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Metallacrown ethers: synthesis and structural investigation of silver metallamacrocycles

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Abstract—The bis-monodentate ligands **1** and **2** based on the interconnection of two pyrazolyl units by CH_2–$(CH_2$–$OCH_2)_n$–CH_2 ($n=3$ or 4) spacers, respectively, lead to the formation of either mono nuclear silver metallamacrocycle **10** in the case of **1** or binuclear silver metallamacrocycle **11** in the case of **2**. Both complexes have been characterised in the solid state by X-ray diffraction on single crystals.

Since the discovery of crown ethers by Pedersen in the 1960s,[1] many derivatives belonging to this class of molecules have been designed and prepared.[2] On the other hand, since a decade, considerable efforts have been invested in the design and synthesis of macro(poly)cyclic structures of the metallamacrocycle type.[3–15] Metallamacrocycles are macrocyclic entities for which at least one endocyclic atom or group of atoms is of metallic nature. In other terms, the formation of a metallamacrocycle results from the bridging of at least one organic fragment bearing coordination sites by at least one metal centre. The majority of metallamacrocycles reported so far are based on bridging of rather rigid pyridine-containing ligands.

Here, we report the design and formation of crown ether type metallamacrocycles based on oligoethyleneglycol fragments bearing at both their extremities monodentate coordinating sites, and the effect of the length of the spacer on the nuclearity of the macrocyclic structure.

Pursuing our effort in the design of new metallamacrocycles,[11–16] we designed ligands **1**–**3** which are based on the interconnection of two pyrazolyl moieties as monodentate coordinating sites by oligoethyleneglycol fragments with different lengths. The junction between the pyrazolyl group and the oligoethyleneglycol was achieved through CN bonds. Oligoethyleneglycol was considered as the spacer between the two monodentate pyrazolyl moieties because on the one hand it provides some flexibility and, on the other hand, it may adopt a helical conformation. Furthermore, the use of polyethyleneglycol could lead to the formation of crownether-type metallamacrocycles. We have previously demonstrated this aspect in the context of the generation of infinite helical coordination networks formed between pyridine-bearing polyethyleneglycol derivatives and the silver cation.[17]

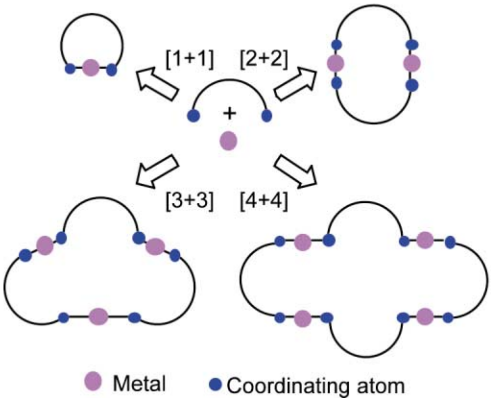

Figure 1. Schematic representations of the formation of metallamacrocycles of different nuclearity between a bis-monodentate fragment and a linearly coordinated metal centre.

Keywords: metallamacrocycle; pyrazole; silver; metallacrownether; coordination; macrocycle.

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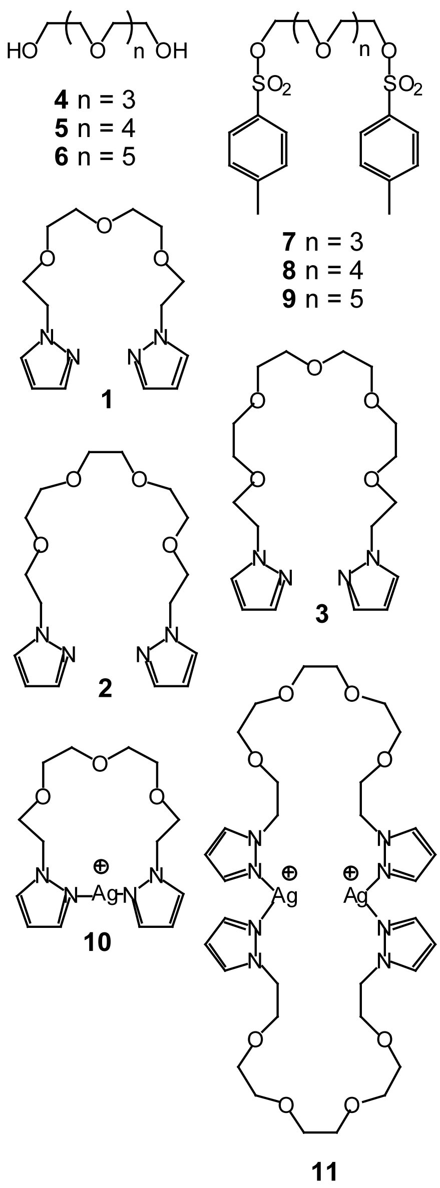

