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Synthesis and Characterization of Homoleptic Copper(I) Complexes with New 1,4,5,8-Tetraazaphenanthrene Derivatives.

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Abstract. The copper(I) complexes of several tetraazaphenanthrene derivatives have been synthesized and characterized. The entwined topography of these complexes in solution has been studied by ^{1}H NMR spectroscopy.

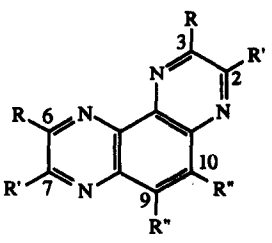
In their work on copper(I) complexes, McMillin and Sauvage observed that ring substituents have a pronounced effect on the excited state lifetimes of 1,10-phenanthroline (phen) complexes [1]: when the metal is well shielded against solvation, the electronically excited state has a longer lifetime [2].

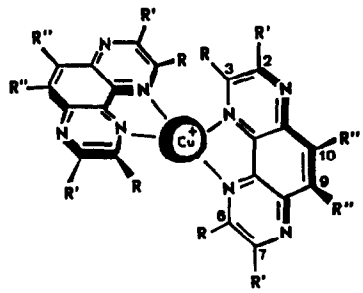
In connection with these results, it is interesting to realize a study of copper(I) complexes with substituted 1,4,5,8-tetraazaphenanthrene (TAP) ligands, taking into account the fact that the two additional nitrogen atoms on each of the two complexed tetraazaphenanthrenes enhance the oxidizing properties of the complexes as compared to their phenanthroline counterparts [3]. For this purpose, we need copper(I) complexes made with different substituted tetraazaphenanthrenes and having the same counter-ion.

Here, we report the synthesis and the characterization of five copper(I) complexes of substituted TAP. The applied procedure is similar to the one used by Sauvage [4] : the complexes $Cu(LL)_2^+BF_4^-$ are obtained by mixing one equivalent of $Cu(CH_3CN)_4BF_4$ **6** (prepared by the literature method [5]) with two equivalents of LL (LL = a chelate). The complexation of **6** with 3,6-dimethyl-1,4,5,8-tetraazaphenanthrene (dmTAP) **1a** (prepared as previously reported [6]), performed under argon in CH_2Cl_2/CH_3CN (1/1) at room temperature, leads to 68 % yield of $Cu(dMeTAP)_2^+BF_4^-$ **1b** as deep red crystals, recrystallized from EtOH, which are characterized by ^{1}H NMR.

The same procedure applied to 2,3,6,7-tetramethyl-1,4,5,8-tetraazaphenanthrene (tmTAP) **2a** [7] and 2,3,6,7,9,10-hexamethyl-1,4,5,8-tetraazaphenanthrene (hmTAP) **3a** (the synthesis of the ligand **3a** is described in note 8) gives a 89 % yield of $Cu(tmTAP)_2^+BF_4^-$ **2b** as orange-red fine needles and a 74 % yield of $Cu(hmTAP)_2^+BF_4^-$ **3b** as red fine needles.

In a similar way, we focused on more bulky substituents and prepared $Cu(tpTAP)_2^+BF_4^-$ **4b** (81% yield, black crystals) from 2,3,6,7-tetraphenyl-1,4,5,8-tetraazaphenanthrene (tpTAP) **4a** [7] and $Cu(dmtpTAP)_2^+BF_4^-$ **5b** (83 % yield, deep red crystals) from 2,3,6,7-tetraphenyl-9,10-dimethyl-1,4,5,8-tetraazaphenanthrene (dmtpTAP) **5a** (the synthesis of **5a** is reported in note 9).





1a,b : R=Me R'=R"=H
2a,b : R=R'=Me R"=H
3a,b : R=R'=R"=Me
4a,b : R=R'=Ph R"=H
5a,b : R=R'=Ph R"=Me

The chemical shifts in ^1H NMR of the ligands **1a-3a, 4a, 5a** and their homoleptic complexes are collected in tables I, II and III respectively [10]. For the compounds **3a** and **3b**, the assignments are based on high resolution spectra and irradiation of the most shielded peak, showing the ^5J coupling between CH_3 3,6 and CH_3 2,7.

Complexation shifts, defined as the difference between the chemical shifts of identical sites of the complex and the ligand, are also mentioned in the tables I to III. These shifts extend from a deshielding of 0,40 ppm to shieldings of 0,9 ppm.

In the series of methylated TAP complexes, both the ligands and the complexes show three singlets.

Compound	dmTAP **1a** and $Cu(dmTAP)_2^+$ **1b**			tmTAP **2a** and $Cu(tmTAP)_2^+$ **2b**			hmTAP **3a** and $Cu(hmTAP)_2^+$ **3b**		
Protons	$CH_{3_{3,6}}$	$H_{2,7}$	$H_{9,10}$	$CH_{3_{3,6}}$	$CH_{3_{2,7}}$	$H_{9,10}$	$CH_{3_{3,6}}$	$CH_{3_{2,7}}$	$CH_{3_{9,10}}$
L	2,97	8,94	8,23	2,92	2,82	8,14	2,88	2,81	2,86
$Cu(L)_2^+$	2,55	9,30	8,52	2,52	2,91	8,33	2,45	2,89	2,96
$\Delta\delta$	-0,42	+0,36	+0,29	-0,40	+0,09	+0,19	-0,43	+0,08	+0,10

Table I : Chemical Shifts and Complexation Shifts ($\Delta\delta$) in the Series PolymethylTAP.

