First Direct Synthesis of a *trans*-III Complex of Tetramethylcyclam − Physicochemical Characterization, Electrochemistry and X-ray Crystal Structure of 1,4,8,11-Tetramethyl-1,4,8,11-tetraazacyclotetradecane Copper(II) Bistetrafluoroborate

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Keywords: Macrocycles / N ligands / Copper / Structure elucidation / Electrochemistry

We report the first direct synthesis of a *trans*-III copper(II) complex of tetramethylcyclam. This new derivative is hexacoordinate in the solid state and square planar in solution. Reduction of this latter leads to a complex voltammetry pattern which could be explained considering an isomerization process.

Introduction

N-substituted polyazamacrocycles have several potential applications: *N*-substituted cyclams, which represent the most widely studied series of tertiary amine macrocycles can be used for medical purposes,[1,2] treatment of water wastes containing heavy metals,[3] or catalysis.[4] Therefore the understanding of the influence of *N*-substitution of the ligand on the coordination mode still remains an important field of interest.

The *N,N′,N′′,N′′′*-tetramethylcyclam derivative (tmc) was first obtained by Barefield and co-workers in the early 70′s.[5,6] A recently described alternative to this seminal synthesis involves the reduction of a bisammonium salt of the bisaminal 1,4,8,11-tetraazatricyclo[9,3,1,1^{4,8}]hexadecane and allows the preparation of tmc without further purification with an overall yield of ca. 80% starting from cyclam.[7]

Metallation of tmc by transition metal ions systematically led to five-coordinate type-I isomers[8] with all substituents (methyl groups and metal axial ligand) pointing in the same direction. This geometry, first suggested by UV/Vis spectroscopy, has since been confirmed by X-ray diffraction studies of numerous tmc complexes of Ni^{II},[9,10] Cu^{II},[11] Fe^{II},[12] Zn^{II},[13] and Co^{II}.[14] Although different conformations were reported for the macrocycle, the isomers were all characterized by the pentacoordination of a metal ion located above the macrocyclic cavity, and bearing one axial ligand, either an anion or a neutral coordinating solvent molecule. Type-III isomers could, until now, only be obtained by tetramethylation of the easily available cyclam type-III homologues;[15,16] clean isomerisation of type-I to type-III isomers could not be achieved, although an interconversion process restricted to nickel species in strongly coordinating solvent has been reported.[9,10,17,18]

Results and Discussion

We report here the first direct synthesis of a type-III $[tmcCu]^{2+}$ starting from the free ligand and the metallic salt: indeed, when tmc was dissolved in a refluxing solution of sodium hydroxide in water followed by addition of copper bis(tetrafluoroborate), only the type-III $[(tmc)Cu](BF_4)_2$ isomer was isolated (See Experimental Section). UV/Vis spectroscopic data correspond to a type-III square-planar (N_4) structure in solution, whereas a *trans*-III configuration with two BF_4^- counterions coordinated to the copper ion could be established in the solid state by X-ray crystallography (see below). Since complexation in water at room temperature affords the pentacoordinated I isomer, it appears that the temperature and basicity of the reaction medium are the key parameters responsible for the stereochemistry of the complexation; a very similar observation has been reported in the case of *N,N′*-difunctionalised derivatives.[19]

The visible spectrum of $(tmc)Cu^{2+}$ is rather insensitive to the nature of the solvent; shifting from coordinating (water) to noncoordinating (nitromethane) solvents led to a shift of λ_{max} from 558 to 530 nm and ε from 193 to 142. This fact suggests that the solvent does not take place in the first coordination sphere and leads us to propose a square-planar (N_4) coordination scheme for $[(tmc)Cu](BF_4)_2$ in solution. These data are close to those observed for related copper complexes known for their square-planar geometry. For example, Elias et al. and Delgado et al. reported absorption maxima (epsilon values) of 520−600 nm (131−139), and 580 nm (192), respectively.[20−22] Moreover, these values differ significantly from those obtained for pen-

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tacoordinate tmc copper complexes ($\lambda_{max} \approx 690$ nm, $\varepsilon \approx 260$)[23] and hexacoordinate cyclam copper complexes ($\lambda_{max} = 586-620$ nm, $\varepsilon \approx 50$).[19]

Conversely, in the solid state, the complex exhibits a hexacoordinate *trans*-III geometry. The asymmetric unit (see ORTEP[24] view in Figure 1) is composed of one half of the complex (with the Cu^{2+} cation lying on an inversion centre) and a BF_4^- anion. The complex presents a distorted octahedral geometry with the copper atom located in the N_4 plane and a fluorine atom coordinating the latter in an axial position on both sides of the macrocycle.

