1,8-Diazabicyclo[6.6.6]eicosa-4,11,17-triyne: a flexible cage for protons, copper(I) and silver(I)

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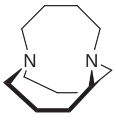
X-Ray structure analysis of the diprotonated cage of 3 and its silver(I) and copper(I) complexes reveals in all three cases the *in,in* conformation and a significant shortening of the intrabridgehead distance from 5.05 Å in 3 to 4.85 Å for 3·2H$^+$, 4.23 Å for 3·Cu$^+$ and 4.61 Å for 3·Ag$^+$.

Investigations of bicyclic compounds with nitrogen atoms at the bridgehead positions prove that mono- and di-protonation depends on the intrabridgehead distance and on the conformation(s) at the nitrogen atoms.[1] In the case of 1,6-diazabicyclo[4.4.4]tetradecane **1**, where the nitrogen atoms adopt the *in,in* conformation,[2] monoprotonation yields a very stable species due to a very strong intramolecular hydrogen bond between the two bridgehead positions,[2] rendering diprotonation rather difficult.[3] For the [1.1.1]cryptand **2**,[4–6] which also shows the *in,in* conformation, inside protonation of both nitrogens has been reported. This finding can be traced back to the larger N···N distance in **2** [3.88(2) Å][5] as against in **1** [2.806(3) Å].[2] In **2**·2H$^+$ the N···N distance was found to be enlarged to 3.91(1) Å.[5] Reports on the accommodation of ions other than H$^+$ in bicyclic bridgehead diamines are sparse. For the encapsulation of Li$^+$ in **2**[6] the other functions were held at least partly responsible.



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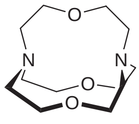

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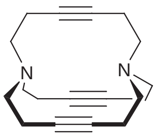

3

Our recently prepared 1,8-diazabicyclo[6.6.6]eicosa-4,11,17-triyne **3**[7] resembles a stretched **1** and shows an even larger N···N distance [5.049(2) Å] than **2**. However, the steric effects of the bridges, as encountered in **1** and related species, should be reduced due to the linear and rigid triple bonds. Therefore we studied the reactions of **3** with protons and metal ions.

The protonation of **3** with TFA was investigated in $CDCl_3$, CD_3OD and D_2O as solvents.† In $CDCl_3$ 1.5 equiv. of TFA are necessary to generate **3**·H$^+$, while in CD_3OD only 0.5 equiv. are required. Monoprotonation reduces the symmetry of **3** (D_3) to C_3, which yields six signals in the ^{13}C NMR spectrum of **3**·H$^+$. In the ^1H NMR spectrum (CD_3OD, 200 MHz) only four lines are found at δ 2.43, 2.79, 3.43 (in a ratio of 2 : 1 : 1) and 7.89 (the proton at the nitrogen atom). Five equivalents of TFA in $CDCl_3$ have to be added to obtain a two-fold protonation of **3**.† The shape of the ^1H NMR spectra of **3**·H$^+$ and **3**·2H$^+$ prove that the rapid equilibration between the two enantiomorphic helical conformations found in **3** is still present.

In all cases the protonation equilibrium is achieved instantly after addition of the acid. Even deprotonation succeeds easily with molar amounts of KOH. In **3**·H$^+$ and **3**·2H$^+$ we find a fast intermolecular proton exchange with solvents such as CD_3OD and D_2O. This behaviour is in contrast to the experiences gained from **1** and **2** and can be classified as the reaction of a normal tertiary amine. X-Ray investigations of **3**·2H$^+$ show‡ that both bridgehead hydrogens are inside the cage [Fig. 1(*a*)].

Interestingly, the encapsulation of two protons in the cavity of **3** causes a contraction of the N···N distance by 0.2 Å to 4.845(3) Å (see Table 1) and an increase of the inward pyramidization of the nitrogens by about 3° to *ca.* 112°, which is close to the ideal tetrahedral angle. The torsional angle between the triple bonds is reduced to 42.7(5)°. The distance between the two bridgehead protons in **3**·2H$^+$ amounts to 3.066(3) Å. An intramolecular proton exchange of **3**·H$^+$ in 1,1,2,2-tetrachloro[$^2H_2$]ethane could not be detected up to 130 °C.

