Unexpected Copper(I) Complexation Behaviour observed in the Synthesis of Novel Polynuclear Chromium(0)–Copper(I) Complexes

Raymond Ziessel[a] **and Jean Suffert**[b]

[a] *Institut Le Bel, Université Louis Pasteur, URA 422 du CNRS, 4, rue Blaise Pascal, 67000 Strasbourg, France*
[b] *EHICS, URA 466 du CNRS, 1, rue Blaise Pascal, 67000 Strasbourg, France*

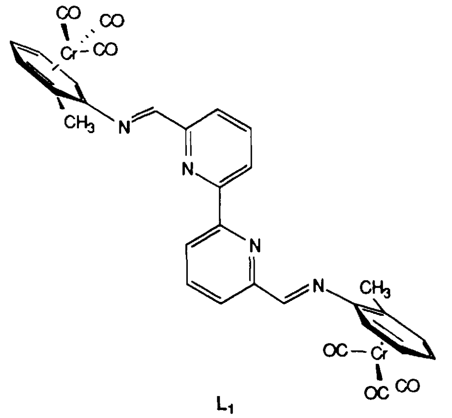
A novel series of penta- and hexa-nuclear chromium(0)–copper(I) complexes, displaying either a two ligand to one copper (thermodynamic product) or a two ligand to two copper (kinetic product) ratio have been synthesized and their properties studied.

Mononuclear copper(I) phenanthroline complexes have been shown to display interesting photophysical properties in both their ground and excited states.[1] With the exception of some halo, carbonyl, or phosphine complexes[2] and one phenanthroline species,[3] all copper(I)–bipyridine or –phenanthroline complexes display a one to two copper to ligand stoicheiometry in a pseudo-tetrahedral geometry. Such complexes have been used recently to prepare metallocatenates,[4] helicates,[5] and a trefoil knot.[6] To our knowledge, however, heteropolynuclear copper(I) complexes have not been studied so far.

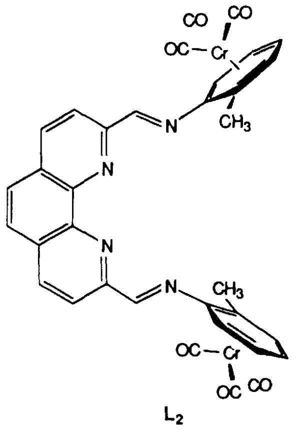
We report here the synthesis, characterization, and spectroscopic properties of novel penta- and hexa-nuclear complexes based on a new family of functionalized tweezer ligands $\mathbf{L_1}$ and $\mathbf{L_2}$ which combine 2,2′-bipyridine (bpy) or 1,10-phenanthroline (phen) with two arenetricarbonylchromium complexes.[7]† Copper complexes of these ligands were readily prepared. Reaction of the deep-orange ligand $\mathbf{L_1}$ (2 equiv.) with $[Cu(CF_3SO_3)]_2\cdot C_6H_6$[8] (0.5 equiv.) in dichloromethane, resulted in an immediate colour change to deep-violet, followed by precipitation of complex $\mathbf{B_1}$ (81%; λ 541 nm, ε 14 900 dm^3 mol^{-1} cm^{-1}). After purification of the mother liquor by column chromatography a second deep-red complex $\mathbf{A_1}$ (14%; λ 462 nm, ε 10 400 dm^3 mol^{-1} cm^{-1}) was isolated. Following the same experimental procedure starting from $\mathbf{L_2}$ complexes $\mathbf{B_2}$ (56%; λ 560 nm, ε 8 970 dm^3 mol^{-1} cm^{-1}) and $\mathbf{A_2}$ (42%; λ 490 nm, ε 10 100 dm^3 mol^{-1} cm^{-1}) were isolated. Complexes $\mathbf{A_1}$ and $\mathbf{A_2}$ correspond by microanalysis to a 2:1 ligand to copper ratio while $\mathbf{B_1}$ and $\mathbf{B_2}$ are species containing a one ligand to one copper stoicheiometry.‡ $\mathbf{A_1}$ and $\mathbf{A_2}$ appear to be the thermodynamic complexation products whereas complexes $\mathbf{B_1}$ and $\mathbf{B_2}$ are the corresponding kinetic species (*vide infra*).

