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# Tetrakis(thiadiazole)porphyrazines. 1. Syntheses and Properties of Tetrakis(thiadiazole)porphyrazine and Its Magnesium and Copper Derivatives

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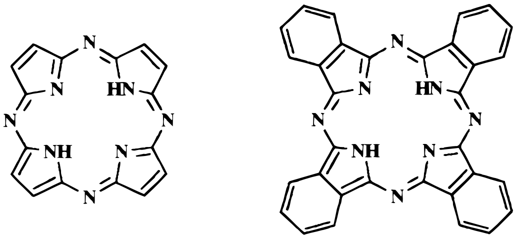
The new macrocycle tetrakis(thiadiazole)porphyrazine, TTDPzH$_2$, has been prepared, in CF$_3$COOH, from its corresponding Mg(II) derivative, [TTDPzMg(H$_2$O)]·CH$_3$COOH, which, in turn, is obtained by the reaction of magnesium(II) propylate and 3,4-dicyano-1,2,5-thiadiazole. The Mg(II) complex is also used for the preparation of the Cu(II) derivative, TTDPzCu, by reaction with copper acetate in CF$_3$COOH. An alternative preparation allows the Cu(II) complex to be obtained from the metal-free macrocycle and Cu(OCOCH$_3$)$_2$ in pyridine. Like the Mg(II) complex, TTDPzH$_2$ and TTDPzCu are obtained as solvated species (carboxylic acid, water). Practically complete elimination of the solvent molecules can be achieved by heating the species under vacuum ($10^{-2}$ mmHg) at 300−310 °C, only the Mg(II) complex retaining water. TTDPzH$_2$ and TTDPzCu can also be obtained by sublimation under vacuum ($10^{-2}$ mmHg, 400−450 °C) from the parent solvated complexes. IR spectra in the range 4000−200 cm$^{-1}$ allow easy identification of the different species. Deuteration of TTDPzH$_2$ has allowed assignments of the NH stretching and bending vibrations. The UV−visible solution spectra in different media all exhibit intense absorptions in the Soret-band (300−400 nm) and Q-band (600−700 nm) regions, showing strong resemblance to those of their corresponding phthalocyanine analogues. A detailed analysis of the spectral behavior allows the electronic structure of the TTDPz macrocyclic ring to be adequately depicted.

**Chart 1**



**a**
**PzH$_2$**

**b**
**PcH$_2$**

## Introduction

Some of the most recent research work on the synthesis, chemical−physical characterization, and reactivity of metal phthalocyanines developed by our and joint laboratories has shown the capacity of different diphthalocyanine molecular units, i.e., Pc$_2$M (M = Ti(IV), Sn(IV)),[1] (PcFe)$_2$C,[2] and (PcRu)$_2$,[3] to result in the formation of linearly elongated electrically conductive materials upon oxidation with I$_2$ or O$_2$, and the role played by the metal centers and by the close $\pi-\pi$ contacts of the adjacent Pc rings in the efficiency of charge transfer along the chained systems has been thoroughly examined.[1−3] We have now started an investigation on porphyrazine (Chart 1a) and substituted porphyrazines and their metal derivatives, a class of materials far less studied, though recently the object of growing interest,[4] than their closely related phthalocyanine[5] (Chart 1b) and porphyrin analogues,[6] and have focused our attention on the synthesis of tetrakis(thiadiazole)porphyrazine, TTDPzH$_2$ (Chart 2a) and its selenium analogue and their metal derivatives as well, because electron-rich and soft substituents such as S or Se inserted into the proximity of the central porphyrazine macrocycle may significantly influence the electronic properties of the latter. This aspect is of importance for

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(1) (a) Ercolani, C.; Paoletti, A. M.; Pennesi, G.; Rossi, G.; Chiesi-Villa, A.; Rizzoli, C. *J. Chem. Soc., Dalton Trans.* **1990**, 1971. (b) Ercolani, C.; Paoletti, A. M.; Pennesi, G.; Rossi, G.; Chiesi-Villa, A.; Rizzoli, C. *Inorg. Chem.* **1993**, *32*, 4605. Abbreviations used in the present paper: Pc = phthalocyaninato anion, $C_{32}H_{16}N_8{}^{2-}$; Pz = porphyrazinato anion, $C_{16}H_8N_8{}^{2-}$; TTDPz = tetrakis(thiadiazole)porphyrazinato anion, $C_{16}N_{16}S_4{}^{2-}$; DMN = diaminomaleonitrile; ClNP = 1-chloronaphthalene; PhCl = chlorobenzene.

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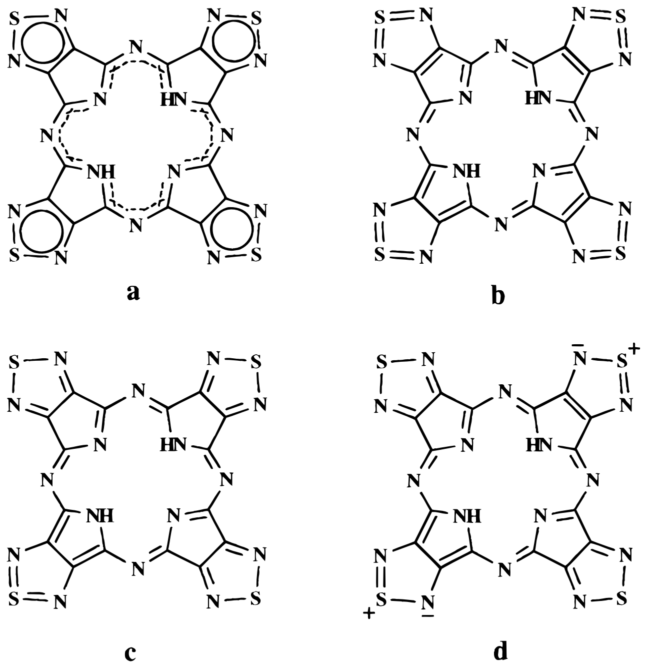
**Chart 2**



