# Formation of Eighteen-membered Metallomacrocyclic Rings by the Sulfur-donor Ligand *N,N'*-ethylenebis(pyrrolidin-2-thione) in the Compounds $[Co(ebpt)Br_2]_2$ and $\{[Cu(ebpt)_2]PF_6\}_n$

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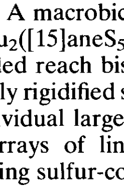
The ligand *N,N'*-ethylenebis(pyrrolidin-2-thione) (ebpt) reacts with cobalt(II) bromide to form $[Co(ebpt)Br_2]_2$ comprising discrete 18-membered rings, and with $Cu(MeCN)_4PF_6$ to produce polymeric $\{[Cu(ebpt)_2]PF_6\}_n$ in which there are chains of spiro-linked 18-membered rings, the ring conformation remaining unchanged.

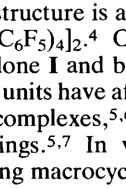
Structurally defined individual large-ring metallocycles involving sulfur-donor ligands coordinated to transition metals are rare. Crystallographically characterised examples include: *trans*-$[Pd_2Cl_4\{Bu^tS(CH_2)_5SBu^t\}_2]$, which forms a 16-membered ring,[1] $[(\eta\text{-}C_5H_5)Zr\{\mu\text{-}S(CH_2)_3S\}]_2$ (12-membered ring),[2] and $[(\eta\text{-}C_5H_5)Zr(\mu\text{-}SCH_2CH_2)_2S]_2$ (16-membered ring).[3] A macrobicyclic structure is also present in the cation of $[Au_2([15]aneS_5)_2][B(C_6F_5)_4]_2$.[4] Our recent studies with extended reach bis-pyridone **I** and bis-lactam **II** ligands with partially rigidified spacer units have afforded several examples of individual large-ring complexes,[5,6] as well as more extensive arrays of linked rings.[5,7] In view of the interest in designing sulfur-containing macrocycles,[8] both for their complex-forming capabilities and potential for redox reactions, we have initiated studies of the thio-analogues of **I** and **II**. We have found that ebpt, **III**, which can be obtained from its pyrrolidone analogue by use of Lawesson's reagent, does, indeed, give large-ring complexes and we report here two examples.

Reaction of **III** with cobalt(II) bromide hexahydrate in hot ethanol–2,2-dimethoxypropane (1 : 1) followed by concentration of the solution *in vacuo* afforded a blue complex $Co(ebpt)Br_2$ **1**. An analogous reaction of **III** with $Cu(MeCN)_4PF_6$ in ethanol–acetonitrile (1 : 2) gave pale yellow $[Cu(ebpt)_2]PF_6$ **2**. Both compounds have been fully characterised by single-crystal X-ray methods.†

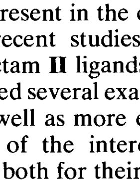
The X-ray analysis of **1** shows the complex to be dimeric, with two ebpt ligands bridging two tetrahedrally coordinated cobalt(II) centres to form a centrosymmetric 18-membered ring (Fig. 1). There are only small differences in the pairs of Co–Br and Co–S bond lengths [Co–Br(1) 2.368(2), Co–Br(2) 2.387(2), Co–S(1) 2.329(3) and Co–S(2) 2.319(3) Å] but the bond angles deviate significantly from idealised tetrahedral and are in the range 98.3(1)–114.3(1)°, the distortions being principally in the form of a twisting of the Br–Co–Br plane with respect to the S–Co–S plane about a $C_2$ axis of the tetrahedron.



**I**



**II**



**III**

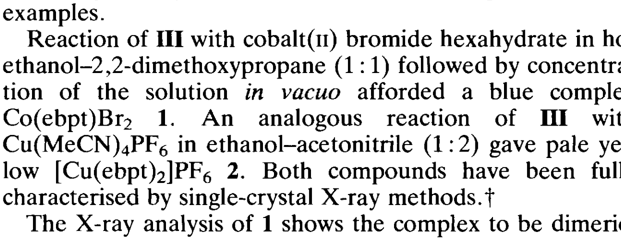


**Fig. 1** The 18-membered metallocycle formed by **1**

The macrocycle has a slightly puckered conformation and is self-filling, with one pair of diametrically opposite S atoms directed inwards and lying within the mean plane of the macrocycle (S···S 4.6 Å), whilst the other pair are pseudo-axially directed. The presence of two inwardly directed sulfur atoms contrasts with the normally observed *exo*-orientation in purely organic sulfur macrocycles.[8] This difference may, in part, be attributable to the steric requirements of the bromine atoms and to the directing role of the ebpt ligand. The conformation about the N–$CH_2$–$CH_2$–N bridging unit is *gauche* (–$CH_2$–$CH_2$– angle = 68°) and consistent with one of the two principal ligand conformations previously observed in the erbium nitrate complex of the bis-lactam analogue.[7]

The crystals contain occluded methanol molecules of solvation [from the reaction of 2,2-dimethoxypropane with the water of hydration of the cobalt(II) bromide]. These lie in channels that extend in the crystallographic *c* direction and are loosely held *via* O–H···Br hydrogen bonds (3.2 Å).