For these three compounds (table I), the complexation induces a constant shielding for the protons of the substituent in ortho position of the coordination site ($-0,43 < \Delta\delta < -0,40$ ppm), similar to that found for $Cu(dmp)_2^+$ [11] ($\Delta\delta$ = -0,44 ppm; dmp = 2,9-dimethyl-1,10-phenanthroline) and $Cu(bcp)_2^+$ ($\Delta\delta$ = -0,38 ppm ; bcp = bathocuproïne). In the same way, the downfield shift induced on $H_{2,7}$ ($\Delta\delta$ = +0,36 ppm) by complexation is identical to the deshielding induced on the analogous positions 3 and 8 of $Cu(bcp)_2^+$ ($\Delta\delta$ = +0,35 ppm).

Concerning the TAPs with more bulky substituents, the complexation induces upfield shifts of aromatic protons on position 3 and 6, similarly to the shifts observed for $Cu(dpp)_2^+$ [11] ($\Delta\delta$ (H_o) = -1,02 ppm ; $\Delta\delta(H_m)$ = -1,08 ppm ; $\Delta\delta(H_p)$ = -0,73 ppm ; dpp = 2,9-diphenyl-1,10-phenanthroline). The deshielding on substituent 9 and 10 (+0.09 ppm) in **5b** is the same as observed for **3b** (+0.10 ppm). The different effects responsible for these important shifts are explained in a detailed ^1H NMR study published by Dietrich-Buchecker and coll. [11] about copper(I) complexes with phenanthroline derivatives. The conclusions of that paper can be extended to complexes with substituted tetraazaphenanthrenes. Specially, the shielding on positions 3 and 6 arising from the intense ring current effect of the TAP nuclei indicates that the two substituents of one TAP are located respectively above and below the other TAP plane of the other coordinate.

Compound	H_o	H_m	H_p	$H_{o'}$	$H_{m'}$	$H_{p'}$	$H_{9,10}$
tpTAP **4a**	7.71	7.37	7.37	7.64	7.37	7.37	8.37
$Cu(tpTAP)_2^+$ **4b**	6.92	6.59	6.84	7.44	7.34	7.34	8.51
$\Delta\delta$	-0.79	-0.78	-0.53	-0.20	-0.03	-0.03	+0.14

Table II: Chemical Shifts and Complexation Shifts ($\Delta\delta$) for tpTAP.
o,m,p represent the ortho, meta and para positions of the phenyl group located on the positions 3 and 6 of the TAP ; o', m' and p' represent the ortho, meta and para positions of the phenyl group located on positions 2 and 7 of the TAP.

Compound	H_o	H_m	H_p	$H_{o'}$	$H_{m'}$	$H_{p'}$	CH_3
dmtpTAP **5a**	7.74	7.37		7.74	7.37		2.99
$Cu(dmtpTAP)_2^+$ **5b**	6.86	6.55	6.79	7.46	7.33		3.08
$\Delta\delta$	-0.88	-0.82	-0.58	-0.28	-0.04		+0.09

Table III: Chemical Shifts and Complexation Shifts ($\Delta\delta$) for dmtpTAP.
o,m,p represent the ortho, meta and para positions of the phenyl group located on the positions 3 and 6 of the TAP ; o', m' and p' represent the ortho, meta and para positions of the phenyl group located on positions 2 and 7 of the TAP.

The synthetic method described in the present report allowed the fast and efficient preparation of copper(I) complexes with polysubstituted tetraazaphenanthrenes. The topography of these complexes in solution has been confirmed by ^1H NMR. Indeed, comparative measurements of chemical shifts clearly demonstrate that the two TAP derivatives are entwined around the copper, leading to complexes containing a metal efficiently protected from its environment.

The photochemical and electrochemical properties of these complexes are under progress and will be described in a further publication.

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8. 2,3-dimethyl-4,6-dinitroaniline **7** is reduced by hydrazine and Pd/C to afford 2,3-dimethyl-4-nitro-o-phenylenediamine **8** (crystallized from benzene ; 58% yield ; m.p.: 160-162°C). **8** is condensed with diacetyl in EtOH providing 2,3,5,6-tetramethyl-7-nitroquinoxaline **9** (crystallized from MeOH/H_2O ; 82% yield ; m.p.: 147-148°C) which reacts readily with hydroxylamine in alkaline medium to give 5-amino-6-nitro-2,3,7,8-tetramethylquinoxaline **10** (crystallized from MeOH ; 55% yield ; m.p.: 176-177°C). 2,3,6,7,9,10-hexamethyl-1,4,5,8-tetraazaphenanthrene **3a** is obtained by reducing **10** with hydrazine and Pd/C in 5,6-diamino-2,3,7,8-tetramethylquinoxaline **11** (sublimation ; 94% yield ; m.p.: 170-171°C) and condensing **11** with diacetyl (**3a** : crystallized from MeOH ; 86% yield ; m.p. : 255-257°C).
9. **5a** is obtained similarly to **3a**. Condensing **8** with benzil in EtOH results in the formation of 2,3-diphenyl-5,6-dimethyl-7-nitroquinoxaline **12** (crystallized from EtOH ; 98% yield ; m.p.: 180-182°C) which is aminated by hydroxylamine to afford 5-amino-6-nitro-7,8-dimethyl-2,3-diphenylquinoxaline **13** (crystallized from EtOH ; 68% yield; m.p.: 194-195°C). **13** is reduced by hydrazine and Pd/C in EtOH and the diaminated product **14** (crystallized from benzene ; 97% yield; m.p.: 216-218°C) condensed with benzil to give **5a** (crystallized from AcOH/H_2O : 84% yield ; m.p.:269-270°C).
10. ^1H NMR spectra were recorded with a Bruker Cryospec WM spectrometer at 250 MHz. Chemical shifts, relative to internal TMS, are given in ppm.
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