**TTDPzH$_2$**

a number of reasons, especially if an attempt is made to modulate the solid state interunit contacts, since the latter play a relevant role in charge transfer processes in appropriately monodimensionally stacked materials, as has been indeed widely shown for the parent class of phthalocyanine compounds.[7]

We report here the synthesis, structure, and chemical−physical properties of TTDPzH$_2$. To our knowledge, the description of this macrocycle is unprecedented. Its Mg(II) and Cu(II) derivatives are also described here. These two metal complexes were recently prepared[8] by using procedures which imply difficult purification of the materials isolated and, in one case (Mg), very low yields. The syntheses of these Mg(II) and Cu(II) complexes are accomplished here via alternative accessible methods, which allow consistent and pure amounts of the complexes to be isolated. Information at hand, which allows some knowledge of the molecular and electronic structure of the present species to be achieved here, has been made available by IR, UV−visible, EPR, and magnetic susceptibility measurements. Selenium containing analogues are also currently under investigation and will be dealt with separately.

## Experimental Section

Solvents (1-propanol, $CH_2Cl_2$, chlorobenzene, $CH_3COOH$, $CF_3COOH$, pyridine, ethyl alcohol, 96% $H_2SO_4$) and reagents ($SOCl_2$, Mg turnings, anhydrous $Na_2SO_4$, $Cu(OCOCH_3)_2\cdot H_2O$) were pure chemicals (Carlo Erba, Merck). The hydrated copper acetate was recrystallized from acetic anhydride to give the anhydrous salt. DMN (diaminomaleonitrile) was a commercially available reagent (Aldrich), used without further purification. Metal-free phthalocyanine, PcH$_2$, and its Cu(II) derivative, PcCu, were commercial products (Eastman-Kodak) and were purified by sublimation under vacuum (450 °C, $10^{-2}$ mmHg).

**Synthesis of 3,4-Dicyano-1,2,5-thiadiazole (I).** This material was prepared by following closely the procedure reported elsewhere:[9] A mixture of DMN (10.8 g, 0.1 mol) and freshly distilled $SOCl_2$ (35.7 g, 0.3 mol) was heated at 50 °C for $^1/_2$ h and then refluxed for 1 h. Excess $SOCl_2$ was eliminated by evaporation and the solid dissolved in 400 mL of $CH_2Cl_2$ . After filtration, the solvent was removed under reduced pressure and the solid obtained was dried under vacuum (11 g; yield 80%).

**Synthesis of [TTDPzMg(H$_2$O)]·CH$_3$COOH.** Magnesium metal (0.75 g, 0.031 mol) was suspended, with stirring, in propyl alcohol (30 mL) in a 100 mL round-bottomed flask in the presence of a small amount of $I_2$. The suspension was heated to reflux for a minimum of 8 h to determine complete conversion of Mg into its corresponding propylate. Hydrogen developed during the reaction. **I** (4.22 g, 30 mmol) was then added, and the mixture was heated at 120 °C for 14 h. During the reaction, the gray mixture became dark green and then dark blue. At the end of the reaction, propanol was eliminated by evaporation under reduced pressure, and $CH_2Cl_2$ was repeatedly added to the solid blue ground material to dissolve excess unreacted **I**. Acetic acid (50% in water) was then added to the solid material to dissolve unreacted magnesium propylate, and the mixture was stirred at room temperature for 1−2 h. After filtration, the cobalt-blue solid material obtained was washed with water to neutrality and then dried under vacuum for 1−2 h (1.58 g; yield 47%, calcd on the amount of **I** used). IR, cm$^{-1}$ (Nujol; bold-type absorptions are characteristic for the species; absorptions due to solvent molecules are given in italics): $\nu$ = *1735* m, *1690*w, *1630*m, *1530*s, 1310w, 1265s, 1215vw, **1095**s, **1050**s, 880w, 853vvw, 825w, 783vw, 764w, **733**s, **690**s, 622vvw, 515s, 450vvw, 285vw. Anal. Calcd for [TTDPzMg(H$_2$O)]·CH$_3$COOH, $C_{18}H_6MgN_{16}O_3S_4$: C, 33.42; H, 0.93; N, 34.64. Found: C, 33.86; H, 0.87; N, 34.86. Heating under vacuum (300 °C, $10^{-2}$ mmHg) of the complex led to elimination of acetic acid and formation of the monohydrate [TTDPzMg(H$_2$O)]. Anal. Calcd for $C_{16}H_2MgN_{16}OS_4$: C, 32.75; H, 0.34; N, 38.19. Found: C, 33.24; H, 0.20; N, 37.68.

