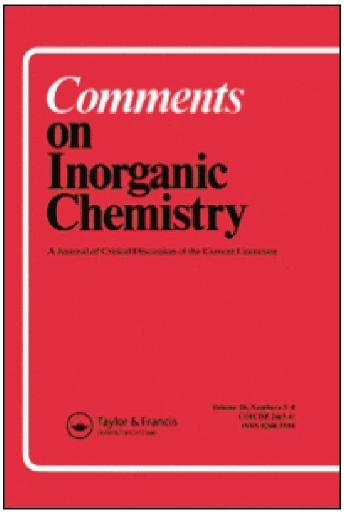

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Structural, Geometrical and Configurational Changes in Metal Complexes of Tetraazamacrocycles with a Pendant Donor Group

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Structural, Geometrical and Configurational Changes in Metal Complexes of Tetraazamacrocycles with a Pendant Donor Group

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Metal complexes of mono-functionalized tetraazamacrocycles show a pH-dependent equilibrium, in which the donor group of the side chain can either bind to the metal ion or not. The structural changes of the metal macrocyclic moiety which take place in this reaction are discussed, and it is shown that the structural problems associated with it are manifold: there are examples in which neither the coordination geometry around the metal ion nor the configuration of the macrocycle are altered; there are cases in which the coordination number of the metal ion is increased, since an additional metal to ligand bond is formed with the side chain donor group, thus giving a new coordination geometry; and finally there is one example in which a drastic rearrangement of the whole metal macrocyclic unit occurs, to give a geometrical and a configurational change.

Key Words: *mono-functionalized tetraazamacrocycles, structural changes, pendant group, copper(II) complexes, nickel(II) complexes*

The field of macrocyclic ligands and of their metal complexes is extremely wide and the developments in it have taken manifold directions.[1] One of these has been the functionalization through the introduction of side chains, which modify the complexation properties of these ligands. Derivatives of crown ethers,[2] of N,O-macrocycles[3] and of cyclic polyaza compounds[4] have been described in the literature.

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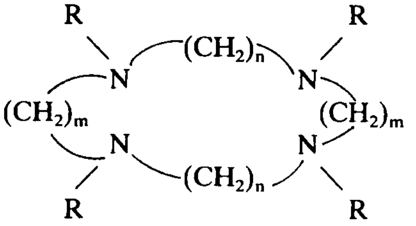
Beside exhibiting several interesting features and application possibilities, functionalized macrocycles are compounds on which the coordination chemist can study structural effects when the donor group present in the side chain binds to the metal ion. Whereas these aspects have extensively been studied for complexes with tetrasubstituted tetraazamacrocycles such as **1**,[5] less has been done for monosubstituted derivatives, probably because the synthesis of such compounds is more demanding than that of the tetrasubstituted ones.



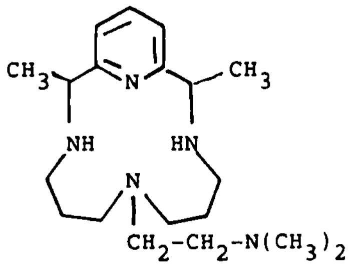
1

R = CH_2-$COOH^{5a}$
R = CH_2-CH_2-NH^{5b}
R = CH_2-CH_2-CN^{5c}
R = CH_2-CH_2-OH^{5d}
m,n = 2 and/or 3

The aim of this Comment is to cover the structural results of metal complexes of monosubstituted tetraazamacrocycles and to discuss geometrical and configurational changes which can take place when the side chain is involved in the coordination to the metal ion through its functional group.

SOLUTION CHEMISTRY AND EQUILIBRIA

Since the discovery of the pH-induced geometry change in the Ni^{2+} complex with **2**,[6]



2

many more examples of this reaction in metal complexes of mono-functionalized tetraazamacrocycles have been described.[7] The on/off equilibrium (1)

(1)

is a direct consequence of the differential reactivity of the macrocyclic unit, which being relatively rigid and kinetically inert, is not displaced from the metal ion by acid addition, and of that of the flexible and kinetically labile side chain functional group, which easily can undergo acid induced dissociation.

