DOI: 10.1002/ejic.200900029

Redox Chemistry of Tetrakis[5,6-di(2-pyridyl)-2,3-pyrazino]porphyrazinatocobalt(II): Isolation and Characterization of Solid Pure Co^{I}, Co^{II}, and Co^{III} Complexes[‡]

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Keywords: Porphyrazines / Cobalt / Redox chemistry

Salt-like hydrated complexes of formulae Na[Py_8TPyzPzCo] and [Py_8TPyzPzCo]($SbCl_6$) containing Co^{I} and Co^{III}, respectively, and the neutral Co^{II}–bis(dimethyl sulfoxide) (DMSO) adduct [Py_8TPyzPzCo(DMSO)$_2$], bearing additional clathrated DMSO molecules, have been prepared and characterized {Py_8TPyzPz = tetrakis[5,6-di(2-pyridyl)-2,3-pyrazino]-porphyrazinato dianion}. The sodium Co^{I} salt, the anion of which, [Py_8TPyzPzCo]$^{1-}$, had previously been identified by electrochemical solution studies, represents the first example of a Co^{I} derivative of a tetrapyrrolic macrocyclic chromophore prepared as a solid pure material. Solutions of Na[Py_8TPyzPzCo] in DMSO, under defined experimental conditions, allow the slow formation (months) of crystals of its corresponding Co^{II} complex of formula [Py_8TPyzPzCo(DMSO)$_2$]·6 DMSO. The structure of the adduct, elucidated by single-crystal X-ray analysis, shows the central Co^{II} ion surrounded by the four pyrrole N atoms of the porphyrazine macrocycle and two O atoms of the axially bonded DMSO molecules. Oxidation of the basic starting material [Py_8TPyzPzCo] with phenoxathiin hexachloroantimonate (phenox-$SbCl_6$) led to the formation of the Co^{III} complex [Py_8TPyzPzCo]($SbCl_6$). Full characterization of the title Co^{I}, Co^{II}, and Co^{III} species has been accomplished by solution studies and from IR, UV/Vis, EPR and X-ray crystallography data.

Introduction

Our studies on porphyrazine systems carrying peripherally annulated electron-deficient heterocycles (thia-/selenodiazole, diazepine, pyrazine) have in recent times been extensively directed towards the synthesis and characterization of a novel series of pyrazino-porphyrazine macrocycles: namely the free base tetrakis[5,6-di(2-pyridyl)-2,3-pyrazino] porphyrazine[1] [Py_8TPyzPzH_2] (Figure 1, A), its metal derivatives [Py_8TPyzPzM] [M = $Mg^{II}(H_2O)$, Mn^{II}, Co^{II}, Cu^{II}, Zn^{II}][2] and their corresponding octacations [(2-Mepy)$_8$TPyzPzM]$^{8+}$ (also shown in part B of Figure 1 as the unmetalated species).[3] Most recently, further studies were extended to include the similarly formulated Pd^{II} complexes [Py_8TPyzPzPd] and [(2-Mepy)$_8$TPyzPzPd]$^{8+}$ and the interesting pentanuclear species [$(PdCl_2)_4$$Py_8$TPyzPzPd], which represents quite a rare type of combined central and exocyclic metal binding,[4] highly distinct in terms of structural features from the similarly formulated pentanuclear analogues.[5] The three Pd^{II} species proved to be active photosensitizers for the generation of singlet oxygen.[6]

It has been widely ascertained[1,2a,3,4] that the presence of the strongly electron-withdrawing peripheral dipyridylpyrazine fragments in these pyrazino-porphyrazine macrocycles (neutral or octacationic) significantly influences the σ–π electronic distributions within the molecular framework heavily affecting their tendency to the uptake and release of electrons. Their electrochemical behaviour[1,2a,3,4] involves four stepwise one-electron reductions, leading to the formation of [Py_8TPyzPzM]$^{n-}$ (n = 1–4) and [(2-Mepy)$_8$-TPyzPzM]$^{n+}$ (n = 7–4) charged species. The reductions, appearing in most cases as reversible or quasi-reversible, well separated processes, take place at much more positive $E_{1/2}$ values (V vs. SCE) than the parallel processes occurring for their phthalocyanine analogues [PcM][7] and related diazepino-[8] and thiadiazolo-porphyrazine[9] macrocycles.

