A self-assembled macrocyclic tetranuclear molecular square $[Co(HL)]_4^{4+}$ [H_2L = tetra(2-pyridyl)thiocarbazone]

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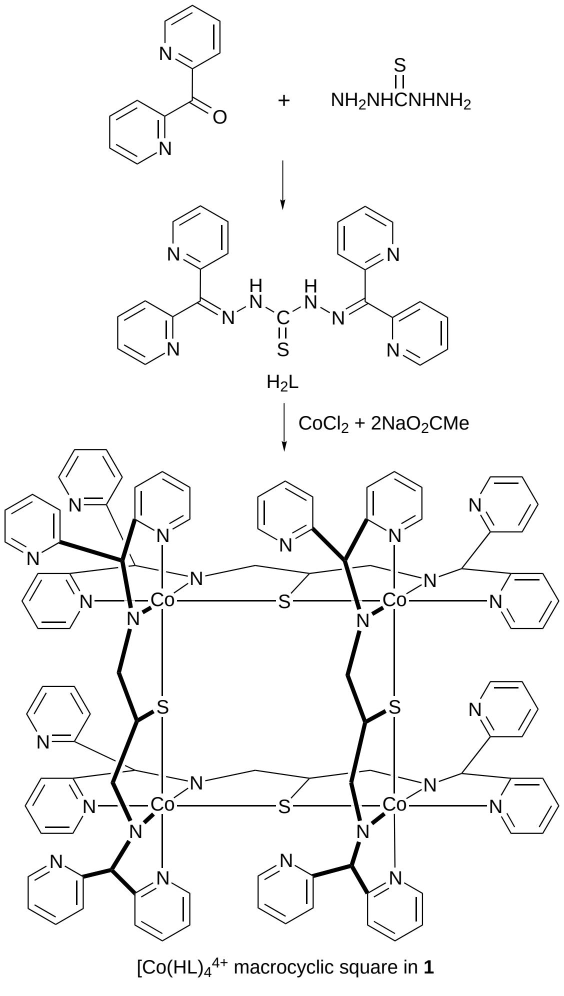
A novel conformationally rigid, cobalt-based cationic molecular square achieved *via* self-assembly from tetra(2-pyridyl)thiocarbazone is synthesized and structurally characterized.

Recently, conformationally rigid, tetranuclear macrocyclic ring systems with approximately 90° bond angles about each corner atom have been prepared in high yields *via* self-assembly from rigidly available precursors, thereby adding a new dimension to supramolecular as well as potentially biomimetic chemistry.[1–7] Hitherto only two related types of supramolecules have been reported. One is a square molecular box bridged by bifunctional nitrogen donors such as 4,4′-bipyridine,[1] 2,6-diazanthracene,[2] 2,6-diazanthracene-9,10-dione,[3] *cis*- or *trans-meso*-dipyridyl porphyrins[4] and the uracil monoanion,[5] where polyvalent iodine or heavy transition metals (Pd and Pt) occupy the corners. A second system is the $n \times n$ inorganic grid bridged by a linear polytopic ligand containing bidentate chelating sites for which the square-matrix arryas are occupied by tetrahedrally coordinating metal centres.[6,7]

In the present work, we report the synthesis and structural characterization of the first example of a cobalt-based cationic molecular square achieved *via* self-asembly with a novel rigid pentadentte ligand containing sulfur and nitrogen donor sites.

When di(pyridyl)ketone was treated with thiocarbazide in methanol at reflux, a yellow solid was readily formed. Elemental analysis supports the formation of the new pentadentate N_4S ligand $(C_5H_4N)_2C{=}NN(H)C(S)N(H)N{=}C(C_5H_4N)_2$, tetra(2-pyridyl)thiocarbazone, H_2L. Interaction of $CoCl_2{\cdot}6H_2O$ with H_2L and NaO_2CMe in methanol at boiling temperature gave the tetranuclear complex $[Co(HL)]_4[O_2CMe]_4{\cdot}H_2O$ **1** *via* self-assembly, as shown in Scheme 1.† Macrocyclic complex **1** is a remarkably stable dark brown crystalline solid and is soluble in most organic solvents. An X-ray crystallographic study‡ has unequivocally confirmed the existence of a tetranuclear cationic molecular square in **1**.

