Tetrakis(thiadiazole)porphyrazines. 2. Metal Complexes with Mn(II), Fe(II), Co(II), Ni(II), and Zn(II)

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The synthesis and general chemical physical characterization of the following new classes of complexes derived from tetrakis(thiadiazole)porphyrazine ($TTDPzH_2$), i.e., $[(TTDPz)M(DMSO)_2]$ (M = Mn(II), Fe(II)), $[(TTDPz)M](H_2O)_2$, and [(TTDPz)M] (M = Mn(II), Fe(II), Co(II), Ni(II), Zn(II)) are reported. The IR spectra in the region 4000−200 cm^{-1} show for all the species typical modes of the TTDPz skeleton and specific absorptions of the thiadiazole ring. The UV−visible spectra in different media show the expected absorptions in the Soret and Q-band regions. Inspection of the IR spectra of the two six-coordinate adducts $[(TTDPz)M(DMSO)_2]$ and of their corresponding species containing DMSO-d_6 clearly indicate that DMSO is O-bonded to the central metal in both species (ν(SO) located at 918 and 940 cm^{-1} for the Fe(II) and Mn(II) species, respectively), differently from the findings for DMSO (S-bonded) in the Fe(II) and Ru(II) phthalocyanine analogues. The complexes $[(TTDPz)M](H_2O)_2$ and [(TTDPz)M] are all tetracoordinate species, the water molecules for the hydrated species being very likely only weakly ligated at the peripheral thiadiazole rings of the macrocycle. Some additional information on the oxidation and spin state of the complexes has been achieved by Mössbauer spectra (Fe) and room-temperature magnetic susceptibility measurements, and data at hand are compared, when allowed, with those of the parallel classes of metal phthalocyanine complexes.

Introduction

We recently reported on tetrakis(thiadiazole)porphyrazine, $TTDPzH_2$ (Scheme 1A) and its Mg(II) and Cu(II) derivatives,[1] and more recently also on the corresponding species containing the tetrakis(selenodiazole)porphyrazine macrocycle (Scheme 1B).[2] These new types of porphyrazine systems can be probably identified, as to their structural and electronic features, as highly representative examples of phthalocyanine-like macrocycles, if it is considered that the external thiadiazole and selenodiazole rings are isoelectronic, in terms of π-electrons, with the benzene rings present in the phthalocyanine skeleton (Scheme 1C), the overall molecular skeleton retaining an essentially square planar molecular structure. The presence of soft atoms such as S or Se in the peripheral heterocyclic rings, in addition to N atoms, may, nonetheless, affect the electronic charge density distribution within the macrocycle and influence the nature of the interunit contacts between adjacent molecules in the solid state, possibly resulting in new types of materials with some distinct behavior with respect to that shown by the class of the phthalocyanine analogues. It is in our mind to extend the investigation for the formation of new metal derivatives of the above S- and Se-containing macrocycles and examine some of their general chemical and physical properties in a perspective of possible practical applications, so widely verified for the parent class of phthalocyanine complexes.

We present here the results concerning the synthesis and chemical physical characterization of a number of M(II) complexes of the macrocyclic sulfur containing ligand $TTDPzH_2$ (Scheme 1A; M(II) = Mn(II), Fe(II), Co(II), Ni(II), and Zn(II)), which have been studied by spectral (IR, UV/visible, Mössbauer) and magnetic susceptibility measurements.

Experimental Section

Solvents and Reagents. Acetone, ethanol, dichloromethane, *n*-hexane, tetrahydrofuran, pyridine, CH_3COOH, CF_3COOH, H_2SO_4, thionyl chloride, bisublimed I_2, $(NH_4)_2Fe(SO_4)_2\cdot 6H_2O$, $(CH_3COO)_2M\cdot 4H_2O$ (M = Mn(II), Co(II), Ni(II)), $(CH_3COO)_2Zn\cdot 2H_2O$, and $NiCl_2\cdot 6H_2O$, were all Carlo Erba pure solvents and reagents and were used as such. Dimethyl sulfoxide (DMSO) was normally freshly distilled over CaH_2 before use. Diaminomaleonitrile (DMN) (99%) was purchased from Aldrich.

Tetrakis(thiadiazole)porphyrazine, $TTDPzH_2$, was obtained from its corresponding Mg(II) complex as previously reported.[1] It normally contains water (1 mole × mole of species, or less), which will be neglected in the formulation given. As indicated below, the metal complexes TTDPzM containing water are normally given as dihydrates and the elemental analyses quoted are those of samples which were more closely found to correspond to the formulation given. However, elemental and thermogravimetric analyses not rarely suggested lower or higher amounts of water present up to four molecules per mole of complex.

$[(TTDPz)Mn(DMSO)_2]$. $TTDPzH_2$ (120 mg, ca. 0.22 mmol) and $(CH_3COO)_2Mn\cdot 4H_2O$ (104 mg, 0.42 mmol) are added to freshly distilled degassed DMSO (10 mL). The mixture is refluxed at 200 °C in an inert atmosphere (N_2) for 3 h, with stirring. After cooling and