**Synthesis of TTDPzH$_2$.** The solvated Mg(II) complex (1.0 g, 1.55 mmol) was suspended in pure $CF_3COOH$ (10 mL), and the mixture was refluxed for 2 h, with stirring. After cautious addition of water (20 mL), the mixture was heated again for 20 min. After cooling and filtration, the dark bluish-green solid material was washed abundantly with water and dried under vacuum (0.34 g, ~0.5 mmol; yield ~35%). IR, cm$^{-1}$ (Nujol): $\nu$ = **3290** w ($\nu$(NH)), *1735*w, *1690*m, *1635*w, **1565**w ($\delta$(NH)), *1530*m, 1505w, 1340w, 1285vw, 1265s, **1215**s, **1131**s, **1054**m, **1014**s, 852w, 815m, **753**s ($\gamma$(NH)), **743**s, **666**s, **590**m, 515s, 450vw, 280w. Elemental and thermogravimetric analyses indicated that this material consists of solvated TTDPzH$_2$ containing, most probably, trifluoroacetic acid and water, both species slightly varying from sample to sample. Complete elimination of acid and water was accomplished by heating the ground material under vacuum ($10^{-2}$ mmHg) at 310 °C for 3 h. Anal. Calcd for $C_{16}H_2N_{16}S_4$: C, 35.16; H, 0.37; N, 41.00. Found: C, 35.41; H, 0.16; N, 41.61. Alternatively, TTDPzH$_2$ could also be obtained in the form of purple, clean microcrystalline material by sublimation under vacuum ($10^{-2}$ mmHg) at 400−450 °C.

**Synthesis of TTDPzD$_2$.** Deuteration of TTDPzH$_2$ was carried out by dissolution of this macrocycle in 98% $D_2SO_4$ (99.0% D) followed by pouring of the solution into cold freshly dried acetone. The precipitate formed was washed with acetone and dried under vacuum. The IR spectra of different samples prepared in this way revealed the presence of residual traces of sulfuric acid, probably attached to the N atoms of the thiadiazole rings, which acetone was unable to remove. IR, cm$^{-1}$ (Nujol): $\nu$ = 2465 cm$^{-1}$ w ($\nu$(ND)), 1740m, 1690s, 1625w, 1530m, 1500w, 1340vw, 1262m, 1218m, 1170s, 1135s, 1050s, 1020m, 870s, 820w, 738s, 670m, 600vw, 585vs ($\gamma$(ND)), 538w, 515s, 450m.

**Synthesis of TTDPzCu.** Finely ground [TTDPzMg(H$_2$O)]·CH$_3$COOH (0.50 g, 0.78 mmol) and anhydrous copper acetate (0.33 g, 1.65 mmol) and pure $CF_3COOH$ (20 mL) were mixed together in a round-bottomed flask (50 mL). The mixture was refluxed, under stirring, for 14 h. A dark-blue material was formed during the reaction. Water was then slowly added from the top of the apparatus, and the mixture was refluxed for a further 20 min. After cooling, the blue solid was washed abundantly with water and dried under vacuum (0.23 g, ~ 0.34 mmol; yield 44%). IR, cm$^{-1}$ (Nujol): $\nu$ = *1735* m, *1690*m, *1620*w,

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*1538*s, 1333vvw, 1272s, **1108**s, 1060vvw, 882m, 829m, 785vvw, 765m, **732**s, **688**s, 621w, 513s, 450vvw, 297vw. Elimination of ligated acid and water was accomplished by heating the blue solid material under vacuum (300 °C, $10^{-2}$ mmHg) to give pure TTDPzCu. Anal. Calcd for $C_{16}N_{16}CuS_4$: C, 31.60; H, 0.00; N, 36.85. Found: C, 31.43; H, 0.00; N, 36.91. Pure TTDPzCu, in the form of a purple microcrystalline powder, was also obtained by sublimation of the solvated species ($10^{-2}$ mmHg, 450 °C).

$TDDPzH_2$ allowed a mild procedure to be alternatively used for the synthesis of the Cu(II) derivative: Solvated $TTDPzH_2$ (715 mg, ~ 1.3 mmol) and anhydrous copper acetate (519 mg, 2.60 mmol) were suspended, partly dissolved, in pyridine (40 mL), and the mixture was stirred at room temperature for 24 h. The blue solid material was separated from the mixture by centrifugation, and washed abundantly with ethanol, and dried under vacuum ($10^{-2}$ mmHg) at 300−310 °C (490 mg; yield ~62%). Anal. Calcd for $C_{16}N_{16}CuS_4$: C, 31.60; H, 0.00; N, 36.85. Found: C, 31.40; H, 0.10; N, 36.63%.

**Physical Measurements.** IR spectra were run on a Perkin-Elmer 783 spectrophotometer in the range 4000−200 $cm^{-1}$ by using Nujol mulls between CsI plates. UV−visible solution spectra were taken on a Varian Cary 5E spectrometer. Room-temperature magnetic susceptibility measurements were obtained by the Gouy method on a permanent magnet (7000 G), by using a $NiCl_2$ solution as calibrant. Analytically pure samples of $TTDPzH_2$ failed to give a reliable value of the diamagnetic correction for the macrocycle because of the presence of paramagnetic contaminants. Thus, the value was calculated by the use of Pascal's constants ($-267 \times 10^{-6}$ cgsu).[10] This value is in good agreement with that obtained by taking 4 times that measured directly on **I** ($-62 \times 10^{-6}$ cgsu). Additional corrections for the metal centers and the solvent molecules were calculated from Pascal's constants. Thermogravimetric analyses were run on a Stanton Re model STA-781 analyzer under a $N_2$ atmosphere (0.5 L/min). EPR data were obtained on a Varian V4502-4 spectrometer (X-band) both at room temperature and at 80 K. Elemental analyses were performed at the Laboratorio di Microanalisi (CNR, Area della Ricerca, Montelibretti).