Cyclic voltammetry and spectroelectrochemical results for the series of [Py_8TPyzPzM] species with M = $Mg^{II}(H_2O)$, Zn^{II}, Cu^{II} and Co^{II}[2a,3b] demonstrate that, irrespective of the solvent used, either pyridine or DMSO, the $E_{1/2}$ values (V vs. SCE) for the first one-electron uptake move progressively towards less negative values, indicative of easier reductions, in the sequence (py, DMSO): $Mg^{II}(H_2O)$ (–0.40; –0.33) → Zn^{II} (–0.34; –0.26) → Cu^{II}

[‡] Tetra-2,3-pyrazinoporphyrazines with Externally Appended Pyridine Rings, VII. Part VI: see ref.[6]

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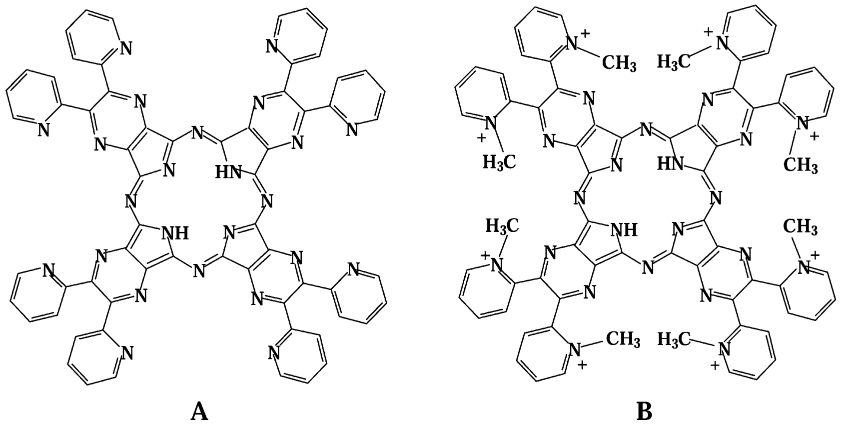

Figure 1. Schematic representation of A) the unmetalated tetrakis[5,6-di(2-pyridyl)-2,3-pyrazino]porphyrazine [$Py_8TPyzPzH_2$], and B) its corresponding octacation [$(2\text{-Mepy})_8TPyzPzH_2]^{8+}$.

(–0.30; –0.22) → Co^{II} (–0.26; –0.06).[2a,3b] Interestingly, the same sequence also holds for their corresponding +8-charged macrocycles [$(2\text{-Mepy})_8TPyzPzM]^{8+}$ in DMSO:[3b] $Mg^{II}(H_2O)$ (–0.19) → Zn^{II} (–0.10) → Cu^{II} (–0.04) → Co^{II} (+0.05). In the explored positive range of potentials +1.0 → 0 V, among the just cited neutral [$Py_8TPyzPzM$] and octacationic [$(2\text{-Mepy})_8TPyzPzM]^{8+}$ complexes, a one-electron oxidation is detected in DMSO only for the Co^{II} complex [$Py_8TPyzPzCo$] (+0.67 V vs. SCE) and its octacationic analogue [$(2\text{-Mepy})_8TPyzPzCo]^{8+}$, for which oxidation occurs with a slightly more positive $E_{1/2}$ value (+0.76 V vs. SCE).[3b]

One of the most important aspects, of great interest for the current work, is that the four observed sequential one-electron reductions take place on the ligand for all metal derivatives, with the sole exception of the first reduction for the neutral and octacationic Co^{II} complexes. In fact, first reduction for both of these species was shown to be *metal-centred*, with implied formation of the corresponding Co^{I} species, as has been established on the basis of UV/Vis and EPR spectral data.[2a,3b] These findings parallel those for the unsubstituted phthalocyanine Co^{II} analogue [PcCo][10] and its substituted tetra-neopentoxy derivative,[11] for which solution studies indicate that the first one-electron reduction also takes place as a metal-centred Co^{II}/Co^{I} process. The same process has been considered to occur in the electrochemical reduction of the tetraquaternized tetra(pyridino)porphyrazinatocobalt(II), deposited as the corresponding Co^{I} species in the form of thin films on graphite electrodes,[12a,12b] and similarly to the same process for the deposited tetracarboxyphthalocyanine cobalt complex.[12c] To the best of our knowledge, however, no description of a porphyrin, phthalocyanine or porphyrazine Co^{I} complex isolated in the solid state as a pure species has so far been reported in the literature.