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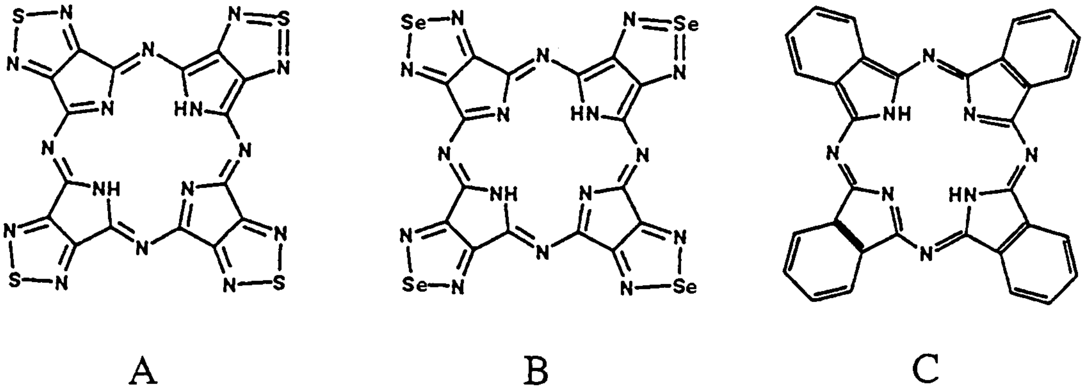
Scheme 1



centrifugation, the solid material is washed with water and brought to constant weight under vacuum (90 mg; yield 70%). The complex is stable in air and shows no tendency to form a hydrate. Calcd for the formula [(TTDPz)Mn(DMSO)$_2$], $C_{20}H_{12}MnN_{16}O_2S_6$: C, 31.79; H, 1.59; N, 29.67; S, 25.46. Found: C, 32.19; H, 1.53; N, 28.98; S, 25.81%. IR, cm^{-1} (Nujol, hereafter absorptions due to H_2O or DMSO are given in italics): ν = *3000(sh)* (ν_{as}(CH$_3$), 1545s, 1500m, *1410w−1400w* (δ_{as}-(CH$_3$)), 1320s, *1297w* (δ_s(CH$_3$)), 1256s, 1127s, 1052vw, 1020(sh), *1010m−988vs* (ρ(CH$_3$)), *940s* (ν(S=O)), 825w, 781s, 765s, 720s, 690s, 510s, 414m. The deuterated species [(TTDPz)Mn(DMSO-d_6)$_2$] could not be obtained by simply refluxing a suspension of the normal bisadduct in deuterated DMSO. It was obtained by first eliminating DMSO from the adduct (see below) to give TTDPzMn, followed by refluxing a suspension of the latter in DMSO-d_6 in a inert atmosphere (N_2).

[(TTDPz)Mn](H$_2$O)$_2$. This hydrated species can be obtained as an amorphous powder from the DMSO adduct by heating this latter at 300 °C under vacuum (10^{-2} mmHg) for 1 $^1/_2$ h to give [(TTDPz)Mn], followed by exposition of the latter to the air. Calcd for the formula [(TTDPz)Mn](H$_2$O)$_2$, $C_{16}H_4MnN_{16}O_2S_4$: C, 30.24; H, 0.63; N, 35.25; S, 20.18. Found: C, 30.44; H, 0.71; N, 33.42; S, 18.79%. IR, cm^{-1} (Nujol): ν = *3330m* (broad), *1650m*, 1530m, 1490m, 1264vs, 1088s, 1055m, 870m, 855w, 826w, 785m, 760w, 730s, 683s, 616w, 512s, 369w.

[(TTDPz)Mn] is formed as a bluish amorphous material from the DMSO adduct (see above). Calcd for the formula [(TTDPz)Mn], $C_{16}MnN_{16}S_4$: C, 32.06; H, 0.00; N, 37.38; S, 21.39. Found: C, 31.98; H, 0.00; N, 35.72; S, 21.39%.

[(TTDPz)Fe(DMSO)$_2$]. TTDPzH$_2$ (272 mg; ca. 0.50 mmol) and $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ (348 mg; 0.89 mmol) are added to freshly distilled DMSO (20 mL) and the mixture is refluxed in an inert atmosphere (N_2) for 3 h. After cooling and filtration, the dark-green crystalline solid separated is repeatedly washed with water and brought to constant weight under vacuum (320 mg; yield 85%). Calcd for the formula [(TTDPz)Fe(DMSO)$_2$], $C_{20}H_{12}FeN_{16}O_2S_6$: C, 31.75; H, 1.60; N, 29.6; S, 25.42; Fe, 7.38. Found: C, 31.2; H, 1.56; N, 28.8; S, 24.9; Fe, 6.98%. Thermogravimetric analysis of [(TTDPz)Fe(DMSO)$_2$] shows the loss of DMSO at ca. 300 °C (calcd weight loss 20.65%; found 20.91%). IR, cm^{-1} (Nujol): ν = *3000sh* (ν_{as}(CH$_3$)), 1537m, 1520s, *1422w−1410w* (δ_{as}(CH$_3$)), 1378w, 1353w, 1332vs, *1297w* (δ_s(CH$_3$)), 1258vs, 1225vw, 1170vw, 1122vs, 1085vw, 1050w, 1042vw, *1025w−m* (ρ(CH$_3$)), 1004vw, *974s* (ρ(CH$_3$)), *918s* (ν(S=O)), 895vw, 828vw, 780m−s, 763m, 746m, 688vs, 617vw, 512s, 495w. Similarly to what has been done for the synthesis of the Mn−DMSO-d_6 adduct, [(TTDPz)Fe(DMSO-d_6)$_2$] was obtained by refluxing a suspension of TTDPzFe (see below) in DMSO-d_6 in an inert atmosphere (N_2).

[(TTDPz)Fe](H$_2$O)$_2$. Similarly to the corresponding Mn species, this complex can be obtained as an amorphous powder by heating the DMSO adduct at 300 °C under vacuum (10^{-2} mmHg) for 1 $^1/_2$ h to give [(TTDPz)Fe], followed by exposition to the air of the latter. Calcd for the formula [(TTDPz)Fe](H$_2$O)$_2$, $C_{16}H_4FeN_{16}O_2S_4$: C, 30.19; H, 0.63; N, 35.21; S, 20.15. Found: C, 29.65; H, 0.85; N, 33.45; S, 20.21%. IR, cm^{-1} (Nujol): ν = *3330m* (broad), *1630m*, 1540s, 1520m, 1335s, 1263vs, 1110vs, 1070w, 1020w, 890w, 830w, 780w, 768m, 742m−s, 690vs, 619w, 511s.