## Results and Discussion

**General Properties.** $[TTDPzMg(H_2O)]\cdot CH_3COOH$ has proved to be particularly important as a source for the preparation of both $TTDPzH_2$ and TTDPzCu. In fact, trifluoroacetic acid is able to extract Mg(II) from the central site of the complex, allowing the formation of the metal-free macrocycle, which, in turn, in the presence of Cu(II), can be converted into TTDPzCu. The IR spectra of the three species are different, particularly in the region 1600−200 $cm^{-1}$ (see Experimental Section). The formation of both $TTDPzH_2$ and TTDPzCu from the Mg(II) complex can be hence easily followed by the related changes in the IR spectra. Thermogravimetric analysis of these materials indicates that they are stable up to temperatures of 350−400 °C under an inert ($N_2$) atmosphere, with gradual and featureless loss of the solvent molecules with increasing the temperature. Thermal treatment under vacuum (310 °C for 2−4 h) or sublimation (450−500 °C, $10^{-2}$ mmHg) determines practically complete loss of the solvent molecules, as shown by the disappearance of the related bands in the pertinent IR regions, exception being made for the Mg(II) derivative, which seems to retain residual water, very likely directly coordinated to the central metal, as is the case for the phthalocyanine analogue $[PcMg(H_2O)]\cdot 2py$,[11] and not simply hydrogen-bonded and positioned in the peripheral part of the macrocycle.

**IR Spectra.** The IR spectra of sublimed $TTDPzH_2$ and TTDPzCu are partially presented in Figure 1. For solvated species, acetic acid and water determine the presence of additional medium-strong bands in the 3400−3200 (broad) and 1750−1600 $cm^{-1}$ regions. The absorptions found in the IR spectrum of $TTDPzH_2$ at 3290 (Figure 1, insert), 1565, and 753 $cm^{-1}$ are assigned as $\nu$(NH), $\delta$(NH), and $\gamma$(NH) vibrations, similarly to what has been suggested for absorptions at 3273, 1539, and 735 $cm^{-1}$ in the case of $PcH_2$.[12] For unsubstituted porphyrazine and for its alkyl- and aryl-substituted derivatives,[13,14] the $\nu$(NH) stretch was observed at 3298−3300 $cm^{-1}$. Such assignments are also supported by deuteration of $TTDPzH_2$, which determines disappearance of the 3290 and 753 $cm^{-1}$ absorptions, with the appearance of new corresponding absorptions at 2465 $cm^{-1}$ ($\nu$(ND) and 585 $cm^{-1}$ ($\gamma$(ND)) in the IR spectrum of $TTDPzD_2$ (Figure 1A, dashed line). The ratios of the positions for NH and related ND absorptions are in good agreement with theoretical expectation (~1.3).[12,15] As to the 1565 $cm^{-1}$ band, which, incidentally, *is not* present in the spectra of the metal complexes, it also disapppears upon deuteration. However, the corresponding $\delta$(ND) vibration, expected at ~1200 $cm^{-1}$, cannot be detected in the spectrum of $TTDPzD_2$, since this region is highly obscured by the solvent absorptions.

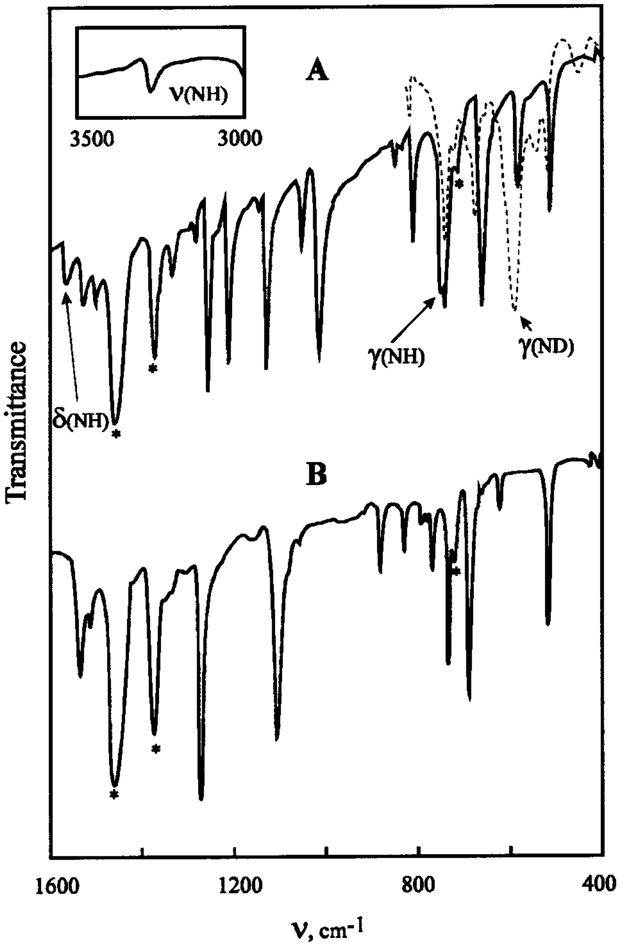

**Figure 1.** Nujol mull IR spectra (* indicates Nujol absorptions) of sublimed $TTDPzH_2$ (A; the dashed line is for the deuterated material) and TTDPzCu (B).

