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# Linked macrocyclic systems. Interaction of copper(I) with tris-ring N<sub>2</sub>S<sub>2</sub>-donor macrocycles and their single-ring analogues

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Dedicated to Professor K. Gloe, Technical University, Dresden on the occasion of his 60th birthday.

## Abstract

The interaction of two tri-linked N<sub>2</sub>S<sub>2</sub>-donor macrocyclic ligands, 1 (R = H) and 2 (R = H), and their related single ring derivatives, 3 (R = H) and 4  $(R = CH_2C_6H_5)$ , with copper(I) is reported. Solid 3:1 (metal:ligand) complexes of type  $[Cu_3L](PF_6)_3$  (L = 1 and 2, R = H) and single ring derivatives of type [CuL]PF<sub>6</sub> (L = 3, R = H; L = 4, R = CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>) were isolated; the X-ray structure of [CuL]PF<sub>6</sub> (L = 3, R = H) showed that the four macrocyclic donor atoms coordinate to the copper(I) in a quasi-tetrahedral manner (Cu-N 2.089, 2.096(4); Cu-S 2.239, 2.264(2) Å, X-Cu-Y 104.5(1)-115.4(1))°. © 2007 Elsevier B.V. All rights reserved.

Keywords: Copper(I); S2N2-donor macrocycle; Trinucleating macrocycle; X-ray

The synthesis of saturated S<sub>2</sub>N<sub>2</sub>-donor macrocycles, together with aspects of their metal coordination chemistry, have now been the focus of a considerable number of studies [1]. For example, we have investigated the use of mixed nitrogen-sulfur donor macrocyclic species as selective reagents for individual transition and post-transition metal ions [2-6]. Our studies have included solution and solid state aspects of the interaction of the three-ring macrocyclic ligands 1 and 2 (R = H or  $CH_2C_6H_5$ ) with palladium(II) [2] and platinum(II) [2] and silver(I) [3]. In each case corresponding trinuclear complex cations of type  $[M_3L]^{n+}$  (L = 1 or 2, R = H or CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>); (M = Ag, n = 3; Pd, Pt, n = 6) were shown to form. The N<sub>2</sub>S<sub>2</sub>-donor set of each macrocyclic ring was expected on HSAB principles to show a strong affinity for these soft metal ions and

the available evidence confirms that this is so. However, in no case has it been possible to obtain crystals suitable for an X-ray structure determination and hence it was not possible to define the solid state coordination geometries of the respective metal centres in these complexes directly. In view of this, corresponding mononuclear complexes of type  $[ML](PF_6)_n$  (M = Ag, n = 1; Pd, Pt, n = 2) incorporating the single ring ligands 3 (R = H or  $CH_2C_6H_5$ ) and 4 (R= H or CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>) were prepared in anticipation that the smaller overall size of these latter species might aid the formation of suitable crystals for X-ray diffraction. In the case of palladium(II) and 3 (R = H), this strategy proved successful and suitable crystals for an X-ray structure determination of mononuclear  $[PdL](PF_6)_2$  (L = 3 R = H) were obtained [2]. The structure shows that the palladium is coordinated to all four donor atoms of the macrocycle in a square planar manner, with the ligand geometry around the 4-coordinate metal ion being slightly puckered; physical measurements suggest that a similar

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coordination geometry occurs for each of the corresponding complexes  $[Pd_3L](PF_6)_6$  (L = 1 and 2, R = H),  $[PdL](PF_6)_2$  (L = 3, R = H) and  $[PdL](PF_6)_2$  (L = 4, R = H).



In a previous investigation Kaden et al. [7] determined stability constants for the copper(I) ( $\log K = 0.17$ ) and copper(II)  $(\log K = 10.27)$  complexes of the parent (trans donor) 16-membered macrocycle, 1,9-dithia-5,13-diazacyclohexadecane, but no solid complexes of copper(I) were reported; nevertheless, based on molecular modelling it was predicted that this ligand is capable of adopting a relatively strain-free configuration around a tetrahedral metal ion such as copper(I). In another study, the 1:1 copper(I)complex of the isomeric cis-donor ligand, 1,5-dithia-9,13diazacyclohexadecane, was isolated and its X-ray structure shows a close to tetrahedral  $(N_2S_2)$  coordination geometry [8]. The coordination of all macrocyclic donors is perhaps unsurprising since it has been proposed that copper(I) has similar affinities for saturated N and thioether S donor atoms [9].



of  $[CoLX_2]$  (X = Cl or Br),  $[CuLCl_2] \cdot 0.5C_7H_8$  [11], [AgL(OCCH\_3)]  $\cdot 2H_2O$ ,  $[RhLCl_2]PF_6$ ,  $[PdL](PF_6)_2$  [13] and  $[PdL]Cl_2 \cdot 2H_2O$  [14] show in each case that square planar (or near square planar) arrangements of the macrocyclic donors occur around the respective central metal ions.