[(TTDPz)Fe]. This species can be obtained as an amorphous powder by heating the DMSO adduct as indicated above, or, alternatively, as a purple microcrystalline powder by sublimation of the same species under vacuum (10^{-2} mmHg) at 500−550 °C. Calcd for the formula [(TTDPz)Fe], $C_{16}FeN_{16}S_4$: C, 32.01; H, 0.00; N, 37.32; S, 21.36. Found: C, 31.53; H, 0.00; N, 36.84; S, 21.28%. The sublimed purple microcrystalline material shows apparently no tendency to assume water molecules in air. IR, cm^{-1} (Nujol): ν = 1535m−s, 1520(sh), 1507(sh), 1330m, 1262−1252vs, 1162vw, 1110vs, 1057vw, 890w−m, 828w, 818vw, 795w, 772−762m−s, 738s, 720vw, 688vs, 625w, 511s, 300w.

[(TTDPz)Co](H$_2$O)$_2$. This complex can be directly prepared as an amorphous powder as follows: TTDPzH$_2$ (104 mg; ca. 0.19 mmol) and $(CH_3COO)_2Co \cdot 4H_2O$ (120 mg; 0.48 mmol) are added to freshly distilled DMSO and the suspension is kept under stirring for 24 h at room temperature. After centrifugation, the blue solid is separated and washed with water and EtOH, and brought to constant weight under vacuum (100 mg; yield 83%). Calcd for the formula [(TTDPz)Co]-(H$_2$O)$_2$, $C_{16}H_4CoN_{16}O_2S_4$: C, 30.05; H, 0.63; N, 35.04; S, 20.05. Found: C, 30.61; H, 0.71; N, 33.14; S, 19.69%. IR, cm^{-1} (Nujol): ν = *3460w, 3340w, 3230sh, 1635w*, 1540s, 1343m−s, 1270vs, 1135w, 1097vs, 1073m, 900w, 830w, 788w−m, 770m, 745m−s, 722w, 692vs, 618w, 513s, 295w.

[(TTDPz)Co] is obtained as an amorphous powder by mild heating (100 °C) under vacuum of the corresponding hydrate, or as a microcrystalline purple material by subliming the solvated complex under vacuum (10^{-2} mmHg) at 500 °C. Anal. Calcd for [(TTDPz)Co], $C_{16}CoN_{16}S_4$: C, 31.84; H, 0.00; N, 37.14; S, 21.25. Found: C, 31.95; H, 0.00; N, 37.14; S, 21.30%. IR, cm^{-1} (Nujol): ν = 1535s, 1515w, 1488w, 1340w−m, 1269vs, 1167vw, 1116s, 1095s, 1068w, 894w, 830w, 820vw, 795w, 767m, 742s, 722vw, 690vs, 623w, 513s, 332w.

[(TTDPz)Ni](H$_2$O)$_2$. A direct synthesis of this complex can be accomplished in DMSO by using alternatively $(CH_3COO)_2Ni \cdot 4H_2O$ or $NiCl_2 \cdot 6H_2O$. By using the acetate (similarly for the chloride) the reaction is exemplified as follows: TTDPzH$_2$ (120 mg; ca. 0.22 mmol) and $(CH_3COO)_2Ni \cdot 4H_2O$ (140 mg; 0.56 mmol) are suspended in DMSO (20 mL) and the mixture is heated at 100 °C for 3 h with stirring. After cooling, the solid purple complex, separated from the mother liquors by centrifugation, is washed with H_2O and brought to constant weight under vacuum (90 mg, yield ca. 70%). Calcd for the formula [(TTDPz)Ni](H$_2$O)$_2$, $C_{16}H_4NiN_{16}O_2S_4$: C, 30.06; H, 0.63; N, 35.06; S, 20.06. Found: C, 31.01; H, 0.81; N, 34.25; S, 20.40%. IR, cm^{-1} (Nujol): ν = *3410w, 3290w, 3200w, 1640w*, 1525w, 1500m, 1267vs, 1130w, 1078s, 1057w, 1048vw, 1013w, 880w, 823w, 780w, 763m, 733m, 718w, 682s, 616w, 512s.

[(TTDPz)Ni]. The complex can be obtained as an amorphous purple material from the corresponding dihydrate by mild heating (100 °C) under vacuum (10^{-2} mmHg) for 1 h, or as a microcrystalline material by sublimation under vacuum (500 °C, 10^{-2} mmHg) of the hydrated complex. Calcd for the formula [(TTDPz)Ni], $C_{16}NiN_{16}S_4$: C, 31.85; H, 0.00; N, 37.15; S, 21.26. Found: C, 32.11; H, 0.00; N, 36.17; S, 20.3%.

[(TTDPz)Zn](H$_2$O)$_2$. TTDPzH$_2$ (120 mg; ca. 0.22 mmol) and (CH$_3$CO$_2$)$_2$Zn·(H$_2$O)$_2$ (1 g; 0.46 mmol) are suspended in freshly distilled DMSO (15 mL). The mixture is stirred at room temperature for 3 h. After centrifugation, the purple solid separated is washed with water and ethanol and brought to constant weight under vacuum (126 mg; yield ca. 90%). Calcd for [(TTDPz)Zn](H$_2$O)$_2$, $C_{16}H_4N_{16}O_2S_4Zn$: C, 29.75; H, 0.62; N, 34.69; S, 19.86. Found: C, 29.85; H, 0.95; N, 33.75; S, 20.56%. IR (Nujol): ν (cm^{-1}) = *3450w, 3310w, 3230w, 1635m*, 1526m, 1494m, 1269vs, 1081s, 1053m, 875w, 828w, 785w, 764m, 732m, 720w, 686s, 618w, 516s, 360w, 295w.