Stirring a solution of **3** under argon in CH_2Cl_2 with a small excess of MOTf (M = Cu, Ag) at room temperature for three days leads to 1 : 1 complexes for both metals in almost quantitative yields. The spectroscopic properties of **3**·Cu$^+$ and **3**·Ag$^+$ suggest that the metal is situated in the center of the cage.† NMR and IR studies give no hints of a binding interaction between the metal ion and the surrounding triple bonds, so it can be said that the ligand coordinates mainly with the bridgehead nitrogens, effecting a linear N–M$^+$–N geometry. The structural assignment is supported by X-ray investigations of single crystals of both complexes.‡ It is seen [Fig. 1(*b*), (*c*)] that the metal ion is located in the center of the cage, forcing the bridgehead positions even closer together. **3**·Ag$^+$ displays, like **3**, D_3 symmetry, while **3**·Cu$^+$ reveals C_{3h} symmetry. The N–

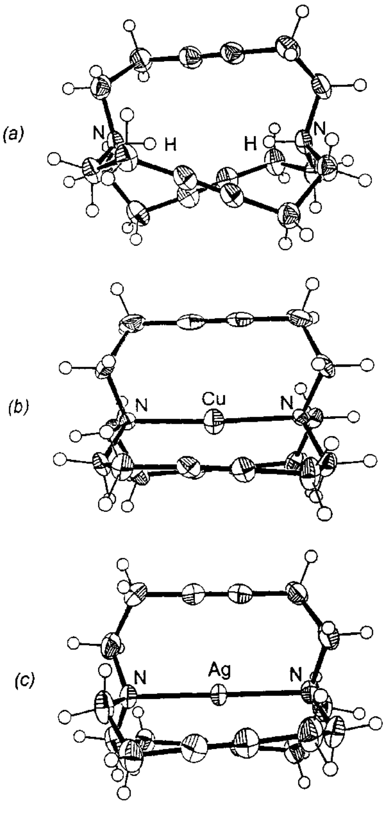

Fig. 1 ORTEP plots (50% ellipsoid probability) of the molecular structures of (*a*) **3**·2H$^+$, (*b*) **3**·Cu$^+$ and (*c*) **3**·Ag$^+$.

Table 1 Most relevant distances and angles for **3**, **3**·2H$^+$, **3**·Cu$^+$ and **3**·Ag$^+$ (standard deviations given in parentheses)

	3^a	**3**·2H$^+$	**3**·Cu$^+$	**3**·Ag^{+b}
N···N/Å	5.049(2)	4.845(3)	4.227(5)	4.614(5) *4.630(5)*
N–M/Å	—	—	2.110(2), 2.118(2)	2.306(3), 2.308(3) *2.313(3), 2.317(3)*
M–X^c/Å	—	—	2.460(4)–2.576(4)	2.493(4)–2.527(4) *2.498(4)–2.539(4)*
Θ^d (°)	55.5(3)	42.5(3)–42.9(3)	6.3(3)–7.9(3)	8.2(3) *16.2(3)*
d(C≡C)/Å	1.188(2)	1.192(4)	1.189(6)–1.195(6)	1.194(6)–1.199(6) *1.195(6)–1.204(6)*

^{a} Ref. 7. ^{b} Data in italics refer to the second independent complex cation in the asymmetric unit. ^{c} M–X is the distance between the metal and the center of the triple bonds. ^{d} Torsional angle between the triple bonds.

M$^+$–N bond angles for **3**·Cu$^+$ and **3**·Ag$^+$ amount to 176.6(3) and 178.9(3)°, respectively. Relevant data for **3**·Cu$^+$ and **3**·Ag$^+$ are collected in Table 1 and compared with **3** and **3**·2H$^+$.

As a consequence of the shortening of the N···N distance in **3**, the torsion angle between the triple bonds is reduced considerably in **3**·Cu$^+$ and **3**·Ag$^+$. The distances between the centers of the alkyne groups and the metal ions [**3**·Cu$^+$: 2.460(4)–2.576(4), **3**·Ag$^+$: 2.493(4)–2.539(4) Å] are larger than for other alkyne silver or copper complexes [Cu$^+$–center of alkyne : 2.02(1) Å, Ag$^+$–center of alkyne : 2.33(1) Å].[8] In both metal complexes the bridgehead atoms show an ideal tetrahedral conformation. The mean N–Ag$^+$ and N–Cu$^+$ distances [2.311(3) and 2.114(2) Å, respectively] are rather expanded with regard to the values reported for homoleptic two-coordinated silver(I) amine complexes, *e.g.* Ag(NH$_3$)$_2$NO$_3$ [2.121(1) Å][9] and comparable complexes of copper(I) (average value: 1.88 Å).[10] Many of the known mononuclear two-coordinated copper(I) complex cations deviate considerably from the ideal linear structure to coordinate further ligands and come up to the preferred four-coordinate tetrahedral geometry. Although in **3**·Cu$^+$ potential ligands (the triple bonds) are within reach, this tendency seems to be effectively blocked due to the extended N–Cu$^+$–N arrangement.