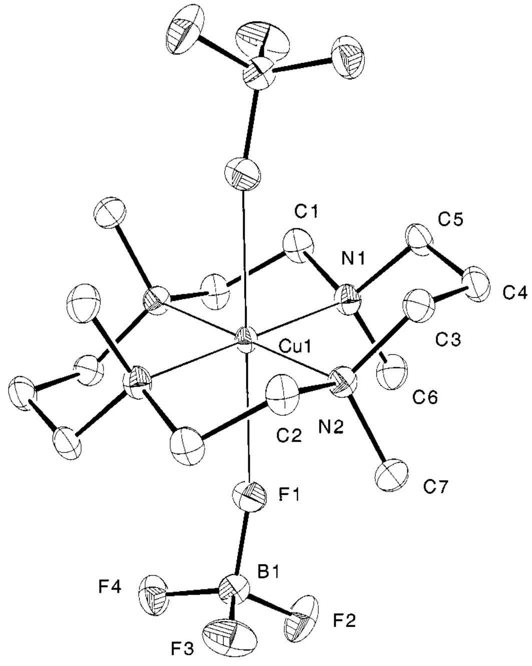

Figure 1. ORTEP drawing of *trans*-III [(tmc)Cu]$(BF_4)_2$; the thermal ellipsoids are at the 50% probability level

The anion coordination is evidenced by the distance F1−Cu (2.529 Å), the almost four right angles F1−Cu−N ($89.30 < \alpha < 90.70°$) and the longer distance B−F1 (1.421 Å) when compared to the other three B−F bond lengths (1.376−1.386 Å). The equatorial Cu−N distances are almost equivalent [2.074(1) and 2.077(1) Å] and the N−Cu−N angles are close to right angle values [86.89(5) and 93.11(5)°]. The N−C and C−C distances range from 1.489 to 1.497 Å and from 1.513 to 1.526 Å, respectively, indicating a very small dispersion around their respective mean values 1.493(5) and 1.519(5) Å. All bond lengths and angles are comparable to typical values found in the literature for this kind of complex.[25] The six- and five-membered rings building the complex have chair and envelope conformations, respectively.

Electrochemical reduction of this type-III [(tmc)Cu]$(BF_4)_2$ dissolved in acetonitrile leads to a complex voltammetry pattern. The reduction happens at a rather high potential (−0.41 V vs. SCE, 2 V/s), in agreement with the general trend of tmc ligands stabilising lower oxidation states than unsubstituted cyclam; however, the reduction wave remains chemically irreversible even at potential scan rates as high as 2000 V s^{-1} and a new redox couple appears at $E^0 = -0.28$ V as shown in Figure 2. This clearly establishes that the initially formed type III $[(tmc)Cu]^+$ has a lifetime shorter than 50 µs and very rapidly evolves to another copper(I) species that is fairly stable on the cyclic voltammetry time scale, as evidenced by its chemically reversible oxidation wave (Figure 2A). At longer time scales, corresponding to slow cyclic voltammetry, this new Cu^I species also undergoes a rearrangement to yield a third form of $[(tmc)Cu]^+$, the reversible oxidation of which now takes place around $E^0 = +0.07$ V (Figure 2B).

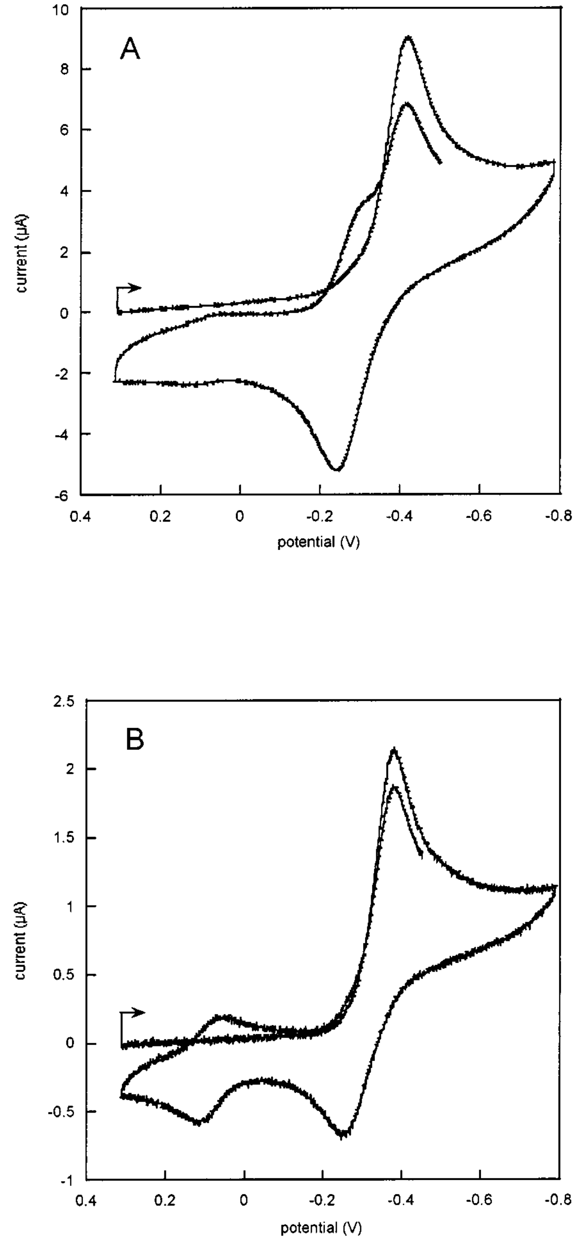

Figure 2. Cyclic voltammograms of a 2 mm solution of type-III [(tmc)Cu]$(BF_4)_2$ in acetonitrile 0.1 M nBu$_4$N(BF_4) recorded at a platinum disc electrode (0.5 mm diameter) at room temperature; potential scan rate 10 V/s (A) and 0.5 V/s (B)