The synthesis of such a type of species, i.e., the Co^{I} complex Na[$Py_8TPyzPzCo$], has now been accomplished. Appropriate experimental conditions were found for the use of [$Py_8TPyzPzCo$] for the preparation, isolation and characterization of the corresponding Co^{III} complex [$Py_8TPyzPzCo](SbCl_6)$. Rather unexpectedly, attempts directed towards the preparation of single crystals of the Co^{I} complex suitable for X-ray work resulted in the isolation of the Co^{II} complex [$Py_8TPyzPzCo(DMSO)_2$], which represents the first 2,3-pyrazino-porphyrazine macrocycle so far structurally elucidated by single-crystal X-ray work. A full description of the Co^{I}, Co^{II} and Co^{III} complexes is given below.

Results and Discussion

Synthesis and Characterization of the Co^{I} Complex Na[$Py_8TPyzPzCo$]·7 H_2O

a) Spectrophotometric Titration of the Reduction of [$Py_8TPyzPzCo$] to the Monoanion [$Py_8TPyzPzCo]^{1-}$ with $NaBH_4$ in DMSO

One-electron uptake by [$Py_8TPyzPzCo$] to form the anion [$Py_8TPyzPzCo]^{1-}$, previously examined by solution electrochemical studies,[2a,3b] can easily be carried out by a chemical pathway to give the salt-like species Na[$Py_8TPyzPzCo$] (hydrated), which can be isolated and studied as a solid material. Preliminary experiments in DMSO solution were carried out in order to define the required experimental conditions.

In a typical experiment, a known volume (3.00 mL) of a deoxygenated (Ar) DMSO solution of the neutral species [$Py_8TPyzPzCo$] [$c = 5.1 \times 10^{-6}$ M; ε (634 nm) = 1.72×10^{5} $M^{-1} cm^{-1}$] was introduced into a 1-cm optical cuvette closed with a rubber septum. By microsyringe, microaliquots of a solution of $NaBH_4$ in DMSO (0.087 mg mL^{-1}, $c = 2.3 \times 10^{-3}$ M), prepared separately under Ar, were added stepwise to the solution of the complex. The spectral changes observed after addition of each $NaBH_4$ aliquot (1.00 ± 0.05 µL) are shown in Figure 2 (top).

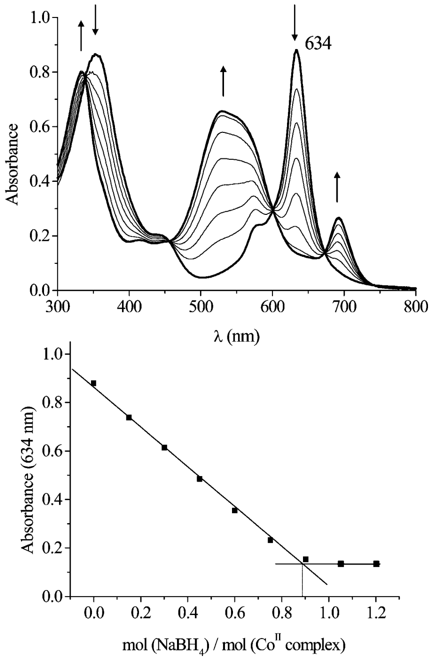

Figure 2. Spectral modifications of a DMSO solution of [Py$_8$TPyzPzCo] by gradual addition of NaBH$_4$ in DMSO (top) and related data analysis (bottom).

