Synthesis of [Tetrakis(1,3-dithiol-2-thiono)-porphyrazinato]magnesium†‡

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[Tetrakis(1,3-dithiol-2-thiono)porphyrazinato]magnesium has been prepared by cyclotetramerization of 4,5-dicyano-1,3-dithiol-2-thione.

Tetrapyrol macrocycles are of considerable interest owing to their fascinating electronic and optical properties.[1] Although porphrines, tetrabenzoporphyrines, porhyrazines and phthalocyanines are the main subgroups of these macrocylic molecules, phthalocyanines have received major attention both from the synthetic point of view and practical applications.[2] In recent years a large number of derivatives have been prepared to facilitate the exploitation of these properties in gas sensors, electrophotography, fuel cells, solar energy conversion, non-linear optics, catalysis and photodynamic cancer therapy.

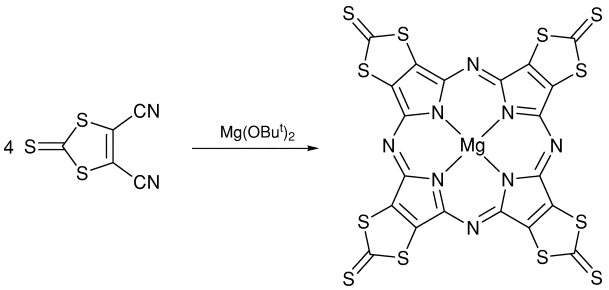
Another important group for contemporary materials chemistry are some chalcogen derivatives.[3,4] It has been pointed out that although sulfur based heterocyclic systems are central building blocks of the chemistry of life (*e.g.* biotin, thiamine pyrophosphate, penicillin), the biological importance of sulfur-containing heterocycles is still minor when compared to the very wide applications of them in modern materials chemistry. The chemistry of the 1,3-dithiole system in particular is interesting mainly because of the exceptionally rich redox chemistry and polarizability of sulfur. Conductivity and superconductivity, non-linear optics (NLO) and organic ferromagnetism have been realized in new materials based on 1,3-dithiol units.[5] In parallel with the 1,3-dithiolium cations which are aromatic 6π electron systems, 1,3-dithiole-2-thiones have been characterized as pseudo-aromatic in aspects of their reactivity.[6]

In the present paper, our aim was to prepare a novel structure in which 1,3-dithiol-2-thione heterocycles are fused on the periphery of a magnesium porphyrazine in order to extend the aromatic core.

The starting point for this compound is the disodium salt of dithiomaleonitrile which is obtained in two steps from carbon disulfide and sodium cyanide.[7,8] The presence of bulky electron donating S-groups is expected to enhance the chemical stability and optical properties of porphyrazines. Treatment of the disodium salt of dithiomaleonitrile with thiophosgene gives the desired unsaturated *o*-dicyano compound, 4,5-dicyano-1,3-dithiole-2-thione. This was previously synthesized by Klinsberger[9] in order to obtain the 1,3-dithiolium cation which was used to prepare tetrathiafulvalene.

The synthesis of the target molecule was accomplished by cyclotetramerization of 4,5-dicyano-1,3-dithiole-2-thione in butanol in the presence of magnesium butanolate (Scheme 1). The dark blue product was isolated from the reaction mixture by Soxhlet extraction with pyridine.

The pseudo-aromatic five-membered dithiole rings attached to the planar porphyrazine macrocycle are forced to lie in the same plane, and thus tetrakis(1,3-dithiol-2-thiono)porphyrazinatomagnesium (MgPzt) should be very similar to phytalocyanine. Very low solubility of this new compound in common organic solvents is an expected consequence of its structure.