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. The value used for the diamagnetic correction of the macrocycle was the same calculated before[1] by using Pascal's constants (-267×10^{-6} cgsu,[4] and addition of the appropriate contribution for the specific metal ions and solvent molecules). Mössbauer spectral data were measured as described previously.[5] Thermogravimetric analyses were performed on a Stanton Redcroft Model STA-781 analyzer under a N$_2$ atmosphere. Elemental analyses (C, H, N, S) were made on an EA 1110 CHNS-O CE instrument at the "Servizio di Microanalisi", Dipartimento di Chimica, "La Sapienza". Fe was quantitatively detected by atomic absorption on a Varian Spectra AA-30.

Results and Discussion

The following three classes of complexes are the object of the present contribution: (i) [(TTDPz)M(DMSO)$_2$] (M = Mn(II), Fe(II)); (ii) [(TTDPz)M](H$_2$O)$_2$ (M = Mn(II), Fe(II), Co(II), Ni(II), Zn(II)); (iii) [(TTDPz)M] (M = Mn(II), Fe(II), Co(II), Ni(II), Zn(II)).

Synthetic Aspects and Some Properties. The synthetic procedures performed in DMSO and described in the Experimental Section show that the complexes prepared directly from the free ligand TTDPzH$_2$, i.e., the two DMSO adducts (i) and the hydrated species of group (ii) [(TTDPz)M](H$_2$O)$_2$ (M = Co(II), Ni(II), Zn(II)) are generally obtained in high yields (70−90%). The two species [(TTDPz)M](H$_2$O)$_2$ (M = Mn(II), Fe(II)) of class (ii)) are obtained by elimination of DMSO (300 °C, 10^{-2} mmHg) from the corresponding adducts (i), followed by their exposition to the air.

The X-ray powder spectra of the Mn(II) and Fe(II) DMSO adducts (i) show that they have a high crystalline character and are practically isomorphous with one another. Surprisingly, these two DMSO adducts are stable to the air, namely, they show apparently no tendency to attract water molecules from the atmosphere. The presence of clathrated water in these complexes is excluded by elemental as well as thermogravimetric analysis, and by the absence in the IR spectra of absorptions above 3000 cm^{-1} and just about 1600 cm^{-1}, regions where the OH stretching and bending modes of H$_2$O are, respectively, expected to appear. The drastic thermal conditions required for the elimination of the DMSO molecules from these adducts (see above), further proved by thermogravimetric analysis in an inert atmosphere (N$_2$), clearly suggest direct coordination of the DMSO molecules to the central metal to give six-coordinate species. A comparable thermal treatment is required for the two known phthalocyanine analogues, namely [PcFe(DMSO)$_2$][6] and [PcRu(DMSO)$_2$][7] (Pc = phthalocyaninato anion, $C_{32}H_{16}N_8{=}$), for which direct ligation of DMSO to the central metal has been proved by X-ray work on PcFe(DMSO)$_2$[6] and is assumed in the strictly isomorphous Ru complex.[7] Both these phthalocyanine species are six-coordinate low-spin (d^6) M(II) species.

The hydrated species (ii) have similar X-ray spectral patterns, typical of practically amorphous materials with a short-range order. The weak binding of water (thermogravimetric analysis indicates that the loss of water starts immediately above room temperature) is certainly attributable to the presence of the peripheral N atoms to which H$_2$O molecules are very likely ligated by hydrogen bonds. The weak binding certainly determines a continuous exchange of these molecules with those present in the external atmosphere, with consequent deterioration of the crystalline character of all the hydrated species isolated.

Appropriate thermal heating under vacuum of adducts (i) or (ii) (see Experimental Section) leads to the formation of the corresponding unligated compounds [(TTDPz)M] (species (iii)) in the form of substantially amorphous powders. They are obtained as microcrystalline powders by sublimation of species (i) or (ii), or even of the amorphous [(TTDPz)M] materials, under more drastic conditions (450−550 °C, 10^{-2} mmHg). The sublimed materials do not show an immediate tendency to assume water. It should be noticed, however, that a sample of [(TTDPz)Co], examined 4 months after its sublimation, clearly indicated the presence of water.

IR Spectra. The tetrakis(thiadiazole)porphyrazines of classes (i), (ii), and (iii) have similar IR spectra in the range 4000−200 cm^{-1}, with characteristic TTDPz skeletal modes appearing in the ranges 1550−1525 (m−s), 1520−1490 (w−s), 1275−1255 (s−vs), 1130−1078 (s), 1070−1040 (w−m), 745−720 (m−s), 692−686 (s), and 625−616 (w) cm^{-1}, in each range the peak position depending on the specific central metal and adduct molecules present (DMSO). Additional absorptions present in the ranges 900−870 (w), 830−820 (w), 770−760 (w−m), and 516−510(s) cm^{-1} are very likely associated with the presence of the thiadiazole rings. In fact, according to the vibrational analysis made for 1,2,5-thiadiazole,[8] intense modes assigned as ring deformation and ring torsion appear for this species, respectively, at 895 and 520 cm^{-1}, whereas the SN stretching modes contribute strongly to the absorptions found at 806 and 780 cm^{-1}. Noticeably, a similar set of absorptions, due to the presence of the peripheral selenodiazole rings, are observed in the IR spectra of tetrakis(selenodiazole)porphyrazines,[2] although shifted to lower frequencies with respect to those of the corresponding S-containing macrocycle, as might be expected consequent to substitution of S by Se.