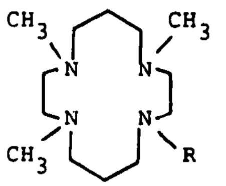
By considering equilibria such as (1), one automatically asks the question, what happens to the macrocyclic unit and to the coordination geometry of the metal ion when the new bond between M and X is formed? In a first approximation one can assume that because of the relatively high inertness of the coordinative bonds of the macrocycle, little or even nothing is going to change. However, let us consider reaction (1) in more detail. A new bond is formed with the donor group X of the side chain and this implies that the overall geometry and, therefore, also the energy of the electronic states must change. In addition, through the coordination of the donor group X, additional steric interactions result, which also could modify the conformation and/or configuration of the macrocycle, since tetraazacycloalkanes are relatively flexible and can adapt themselves to such steric constraints.

It is clear that questions like these cannot be solved by studies in solution, but only through structural results obtained by X-ray diffraction analysis.

STRUCTURAL ASPECTS IN THE SOLIDS

In the literature the structures of several tetraazamacrocycles carrying a side chain able to coordinate, such as derivatives of 1,4,8-trimethyl-1,4,8,11-tetraazacyclotetradecane (trimethylcyclam), derivatives of 1,4,8,11-tetraazacyclotetradecane (cyclam), and derivatives of 1,4,7,11-tetraazacyclotetradecane (iso-cyclam) have been described. In most cases the structure of the parent compound and that of the functionalized derivative are both available so that a direct comparison of the geometrical environment of the metal ion and of the macrocycle configuration is possible.

The first examples we shall discuss are the Cu^{2+} complexes of mono-N-functionalized derivatives of trimethylcyclam, a macrocycle with tertiary amino nitrogens.



3 R = CH_3

4 R = $CH_2-CH_2-COOEt$

5 R = $CH_2-CH_2-PO(OEt)_2$

In the parent compound **3** the trans-I configuration[8] of the macrocycle is found and the metal ion is displaced from the best plane of the four nitrogens by 0.220 Å.[9] The Cu^{2+} is pentacoordinated by the four nitrogens of the macrocycle and one water molecule. The geometry is somewhere between a square pyramidal and a trigonal bipyramidal one (Fig. 1(a)). The N_1-Cu-N_3 angle is nearly linear with 178.1°, whereas the N_2-Cu-N_4 angle is 154.6°.

The structures of two Cu^{2+} complexes with a carboxylate (**4**) and phosphonate (**5**) ester side chain have also been characterized by X-ray diffraction measurements.[10] In both cases the Cu^{2+} is as in the parent macrocycle **3** pentacoordinate, surrounded by the four nitrogens of the macrocycle and an oxygen of the functional group of the side chain (Fig. 1(b)). The geometry can be described either by a distorted square pyramid or a distorted trigonal bipyr-

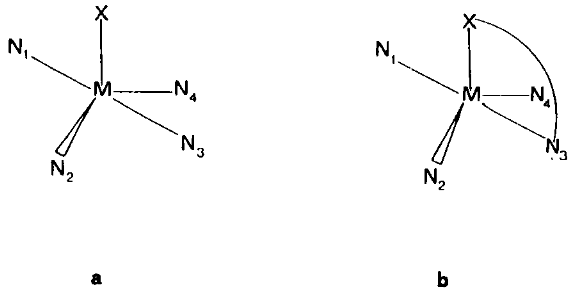
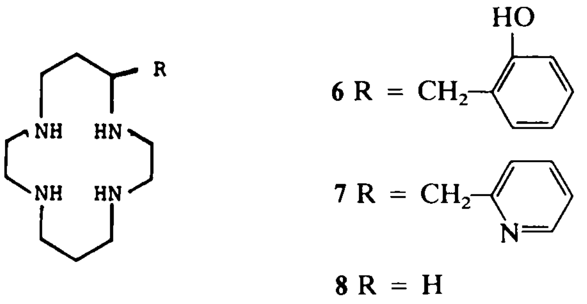


FIGURE 1 Structures of the parent compound $Cu(\mathbf{3})^{2+}$ (a) and of the two pendant arm complexes $Cu(\mathbf{4})^{2+}$ and $Cu(\mathbf{5})^{2+}$ (b).

amid. The best plane through the four nitrogens shows deviations of ± 0.22 Å and ± 0.24 Å for Cu(**4**)$^{2+}$ and Cu(**5**)$^{2+}$, respectively. In addition the Cu^{2+} is out of this plane by 0.21 Å and 0.30 Å for Cu(**4**)$^{2+}$ and Cu(**5**)$^{2+}$, respectively, in the direction of the apical oxygen. As in **3** we have a nearly linear arrangement for N_1–Cu–N_3 (178.9° and 176.9°, respectively). However, the angles in the equatorial plane differ considerably from the ideal one. The largest deviation is found for N_2–Cu–N_4 with 155.8° and 149.9°, respectively. The macrocycle is folded along the N_1–Cu–N_3 axis and assumes the trans-I configuration with all nitrogen substituents on the same side of the four nitrogen plane. These examples show that for such Cu^{2+} complexes the coordination of a side chain does not significantly alter the geometry around the metal ion nor the conformation of the macrocycle, although one would expect that an additional steric interaction between the side chain and the three methyl groups could arise because of the trans-I configuration.