Scheme 1

The low solubility of MgPzt hindered an extensive ^{13}C NMR investigation. Elemental analysis results closely match the calculated values and the electronic spectrum provides evidence for porphyrazine formation. In donor solvents such as DMF or pyridine, the axial positions can be occupied by donor solvent molecules, but the porphyrazine core still retains D_{4h} symmetry. A consequence of this is two intense absorptions with maxima at 646 nm (Q band) and 382 nm (B band) (Fig. 1). The IR spectrum is consistent with the proposed structure and the intense C≡N stretching vibrations of the starting maleonitrile derivative are absent. Mass spectrometry might be a promising technique to verify the structure; however, the mass spectrum of MgPzt obtained by the FAB method did not give the molecular ion peak as is also the case for some other unsaturated multisulfur complexes (*e.g.* dithiolenes[10]) which are known to have low volatility and decompose near the melting point. Consequently, we need to search for suitable fragmentation patterns which are observed in this case at

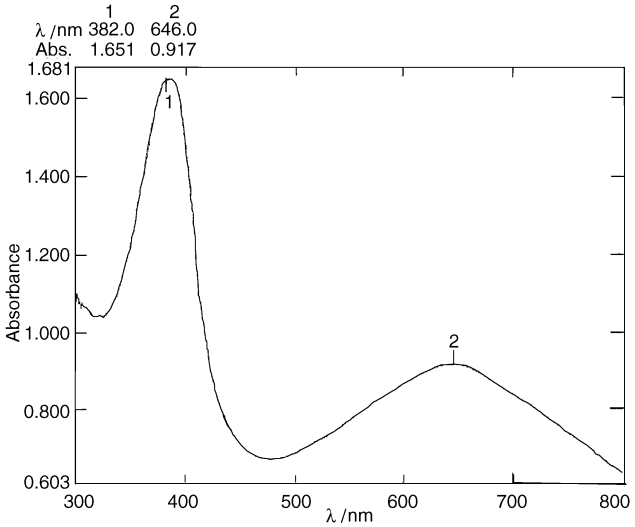


Fig. 1 UV–VIS spectrum of [tetrakis(1,3-dithiol-2-thiono)-porphyrazinato]magnesium (MgPzt)

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m/*z* 639.6 and 550.8 which might correspond to fragments formed by cleavage of multisulfur units such as ($CS_2 + CS$) and ($2CS_2 + CNS$), respectively.

The general route to insert various metal ions in the porphyrazine core is to demetallate the magnesium derivative by treatment with a suitable acid and then incorporate a metal ion by reaction with an excess of the metal ion.[11] This procedure was attempted for the tetrakis(1,3-dithiol) substituted porphyrazine using acetic acid, trifluoroacetic acid or conc. HCl. However, the metal-free derivative could not be isolated. Depending on the reaction conditions, either MgPzt was unaffected or it was completely decomposed. This unexpected result might be also attributed to the insolubility of the porphyrazine in these acids under mild conditions.

Experimental

[*Tetrakis*(1,3-*dithiol*-2-*thiono*)*porphyrazinato*]*magnesium*.—Magnesium powder (68 mg, 2.9 mmol) was refluxed overnight in 10 ml of butanol with the addition of a few crystals of I_2. To this magnesium butanolate mixture, 4,5-dicyano-1,3-dithiole-2-thione[9] (184 mg, 1 mmol) was added and after refluxing for 3 h, a dark blue suspension was obtained. After cooling to room temperature, diethyl ether (50 ml) was added to completely precipitate the product. It was filtered off, washed first with water, then with ethanol and diethyl ether. This crude product was extracted with pyridine (30 ml) in a Soxhlet extractor. After evaporation of the solvent from the dark blue solution, pure porphyrazine was obtained by washing the residue from traces of pyridine first with ethanol and then with diethyl ether. Yield: 88 mg (46%). This porphyrazine was only slightly soluble in DMF, DMSO and pyridine.

ν_{max}/cm^{-1} (KBr pellet) 1480, 1250, 1110, 1020, 840, 650. λ_{max}/nm (DMF) 646, 382 (Found: C, 31.56: H, 0.0; N, 14.97; S, 50.35; Mg, 3.0. $C_{20}H_0N_8S_{12}Mg$ requires C, 31.58; H, 0.0; N, 14.74; S, 50.52; Mg, 3.16%). *m*/*z* 639.6, 550.8, 391.4, 259.3, 173.2.

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