In compound **1**, the sulfur atom of the HL^- monocation exhibits twofold positional disorder, and its scattering power is represented by two 'half-atoms' S(1) and S(1′) separated by 0.93 Å. For the sake of clarity, only S(1) is shown in Fig. 1 and referred to in subsequent discussion. The tetranuclear $[Co(HL)]_4^{4+}$ cation is located at the $\bar{4}$ site with four cobalt(ii) atoms at the corners of a square of edge length Co···Co of 4.43 Å, each metal centre being octahedrally coordinated by atoms S(1), N(2) and N(3) of one HL^- ligand and S(1a), N(6a) and N(7a) from a second ligand (Fig. 1). These two HL^- ligands bind to cobalt(ii) in the *mer* configuration (with pairs of S atoms and pyridyl N atoms each bearing a *cis* relationship, whereas the thiocarbazone N atoms are *trans* to each other) as found in related octahedral cobalt thiocarbazone complexes.[8] The sulfur atoms lie alternately above and below the mid-points of the edges of the square, each being connected to two cobalt atoms with a bond angle Co–S–Co of 151°. The measured C–S bond distance of 1.814(4) Å is within the normal range of a C–S single bond,[9] indicating that the thiocarbazone moiety HL^- adopts the thiol tautomeric form in acting as a mononegative ligand.[10] The C–N and N–N bond distances in HL^- are intermediate between formal single and double bonds (see Fig. 1), pointing to extensive electron delocalization over the entire molecular skeleton. The imino H atom of the HL^- monocation could not be located from the difference Fourier map, and is most likely disordered over both N(1) and N(5) sites. Except for the uncordinated pyridine rings and the disordered sulfur atom, the atoms in the monoanion are nearly coplanar, the mean deviation from the best plane being 0.080 Å. The dihedral angle between two HL^- ligands coordinated to the same Co^{II} atom is exactly 90° due to the symmetry of the $I4_1/a$ space group, the closest intermolecular distance between two HL^- planes coordinated to different Co^{II} centres is 4.43 Å, indicating weak π–π interaction. The crystal structure of **1** consists of a packing of tetranuclear $[Co(HL)]_4^{4+}$ cations



Scheme 1

imbedded in a matrix of highly disordered acetate ions and water molecules.

The UV–VIS spectra of **1** in methanol shows a strong broad absorption band at *ca.* 264 nm (log ε = 5.3) which is assigned to intraligand transitions and a quite broad band at *ca.* 490 nm (log ε = 4.2) which might be assigned to an MLCT transition. This result suggests that the square molecular box may be retained in solution. Solid-state spectra in the range 550–850 nm exhibit only a strong bond at *ca.* 600 nm, which can be assigned to d–d transitions of the central metal.

The components used in the construction of the cationic molecular square $[Co(HL)]_4^{4+}$ by self-assembly are novel in several respects. Previous studies generally made use of bidentate nitrogen donor ligands as the edges and iodonium or heavy transition-metal ions as the corners of the square unit. In our synthesis of this type of tetranuclear macrocycle we have introduced a newly designed, rigid pentadentate N_4S ligand for binding to a first-row transition metal, thereby offering the potential of broadening the scope of further work in this area.

