V/SCE in $CH_2Cl_2 + 0.1$ *M* TBAP and at +0.37 V/SCE in $CH_3CN + 0.1$ *M* TEAP under our experimental conditions. [a] Peak potential and [b] formal redox potential of the first oxidation of the arenechromium tricarbonyl. [c] Not observed. [d] Present as an irreversible shoulder on the oxidation peak of the arenechromium tricarbonyl. [e] Observed as a reversible redox couple at low sweep rates.

solution. Alternatively the addition of copper(II) salts to **5c** gave a green solution ($\lambda = 612$ nm, $\epsilon$ 1300 $M^{-1}$ cm$^{-1}$, $\lambda = 357$ nm, $\epsilon = 8800$ $M^{-1}$ cm$^{-1}$) of stable copper(II) complex having a 2/1 ligand copper stoichiometry (*m/z* 1174.0 [Cu(**5c**)$_2$, CF$_3$SO$_3$]$^+$). This Cu$^{II}$ complex was reversibly reduced at the potential at which the corresponding copper(I) complex oxidizes. In the case of ligand **5c** for a 2/1 ligand/copper(I) stoichiometry, only one redox couple is observed at the potential given in Table 1. Upon further addition of copper(I) to the **5c** solution, a second redox couple was observed at +0.34 V/SCE in CH$_3$CN, corresponding to the formation in solution of a new species, whose 1/1 ligand copper stoichiometry was confirmed by FAB$^+$ mass spectroscopy.

The presence of the arenechromium tricarbonyl subunits does not change the copper(I) coordination geometry; the MLCT absorption band for each of the copper(I) complexes of **5a**, **5b** and **5c** is identical with those for **4a**, **4b** and **4c**. Geometric changes towards more square planar [19] or T-shaped copper(I) complexes [20] would shift the bands to the UV. The absence in acetonitrile of the Cu$^{II/I}$ couples in complexes of **4a–c** in contrast to those observed for **5a–c** (Table 1), is probably due to the shift of the Cu$^{II/I}$ couple to more positive potentials, so that the $E°$ of these redox couple is located beyond the oxidation of the chromium tricarbonyl subunits.

Comparison of the potentials in Table 1 shows that the potentials of the Cu$^{II/I}$ couple are more positive in the presence of arenechromium tricarbonyl complexes [Cu(**4a–c**)$_2$]$^+$ than in the [Cu(**5a–c**)$_2$]$^+$ complexes. As was expected, the anodic potential shift of the copper couple in **4a–c** is highest for complex **4a**, since in the latter the copper phenanthroline complex is only separated from the *o*-toluidine-chromium tricarbonyl by a methylene link. Such a potential shift due to the electron-withdrawing effect was previously observed in dinuclear species even with a methylene linkage between the two complexes [4]. However, in the present study a steric contribution to the Cu$^{II/I}$ redox couple cannot be excluded.

Further studies of this new class and related Cu$^{II}$, Co$^{II}$, Mn$^{II}$ complexes are in progress in order to gain more insight into their physico-chemical properties.

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