This general pattern is reminiscent of what has been observed and described for a related *trans*-III derivative of copper(II) coordinated to a hexadentate tetra-*N*-substituted cyclam derivative.[19] In the latter case, the observation of two subsequent isomerisations of the initial copper(I) complex has been attributed to partial decoordination associated with a modification from a type-III to a type-I configuration. Further investigations concerning the assignment of the structure of the electrogenerated (tmc)Cu$^+$ derivatives are required to confirm the analogy and establish the occurrence of a related type-III to type-I transformation process taking place at the level of the tmc copper(I) derivative.

Work is in progress to clearly establish the influence of the experimental conditions (pH, temperature, ...) on the stereochemistry of tetra-*N*-substituted cyclam complexes.

Experimental Section

General: UV/Vis spectroscopic data were collected on a Varian Cary 5 spectrophotometer. Mass spectra were recorded on a Bruker ProFlex III MALDI/TOF mass spectrometer using dithranol as matrix. X-ray diffraction data were collected on an Enraf−Nonius Kappa-CCD diffractometer equipped with an Oxford Cryostream low temperature device.

All the electrochemical experiments were run under argon. $n\mathrm{Bu_4NBF_4}$ was used as the supporting electrolyte; it was obtained from $n\mathrm{Bu_4N(HSO_4)}$ and $\mathrm{NaBF_4}$, recrystallized from ethyl acetate/hexane and dried at 60 °C under vacuum.

Cyclic voltammetry experiments were performed in an air-tight, three-electrode cell connected to a vacuum line. The reference electrode was SCE (Tacussel) separated from the solution by a bridge compartment filled with the same solvent supporting electrolyte solution as that used in the cell. The counter electrode was a platinum spiral wire with ca. 1 cm^2 apparent surface area. The working electrodes were disks obtained from cross sections of gold wires (diameters 25 to 500 μm). An EG & G PAR-175 signal generator was used; the potentiostat was home-made, with a positive feedback loop for ohmic drop compensation. The currents and potentials were recorded on a Nicolet 310 oscilloscope.

[(tmc)Cu](BF$_4$)$_2$: Tetramethylcyclam (0.64 g, 2.5 mmol) and NaOH (0.3 g, 7.5 mmol) in 20 mL of water were heated under stirring at 90 °C. $\mathrm{Cu(BF_4)_2{\cdot}H_2O}$ (0.64 g, 2.5 mmol) was then added. The mixture was stirred at 90 °C for one hour. After filtration and slow evaporation of the solvent, purple crystals of *trans*-III $\mathrm{[(tmc)Cu](BF_4)_2}$ suitable for an X-ray study were collected (0.62 g, 50%). − MS (MALDI/TOF): m/z = 319 [(tmc)Cu]$^+$. − $\mathrm{C_{14}H_{32}B_2CuF_8N_4}$ (493.58): calcd. C 34.07, H 6.53, N 11.35; found C 34.48, H 6.22, N 11.33.

X-ray Crystallographic Study: Crystal data for $\mathrm{[C_{14}H_{32}N_4Cu][2(BF_4)]}$, dark blue prismatic crystal of dimension 0.42 × 0.20 × 0.14 mm, M = 493.60, monoclinic, space group $P2_1/n$, $Z = 2$, a = 8.9279(3) Å, b = 9.2302(2) Å, c = 12.6028(4) Å, β = 91.55(1)°, U = 1038.17(5) Å^3, D_c = 1.579 g cm^{-3}, T = 130(2) K, $F(000)$ = 510, Mo-K_α radiation (λ = 0.71073 Å), μ = 1.130 mm^{-1}, 16925 reflections measured in the range 2.74° ≤ θ ≤ 30.02°, with 3016 being unique (R_int = 0.0752) which were used in all calculations. The structure was solved by direct methods and refined using full-matrix least-squares on F^2 to $R1$ = 0.0330, S = 1.009, for 2548 reflections with $I > 2\sigma(I)$ and 133 refined parameters, $wR2$ (all data) = 0.0805. Programs used: SHELXS-97 for structure determination and SHELXL-97 for refinement (G. M. Sheldrick, University of Göttingen).

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-150973. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

This work was supported by grants from the French Ministry of Research (MENRT) and CNRS (UMR 5633, UMR 8640). The authors are also grateful to M. Soustelle for assistance in the synthesis of the tmc precursor.

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Received October 30, 2000
[I00413]