Scheme 1.

The pyrazolyl group was chosen as the coordinating site because of its binding ability towards metal cations and, when connected to the polyethyleneglycol type spacer through its amino group, the proper disposition of the imine nitrogen for metal coordination. We have previously demonstrated the ability of pyrazolyl-based ligands to form either metallamacrocycles[12] or infinite tubular coordination networks.[13]

Ligands **1**–**3** are bis-monodentate fragments and, when associated with a metal cations adopting a linear coordination geometry, they may either generate metallmacrocycles of different nuclearity (Fig. 1) or infinite coordination networks. In principle, depending on the spacer connecting the two coordination sites, i.e. its flexibility and the nature of hetero atoms, one may orientate the system towards the formation of discrete or infinite molecular assemblies. As for discrete metallamacrocyclic structures, when an appropriate metal cation allowing reversible binding is used, again the nuclearity of the metallamacrocycle (Fig. 1), i.e. (nL,nM, $n=1$, 2, 3, etc...) should depend on the geometric characteristics of the organic ligand. For the reason mentioned above, the Ag^+ cation was chosen as the connecting metallic centre because on one hand it may adopt a linear coordination geometry and on the other hand, its binding by ligands bearing N atoms as coordination sites is reversible.

The synthesis of **1**–**3**[18] (Scheme 1) was straightforward and achieved in high yields through the reaction of sodium pyrazolate, generated by treatment of pyrazole with sodium hydride, with the ditosylate derivatives **7**–**9**. The latter compounds may be readily prepared from the corresponding diols **4**–**6** upon treatment with tosyl chloride.

By slow diffusion at room temperature of a solution of $AgPF_6$ (6 mg) in *i*PrOH (4 ml) into a $CHCl_3$ (2 ml) solution containing the ligand **1** (4 mg), crystalline material was obtained. The X-ray diffraction[19] on a single crystal revealed the exclusive presence of the monocationic silver metallamacrocycle **10** and the PF_6^- anion. The mononuclear metallamacrocycle of the (1L,1M) type is formed by bridging of the two pyrazolyl moieties of **1** by the Ag^+ cation ($d_{Ag–N}=2.09$ and 2.11 Å). The CH_2–$(CH_2$–$OCH_2)_3$–CH_2 fragment adopts an helical conformation (OCCO and NCCO dihedral angles of −75.9, 70.7° and −69.6, 63.0°, respectively). The coordination sphere around the Ag^+ cation is composed of two N atoms of the imine type (NAgN angle = 175.9°) and one O atom belonging to **1** ($d_{Ag–O}=$ 2.75 Å). The coordination geometry around the metal centre may be regarded as a distorted T (Fig. 2, top). Due to the helical conformation adopted by the

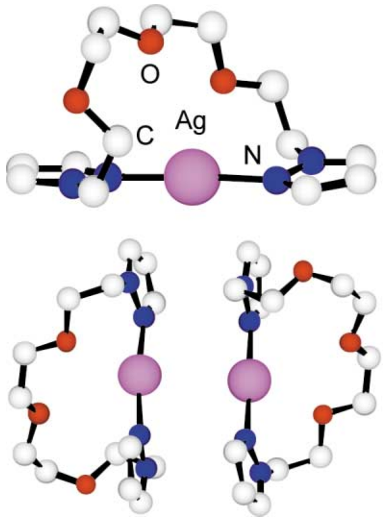

Figure 2. Solid-state structure of the mono-metallic silver crown ether **10** obtained by obturation of the ligand **1** by the silver cation adopting a linear coordination geometry (top) and the arrangement leading to a racemic pair of two complexes **10** with a fairly short Ag–Ag distance of ca. 3.6 Å (bottom). H atoms and PF_6^- anions are not represented for clarity. For bond distances and angles, see text.