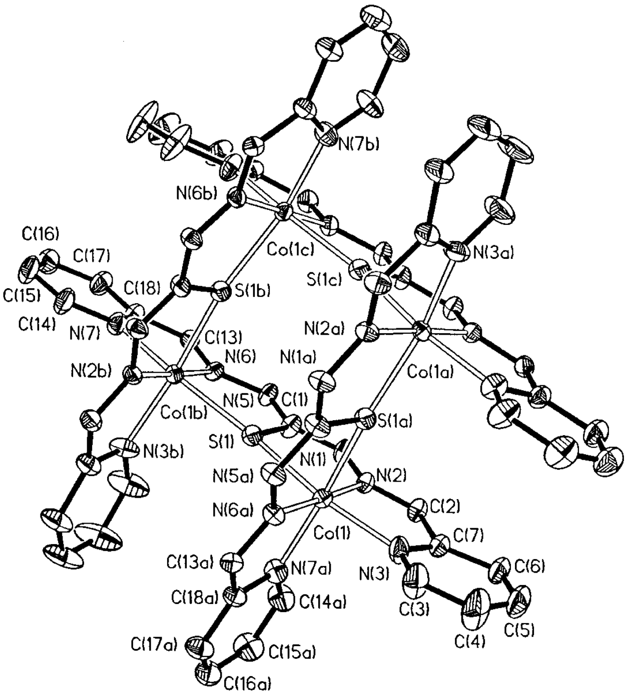


Fig. 1 Perspective view of the molecular skeleton of the square macrocycle $[Co(HL)_4]^{4+}$ in **1**, showing the non-hydrogen atoms as 25% probability thermal ellipsoids. The uncoordinated pyridine rings and hydrogen atoms are omitted for clarity. The Co···Co separation is 4.43 Å. Selected bond lengths (Å) and angles (°): Co(1)–S(1) 2.268(3), Co(1)–N(2) 1.905(5), Co(1)–N(3) 1.983(5), Co(1)–S(1a) 2.300(3), Co(1)–M(6a) 1.915(5), Co(1)–N(7a) 1.971(5). S(1)–C(1) 1.813(6), C(1)–N(1) 1.318(7), C(1)–N(5) 1.321(6), N(2)–C(2) 1.314(7), N(6)–C(13) 1.317(6), N(1)–N(2) 1.353(6), N(5)–N(6) 1.356(6); S(1)–Co(1)–N(2) 84.7(1), S(1)–Co(1)–N(3) 162.4(2), S(1)–Co(1)–S(1a) 115.4(1), S(1)–Co(1)–N(6a) 93.5(1), S(1)–Co(1)–N(7a) 78.9(2), N(3)–Co(1)–N(2) 81.4(2), N(3)–Co(1)–S(1a) 77.2(2), N(3)–Co(1)–N(6a) 100.3(2), N(3)–Co(1)–N(7a) 92.2(2), Co(1)–S(1)–Co(1b), 151.3(1). Symmetry codes: a $-0.25 + y$, $1.25 - x$, $0.25 - z$; b $1.25 - y$, $0.25 + x$, $0.25 - z$.

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Footnotes

† Complex **1** was synthesized by combining methanol solutions of H_2L^1 (0.44 g, 1 mmol), $CoCl_2 \cdot 6H_2O$ (0.24 g, 1 mmol) and NaO_2CMe (0.16 g, 2 mmol). The dark brown crystalline solid which formed after refluxing for 2 h was isolated and dried under vacuum to give **1** in 62% yield. Crystals suitable for an X-ray structure determination were obtained from slow evaporation of a DMF solution of **1** in air. Anal. Found: C, 54.1; H, 3.9; N, 19.5. Calc. for $C_{100}H_{80}Co_4N_{32}O_8S_4 \cdot H_2O$: C, 53.6; H, 3.7; N, 20.0%.

‡ *Crystal data* for **2**: tetragonal, space group $I4_1/a$ (no. 88); a = 14.467(1), c = 47.411(1) Å, U = 9923(5) Å^3, Z = 4, $F(000)$ = 4560, μ = 0.82 mm^{-1}; 5240 independent reflections measured, 2662 observed [$F > 6.0\sigma(F)$], number of parameters = 408; R = 0.057, R_w = 0.079. The intensities were collected at 294 K on a Rigaku Raxis IIC imaging-plate diffractometer using Mo-Kα radiation (λ = 0.710 73 Å) from a rotating-anode generator operating at 50 kV and 90 mA ($2\theta_{max}$ = 55.2°); 60 oscillation frames in the range 0–180°, exp osure time 8 min per frame. The crystal structure was solved by direct methods with distance restraints of C–C = 1.38 ± 0.01 Å and C–N = 1.34 ± 0.01 Å for uncoordinated pyridyl groups. The S atom [site occupancy factor (sof) for S(1) and S(1′) fixed at 0.5] and acetate ions [sof = 0.5 for O(1), O(2), C(24) and C(25) of one acetate group, sof = 1/4 for O(3), O(4) C(26), C(27) and O(5), O(6), C(28) and C(29) of the two other acetate groups with distance restraints of C–C = 1.520 ± 0.005 Å, C–O = 1.254 ± 0.005 Å, O···O = 2.16 ± 0.01 Å], as well as the water molecule (sof = 0.25) were found disordered. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares. Hydrogen atoms were placed in their calculated positions with C–H = 0.96 Å, assigned fixed isotropic thermal parameters and allowed to ride on their respective parent atoms. The contributions of these hydrogen atoms were included in the structure-factor calculation. All computations were carried out on a PC-486 usig the SHELXTL-PLUS program package. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/356.

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