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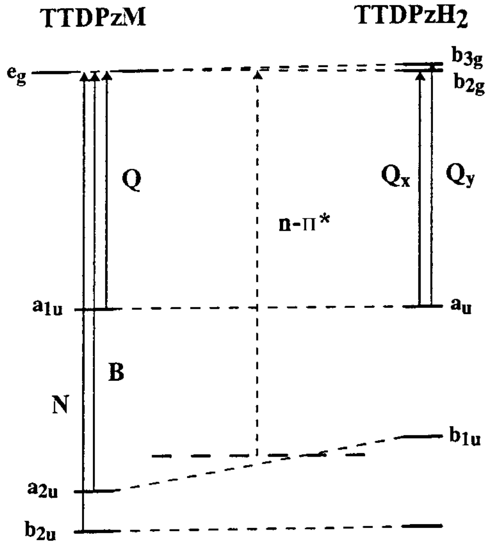

**Figure 2.** Schematic presentation of the electronic transitions in the visible and close UV regions for the present tetrakis(thiadiazole)porphyrazine macrocycles. The scheme is constructed in accordance with the theory of the electronic absorption spectra of porphyrins[16] and the transition energies are estimated from the experimental spectra of TTDPzCu and $TTDPzH_2$ in chlorobenzene. The underlying n → $\pi^*$ transitions which could be responsible for a diffuse character of the Soret band[16,17] and the level of the corresponding filled N $p_\sigma$ orbitals originating mostly from meso nitrogens are depicted with dashed lines.

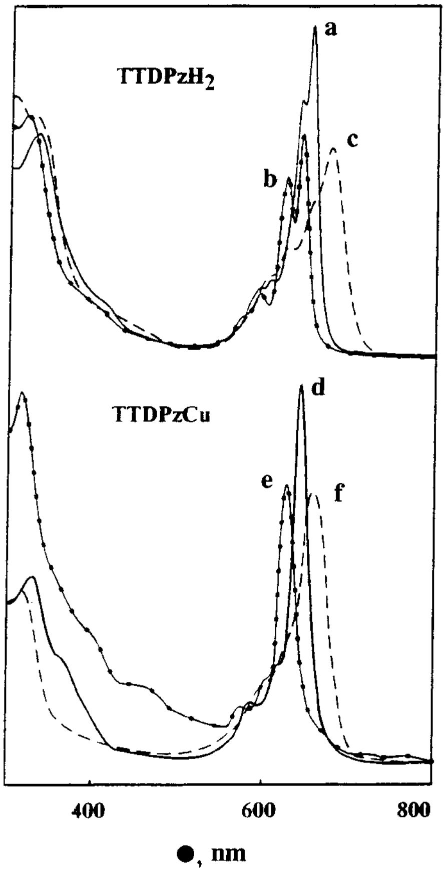

**Figure 3.** UV–vis spectra of $TTDPzH_2$ in PhCl (a), $CH_3COOH$ (b), and 100% $H_2SO_4$ (c) and of TTDPzCu in PhCl (d), $CH_3COOH$ (e), and 96% $H_2SO_4$ (f).

**UV–Visible Spectra and Structural and Electronic Properties.** UV–visible solution spectra of the present species, taken qualitatively in nondonor (chlorobenzene, $CH_2Cl_2$) and acidic solvents ($CF_3COOH$, $H_2SO_4$) and measured quantitatively in pyridine, allow some discussion to be developed on the following points: (a) comparison between the spectral behaviors of porphyrazines and their corresponding phthalocyanine analogues; (b) assignments of the absorptions in the Q- and Soret-band regions; (c) solvent dependence of the spectral features; (d) nature of the electronic distribution in the macrocycle and associated adequate representation of the latter.

$TTDPzH_2$ and its Mg(II) and Cu(II) derivatives show UV–visible solution spectral features closely resembling those of their phthalocyanine analogues in that they exhibit very intense absorptions in the 600–700 and 300–400 nm regions. These absorptions are assigned, for the phthalocyanine species, to the allowed HOMO–LUMO intraligand $\pi-\pi^*$ transitions.[16] We anticipate here that similar assignments apply, reasonably, for the present porphyrazine materials. This points out the overall similarity of the electronic distribution for the two classes of compounds, which implies extensive $\pi$-electron delocalization occurring throughout the skeleton of the porphyrazine macrocycle, with considerable involvement of the peripheral thiadiazole rings. Nevertheless, a detailed examination of the spectral data (see below) reveals several spectral differences, worthy of mention, which are directly related to the specific nature of the TTDPz and Pc macrocycles.

It is necessary to claim here that for $PcH_2$ ($D_{2h}$ symmetry) split Q (600–700 nm) and B (300–400 nm) bands are expected, assigned respectively as $a_u \rightarrow b_{2g}$ ($Q_x$), $a_u \rightarrow b_{3g}$ ($Q_y$) and $b_{1u} \rightarrow b_{2g}$ ($B_x$), $b_{1u} \rightarrow b_{3g}$ ($B_y$).[16] For its metal derivatives, PcM, the symmetry of the $\pi$-chromophore is $D_{4h}$ and the two LUMOs $b_{2g}$ and $b_{3g}$ give rise to a 2-fold degenerate $e_g$ level. Thus, unsplit Q and B absorptions are expected, associated with transitions $a_{1u} \rightarrow e_g$ and $a_{2u} \rightarrow e_g$, respectively. Figure 2 gives a schematic representation of these electronic transitions for the TTDPz systems. Whereas the Q-band region normally allows the correct assignments, showing only additional vibronic satellites of weak intensity, the Soret band region is often complicated by some overlapping of B bands with absorptions due to N and n → $\pi^*$ transitions.[16,17] This appears be the case also for the present complexes (see below).