We now report the synthesis of the four new copper(I) species:  $[Cu_3L](PF_6)_3$  (L = 1 and 2; R = H) and  $[CuL]PF_6$  (L = 3, R = H; L = 4, R = CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>); the synthesis and characterisation of the respective ligands has been reported previously [2,3]. Reaction of  $[Cu(CH_3CN)_6]PF_6$  with 1 (R = H) or 2 (R = H) in a 1:3 molar ratio or with 3 (R = H) or 4 (R = CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>) in a 1:1 molar ratio in an acetonitrile/methylene chloride solvent mixture under nitrogen led to isolation of the corresponding 3:1 complexes,  $[Cu_3L](PF_6)_3$  (L = 1, R = H) and (L = 2, R = H) [15], and 1:1 complexes,  $[CuL]PF_6$  (L = 3, R = H) and (L = 4, R = CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>) [16]. All products yielded satisfactory microanalyses.

As also occurred for the palladium complex of **3** ( $\mathbf{R} = \mathbf{H}$ ), we were only successful in isolating suitable crystals for X-ray investigation in the case of the mononuclear copper(I) complex of **3** ( $\mathbf{R} = \mathbf{H}$ ); crystals of [CuL]PF<sub>6</sub> ( $\mathbf{L} = \mathbf{3}, \mathbf{R} = \mathbf{H}$ ) were obtained by dissolving the product isolated from the synthetic procedure in methylene chloride and then adding a small amount of carbon tetrachloride; crystals formed at room temperature over several days [16].

In contrast to the square planar arrangement found in  $[PdL](PF_6)_2$  (L = 3, R = H), the X-ray structure [17] of  $[CuL]PF_6$  (L = 3, R = H) shows that the copper(I) site is



Complexes of an octamethyl derivative **5** of the above 'parent' 16-membered macrocycle [10] with cobalt(II), nickel(II), copper(I), zinc(II), palladium(II), rhodium(III) [11], silver(I) [12], cadmium(II), lead(II) and mercury(II) [11] have been reported. The crystal structures

Fig. 1. Projection of the  $[CuL]^+$  (L = 3; R = H) cation, showing nonhydrogen atoms with 20% probability amplitude displacement envelopes, hydrogen atoms having arbitrary radii of 0.1 Å. Cu–N(1,9) are 2.089, 2.096(4); Cu–S–(5,5') 2.264(2), 2.239(2) Å; N(1)–Cu–N(9), S(5,5'), N(9)– Cu–S(5,5'), S(5)–Cu–S(5') are 114.6(2), 109.4(2), 107.2(1), 105.9(1), 104.5(1), 115.4(2)°; the bond distances are similar to those in the 1:1 copper(I) complex of the cis-donor ligand, 1,5-dithia-9,13-diazacyclohexadecane [8]: Cu–N 2.050(6), 2.063(8); Cu–S 2.253(2), 2.255(2) Å.

quasi-tetrahedrally coordinated, being bound to all four donors of the macrocycle (Fig. 1).

A single formula unit, devoid of crystallographic symmetry, comprises the asymmetric unit of the structure. The cation, shorn of the benzyl pendant, has quasi-2 symmetry, but, although chiral and in a non-centrosymmetric space group, the structure overall is racemic. All chelate rings are six-membered 'chairs', 'flatter' at the copper atom, those defined by C(6,7,8), C(2',3',4') more distorted than the other pair. The amino-hydrogen H(9) is hydrogen-bonded to a face of the PF<sub>6</sub> anion, being essentially equidistant (2.5<sub>5</sub>–2.7<sub>0</sub> Å (est.)) from F(4–6); it lies to the same side of the macrocycle as the benzyl pendant, as in the palladium(II) complex.

The 1:1 copper(I) complex of the related 'trans'  $N_2S_2$  donor, dibenzo-substituted, unsaturated macrocycle **6** has also been investigated by X-ray diffraction [18]. This complex adopts a distorted tetrahedral arrangement with the N(1)–Cu–N(2) bond angle = 118.00° and the S(1)–Cu–S(2) bond angle = 132.07°; Cu–N are 1.981, 1.989(2) and Cu–S 2.246, 2.247(1) Å. The counter ion in this case is triflate. Related copper(I) complexes of double ring,  $N_{2(imine)}$ -S<sub>2</sub>-macrocycles have also been reported [19].

In this report we have demonstrated that both the present tritopic ligands readily give 3:1 (metal:ligand) complexes with copper(I) hexafluorophosphate while the related single rings **3** ( $\mathbf{R} = \mathbf{H}$ ) and **4** ( $\mathbf{R} = CH_2C_6H_5$ ) yield analogous 1:1 products. These complexes expand the known examples of the otherwise little studied [20] category of N<sub>2</sub>S<sub>2</sub>-donor macrocyclic complexes incorporating copper(I). The structure of [CuL]PF<sub>6</sub> ( $\mathbf{L} = \mathbf{3}$ ,  $\mathbf{R} = \mathbf{H}$ ) once again confirms that the 16-membered ring is able to span four tetrahedral positions around copper(I) in an unstrained fashion; it seems likely that a similar geometry occurs for each metal site in the remaining three complex species prepared in the present study.