The triflate salts of **3**·Cu$^+$ and **3**·Ag$^+$ are stable to air and not light sensitive. None of the silver(I) halides is obtained by treatment of solutions of **3**·Ag$^+$ TfO$^-$ in CH$_2$Cl$_2$ or MeOH with Me$_2$NH$_2$Cl, Et$_3$NHBr and Bu$_4$NI at room temperature, indicating remarkable stability. The aptitude of **3** as a flexible ligand for further metal ions is currently under investigation.

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Notes and references

† *Selected data* for **3**·2H$^+$(CF$_3$CO$_2$$^-$)$_2$: δ_H(CD$_3$OD, 200 MHz) 3.01 (t, *J* 5.6, 12H), 3.60 (t, *J* 5.4, 12H), 7.87 (s, 2H); δ_C(CD$_3$OD, 50.3 MHz) 16.6, 55.5, 81.1, 113.2, 114.1, 118.9, 119.8, 158.6, 159.4, 160.3, 161.0. For **3**·Cu$^+$ TfO$^-$: δ_H(CD$_2$Cl$_2$, 300 MHz) 2.63 (s, 24H); δ_C(CH$_2$Cl$_2$, 50.3 MHz) 18.9, 53.0, 80.3; Calc. for C$_{18}$H$_{24}$N$_2$^{65}Cu: 331.1235, found: 331.1241. For **3**·Ag$^+$ TfO$^-$: δ_H(CD$_3$OD, 500 MHz) 2.64 (s, 12H), 2.69 (s, 12H); δ_C(CD$_3$OD, 125 MHz) 18.9, 54.1, 79.0; Calc. for C$_{18}$H$_{24}$N$_2$^{107}Ag: 375.0990, found: 375.0986.

‡ *Crystal data* for **3**·2H$^+$ (CF$_3$CO$_2$$^-$·CF$_3CO_2$H)$_2$: C$_{26}H_{28}F_{12}N_2O_8$, *M* = 724.50, colourless crystals from CDCl$_3$, monoclinic, *a* = 16.0744(1), *b* = 10.2190(2), *c* = 18.9058(3) Å, β = 91.5930(1)°, *V* = 3104.35(8) Å^3, ρ_c = 1.55 Mg m^{-3}, *T* = 200(2) K, space group *C*2/*c*, *Z* = 4, μ(Mo-Kα) = 0.16 mm^{-1}, 11183 reflections collected, 2687 independent reflections (R_{int} = 0.0239), R_1 (*F*) = 0.046, wR_2 (F^2) = 0.112. The structure contains two hydrogen-bonded trifluoroacetate dimers as anions for each dication.

For **3**·Cu$^+$ TfO$^-$: C$_{19}$H$_{24}$CuF$_3$N$_2$O$_3$S, *M* = 481.00, colourless crystals from MeOH, monoclinic, *a* = 11.7163(4), *b* = 7.4458(3), *c* = 23.4107(8) Å, β = 99.8520(1)°, *V* = 2012.17(13) Å^3, ρ_c = 1.59 Mg m^{-3}, *T* = 200(2) K, space group *P*2$_1$/*n*, *Z* = 4, μ(Mo-Kα) = 1.24 mm^{-1}, 14503 reflections collected, 3478 independent reflections (R_{int} = 0.0291), R_1 (*F*) = 0.029, wR_2 (F^2) = 0.069. The copper atom is refined with a free site occupancy factor (it refines to a partial site occupancy of 0.8), because the copper position is partially occupied by a proton (20% occupancy). 10% of the complex cations are disordered, showing a D_3 symmetry like **3**·Ag$^+$.

For **3**·Ag$^+$ (TfO$^-$·0.25 CH$_2$Cl$_2$): C$_{19.25}$H$_{24.50}$AgCl$_{0.50}$F$_3$N$_2$O$_3$S, *M* = 546.56, colourless crystals from CH$_2$Cl$_2$, triclinic, *a* = 13.4273(2), *b* = 13.9115(3), *c* = 14.0299(3) Å, α = 65.5820(1), β = 73.2750(1), γ = 64.6590(1)°, *V* = 2137.02(7) Å^3, ρ_c = 1.70 Mg m^{-3}, *T* = 200(2) K, space group $P\bar{1}$, *Z* = 4, μ(Mo-Kα) = 1.15 mm^{-1}, 15934 reflections collected, 7079 independent reflections (R_{int} = 0.0200), R_1 (*F*) = 0.032, wR_2 (F^2) = 0.075. Two independent complex cations in the asymmetric unit. The unit cell contains four complex cations, four triflate anions and one disordered CH$_2$Cl$_2$ molecule. CCDC 182/1102. Crystallographic data is available as .cif files from the RSC web site, see: http://www.rsc.org/suppdata/cc/1999/171

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