CH_2–$(CH_2$–$OCH_2)_3$–CH_2 unit, the metallamacrocycle is chiral. However, in the crystal, both enantiomers are present and consequently a racemate is formed. Interestingly, two enantiomers form a pair with face-to-face arrangement. A possible reason for such an arrangement may be the rather short Ag–Ag distance of ca. 3.66 Å (Fig. 2, bottom). The PF_6^- anions are filling empty spaces between cationic units and no peculiar interactions between them is observed. A possible reason why in the case of **1**, only the mononuclear complex is observed may be based on the reversibility of the pyrazole–Ag^+ interaction. Indeed, whereas in principle any metallamacrocycle of the (nL,nM, $n=1$, 2, 3, etc...) type may be formed, perhaps due to the rather short length of the spacer, the most stable complex is the mononuclear specie **10**. Since the cyclisation processes are reversible, the system is allowed to reach the most thermodynamically stable situation.

By slow diffusion at room temperature of a solution of $AgSbF_6$ (6 mg) in *i*PrOH (4 ml) into a $CHCl_3$ (2 ml) solution containing the ligand **2** (4 mg), crystalline material was obtained and studied in the solid state by X-diffraction[19] on a single crystal, exclusively composed of the cationic bimetallic silver metallamacrocycle **11** and the SbF_6^- anion. The metallamacrocycle of the (2L,2M) type adopts a centre of symmetry and is formed by bridging of the two ligands **2** by two Ag^+ cations ($d_{Ag-N}=2.16$ Å). The two CH_2–$(CH_2$–$OCH_2)_4$–CH_2 fragments adopt again a helical conformation with opposite chirality affording thus an achiral macrocycle (OCCO and NCCO dihedral angles of −64.4, 77.3, 53.0° and −78.2, 71.7°, respectively). The coordination sphere around the Ag^+ cation is composed of two N atoms of the imine type belonging each to a fragment **2** (NAgN angle = 168.0°) (Fig. 3) and two O atoms belonging to the CH_2–$(CH_2$–$OCH_2)_5$–CH_2 unit ($d_{Ag-O}=2.68$ and 2.91 Å). The coordination geometry around the metal centre may be regarded as a severely distorted tetrahedron. The PF_6^- anions are again filling empty spaces between dicationic units with no specific interactions with the metallamacrocyclic units. Again, based on the reversibility of the coordination process, a possible reason why in that case only the bimetallic metallamacrocyclic structure is formed may be based on the thermodynamic stability of the complex resulting from the longer spacer which allows further charge–dipole interactions between the O atoms of the spacer and the cationic centres.

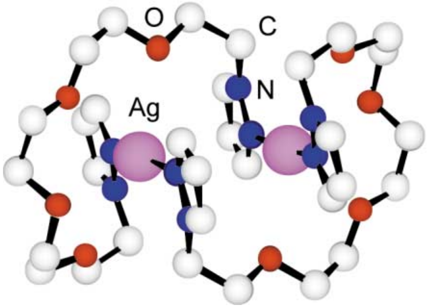

Figure 3. Solid-state structure of the bi-metallic silver crown ether **11** obtained by interconnection of two ligands **2** by two silver cations, adopting a linear coordination geometry. The two moieties **2** adopt helical conformation with opposite handedness. H atoms and SbF_6^- anions are not represented for clarity. For bond distances and angles, see text.