**(A) Nondonor Solvents (PhCl, $CH_2Cl_2$).** Sonication and mild heating were required, because of low solubility, for a qualitative exploration of UV–visible solution spectra of $TTDPzH_2$ in PhCl and $CH_2Cl_2$. Only PhCl could be used for the Mg(II) and Cu(II) complexes, since dissolution of the Mg(II) species in the slightly acidic $CH_2Cl_2$ causes demetalation and formation of $TTDPzH_2$, whereas the Cu(II) complex is not soluble enough in this medium to give reliable results. The spectrum of $TTDPzH_2$ shows splitting of the Q-band, as expected in $D_{2h}$ symmetry, with peaks at 641 and 653 nm and with peaks at 636 and 649 nm for PhCl (Figure 3a) and $CH_2Cl_2$, respectively (see assignments above). TTDPzCu and its Mg(II) analogue show similar spectra in PhCl (see Figure 3d for TTDPzCu) in that they both exhibit a single Q absorption, respectively at 642 and 647 nm, indicative of $D_{4h}$ symmetry, as expected in the case of TTDPzCu, but clearly substantially maintained even for the $\pi$-chromophore of the Mg(II) complex, although the presence of a water molecule ligated to the metal

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center would require the assignment of a $C_{4v}$ symmetry. A definite hypsochromic shift of the Q band is observed when one compares the spectra in PhCl of the present species (641−653 nm) with those of the corresponding phthalocyanine analogues in an equivalent non donor solvent (ClNP) (698 and 664 nm for $PcH_2$; 678 nm for both PcCu and PcMg). A similar shift was observed for tetrapyrazinoporphyrazine (Q band at 642 nm).[18] This shift might be explained by the presence in the TTDPz unit of the annulated thiadiazole rings, which, experiencing $\pi$-deficiency as compared to the isoelectronic benzene rings present in the Pc unit, cause a lowering of the HOMO $a_u$ ($a_{1u}$ for metal complexes) larger than that of the LUMO $b_{2g}$ ($e_g$), with consequent increase of the HOMO−LUMO energy gap.

In the Soret region, solutions of $TTDPzH_2$ in PhCl and $CH_2Cl_2$ each show a broad absorption with a maximum at 330−335 nm, certainly due to strong contributions from B transitions and accompanied, in the latter solvent, by a very intense peak at 275 nm, most likely due to the $\pi \rightarrow \pi^*$ transition of the thiadiazole rings (3,4-dicyano-1,2,5-thiadiazole has $\lambda_{max}$ at 272 nm in methanol).

**(B) Acidic Solvents ($CF_3COOH$, $H_2SO_4$).** Proton interaction of $TTDPzH_2$ in acidic media can take place at the two internal pyrrole-type N atoms (i), at the four meso nitrogens (ii), and at the eight N atoms of the peripheral thiadiazole rings (iii), with different effects on the symmetry of the molecule and the HOMO−LUMO energy levels and, hence, on the UV−visible spectra. Type i might raise the symmetry of the molecule from $D_{2h}$ to $D_{4h}$, and an unsplit Q band should be observed; type ii would stabilize the LUMOs, leaving unchanged the HOMO $a_u$ ($a_{1u}$ for metal complexes), implying a bathochromic shift of the Q band; type iii implies a marked stabilization of the HOMO $a_u$ ($a_{1u}$) and, hence, a hypsochromic shift of the Q band. By spectral examination, type i was seen for porphyrins[13] and (tetrakis(tetramethylene)porphyrazine),[19] type ii for $PzH_2$[20] and $PcH_2$,[4c] and type iii for tetra-2,3-pyridino- ($TPyPzH_2$) and tetrapyrazinoporphyrazines.[21]

Spectra could be measured in $CF_3COOH$ and in $H_2SO_4$ for $TTDPzH_2$ and the Cu(II) complex, but not for the Mg(II) complex because of unequivocal demetalation. The spectrum of $TTDPzH_2$ in $CF_3COOH$, a strongly acidic and proton-donating solvent, again shows a double-peaked Q absorption (peaks at 624 and 642 nm; see Figure 3b), which suggests no additional protonation at the inner $N_4$ system and, on the whole, essential retention of $D_{2h}$ symmetry. As to the very small hypsochromic shift of the Q band observed in going from the spectrum in PhCl to that in $CF_3COOH$ ($\Delta E(Q_x) = 270\ cm^{-1}$), suggestive of protonation confined only at the thiadiazole N atoms, it appears too small to be taken as significant. However, it is true that, although in a range of very weak basicities, protonation at the external thiadiazole N atoms ($pK_a = -4.7$ for **I**)[22] should be preferred to that of the meso N nitrogens ($pK_a = -8.2$ for $TPyPzH_2$[21c]). In 100% $H_2SO_4$ and weak oleum (5%), the Q-band peak in the spectrum (Figure 3c) is shifted bathochromically to 676 nm ($\Delta E(Q_x) = 790\ cm^{-1}$ with respect to $CF_3COOH$). This reversed shift is evidently caused by the additional acid−base interaction occurring at only one of the meso N atoms, with type ii effects predominating over type iii effects. In the case of $PcH_2$, acid−base interaction with one of the meso N atoms results in a comparable bathochromic shift ($\Delta E(Q_x) = 960\ cm^{-1}$ in $CF_3COOH$ as compared to ClNP), whereas in 100% $H_2SO_4$ all four meso N atoms of $PcH_2$ are involved in such an interaction and a quadruplicated bathochromic shift is observed ($\Delta E(Q_x) = 3610\ cm^{-1}$).[4c] Protonation of only one meso N atom for $TTDPzH_2$ in 100% $H_2SO_4$ is very likely explained by the weaker basicity of the meso N atoms, as due to the strong electron-withdrawing effect of the protonated thiadiazole rings. A similar situation was described for tetrakis(2,3-pyridine)porphyrazines.[4c,21c] Incidentally, $TTDPzH_2$ is not stable in 90−98% aqueous $H_2SO_4$, probably undergoing rapid hydroprotolytic destruction.