The second group includes cyclam derivatives with a side chain starting from a carbon atom of the macrocyclic ring.



The structures of two Ni^{2+} complexes with a phenolate **6**[11] and a pyridine **7**[12] in the pendant group have been described by Kimura *et al.* and can be compared with the Ni^{2+} complex of the parent compound cyclam **8**.

The geometry around the Ni^{2+} ion in the complex with **6** has been described as square pyramidal with four nitrogen donors in the basal plane and the phenolate oxygen apically bound.[11] However, there is a perchlorate oxygen at 2.402 Å in the other apical position so that a distorted octahedral geometry results (Fig. 2(b)).

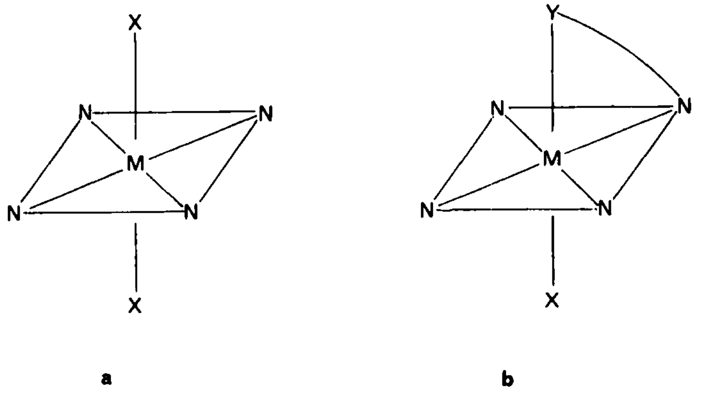
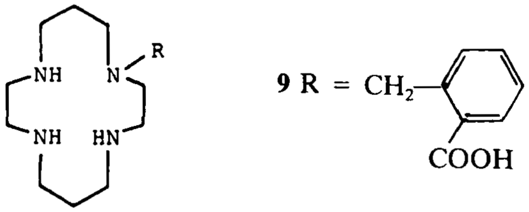


FIGURE 2 Structures of the parent compound Ni(**8**)$^{2+}$ (a) and of the two pendant arm complexes Ni(**6**)$^{2+}$ and Ni(**7**)$^{2+}$ (b).

The Ni–N bonds are between 2.05 and 2.08 Å, whereas that to the phenolate oxygen is somewhat shorter, 2.015 Å. Interestingly, the four nitrogens and the Ni^{2+} ion are coplanar and the macrocycle assumes the trans-III configuration. The structure of the Ni^{2+} complex with the methylpyridine side chain 7[12] is very similar to that just described. The Ni^{2+} is in a distorted octahedral arrangement coordinated by the four nitrogens of the macrocyclic ring, by the pyridyl group in one of the axial positions and a water molecule in the other (Fig. 2(b)). Bond lengths are: Ni–N (macrocycle) 2.056–2.093 Å, Ni–N (pyridine) 2.124 Å and $Ni-OH_2$ 2.237 Å. Again the four nitrogens of the macrocycle and the Ni^{2+} are coplanar and the Ni-cyclam moiety is in the thermodynamically stable trans-III configuration. A comparison with the structures of $[Ni(cyclam)]Cl_2$[13] and $[Ni(cyclam)](NO_3)_2$[14] with Ni–N bonds of 2.05–2.06 Å and two axial Cl^- or NO_3^- as ligands show a similar coordination geometry: the NiN_4 moiety forms a planar arrangement and the macrocycle assumes the trans-III configuration (Fig. 2(a)). These examples clearly show that in the case of the Ni^{2+} complexes with C-substituted cyclam derivatives the additional coordination of the pendant group does not alter the structure of the metal-macrocycle unit.

It is interesting to compare these results with those obtained for a N-substituted cyclam derivative.



