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Thia-calix[*n*]pyridines, synthesis and coordination to Cu(I,II) ions with both N and S donor atoms†

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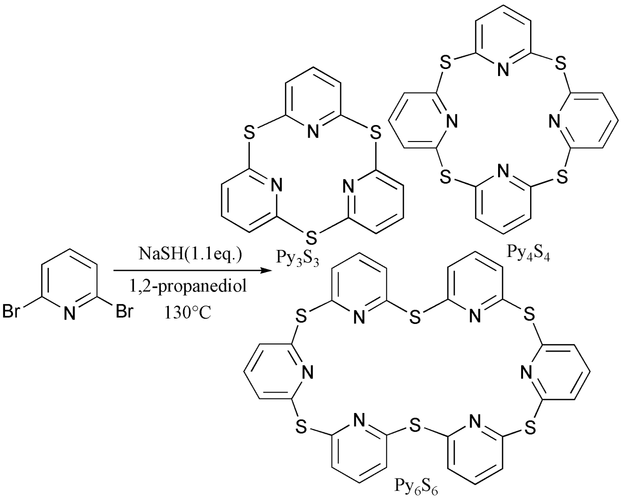
The novel thia-calix[*n*]pyridines ($n = 3, 4, 6$) coordinated to copper ions through nitrogen and sulfur atoms to give multinuclear complexes whose structures have been determined by X-ray crystallography and NMR spectra.

Calixarenes with hetero-atoms have attracted much attention due to the special functionality imparted by the hetero-atoms. In the case of calix[4]pyrrole, it was shown that they have a preference for binding F^- over other anions.[1]

By expanding the pyrrole ring of calix[4]pyrrole, Sessler and coworkers prepared calixpyrrole/pyridine and calix[4]pyridine,[2] but only a small number of complexes have been prepared using them as ligands.[3] Because the pyridine rings in calix[4]pyridine are linked together in the 2 and 6 position by an sp^3 hybridized carbon, steric effects make the formation of a macrocyclic complexes difficult. However exchanging the linking C with sulfur atoms should increase the flexibility and coordinating ability of the calixpyridine. In addition, metal atoms can coordinate to the S atoms creating possible metallothionein mimics.[4] Thia-calix[3]pyridine(Py_3S_3) has been known for years,[5] but its coordination abilities have never been examined. We report the preparation of thia-calix[*n*]pyridines (Py_nS_n), where $n = 3, 4, 6$, and the coordination abilities of Py_3S_3 and Py_4S_4 toward copper ions.

Using a convenient one-pot reaction of 2,6-dibromopyridine with sodium hydrosulfide, thia-calix[3], [4] and [6]pyridine were prepared in 40, 8 and 4% yields, respectively (Scheme 1). The structure of thia-calix[4]pyridine was determined by X-ray crystallography (see Fig. 4).‡



Scheme 1 Synthesis of thia-calix[*n*]pyridines.

The coordination ability of Py_3S_3 was examined using $[Cu(CH_3CN)_4](PF_6)$. In CH_2Cl_2, a dimeric complex, $[Cu(Py_3S_3)]_2(PF_6)_2$ (**1**) (eqn. (1)), was produced which is stable only in the solid state and in non-coordinating solvents.

$$2[Cu(CH_3CN)_4](PF_6) + 2Py_3S_3 \rightarrow [Cu(Py_3S_3)]_2(PF_6)_2 \quad (1)$$

$$[Cu(Py_3S_3)]_2(PF_6)_2 + 2CH_3CN \rightleftharpoons 2[Cu(Py_3S_3)(CH_3CN)](PF_6) \quad (2)$$

Recrystallization of **1** from an acetonitrile solution produced monomeric $[Cu(Py_3S_3)(CH_3CN)](PF_6)$ (**2**) accompanied by cleavage Cu–S bond and ligation of an CH_3CN to the Cu atom. The equilibrium in eqn. (2) shifted toward the right in the presence of an excess amount of acetonitrile.