The differences in the IR spectra of series (i), (ii), and (iii) consist mainly of the presence of additional absorptions due to the stretching (>3000 cm^{-1}) and bending absorptions of H$_2$O (ca. 1630 cm^{-1}) in the spectra of the hydrated species (ii), and to the DMSO modes in the adducts (i) [TTDPzM(DMSO)$_2$] (M = Mn(II), Fe(II)). These latter complexes deserve some detailed discussion as to the type of binding of DMSO, since it is known that DMSO can ligate to a central metal through either sulfur or oxygen.[9] The bond order 2 for the S=O group in free DMSO is a combination of an S→O σ and a reverse O→S (pπ−dπ)

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Table 1. Assignment of the DMSO and DMSO-d_6 Vibrations in the IR Spectra of [(TTDPz)M(DMSO)$_2$] and [(TTDPz)M(DMSO-d_6)$_2$] (M = Mn, Fe)

assignment	free DMSO	[(TTDPz)M(DMSO)$_2$] M = Fe	[(TTDPz)M(DMSO)$_2$] M = Mn	free DMSO	[(TTDPz)M(DMSO-d_6)$_2$] M = Fe	[(TTDPz)M(DMSO-d_6)$_2$] M = Mn
ν_{as}(Me)	3000m	3000sh	3000sh	2250m	2260m	2260w
ν_s(Me)	2918m	*a*	*a*	2133w	2125m	2125w
δ_{as}(Me)	1436s	1422w	1410w	1084s	1050m	1044w
	1416m	1410vw	1400w	1043m	1028m	
δ_s(Me)	1306m	1297w	1297w	1034m	1012m	1015m
				1005m	990w	990m
ρ(Me)	1012s	1025w	1010m	811m	826m	827m
	946s	973s	988vs			
ν(S=O)	1055vs	918s	940s	1064vs	932vs	965vs
ν_{as}(C−S)	690s	n.o.[b]	n.o.[b]	619	n.o.[b]	n.o.[b]
ν_s(C−S)	661m	n.o.[b]	n.o.[b]	611	611	n.o.[b]

[a] Obscured by the Nujol absorption. [b] n.o. = not observed.

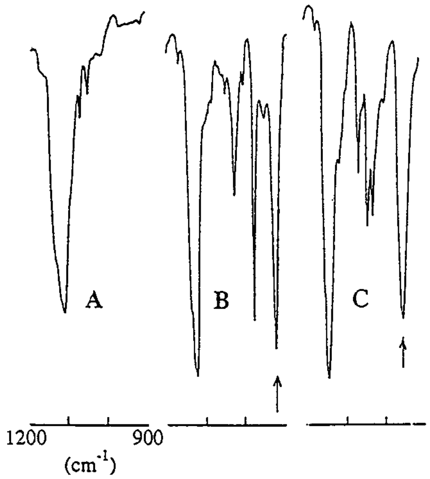

Figure 1. Nujol mull IR spectra in the region 1200−900 cm^{-1} of [(TTDPz)Fe](H$_2$O)$_2$ (A), [(TTDPz)Fe(DMSO)$_2$] (B), and [(TTDPz)Fe(DMSO-d_6)$_2$] (C).

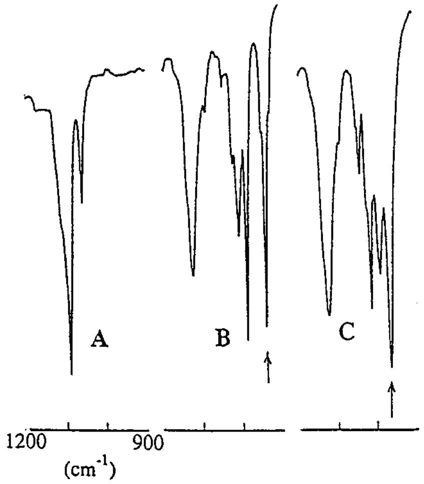

Figure 2. Nujol mull IR spectra in the region 1200−900 cm^{-1} of [(TTDPz)Mn](H$_2$O)$_2$ (A), [(TTDPz)Mn(DMSO)$_2$] (B), and [(TTDPz)Mn(DMSO-d_6)$_2$] (C).