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## Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2007. 06.002.

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- [15] Synthesis of  $[Cu_3L](PF_6)_3$  (L = 1, R = H or 2, R = H).  $[Cu(CH_3CN)_4](PF_6)$  (0.193 mmol) in acetonitrile (5 cm<sup>3</sup>) was added 1 (R = H) or 2 (R = H) (0.064 mmol) in methylene chloride (8 cm<sup>3</sup>). The solution was stirred under nitrogen for 0.5 h, after which acetonitrile was added dropwise until no more precipitate formed. The greenish white solid was collected by filtration and washed twice with acetonitrile and then twice with diethyl ether. The precipitate was initially dried under an atmosphere of nitrogen and then *in vacuo*.  $[Cu_3L](PF_6)_3$  (L = 1, R = H) (yield, 92%). [Found: C, 35.40; H, 5.66; N, 5.56; S, 12.98%.  $C_{45}H_{84}Cu_3N_6S_6$  (PF<sub>6</sub>)<sub>3</sub> requires C, 35.39; H, 5.54; N, 5.50; S, 12.60%]. [Cu<sub>3</sub>(L)](PF<sub>6</sub>)<sub>3</sub> (L = 2, R = H) (yield 81%). [Found: C, 35.45; H, 5.70; N, 5.11%.  $C_{48}H_{90}Cu_3N_6O_3S_6(PF_6)_3$ requires C, 35.65; H, 5.61; N, 5.20%].
- [16] Synthesis of  $[CuL]PF_6$  (L = 3, R = H or 4, R = CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>): [Cu(CH<sub>3</sub>CN)<sub>4</sub>]PF<sub>6</sub> (70.8 mg, 0.19 mmol) in methylene chloride (5 cm<sup>3</sup>) and added to 3 (R = H) or 4 (R = CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>) (0.19 mmol) in acetonitrile (8 cm<sup>3</sup>). The solution was stirred under nitrogen for 0.5 h, after which a small volume of acetonitrile was added until no more precipitate formed. The greenish white precipitate was collected by filtration and washed with a small volume of acetonitrile and then twice with diethyl ether. The product was initially dried under an atmosphere of nitrogen and then *in vacuo*. [CuL]PF<sub>6</sub> (L = 3, R = H) (yield 86%). [Found: C, 40.98; H, 5.56; N, 5.23; S, 11.49%. C<sub>19</sub>H<sub>32</sub>CuN<sub>2</sub>PF<sub>6</sub>S<sub>2</sub> requires C, 40.67; H, 5.75; N, 4.99; S, 11.43%]. [CuL]PF<sub>6</sub> (L = 4, R = CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>) (yield 77%). [Found: C, 47.49; H, 5.81; N, 4.22; S, 9.65%. C<sub>27</sub>H<sub>40</sub>CuN<sub>2</sub>OPF<sub>6</sub>S<sub>2</sub> requires C, 47.60; H, 5.92; N, 4.11; S, 9.41%].
- [17] Crystallrefinement data: [CuL]PF<sub>6</sub> (L = 3; R = H) = C<sub>19</sub>H<sub>32</sub>CuF<sub>6</sub>-N<sub>2</sub>PS<sub>2</sub>, M = 561.1 Orthorhombic, space group  $Pca2_1$  ( $C_{2v}^5$ , No. 29), a = 16.173(8), b = 8.277(2), c = 17.885(4) Å, V = 2394 Å<sup>3</sup>.  $D_c$ (Z = 4) = 1.557 cm<sup>-3</sup>.  $\mu_{Mo} = 1.21$  mm<sup>-1</sup>; specimen:  $0.58 \times 0.22 \times$ 0.18 mm<sup>3</sup>;  $T_{min,max} = 0.76$ , 0.81 (gaussian correction).  $2\theta_{max} = 60^\circ$ ;

3595 unique single-counter diffractometer reflections (*T ca.* 295 K; monochromatic Mo Kα radiation,  $\lambda = 0.7107_3$  Å;  $2\theta/\theta$  scans), 2657 with  $I > 2\sigma(I)$ ; RI = 0.045, wR2 = 0.12 (weights  $((\sigma^2(F^2) + (0.049P)^2 + 0.3969P)^{-1}(P = (F_o^2 + 2F_c^2)/3)))$ ,  $x_{abs} = -0.12(2)$ .  $|\Delta \rho_{max}| = 0.46$  e Å<sup>-3</sup>. CCDC: 638640.

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