The closest type of cobalt(II) complex hitherto reported is the bis(diphenylphosphine oxide) complex $[\{CoCl_2[Ph_2P(O)CH_2CH_2P(O)Ph_2]\}_2]$ which forms a 14-membered ring.[9]

The X-ray analysis of **2** shows that each copper(I) ion is tetrahedrally bonded to four sulfur atoms, one from each of four different ebpt ligands (Fig. 2). The Cu–S bond lengths [2.334(2)–2.348(2) Å] do not differ significantly and they are similar to those found for other tetrahedral $Cu^IS_4$ systems.[10] The S–Cu–S bond angles [103.8(1)–120.8(1)°] again depart from an idealised tetrahedral value {*cf.* 98.8–117.8° in $Cu(ethylenethiourea)_4(NO_3)$[10] and 93.8–117.8° in $[Cu(thiourea)_4]_2(SiF_6)$[11]}.

Pairs of ebpt ligands serve to link adjacent copper centres so as to form a chain of 18-membered rings propagated in the crystallographic $10\bar{1}$ direction, with each pair of rings being linked at lattice translated copper centres. Adjacent, spiro-linked macrocycles are disposed about crystallographically independent centres of symmetry. Their conformations are essentially identical (mean deviation of their best fit = 0.28 Å) as a consequence of a consistent *gauche* relationship of each pair of thiolactam rings about their ethylene bridges (the N–

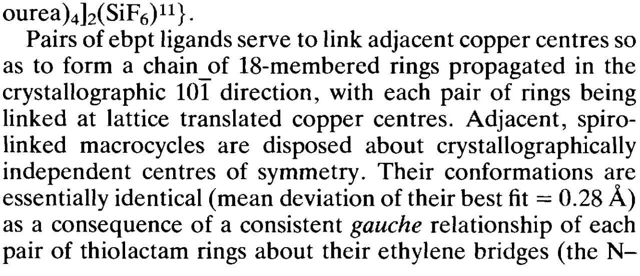


**Fig. 2** Part of the extended chain of 18-membered macrocycles formed by **2**

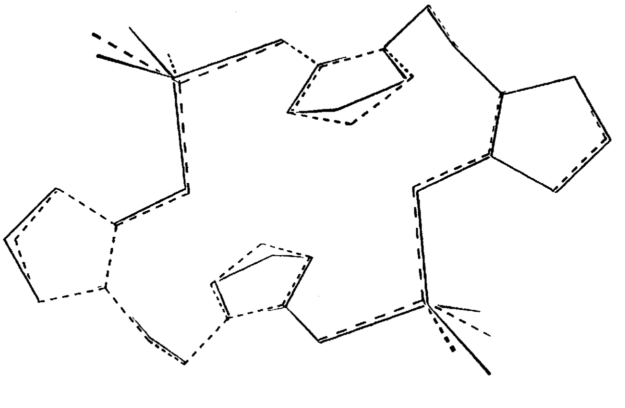


**Fig. 3** Least-squares-fit of the macrocyclic components of **1** (----) and **2** (—)

$CH_2$–$CH_2$–N torsion angles are 64 and 70°, *cf.* 68° in **1**). The ring conformation observed for **2** is remarkably close to that adopted by **1** (Fig. 3); the mean deviation between equivalent atoms in the rings is *ca.* 0.2 Å. The shortest transannular S···S distances are 4.57 and 4.75 Å.

The anions in **2** lie in channels formed between adjacent polymer chains and are loosely linked to the thiolactam units *via* weak C–H···F hydrogen bonds. The acetonitrile molecules of solvation, which are disordered, also lie in channels between the polymer chains.

These two structural results presage a family of large-ring polymeric complexes with extended reach sulfur donor ligands as potentially rich and diverse as those formed by their O-donor analogues.[5–7,12–14] In particular, the consistency of macrocycle conformation for both **1** and **2**, which is clearly independent of crystal packing, would appear to offer an important predictive capability of how this unit may be used in the generation of extended metallocyclic arrays. Indeed, the use of appropriately designed sulfur donors of this type offers entry into new types of large ring frameworks involving *e.g.* platinum metals.

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## Footnote

† *Crystal data* for **1**: $C_{20}H_{32}Br_4Co_2N_4S_4\cdot 1.5MeOH$, monoclinic, space group $P2_1/n$, $a = 10.526(3)$, $b = 12.541(4)$, $c = 13.366(3)$ Å, $\beta = 97.58(2)°$, $U = 1749.0(8)$ Å$^3$, $Z = 2$, $M = 942.3$, $D_c = 1.789$ g cm$^{-3}$, $\mu$(Mo-K$\alpha$) = 57.8 cm$^{-1}$.

For **2**: $C_{20}H_{32}CuF_6N_4PS_4\cdot 0.5MeCN$, triclinic, space group $P\bar{1}$, $a = 9.166(4)$, $b = 13.646(6)$, $c = 13.684(4)$ Å, $\alpha = 67.22(2)$, $\beta = 72.08(2)$, $\gamma = 83.70(2)°$, $U = 1481.4(10)$ Å$^3$, $Z = 2$, $M = 685.8$, $D_c = 1.537$ g cm$^{-3}$, $\mu$(Cu-K$\alpha$) = 47.1 cm$^{-1}$.

Data for both **1** and **2** were measured on a Siemens P4/PC diffractometer with, for **1**, graphite-monochromated Mo-K$\alpha$ radiation and, for **2**, Cu-K$\alpha$ radiation, using $\omega$-scans. Both structures were solved by the heavy-atom method and refined anisotropically to give for **1** $R = 0.053$, $R_w = 0.049$ for 1810 independent observed reflections $[|F_o| > 4\sigma(|F_o|)]$, $2\theta = 3$–$50°$ and for **2** $R = 0.046$, $R_w = 0.054$ for 4067 independent observed reflections $[|F_o| > 4\sigma(|F_o|)]$, $2\theta = 3$–$122°$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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