In conclusion, compounds **1**–**3** based on oligoethyleneglycol spacer of different lengths bearing at both extremities a pyrazolyl coordinating moiety were synthesised. In the presence of Ag^+ cation, whereas for the short member of the series, namely compound **1**, the mono silver metallacrown ether **10** was formed in the solid state, for the longer analogue **2** the binuclear silver metallacrown ether **11** was generated. The formation of other metallacrown ethers with higher nuclearity and other metallic centres is currently under investigation.

Acknowledgements

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References

1. Pedersen, C. J. *J. Am. Chem. Soc.* **1967**, *89*, 7017–7036.
2. Bradshaw, J. S.; Izatt, R. M.; Bordunov, A. V.; Zhu, C. Y.; Hathaway, J. K. In *Comprehensive Supramolecular Chemistry*; Atwood, J. L.; Davies, J. E. D.; MacNicol, D. D.; Vögtle, F., Eds., Vol. 1 (Gokel, G. W., Vol. Ed.); Elsevier: Oxford, 1996; pp. 35–95.
3. Saalfrank, R. W.; Stark, A.; Peters, K.; von Schnering, H.-G. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 851–853.
4. Swiegers, G. F.; Malefetse, T. J. *Chem. Rev.* **2000**, *100*, 3483–3537.
5. Fujita M. In *Comprehensive Supramolecular Chemistry*; Atwood, J. L.; Davies, J. E. D.; MacNicol, D. D.; Vögtle, F., Eds., Vol. 9 (Sauvage, J. P.; Hosseini, M. W., Vol. Eds.); Elsevier: Oxford, 1996; pp. 253–282.
6. Fujita, M. *Acc. Chem. Res.* **1999**, *32*, 53–61.
7. Stang, P. J.; Olenyuk, B. *Acc. Chem. Res.* **1997**, *30*, 502–518.
8. Johnson, D. W.; Xu, J.; Saalfrank, R. W.; Raymond, K. N. *Angew. Chem., Int. Ed.* **1999**, *38*, 2882–2885.
9. Sanders J. K. M. In *Comprehensive Supramolecular Chemistry*; Atwood, J. L.; Davies, J. E. D.; MacNicol, D. D.; Vögtle, F., Eds., Vol. 9 (Sauvage, J. P.; Hosseini, M. W., Vol. Eds.); Elsevier: Oxford, 1996; pp. 131–164.
10. Drain, C. M.; Lehn, J.-M. *Chem. Commun.* **1994**, 2313–2314.
11. Schneider, R.; Hosseini, M. W.; Planeix, J.-M.; De Cian, A.; Fischer, J. *Chem. Commun.* **1998**, 1625–1626.
12. Jouaiti, A.; Loï, M.; Hosseini, M. W.; De Cian, A. *Chem. Commun.* **2000**, 2085–2086.
13. Loï, M.; Hosseini, M. W.; Jouaiti, A.; De Cian, A.; Fischer, J. *Eur. J. Inorg. Chem.* **1999**, 1981–1985.
14. Jullien, V.; Planeix, J.-M.; Hosseini, M. W.; De Cian, A. *J. Org. Met. Chem.* **2002**, *643–644*, 376–380.
15. Jouaiti, A.; Hosseini, M. W.; Kyritsakas, N. *Eur. J. Inorg. Chem.* **2002**, in press.