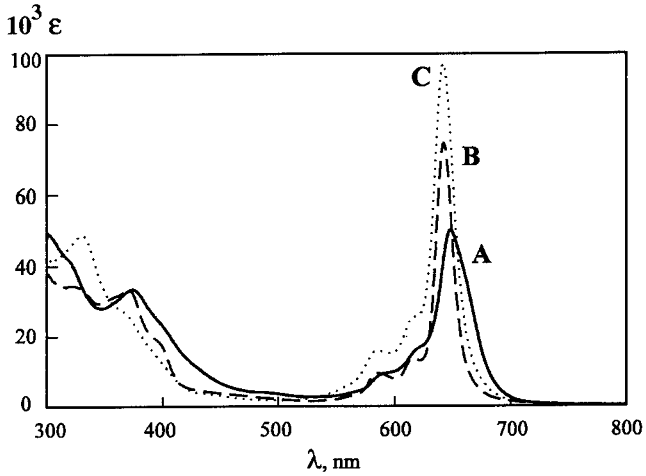

**Figure 4.** UV−vis spectra in pyridine solution of $TTDPzH_2$ (A), TTDPzMg (B), and TTDPzCu (C).

Unlike the Mg complex, TTDPzCu is stable in strong acids. In a solution of $CF_3COOH$, the Cu(II) complex shows a single Q absorption at 631 nm (Figure 3e), which is hypsochromically shifted with respect to that measured in PhCl ($\Delta E(Q_x) = 260\ cm^{-1}$). In 96% $H_2SO_4$, the same absorption moves oppositely to 661 nm ($\Delta E(Q_x) = 690\ cm^{-1}$) (Figure 3f). This is in agreement with the protonation processes already outlined for $TTDPzH_2$.

**(C) Pyridine.** Sonication and mild heating for 30−45 min allowed quantitative solution spectral data to be taken on samples of unsolvated $TTDPzH_2$ and TTDPzCu and of the monohydrated Mg(II) complex (Table 1). Within 24 h, no change of the peak intensities was observed for the Cu(II) and Mg(II) species over the range explored, whereas solutions of $TTDPzH_2$ showed about 30% decrease. The $\epsilon$ values measured, in the range $(1-10) \times 10^4$, are comparable to those found for the phthalocyanine analogues.

A pyridine solution of $TTDPzH_2$, unlike solutions in nondonor or acidic solvents, shows a single, though slightly asymmetric, Q absorption with a maximum at 648 nm (Figure 4A), which clearly implies attainment of $D_{4h}$ symmetry. This suggests substantial deprotonation of the inner NH groups. A similar behavior was also observed for other porphyrazines, i.e., tetraazaporphine and its substituted derivatives,[23] but not for

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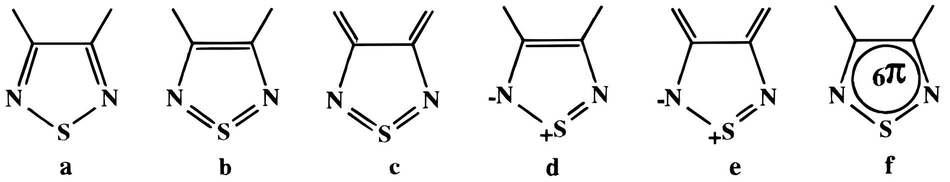
**Table 1.** UV−Visible Spectral Data for $TTDPzH_2$ and Its Mg(II) and Cu(II) Derivatives[a]

| solvent | $\lambda$, nm ($\epsilon \times 10^{-4}$)<br>Soret band (N, B, and $n \rightarrow \pi^*$ transitions) | | | Q(0−1) | Q(0−0) |
|---|---|---|---|---|---|
| | | | $TTDPzH_2$ | | |
| PhCl | | 333 | 415 sh | 593; 607 | 641; 653 |
| $CH_2Cl_2$ | 275 | 331 | 413 sh | 590 sh; 604 | 636; 649 |
| $CF_3COOH$ | 275 | 319 | 405 sh | 575 sh; 594 | 624; 642 |
| $H_2SO_4$ | 272 sh | 302 | 327 | 605 sh; 626 | 656 sh; 676 |
| py ($c = 2.05 \times 10^{-5}$ M) | | 318 sh (4.29); 375 (3.41) | 397 sh (2.54); 483 (0.49) | 591 sh (0.98); 622 (1.85) | 648 (5.07) |
| | | | TTDPzMg | | |
| PhCl | | 330 | 410 sh | 590; 620 | 647 |
| py ($c = 2.35 \times 10^{-5}$ M) | | 322 (3.32); 371 (3.23) | 398sh (1.79) | 585 (1.02); 615 (1.36) | 642 (7.06) |
| | | | TTDPzCu | | |
| PhCl | | 337 | | 584; 618 | 642 |
| py ($c = 1.61 \times 10^{-5}$ M) | | 331 (4.47); 363 sh (2.73) | 439 (0.37) | 586 (1.61); 618 (2.48) | 642 (9.69) |
| $CF_3COOH$ | 275 | 325 | 395 sh; 457 sh | 575; 609 sh | 631 |
| $H_2SO_4$ | 270 | 306 sh; 322 | | 598 sh; 627 sh | 661 |

[a] $TTDPzH_2$ and TTDPzCu are samples desolvated at 300 °C ($10^{-2}$ mmHg). Under the same experimental conditions, the Mg(II) complex was assumed to be a monohydrated species.