In the Cu^{2+} complex of **9** the Cu^{2+} ion is displaced by about 0.11 Å from the best plane through the four nitrogens towards the apical carboxylate oxygen.[15] In addition the four nitrogens are not exactly coplanar, N_1 and N_3 being displaced by 0.05 Å from the best plane on the same side as the Cu^{2+} ion, whereas N_2 and N_4 are displaced by the same amount in the other direction (Fig. 3(b)). The angles $O-Cu-N_2$ and $O-Cu-N_4$ are 99.6° and 89.9°, respectively, and indicate that N_2 is more strongly displaced probably to make room for the benzene ring of the side chain, which attached to N_1 bends over that part of the macrocycle to which N_2 belongs. The configuration of the Cu^{2+}-cyclam unit is trans-III. Compared to the structure of $[Cu(cyclam)](ClO_4)$,[16] which shows a perfectly planar CuN_4 unit, the coordination of the pendant donor group modifies the structure, displacing the metal ion and the nitrogens from their original positions.

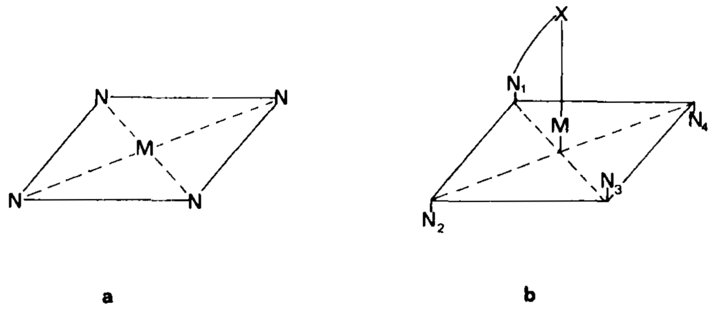
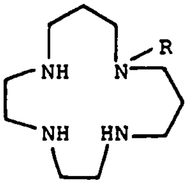


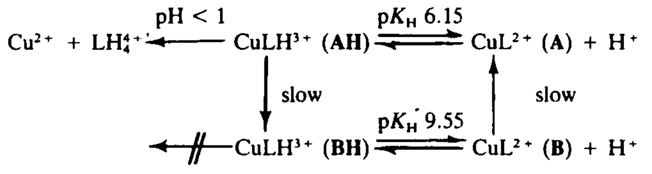
FIGURE 3 Structures of the parent compound $Cu(\mathbf{8})^{2+}$ (a) and of the pendant arm complex $Cu(\mathbf{9})^{2+}$ (b).

The last example describes the on/off equilibrium of a Cu^{2+} complex with an iso-cyclam derivative, carrying a 3-aminopropyl side chain **10** (L).[17]



10 R = CH_2-CH_2-CH_2-NH_2

Depending on the pH conditions and on the age of the solution, four species instead of only two, as described in the previous cases, can be observed. Two of them are protonated species (**AH**, **BH**), the other two deprotonated ones (**A**, **B**), thus giving two acid–base equilibria with two different pK_H values (2).



(2)

If one dissolves the solid $[CuL](ClO_4)_2$ (**A**), the structure of which will be discussed below, in slightly acid solution, one finds for the protonated form **AH** an absorption maximum at 570 nm. This species shows the typical color change when the pH is increased above 6. The observed pK_H = 6.15 and the shift of λ_{max} to 733 nm with a shoulder at 618 nm are in complete agreement with the on/off equilibrium in which the amino group of the side chain binds axially to the Cu^{2+}.

If a slightly acidic solution of **AH** is left at room temperature for several days, a shift of the absorption maximum to 547 nm is found. The reaction is very slow and the relatively small shift of λ_{max} could be interpreted as a side reaction. However, the new species **BH** has properties which are completely different from those of **AH**. **BH** is kinetically much more stable against H^+ than **AH**. In fact fresh solutions containing **AH** dissociate at pH < 1 to Cu^{2+} and the protonated macrocycle, whereas old solutions with

BH do not dissociate appreciably at this pH. In addition, when a solution of **BH** is titrated with base to study the on/off equilibrium, no color change is observed spectrophotometrically, although a potentiometric titration gives a $pK_H = 9.55$. We thus infer that in **BH** the ammonium proton can indeed be titrated, but that the so-formed amino group is not able to coordinate to the Cu^{2+} ion, as in all the other examples discussed above. Interestingly, also, in alkaline solution **B** slowly interconverts to **A**. The rate of this reaction, measured spectrophotometrically, is dependent on $[OH^-]$ and follows the law (3), which is typical for a N-isomerisation through a conjugate base mechanism.

$$v_{\mathbf{B},\mathbf{A}} = k.[\mathbf{B}].[OH^-] \qquad (3)$$

From these observations we infer that **AH** and **BH** as well as **A** and **B** must be isomers which differ from each other by their N-configuration. **BH** is the most stable form at low pH, whereas **A** is preferentially formed at high pH. So a configuration change must take place from acidic solutions containing **BH** to alkaline ones with **A**, the driving force of it being the additional energy of the Cu–N bond with the amino group of the side chain.