Complex **1** has a dimeric structure (Fig. 1)§ in the absence of coordinating ligands other than Py_3S_3. Each Cu(I) center is coordinated by a Py_3S_3 through three pyridines and by another Py_3S_3 through a sulfur atom with a Cu–S bond distance of 2.206(1) Å. The C–S–C angle of bridged sulfur atom is wider (102.4(2)°) than any other C–S–C angles (99.4(2)–99.6(2)°). The two Cu ions are crystallographically identical. The N–Cu–N angles (94.6(1)–96.1(1)°) in **1** are larger than in **2** as the result of the dimerization. Py_3S_3 can incorporate a copper ion in the middle forming flatter structure making the sulfur atoms more accessable for dimerization. A similar dimerization through a Cu–S bond was also observed in a thiophenophane complex of copper.[7]

Complex **2** (Fig. 1)§ is a discrete monomer with the Py_3S_3 and the acetonitrile ligand forming distorted T_d structure. The N–Cu–N angles in both **1** and **2** (92.1(6)–96.1(1)°) are larger than in $[Cu(1,4,7\text{-triisopropyl-}1,4,7\text{-triazacyclononane})(CH_3CN)]^+$ (85.4(1)–86.2(1)°).[6]

The NMR spectrum of **2** in CD_2Cl_2 at 233 K shows an AB_2 pattern (7.83 ppm) for the monomer structure along with an additional set of AB_2 and ABC patterns. The latter signals coalesced at 273 K and reformed as a broad peak (7.98 ppm) at 298 K accompanied by a decreasing in the signal intensity for **2** (7.83 ppm) (Fig. 2). Complex **1** shows the same NMR signals as complex **2** at different temperatures. When acetonitrile was added to this solution, the signal intensity between 7.87–8.12 ppm decreased and the AB_2 pattern at 7.83 ppm increased in intensity. The NMR results establish the presence of both the dimer and monomer in CD_2Cl_2 solution of **2**. Absorption spectrum of **1** changed to that of **2** upon addition of acetonitrile

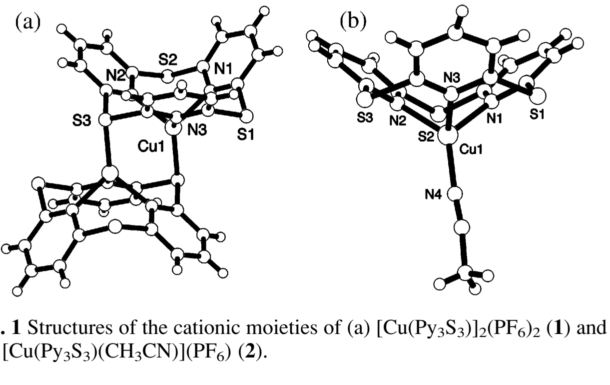


Fig. 1 Structures of the cationic moieties of (a) $[Cu(Py_3S_3)]_2(PF_6)_2$ (**1**) and (b) $[Cu(Py_3S_3)(CH_3CN)](PF_6)$ (**2**).

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† Electronic supplementary information (ESI) available: emission spectra of compound **1**. See http://www.rsc.org/suppdata/cc/b2/b203540e/

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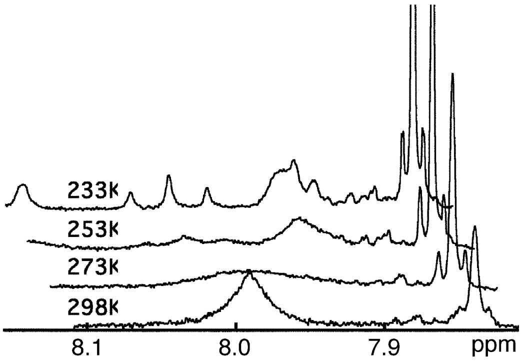

Fig. 2 Variable temperature ^{1}H NMR spectra of the pyridine ring of **2** in CD_2Cl_2.

(5×10^{-2} mol dm^{-3}) (Fig. 3), as well as the disappearance of the emission from **1** peaked at 580 nm.†

We have examined the coordination ability of Py_4S_4 toward metal ions by use of CuBr.

The reaction in air in CH_2Cl_2 produced polymer structure of $[\{Cu(Py_4S_4)\}(CuBr_2)_2{\cdot}CH_2Cl_2]_n$ (**3**) (eqn. (3)).¶ The structure of compound **3** was determined by X-ray crystallography (Fig. 4).‖

$$CuBr + Py_4S_4 \rightarrow [\{Cu(Py_4S_4)\}(CuBr_2)_2]_n \qquad (3)$$

In compound **3**, a Cu(II) ion is surrounded by the four pyridine rings of a Py_4S_4 forming planar coordination structure.

Because the pyridine rings in the ligand tilt alternatively toward the Cu–N coordination plane, C–S–C bridges fold up and down alternatively, and a Cu(I) ion is coordinated by a sulfur atom and bound to a Cu(I) of the next unit, forming one dimensional network.