The spectral modifications are practically identical to those previously observed by spectroelectrochemical experiments for the first one-electron reduction in pyridine or DMSO,[2a,3b] thus confirming the formation of the –1-charged species during the titration. Starting from the UV/Vis spectrum of the Co^{II} complex [Py$_8$TPyzPzCo] (Q band at 634 nm), addition of each aliquot of the NaBH$_4$ solution causes an instantaneous change in the spectrum, which is gradually modified, leading to the final spectrum of the –1-charged species [Py$_8$TPyzPzCo]$^{1-}$ after addition of the appropriate amount of the reducing agent. During this process, the complete disappearance of the Q band at 634 nm is accompanied by the appearance of an intense broad band with maximum intensity at ca. 530 nm and a lower-intensity absorption at 692 nm, the peak in the Soret region being shifted to higher energies (from 355 to 334 nm). As a result, the colour of the solution changes from green to purple. Clean isosbestic points (at 339, 456, 600, 673, 740 nm) indicate the lack of any spectrally detectable intermediate. The plot of the 634 nm absorbance against the (mol NaBH$_4$)/(mol [Py$_8$TPyzPzCo]) ratio (Figure 2, bottom) gives a stoichiometric NaBH$_4$/[Py$_8$TPyzPzCo^{II}] ratio of 0.90 ± 0.05 for the reduction process, very close to the 1:1 ratio expected for a one-electron reduction. Quantitative spectral data for the –1-charged complex are as follows (nm, log ε): 692, 4.72; 560, 5.08; 530, 5.11; 447(sh), 4.54; 415, 4.56; 334, 5.19.

If the system is maintained under an inert atmosphere, the spectrum of [Py$_8$TPyzPzCo]$^{1-}$ is stable for several hours or even days. Moreover, even if contact with air is not precluded, the titration is only little disturbed by the presence of O$_2$ and the (mol NaBH$_4$)/(mol [Py$_8$TPyzPzCo]) ratio found for complete reduction is only slightly above 1. The broad envelope at 500–600 nm in the UV/Vis spectrum of the anion [Py$_8$TPyzPzCo]$^{1-}$ (Figure 2, top) was previously assigned as a M→L charge-transfer band; the related discussion, also developed in connection with similar assignments for the phthalocyanine analogues, has already been reported[2a,3b] and is not reiterated here.

b) Preparative Aspects and Physicochemical Characterization

On the basis of the preliminary study conducted in DMSO solution, the preparative procedure for the hydrated sodium salt Na[Py$_8$TPyzPzCo] was performed by treating the neutral Co^{II} complex with NaBH$_4$ in DMSO as described in the Experimental Section. Figure 3 shows the IR spectra of the unreduced species and its corresponding monoanion. No significant changes due to the formation of the complex Na[Py$_8$TPyzPzCo] are observed in the explored region, except for the range 1100–1200 cm^{-1}, where the reduction process determines the disappearance of the bands at 1130 and 1193 cm^{-1} and concomitant appearance of new bands at 1155 and 1184 cm^{-1}. The interchange of peak position and intensity of the two pairs of absorptions can be useful for following the complete formation of the sodium salt.

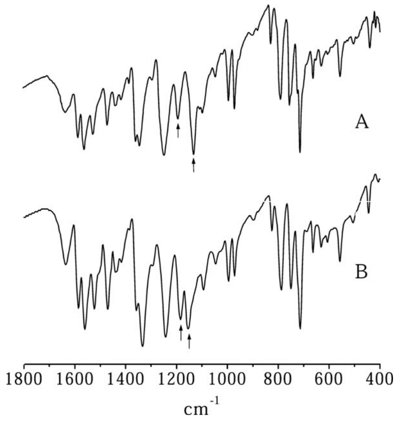

Figure 3. IR spectra in the 1800–400 cm^{-1} range for A) the neutral Co^{II} complex [Py$_8$TPyzPzCo], and B) the related Co^{I} monoanion [Py$_8$TPyzPzCo^{I}]$^{1-}$.

The obtained solid is a deep purple material sufficiently stable if kept under inert atmosphere. Stable in air for a few hours, it is fully reoxidized to the neutral species after several weeks. The amount of clathrated water, always present, is variable depending on the different batches prepared. Thermogravimetric analysis shows that the water molecules are completely eliminated over the temperature range of 25–150 °C. Further heating up to a temperature of 300 °C indicates that no significant decomposition of the unsolvated complex takes place, as it is shown by comparison of the IR and UV/Vis spectra of the materials before and after heating.