**Chart 3**



free phthalocyanine, since, as verified by us and indicated by previous observations,[24] $PcH_2$ exhibits, in pyridine solution, two distinct peaks located at 694 and 659 nm, in agreement with expectation for an undissociated molecule ($D_{2h}$ symmetry). This means that, under the comparable experimental conditions examined, pure pyridine is able to detach protons from $TTDPzH_2$ *and not* from $PcH_2$, definitely indicating the stronger acidity of the NH groups for $TTDPzH_2$. The main maximum in the Soret region for $TTDPzH_2$ (375 nm, Figure 4A), whereas significantly bathochromically shifted as compared to that of TTDPzCu (332 nm, Figure 4C) approaches, instead, closely, that observed for the Mg(II) complex (371 nm, Figure 4B), a species which is certainly characterized by the marked ionic nature of the Mg(II)−$N_4$ bond system. This seems to suggest substantial negative charge location on the TTDPz fragment in the free ligand. It is presently still uncertain, however, whether interaction with pyridine implies the formation of true "pyridinium salts" or, rather, of proton-bridged species of the type $Pz^{2-}\cdots(H^+\cdots Py)_2$, as proposed elsewhere.[4c]

Again, with reference to the spectral behavior of the Mg(II) and Cu(II) complexes in pyridine, similar to that in PhCl over the region explored (Table 1, Figure 4B,C), it is claimed that the Soret-band region, containing large B-band contributions, is certainly the site for the occurrence of closely lying or overlapping N and $n \rightarrow \pi^*$ transitions, as shown by the presence of multiple peaks or shoulders. The above-mentioned bathochromic shift in the direction Cu(II) → Mg(II) implies destabilization of the $a_{2u}$ orbital (characterized by nonzeroth coefficients on the internal and meso N atoms) and, hence, the energy lowering of the transition $a_{2u} \rightarrow e_g$. Instead, the $a_{1u}$ orbital nodes are located on the same atoms; thus, this orbital and, in turn, the $a_{1u} \rightarrow e_g$ transition (Q band) should be only slightly affected by the nature of the metal center, which is, indeed, the case. In fact, the Q band is located in exactly the same position for both the Cu(II) and the Mg(II) complexes (642 nm).

No charge-transfer absorptions (LMCT or MLCT) are observed in the spectra of the present species either in the 500 nm "window" or on the red site of the Q band. Exploration below 300 nm cannot be performed in pyridine because of the solvent absorptivity.

1,2,5-Thiadiazole is an aromatic heterocycle with six $\pi$ electrons.[22,25] Thus, tetrakis(thiadiazole)porphyrazines, with regard to the number of inner and outer $\pi$-electrons involved, are isoelectronic with the parent phthalocyanine analogues. None of the classic structures of the 1,2,5-thiadiazole unit reported in Chart 3, i.e., **3a** with the S atom in the oxidation state +2, **3b** and **3c** containing S(+4), and mesoionic structures **3d** and **3e**, can individually represent the structural and chemical properties of the 1,2,5-thiadiazole derivatives.[25,26] Structures **3a**, **3b**, and **3d** mainly contribute to the real quasi-aromatic structure, adequately depicted as **3f**,[26c] whereas the influence of structures **3c** and **3e** is definitely less important. In light of this, a number of resonance structures can be written for the TTDPz unit in $TTDPzH_2$. Structure **2b**, previously suggested,[8] implying all S atoms in the oxidation state +4, overestimates the importance of the **3b** and **3c** mesomers and is very likely scarcely contributing to the global resonance structure. Our preliminary calculations of atomic charges on the S and N atoms of the thiadiazole ring in $TTDPzH_2$ (AM1 method of Hyperchem[27] was applied for the geometry optimized with the MM+

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method) suggest that the resonance structures **2c** and **2d**, implying an average oxidation state of +2.5 on each of four S atoms of the TTDPz macrocycle, should give the main contribution to the global resonance structure **2a,** which can be considered as the most adequate representation of the TTDPz molecular system. Pertinent helpful information might be obtained for the system from crystallographic data; hence, attempts to prepare of single crystals suitable for X-ray analysis are presently in progress.

**Magnetic Susceptibility and EPR Spectra.** The room-temperature magnetic susceptibility was directly measured for **I** and then also for $TTDPzH_2$ and its Mg(II) and Cu(II) derivatives. Both $TTDPzH_2$ and the Mg(II) derivative give $\mu_{eff}$ values of in the range 0−1.0 $\mu_B$, indicating the presence of paramagnetic impurities. A value of $\mu_{eff}$ of 1.93 $\mu_B$ has been obtained for the Cu(II) complex, in keeping with expectation. Its EPR spectrum has been measured at room temperature as well as at 80 K, with no significant differences. The spectrum shows a partially resolved peak with $g_{\|}$ and $g_{\perp}$ values of 2.13 and 2.05, respectively, as expected for a tetragonally elongated symmetry.

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