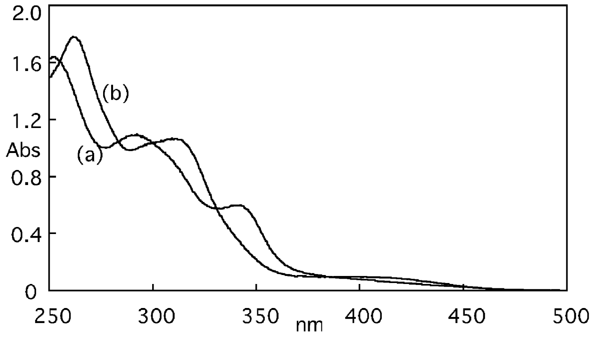

Fig. 3 (a) Absorption spectrum of **1** (5.68×10^{-5} mol dm^{-3}) in CH_2Cl_2, (b) in the presence of acetonitrile (5×10^{-2} mol dm^{-3}).

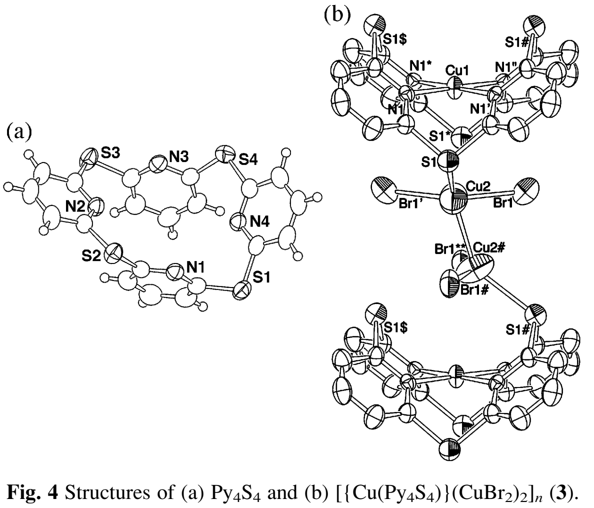

Fig. 4 Structures of (a) Py_4S_4 and (b) $[\{Cu(Py_4S_4)\}(CuBr_2)_2]_n$ (**3**).

The complexes herein are the first examples involving thia-calix[3] and [4]pyridine as ligands. It is conceivable that the flexibility of thia-calix[4]pyridine allowed for the formation of the 1-D extended structure of **3**, whereas the coordination abilities of the sterically constrained calix[4]pyridine are limited.

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Notes and references

‡ *Crystal data for* Py_4S_4: $C_{20}H_{12}N_4S_4$, $M = 436.58$, triclinic, $P\bar{1}$ (No. 2), $a = 8.680(2)$, $b = 9.7776(5)$, $c = 11.5637(7)$ Å, $\alpha = 97.695(4)°$, $\beta = 97.170(10)°$, $\gamma = 90.681(9)°$, $V = 964.5(2)$ Å^3, $Z = 2$, $T = 296.2$ K, $d_{calcd} = 1.503$ g cm^{-3}, $F(000) = 448.00$, μ(Cu-Kα) = 46.37 cm^{-1}, λ(Cu-Kα) = 1.54178 Å, 3079 reflections measured, 2863 observed, 301 variables, $R_1 = 0.031(I > 2.00\sigma(I))$, $wR(F^2) = 0.096$ (all data). CCDC 183866. See http://www.rsc.org/suppdata/cc/b2/b203540e/ for crystallographic files in .cif or other electronic format.

§ *Crystal data for* **1**: $C_{17}H_{13}Cl_2Cu_1F_6N_3P_1S_3$, $M = 634.91$, monoclinic, $P2_1/n$ (No. 14), $a = 13.6779(6)$, $b = 20.4121(9)$, $c = 8.5003(4)$ Å, $\beta = 102.049(2)°$, $V = 2321.0(2)$ Å^3, $Z = 4$, $T = 296.2$ K, $d_{calcd} = 1.817$ g cm^{-3}, $F(000) = 1264.00$, μ(Mo-Kα) = 15.70 cm^{-1}, λ(Mo-Kα) = 0.71069 Å, 10353 reflections measured, 4258 observed, 298 variables, $R_1 = 0.057(I > 3.00\sigma(I))$, $wR(F) = 0.095$ $(I > 3.00\sigma(I))$. CCDC 183864.