Previous studies in pyridine solution[2a] provided basic information on the site of the first one-electron reduction of the Co^{II} complex. Whereas the EPR spectrum of

[$Py_8TPyzPzCo$] in pyridine (77 K) is in keeping with the presence of Co^{II} in a low-spin d^7 ground state, the corresponding –1-charged complex [$Py_8TPyzPzCo$]$^{1-}$ is EPR-silent and hence indicative of the $Co^{II} \rightarrow Co^{I}$ reduction. The low-temperature EPR spectrum of the solid material Na[$Py_8TPyzPzCo$] fully confirms that the site of reduction is the central metal. Figure 4 depicts the EPR spectra at 77 K of solid samples of [$Py_8TPyzPzCo$] (spectrum A) and Na[$Py_8TPyzPzCo$] (spectrum B). Spectrum A reveals the presence of Co^{II} in a tetragonal environment, as expected. Interestingly, spectrum B shows a very evident hyperfine structure for *g*// (dashed lines) typical of Co^{II} in a magnetically diluted environment. Noticeably, this spectrum strictly reproduces that previously obtained for the solid material prepared in DMSO and containing the Co^{II} complex appropriately diluted in its corresponding Zn^{II} analogue [$Py_8TPyzPzZn$], which is also shown for comparison (spectrum C). An accurate examination of the spectrum of Figure 4 (B) indeed shows the presence of a minor amount of an additional form of the Co^{II} complex (black lines on *g*//), with EPR spectral features (*g*// and *A*// values) slightly different from those of the main component. Curiously, the same minor form seems also to be detectable in the magnetically diluted Co^{II}/Zn^{II} material (Figure 4, C). The two components might be generated by the contact of the Co^{II} complex with DMSO, the coordinating ability of which might give rise to two different central Co^{II} coordination sites for the macrocycle. Evidently, the spectrum in Figure 4 (B) belongs to residual subtle amounts of unreduced Co^{II} macrocyclic species dispersed in the diamagnetic –1-charged complex [$Py_8TPyzPzCo$]$^{1-}$. The spectrum in itself, then, is well in keeping with the hypothesis of the metal-centred $Co^{II} \rightarrow Co^{I}$ reduction process.

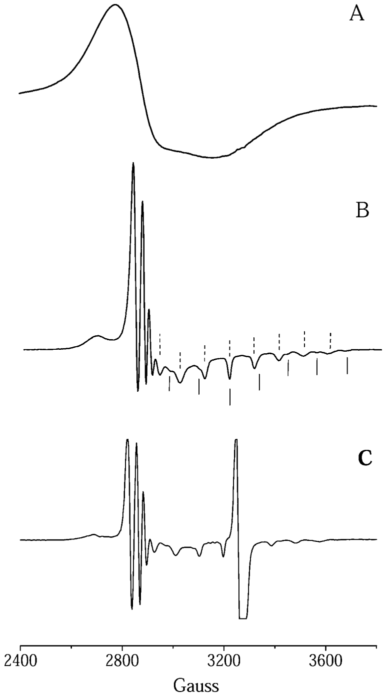

Figure 4. Low-temperature (77 K) EPR spectra of solid samples of A) [$Py_8TPyzPzCo$], B) Na[$Py_8TPyzPzCo$], and C) [$Py_8TPyzPzCo$],[3b] this last magnetically diluted in the corresponding Zn^{II} matrix. In spectrum C, the peak present at ca. 3250 G is due to a π-radical impurity found also to be present in the parallel sample of the pure Zn^{II} complex.

Formation and X-ray Crystal Structure of the Co^{II} Complex [$Py_8TPyzPzCo(DMSO)_2$]·6 DMSO

In an attempt to prepare single crystals of the Co^{I} complex Na[$Py_8TPyzPzCo$], an appropriate amount of the complex was dissolved (partly suspended) in DMSO under N_2 at room temperature. The suspension was stirred for a few minutes and, after separation of the undissolved complex by centrifugation, the saturated solution was left to stand under nitrogen for long periods (months), during which nicely shaped purple crystals slowly formed. Formation of identical crystals was repeatedly observed in several different attempts conducted under similar experimental conditions. The obtained crystals cannot be easily handled because they often undergo rapid fragmentation if singly brought out into air from their mother liquors, most probably due to their tendency to release excess embedded or clathrated DMSO. Despite these difficulties, rapid positioning of a suitable crystal in the diffraction apparatus under N_2 made successful collection of X-ray data possible.