back-donation. Coordination through S is expected to increase the O→S π back-donation, and in turn the SO bond order; as a consequence, the SO stretching frequency, which is located at 1055 cm^{-1} (in solution of CHCl$_3$ or CS$_2$) for unligated DMSO,[10] is expected to be shifted to a higher energy (range 1150−1100 cm^{-1}). On the contrary, coordination through O causes weaker π back-donation; i.e., the SO stretching mode is shifted to lower energy, roughly in the range 950−900 cm^{-1}. DMSO coordination through S, which appears less frequently observed than that through O, was unequivocally established for [PcFe(DMSO)$_2$] by single-crystal X-ray work,[6] and is very likely also occurring in the isomorphous Ru(II) analogue.[7] The problem has been faced here as to which type of DMSO coordination to the central metal takes place in the species [(TTDPz)Fe(DMSO)$_2$] and [(TTDPz)Mn(DMSO)$_2$]. The IR spectra have been recorded for both species (see Experimental Section), as well as for their corresponding samples containing deuterated DMSO, in the region 4000−200 cm^{-1}. Selected absorptions and suggested assignments are summarized in Table 1. The spectra in the range of main interest (1200−900 cm^{-1}) are reported in Figures 1 and 2 for the Fe and Mn species, respectively. In Figure 1A the hydrated species [(TTDPz)Fe](H$_2$O)$_2$) shows that the region 1200−900 cm^{-1} is favorably clean from absorptions, made exclusion for the presence of an intense peak with maximum at 1110 cm^{-1} belonging to the TTDPz skeleton (similar is the case for the Mn complex, see below). Figure 1B and Figure 1C show the spectra of [(TTDPz)Fe(DMSO)$_2$] and of its deuterated species [(TTDPz)Fe(DMSO-d_6)$_2$], respectively. As shown for [(TTDPz)Fe(DMSO)$_2$] in Figure 1B, three main absorptions are present in the region under consideration: (1) the very strong one at 1120 cm^{-1}, which is the TTDPz skeleton mode, only slightly shifted; (2) the two modes at 1025 and 973 cm^{-1}, assigned as ρ(CH$_3$) (absent in Figure 1C, being displaced to lower frequencies upon deuteration; see pertinent assignments in Table 1); and (3) the very intense absorption at 918 cm^{-1}, which is assigned as the SO stretching mode, still present in Figure 1C, although slightly shifted (932 cm^{-1}) as a result of deuteration.[10] The couples of new absorptions 1050m−1028m and 1012m−990vw present in Figure 1C are assigned as δ_{as}(CD$_3$) and δ_s(CD$_3$), respectively (see Table 1). Figure 2 shows the case of the Mn species, with observed similar effects upon deuteration on the various modes of the CH$_3$ groups (ν, δ, ρ) and the intense peak in Figure 2B at 940 cm^{-1}, assigned to the SO stretching mode, found shifted to 965 cm^{-1} in Figure 2C. In conclusion, then, the SO stretching frequencies are found for both [(TTDPz)Fe(DMSO)$_2$] and [(TTDPz)Mn(DMSO)$_2$] in the range 950−900 cm^{-1}, which conclusively allows the statement that the DMSO molecule is O-bound to the central metals in both species. Noteworthy, this is different from what has been observed for the two phthalocyanine Fe(II) and Ru(II) species in which DMSO is S-bonded.[6,7] Some explanation of this different behavior might be connected with the different π-bonding properties of the TTDPz and Pc skeletal units. The

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Table 2. UV−Visible Spectral Data for Tetrakis(thiadiazole)porphyrazine Complexes (λ, nm)

compound	solvent	Soret region			CT region		Q region			other
[(TTDPz)Zn]	Py	336	367	396sh			588	619	645	
	DMSO	329	353	398sh			585	609sh	638	
	HCOOH	331					589	612sh	639	
	CF_3COOH	327					583	613sh	643	
	H_2SO_4	323					603	632sh	664	
[(TTDPz)Ni]	Py	311	327sh	365			578	605sh	631	
	DMSO	305		358			571	603	627	
	HCOOH	331					583	613	638	
	CF_3COOH	322		390sh			576sh	597sh	635	
	H_2SO_4	317					601	627sh	660	
[(TTDPz)Co]	Py	341			445		585sh	605sh	639	
	DMSO	331			458		580sh	605sh	632	664sh
	HCOOH	332							635	
	CF_3COOH	315					578sh	602sh	632	678sh
	H_2SO_4	314					593sh	631sh	656	
[(TTDPz)Fe]	Py	344		411	443	504	603sh	646sh	676	
	CF_3COOH	320			472	577sh	599sh	627sh	643	684sh
	H_2SO_4	306			481			667sh	693	
[(TTDPz)Mn]	DMSO	309	352sh	375sh	466sh	498sh	599sh	623sh	653	708sh
	CF_3COOH	330			513		593sh	618sh	646	681
	H_2SO_4	316sh	384sh				601sh	642sh	662	

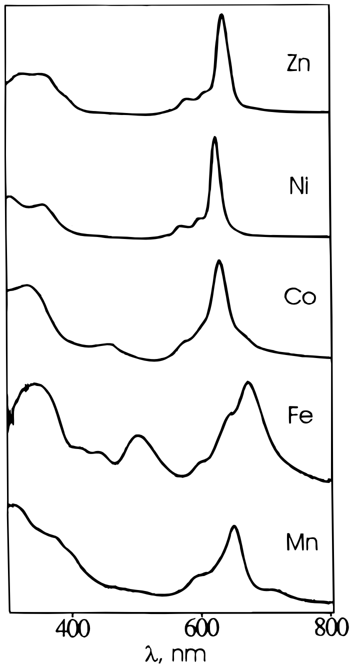

Figure 3. UV−visible spectra of [(TTDPz)M] in DMSO (M = Zn, Ni, Co, Mn) and pyridine (M = Fe).

stronger π-acceptor (and weaker σ-donor) properties of the TTDPz macrocycle are probably more favorable for O-coordination of DMSO, while the more available π-electrons of the Pc macrocycle can contribute to the Fe→S π-back-donation. The weak−medium bands at 495 and 425 cm^{-1} for the Fe(II) complex and at 415 cm^{-1} for the Mn(II) complex can be presumably assigned to the M−O stretching vibrations. The ν(M−O) bands were observed at 438, 415 cm^{-1} for $[Fe(DMSO)_6]^{2+}$ and at 418 cm^{-1} for $[Mn(DMSO)_6]^{2+}$.[11]

UV−Visible Spectra. Similarly to their related analogues,[1] all the present species are completely insoluble in neutral, essentially nondonor solvents, namely acetone, tetrahydrofuran, dichloromethane, and chlorobenzene. They are very poorly soluble in donor solvents such as pyridine and DMSO, and hence, only qualitative UV−visible spectral data could be taken in these solvents (Table 2). For the run of the spectra use was made of the hydrated [(TTDPz)M] species (M = Mn(II) → Zn(II)). As is typical for metal phthalocyanines and porphyrazines, and closely recalling the spectral behavior of the previously reported TTDPzM analogues,[1] intense $\pi \rightarrow \pi^*$ transition bands appear for the present species in the Soret (380−300 nm) and Q band regions (690−630 nm) (Figure 3). The intense narrow Q-band is accompanied by the characteristic vibronic satellites on the blue side, and the Soret band appears as a broad domed envelope due to the presence of the overlapping $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. For complexes of Mn(II), Fe(II), and Co(II) containing vacancies on the $d\pi$ and/or d_{z^2} orbitals these $\pi \rightarrow \pi^*$ transition bands are somewhat broadened and additional charge-transfer bands appear between them.