Crystal data for **2**: $C_{17}H_{12}Cu_1F_6N_4P_1S_3$, $M = 577.00$, orthorhombic, $Pca2_1$ (No. 29), $a = 23.748(3)$, $b = 12.198(2)$, $c = 14.594(1)$ Å, $V = 4227(1)$ Å^3, $Z = 8$, $T = 200.2$ K, $d_{calcd} = 1.813$ g cm^{-3}, $F(000) = 2304.00$, μ(Mo-Kα) = 14.71 cm^{-1}, λ(Mo-Kα) = 0.71069 Å, 32392 reflections measured, 8038 observed, 609 variables, $R_1 = 0.058(I > 2.00\sigma(I))$, $wR(F^2) = 0.063$ (all data). The asymmetric unit contains two crystallographically independent molecules. One of two PF_6^- ions was modeled as being desordered. CCDC 183863.

¶ CuBr (23.0 mg, 0.155 mmol) was added to a $CHCl_3$ solution of (n-Bu)$_4$NBr (50.0 mg, 0.155 mmol), and a $CHCl_3$ solution of Py_4S_4 (13.0 mg, 0.030 mmol) was added to the resulting green solution. The orange suspension was obtained after 30 min stirring. Orange powder of **3** was obtained by filtration (7%).

‖ *Crystal data for* **3**: $C_{22}H_{16}Br_4Cl_4Cu_3N_4S_4$, $M = 1116.70$, tetragonal, $P4_2/nmc$ (No. 137), $a = b = 13.3084(7)$, $c = 9.2055(4)$ Å, $V = 1630.4(1)$ Å^3, $Z = 2$, $T = 296.2$ K, $d_{calcd} = 2.275$ g cm^{-3}, $F(000) = 1070.00$, μ(Mo-Kα) = 74.63 cm^{-1}, λ(Mo-Kα) = 0.71069 Å, 14971 reflections measured, 641 observed, 65 variables, $R_1 = 0.058(I > 3.00\sigma(I))$, $wR(F^2) = 0.148(I > 3.00\sigma(I))$. Cu2 has half occupancy because it is located off the special position about the symmetry operation of the 4_2 screw axis. Only one site is shown in Fig. 4(b). CCDC 183865.

1 P. A. Gale, J. L. Sessler and V. Kral, *Chem. Commun.*, 1998, 1 and references therein.
2 V. Kral, P. A. Gale, P. Anzenbacher, K. Jursikova, V. Lynch and J. L. Sessler, *Chem. Commun.*, 1998, 9.
3 (*a*) R. Crescenizi, E. Solari and C. Floriani, *Organometallics*, 1999, **18**, 606; (*b*) R. Crescenizi, E. Solari, C. Floriani, A. Chiesi-Villa and C. Rizzoli, *Inorg. Chem.*, 1998, **37**, 6044.
4 (*a*) H. Kumagai, M. Hasegawa, S. Miyanari, Y. Sugawara, Y. Sato, T. Hori, S. Ueda, H. Kamiyama and S. Miyano, *Tetrahedron Lett.*, 1997, **38**, 3971; (*b*) N. Iki, C. Kabuto, T. Fukushima, H. Kumagai, H. Takeya, S. Miyanari, T. Miyashi and S. Miyano, *Tetrahedron*, 2000, **56**, 1437; (*c*) N. Iki, N. Morihashi, F. Narumi and S. Miyano, *Bull. Chem. Soc. Jpn.*, 1998, **71**, 1597; (*d*) N. Iki, N. Morihashi, C. Kabuto and S. Miyano, *Chem. Lett.*, 1999, 219.
5 (*a*) K. R. Reistad, P. Groth, R. Lie and K. Undheim, *J. Chem. Soc., Chem. Commun.*, 1972, 1059; (*b*) P. Groth, *Acta Chem. Scand.*, 1973, **27**, 5; (*c*) H. B. Romdhane, M. Bartholin, B. Sillion and S. Boileau, *C. R. Acad. Sci., Ser. II*, 1990, **311**, 525.
6 B. M. T. Lam, J. A. Halfen, V. G. Young Jr., J. R. Hagadorn, P. L. Holland, A. Lledos, L. Cucurull-Sanchez, J. J. Novoa, S. Alvarez and W. B. Tolman, *Inorg. Chem.*, 2000, **39**, 4059.
7 L. R. Hanton, C. Richardson, W. T. Robinson and J. M. Turnbull, *Chem. Commun.*, 2000, 2465.