16. Oddon, G.; Hosseini, M. W. *Tetrahedron Lett.* **1993**, *34*, 713–7416.
17. Schmaltz, B.; Jouaiti, A.; Hosseini, M. W.; De Cian, A. *Chem. Commun.* **2001**, 1242–1243.
18. *General procedure for the synthesis of compounds* ***1–3***: To a solution of pyrazole (1 mmol) in anhydrous DMF (5 ml), a suspension of NaH in oil (50%) was added under argon and the mixture stirred at rt for 30 min. To the mixture, the ditosylate **7**, **8** or **9** (0.5 mmol) was added and the solution heated to 80°C for 12 h. The solvent was evaporated to dryness and the residue was taken up in ether (100 ml). The suspension was filtered before the solvent was removed. The residue thus obtained was purified by column chromatography (SiO_2, CH_2Cl_2/MeOH: 7/3) and afforded the desired compounds **1** (79%), **2** (85%) and **3** (76%) as colourless oils. Compound **1**: ^1H NMR (300 MHz, $CDCl_3$, 25°C): δ (ppm) 3.42 (s, 8H, CH_2O), 3.72 (t, 4H, $J=5.4$ Hz, CH_2O), 4.19 (t, 4H, $J=5.4$ Hz, CH_2N), 6.11 (t, 2H, $J=1.95$ Hz, $CH{=}C$), 7.38 (d, 4H, $J=1.95$ Hz, CHN); ^{13}C NMR (50 MHz, $CDCl_3$, 25°C): δ (ppm) 51.94, 69.83, 70.35, 70.50, 105.29, 130.05, 139.21. Compound **2**: ^1H NMR (300 MHz, $CDCl_3$, 25°C): δ (ppm) 3.60 (m, 12H, CH_2O), 3.80 (t, 4H, $J=5.1$ Hz, CH_2N), 4.30 (t, 4H, $J=5.1$ Hz, CH_2O), 6.20 (t, 2H, $J=2.1$ Hz, $CH{=}C$), 7.50 (d, 4H, $J=2.1$ Hz, CHN); ^{13}C NMR (50 MHz, $CDCl_3$, 25°C): δ (ppm) 21.5, 51.9, 69.8, 70.5, 105.2, 127.9, 130.0, 139.2. Compound **3**: ^1H NMR (300 MHz, $CDCl_3$, 25°C): δ (ppm) 3.58 (m, 8H, CH_2O), 3.83 (t, 4H, $J=5.2$ Hz, CH_2N), 4.29 (t, 4H, $J=5.3$ Hz, CH_2O), 6.22 (t, 2H, $J=2.1$ Hz, $CH{=}C$), 7.50 (d, 4H, $J=2.1$ Hz, CHN); ^{13}C NMR (50 MHz, $CDCl_3$, 25°C): δ (ppm) 52.0, 69.9, 70.4, 70.5, 105.3, 130.0, 139.3.
19. *X-Ray studies*: For both complexes **10** and **11**, obtained by slow diffusion at room temperature of a solution of $AgPF_6$ (6 mg) and $AgSbF_6$ (6 mg), respectively, in *i*PrOH (4 ml) into a $CHCl_3$ (2 ml) solution containing the ligand **1** and **2**, respectively, data were measured at 173 K on a κ CCD diffractometer with graphite monochromated Mo Kα radiation. Compound **10**: $C_{14}H_{22}AgN_4O_3{\cdot}PF_6$, $M=547.19$, triclinic, $a=9.0365(2)$, $b=10.1708(3)$, $c=12.0375(3)$ Å, $\alpha=73.974(5)$, $\beta=70.875(5)$, $\gamma=80.107(5)$, $U=1000.62(4)$ Å^3, space group $P\bar{1}$, $Z=2$, $D_{calcd}=1.82$ g cm^{-3}, μ(Mo Kα)$=1.165$ mm^{-1}, $R=0.034$, $R_w=0.054$ for 2906 independent observed reflections $[|F_o|>3\sigma(|F_o|]$. Compound **11**: $C_{16}H_{26}AgF_6N_4O_4Sb$, $M=682.02$, monoclinic, $a=12.2391(2)$, $b=13.4637(3)$, $c=14.7955(4)$ Å, $\beta=108.036(5)$, $U=2318.25(11)$ Å^3, space group $P2_1/c$, $Z=4$, $D_{calcd}=1.95$ g cm^{-3}, μ(Mo Kα)$=2.087$ mm^{-1}, $R=0.027$, $R_w=0.029$ for 3956 independent observed reflections $[|F_o|>3\sigma(|F_o|]$. Both structures were solved by direct methods using OpenMoleN 2.2[20] and refined anisotropically using absorption corrected data. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre under the following numbers: CCDC 198512 and 198513.
20. OpenMolenN, Interactive Structure Solution, Nonius BV, Delft, The Netherlands, 1997.