Essentially similar spectra are obtained in acidic solvents (HCOOH, CF_3COOH, H_2SO_4), in which the acid−base interaction with the *meso* and external N atoms determines considerable solubility. All investigated complexes are stable in these acids at room temperature, and no spectral changes attributable to demetalation are observed on long keeping of the solutions even in concentrated H_2SO_4 (96%). Slow spectral changes, which were observed for the Fe(II) and Mn(II) derivatives in acidic media, are evidently due to some axial ligand exchange and/or redox processes and need further study.

As can be seen from Table 2 and Figure 4 showing representative spectra of the Ni(II) complex, the Q-band position of the species [(TTDPz)M] in the HCOOH and CF_3COOH solutions differs very little from that for the DMSO or pyridine solutions (the shift does not exceed 8 nm). This is indicative of simple solvation of the weakly basic bridging (*meso*) N atoms. More significant is the bathochromic shift observed in H_2SO_4 (15−30 nm, 500−1000 cm^{-1}), indicative of effective protonation of at least one *meso*-N atom, as discussed elsewhere.[12,1] The N atoms of the thiadiazole rings also have very low basicity ($pK_{a1} = -4.90$ for 1,2,5-thiadiazole[13]). Taking into account the values of the Hammett acidity function H_0 of the solvent used, one can suppose that at least one N atom of each thiadiazole ring is very likely protonated in H_2SO_4 ($H_0 = -11.1$[14]) and

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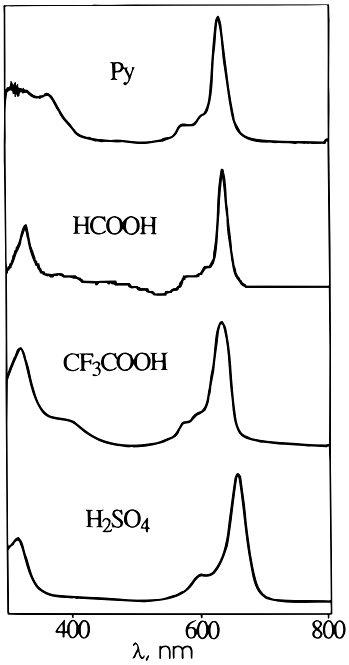

Figure 4. UV−visible spectra of [(TTDPz)Ni] in Pyridine, HCOOH, CF_3COOH and H_2SO_4.

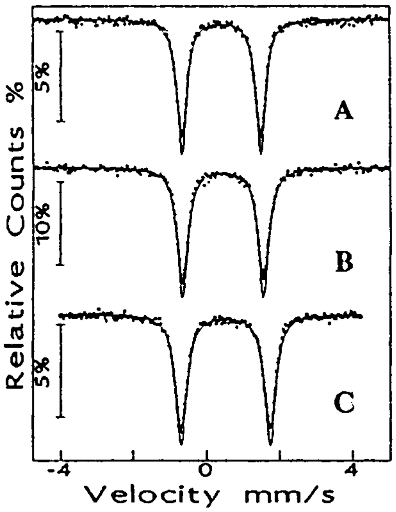

Figure 5. Mössbauer spectra of [(TTDPz)Fe(DMSO)$_2$] (A), [(TTDPz)-Fe](H$_2$O)$_2$ (B), and [(TTDPz)Fe] (C).

less likely in CF_3COOH ($H_0 = -3.09$[13]) or HCOOH ($H_0 = -2.22$[15]). Protonation of N atoms should result in the disappearance of the corresponding n→π* transitions, and specific acid solvation should shift them to higher energies, thus resulting in narrower Soret peaks and disappearance of shoulders on its red site, as was indeed observed (see Figure 4). Evidently the N atoms of the thiadiazole rings and corresponding n→π* transitions are strongly involved in the origin of these shoulders.

Mössbauer and Magnetic Data. The Mössbauer spectra of the Fe-containing species are shown in Figure 5; data are given in Table 3, together with those of some of their phthalocyanine analogues. Data of all the room-temperature magnetic susceptibility measurements are given in Table 4.

(a) DMSO Adducts. The Mössbauer spectrum of [(TTDPz)-Fe(DMSO)$_2$] (Figure 5A) shows one clean doublet, indicative of the presence of only one type of Fe center, with isomer shift and quadrupole splitting values remarkably close to those of [PcFe(DMSO)$_2$] (Table 3). Only a slight variation of the measured values is observed at two different temperatures. The value of $\mu_{\rm eff} = 1.04\ \mu_{\rm B}$ (Table 4) suggests that the complex is diamagnetic, the low observed paramagnetism being certainly attributable to the presence of low amounts of paramagnetic contaminants, as is normally found for such kinds of tetrapyrrolic systems. In conclusion, then, [(TTDPz)Fe(DMSO)$_2$] is a six-coordinate Fe(II) low-spin complex. The $\mu_{\rm eff}$ value measured for [(TTDPz)Mn(DMSO)$_2$] is 4.17 $\mu_{\rm B}$ (Table 4), close to the expected spin-only magnetic moment for a Mn(II) (d^5) having three unpaired electrons. Clearly, the identification of the ground state for this complex awaits a more detailed magnetic study over a wide range of temperature (4−300 K). Curiously, no DMSO adducts of PcMn have so far been reported in the literature, although manganese phthalocyanine has been very extensively studied in solutions of many solvents, including DMSO.[17]