To understand this from a structural point of view, we shall now discuss the X-ray diffraction results of **A** and **BH**. In **A** the amino group of the side chain is bound to the Cu^{2+}, thus giving a pentacoordinate arrangement. The geometry is either a distorted trigonal bipyramid or a distorted square pyramid (Fig. 4(a)). Whereas the N_2–Cu–N_4 bond is nearly linear (171°), as one would expect for a trigonal bipyramid, the equatorial angles are very different from the ideal value of 120°, the N_1–Cu–N_3 being larger (142°), the other two, N_3–Cu–N_5 and N_5–Cu–N_1, being smaller (107° and 110°, respectively).

The X-ray structure of **BH**, the thermodynamically stable form in acidic solution, shows a Cu^{2+} ion in a distorted octahedral environment, coordinated by the four nitrogens of the macrocycle and two perchlorate ions (Fig. 4(b)). The best plane through the four nitrogens gives deviations of ± 0.14–± 0.17 Å. The Cu^{2+} is displaced from it by 0.12 Å. The macrocycle, folded along the N_2–Cu–N_4 axis, the angles N_2–Cu–N_4 and N_1–Cu–N_3 being 177.8° and 160.7°, respectively, is in the trans-II configuration with the

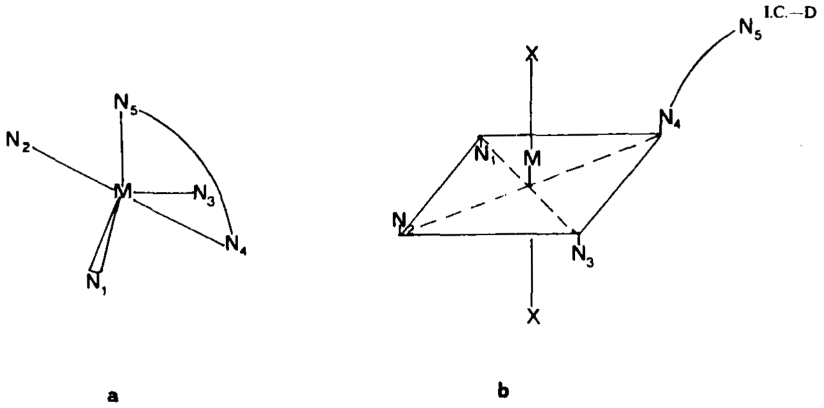


FIGURE 4 Structures of the Cu^{2+} complex **A** (a) and of the isomeric Cu^{2+} complex **BH** (b) with the macrocycle **10**.

unique hydrogen at the junction of the five membered chelate rings.

A comparison of the two structures of **A** and **BH** shows that the binding of the side chain donor group not only modifies the coordination geometry of the metal ion, but also involves a configurational rearrangement of the macrocycle (Fig. 5).

Summarizing the results presented above, we can state that the structural problems associated with the on/off equilibrium (1) of

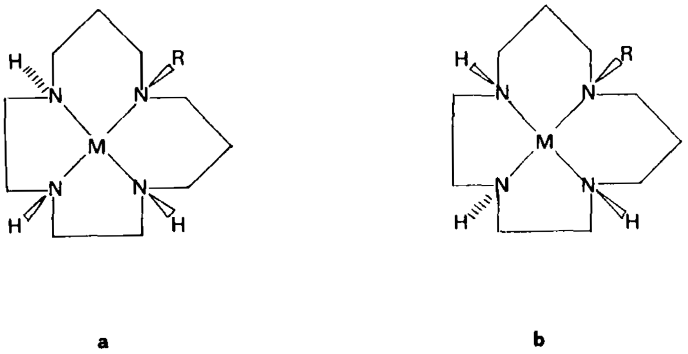


FIGURE 5 Configuration of the macrocycle **10** in the Cu^{2+} complex **A** (a) and **BH** (b).

a side chain exhibit several different aspects. In some cases practically nothing is changed in the coordination sphere of the metal ion and for the configuration of the macrocycle; in other cases a geometrical change takes place, since an additional bond is formed; and finally in other cases a drastic rearrangement of the whole metal–macrocyclic unit occurs, so that not only the geometry around the metal ion, but also the configuration of the macrocycle is changed.

Acknowledgment

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