The ^{1}H NMR spectra of complexes $\mathbf{A_1}$ and $\mathbf{A_2}$ show an upfield shift of the H^6 resonance signal of the arenechromium subunit by 1.5 ppm for $\mathbf{A_1}$ and 1.6 ppm for $\mathbf{A_2}$. Such a characteristic shielding is attributed to the ring-current effect of the bpy or phen nucleus which is the result of the ligands being interlocked around the copper cation. Almost no change (compared to ligands $\mathbf{L_1}$ and $\mathbf{L_2}$) in the imine stretchings is observed in the IR spectra of complexes $\mathbf{A_1}$ and $\mathbf{A_2}$ indicating that no co-ordination of the imine occurs. The fast-atom bombardment (FAB) mass spectra of complexes $\mathbf{A_1}$ and $\mathbf{A_2}$ show molecular peaks at *m/z* 1431 and 1388. Spectroscopic studies as well as microanalyses provide strong evidence for the formulation of $\mathbf{A_1}$ and $\mathbf{A_2}$ as pentanuclear complexes.

Surprisingly, the ^{1}H NMR spectra of complexes $\mathbf{B_1}$ and $\mathbf{B_2}$ show only weak shielding of the H^6 resonance signal of the arenechromium subunit, allowing us to propose a new type of complexation. Only one imine signal (deshielded by 0.15 ppm) is observed for $\mathbf{B_1}$ in the ^{1}H NMR spectrum while in the IR spectrum the imine stretching frequency is shifted by 25 cm^{-1} compared to the free ligand $\mathbf{L_1}$. This is consistent with Cu^I co-ordination as previously determined for Cu^I-Schiff's base complexes.[9] The FAB mass spectrum of complex $\mathbf{B_1}$ shows the molecular ion peak at *m/z* 1661 with an isotopic profile indicating two copper atoms and the absence of peaks at higher *m/z* which excludes a slipped polymeric structure. In the case of $\mathbf{B_2}$ two different imine signals (one at a position



$\mathbf{L_1}$



$\mathbf{L_2}$

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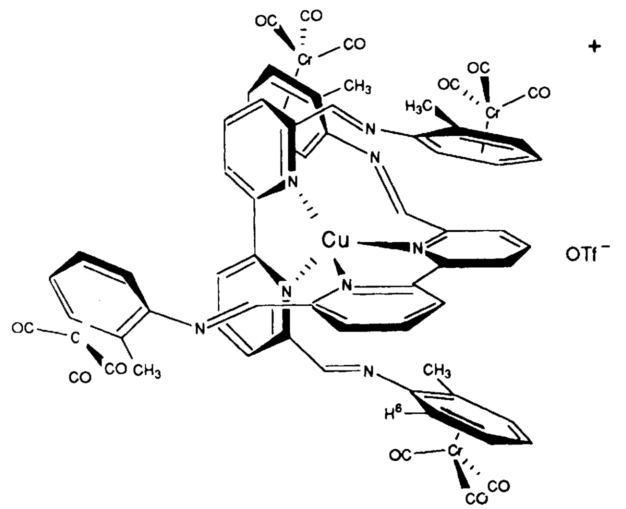
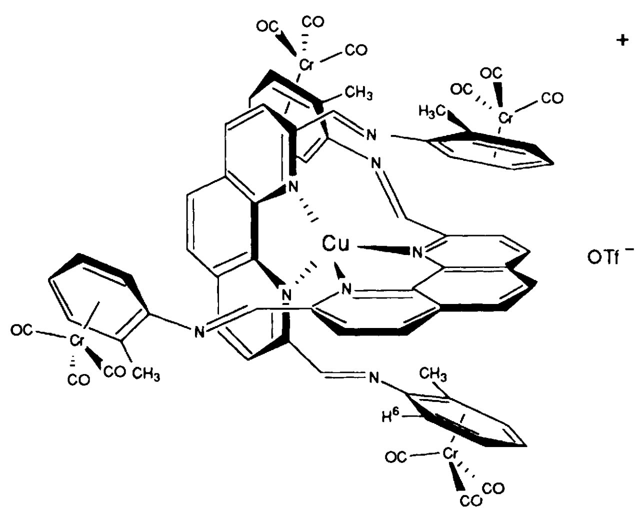
† The synthesis will be reported separately in full. It involves reaction of 2,2′-bipyridine-6,6′-dicarbaldehyde (J. E. Parks, B. E. Wagner, and R. H. Holm, *J. Organomet. Chem.*, 1973, **56**, 53) or 1,10-phenanthroline-2,9-dicarbaldehyde (C. J. Chandler, L. W. Deady, and J. A. Reiss, *J. Heterocycl. Chem.*, 1981, **18**, 599) with (*o*-toluidine)tricarbonylchromium (B. Nicholls and M. C. Whiting, *J. Chem. Soc.*, 1959, 551) in refluxing benzene: $\mathbf{L_1}$ (88%, FAB$^+$ mass spectrum *m/z* 663 $[M + H]^+$); $\mathbf{L_2}$ (82%, FAB$^+$ *m/z* 687 $[M + H]^+$).