Table 3. Mössbauer Spectral Data of the Tetrakis(thiadiazole)porphyrazine and Related Phthalocyanine Fe Derivatives

complex	sample	T (K)	δ^a (mm/s)	ΔE_Q (mm/s)	Γ (mm/s)
[(TTDPz)Fe(DMSO)$_2$]	1	84	0.414	2.169	0.16
		135	0.407	2.178	0.15
	2	84	0.416	2.163	0.15
[(TTDPz)Fe](H$_2$O)$_2$	1^b	84	0.452	2.220	0.15
	2^c	84	0.426	2.141	0.18
[(TTDPz)Fe]		84	0.533	2.481	0.19
[PcFe(DMSO)$_2$]		84	0.50	2.08	
[PcFe]			0.63	2.62	

[a] Referred to metallic ion. [b] Sample obtained by thermal treatment of the DMSO adduct. [c] Sample obtained by dissolving the DMSO adduct in concentrated H_2SO_4 (96%) followed by reprecipitation by pouring the solution into iced water.

(b) Hydrated [(TTDPz)M](H$_2$O)$_2$ and Unsolvated [(TTDPz)M] Complexes (M = Mn(II), Fe(II), Co(II), Ni(II), Zn(II)). The isomer shift and quadrupole splitting values for the single doublet observed in the Mössbauer spectrum of [(TTDPz)-Fe](H$_2$O)$_2$ and [(TTDPz)Fe] (Figure 5B,C, Table 3) are very close to each other and to those of the DMSO adduct. The δ value confirms the presence of Fe(II) in both species. The observed paramagnetism for the two species (Table 4) is not in disagreement with a square planar tetracoordination. Clearly, the observed significant difference in the $\mu_{\rm eff}$ values for the [(TTDPz)Fe](H$_2$O)$_2$ and [(TTDPz)Fe] is of no immediate explanation and calls for a more in-depth magnetic investigation. Noteworthy is the closeness of the $\mu_{\rm eff}$ value for [(TTDPz)Fe] to that of [PcFe], which has been assigned an $S = 1$ spin state,[18] suggesting a similar assignment for the TTDPz complex. The magnetic moment for [(TTDPz)Mn], while indicative of a high spin state for Mn(II) (d^5), is significantly different from that of [PcMn], assigned an $S = {}^3/_2$ spin state.[19] The complex [(TTDPz)Co](H$_2$O)$_2$ is clearly a Co(II) low-spin species, in keeping with findings for PcCo.[16] The listed $\mu_{\rm eff}$ values for the Ni(II), Cu(II),[1] and Zn(II) complexes (Table 4) are as expected, when assuming a four-coordinate square planar symmetry for

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Table 4. Room-Temperature Magnetic Moments of the Tetrakis(thiadiazole)porphyrazine and Phthalocyanine Derivatives

complex	μ_{eff} (μ_{B})	ref[a]	complex	μ_{eff} (μ_{B})	ref
[(TTDPz)Mn(DMSO)$_2$]	4.17 ± 0.03	t.p.			t.p.
[(TTDPz)Fe(DMSO)$_2$]	1.04 ± 0.06	t.p.	[PcFe(DMSO)$_2$]	diam.	
[(TTDPz)Mn]	5.94[c]		[PcMn]	4.34	16
[(TTDPz)Fe](H$_2$O)$_2$[b]	1.96[c]	t.p.			
[(TTDPz)Fe]	3.56 ± 0.15	t.p.	[PcFe]	3.85	16
[(TTDPz)Co](H$_2$O)$_2$	2.06[c]	t.p.	[PcCo]	2.72	16
[(TTDPz)Ni](H$_2$O)$_2$	1.29 ± 0.01	t.p.	[PcNi]	diam.	
[(TTDPz)Ni]	0.90[c]	t.p.	[PcNi]	diam.	
[(TTDPz)Cu](H$_2$O)$_2$	1.93	1	[PcCu]	1.75	16
[(TTDPz)Zn](H$_2$O)$_2$	0.87[c]	t.p.	[PcZn]	diam.	

[a] t.p. = this paper. [b] Sample obtained from the DMSO adduct after dissolution of the latter in concentrated H_2SO_4 (96%) followed by reprecipitation by pouring the solution into iced water. [c] Measured only once.

the central metal in these species. In fact, the low paramagnetism measured for the Ni(II) and Zn(II) complexes is certainly due to the presence of traces of paramagnetic contaminants.

Conclusions

In light of the previous[1] and present results, it can be conclusively stated that the tetrakis(thiadiazole)porphyrazines resemble closely their phthalocyanine counterparts in terms of structural features (essentially square planar symmetry of the porphyrazine skeleton), tendency to axial ligation, and physical properties, such as thermal stability, sublimability, solubility properties, UV−visible spectral, and, partly, magnetic behavior. Implicitly, differences must be in the electronic distribution inside the two tetrapyrrolic units, due obviously to the presence of different peripheral rings present in the two types of macrocycles. The observed different type of DMSO coordination for the two classes of materials is certainly a result of this distinct ring current distribution in the two tetrapyrrolic units.

It has been shown that [(TTDPz)M] complexes can exist in the form of amorphous and microcrystalline powders. Presently, one of our research items is to investigate the type and extension of molecular aggregation in these new materials by using the LAXS (large-angle X-ray scattering) technique for the [(TTDPz)-M](H$_2$O)$_2$ and [(TTDPz)M] amorphous powders and the Rietveld method for the microcrystalline materials. Thin films of the same species are also being structurally investigated.

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