‡ Complexes $\mathbf{A_1}$, $\mathbf{A_2}$, $\mathbf{B_1}$, and $\mathbf{B_2}$, isolated as diastereoisomeric mixtures, were characterized by ^{1}H NMR (200, 400 MHz), ^{13}C NMR (50, 100 MHz), IR, UV-VIS, and FAB$^+$ mass spectroscopy and gave satisfactory elemental analyses for C, H, and N.

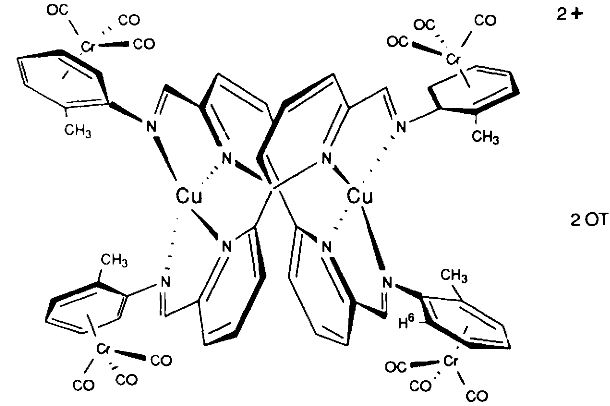


A_1

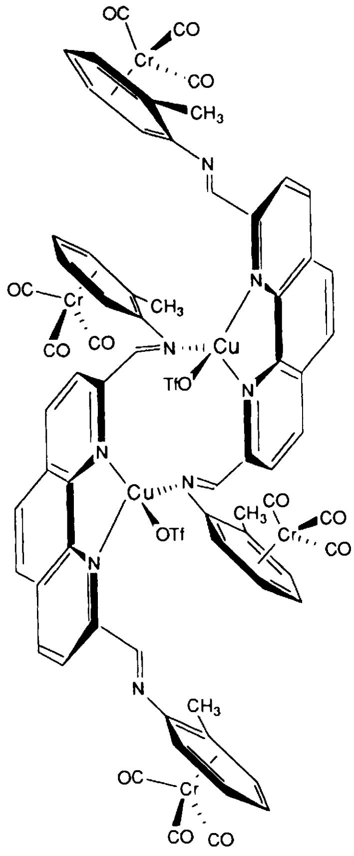


A_2

Tf = CF_3SO_2



B_1



B_2

close to that of L_2 and the second deshielded by 0.19 ppm) were observed in the ^1H NMR spectrum, while in the IR spectrum two different imine stretching frequencies of equal intensity (one being at the same frequency as ligand L_2 and the other shifted by 35 cm^{-1}), as well as a co-ordinated sulphonate group were detected.[10] The FAB mass spectrum also gave a molecular ion peak at *m/z* 1649 with a pattern typical of the presence of two copper atoms. From these combined spectroscopic analyses it appears that the unexpected products $\mathbf{B_1}$ and $\mathbf{B_2}$ are the hexanuclear complexes containing: for $\mathbf{B_1}$, two twisted bpy and two copper(I) cations, each co-ordinated to the imine of the bridge and to one pyridine of the bpy ligand; for $\mathbf{B_2}$, two copper(I) cations, each of which is chelated by one phen ligand and one imine of the second phen ligand.

Corey–Pauling–Koltun (CPK) molecular models of $\mathbf{B_1}$ showed that a 2:2 copper:bpy ligand stoicheiometry is allowed only if a helical arrangement is adopted.[11] Owing to ligand rigidity the phen cannot twist and hence $\mathbf{B_2}$ gives rise to a ladder complex. On dissolving $\mathbf{B_1}$ and $\mathbf{B_2}$ in CD_3CN, clean conversion to $\mathbf{A_1}$ and $\mathbf{A_2}$ (thermodynamic species) can be followed by ^{1}H NMR and UV–VIS absorption spectroscopy. Only $\mathbf{A_1}$ and $\mathbf{A_2}$ were isolated when the reaction was carried out in a more polar solvent.

If the bridge between the bpy or phen subunit and the arenetricarbonylchromium is NH, OCH_2, or SCH_2 none of the kinetic products is isolated. These observations corroborate the fact that $\mathbf{B_1}$ and $\mathbf{B_2}$ formation is feasible only when Cu^I–imine interactions are present.

Work in progress is aimed at the synthesis of the corresponding optically pure copper complexes as well as the preparation of new polyimine ligands based on, *e.g.* 1,8-naphthyridine and 1,9,10-anthyridine in place of bpy or phen.

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