The X-ray data unequivocally show that, under the experimental conditions specified above, the crystals formed in DMSO belong to the neutral original Co^{II} species [$Py_8TPyzPzCo$], which is isolated in the form of its bis-DMSO adduct. It can be assumed that either DMSO or trace amounts of an unknown impurity and/or dioxygen act as the oxidant of the initial Co^{I} species in a very slow process.

Figure 5 shows the structure of the complex. Interatomic distances and angles in the central coordination site and additional data for discussion are listed in Table 1. The asymmetric unit comprises half of the 2,3-pyrazino-porphyrazine macrocycle and three clathrated DMSO molecules (two of them are disordered), disposed about the inversion centre coincident with the central hexacoordinate Co^{II} ion. The in-plane metal centre forms four Co–N bonds with the inner N atoms of the macrocycle with an average Co–N bond length of 1.940(5) Å. With reference to similar tetrapyrrolic porphyrazine analogues also containing Co^{II} located in-plane and with low-spin d^7 configurations, this value is slightly longer than that found in β-[PcCo] [1.908(2) Å][13] and practically coincident with that found [1.942(6) Å] for the Co^{II} complex of tetrakis(thiadiazolo)porphyrazine, [TTDPzCo], in its β-polymorph, isomorphous with its Fe^{II} and Zn^{II} analogues.[14] Notably, recent detailed DFT calculations on the different possible conformers for the Pd^{II} analogue [$Py_8TPyzPzPd$] indicate average bond lengths of ca. 1.99 Å for the inner Pd–N bonds.[4] This longer distance in relation to the Co–N distance in

Table 1. Selected crystal data for [$Py_8TPyzPzCo(DMSO)_2$]·6 DMSO.

Interatomic distances [Å] and angles [°]					
Co1–N1	1.939(5)	N1–Co1–N3	89.8(2)	O1–S1–C33	106.3(3)
Co1–N3	1.940(5)	N1–Co1–O1	91.6(2)	O1–S1–C34	106.0(4)
Co1–O1	2.256(4)	N3–Co1–O1	89.5(2)	C33–S1–C34	97.3(4)
S1–O1	1.518(5)	S1–O1–Co1	119.8(3)		
Dihedral angles [°]					
A–C[a]	38.0(3)	B–C[a]	39.0(3)		
Ai–Ci[a]	35.3(3)	Bi–Ci[a]	44.1(3)		
A–B[b]	48.3(3)	Ai–Bi[b]	54.5(3)		

[a] Dihedral angles between the pyridine and related pyrazine rings. The dihedral angles formed by the pyridine rings A, Ai, B and Bi with respect to the inner pyrazino-porphyrazine ring are 35.8(2), 29.9(2), 35.7(2), 41.4(2)°, respectively. [b] Dihedral angles between proximate pyridine rings.

[TTDPzCo] can reasonably be explained solely on the basis of the different ionic radii of the two bivalent metal centres.[15]

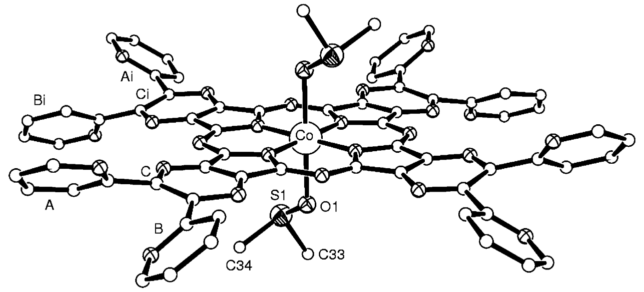

Figure 5. ORTEP[16] drawing of the molecular structure of [$Py_8TPyzPzCo(DMSO)_2$]. Hydrogen atoms have been omitted for clarity.

Six-coordination for [TTDPzCo] is attained by axial ligation of DMSO, which, potentially a bidentate ligand, is known to coordinate to metal centres either through its O (usual) or through its S atoms.[17] In this complex, the two DMSO molecules are *O*-bonded to Co^{II}, with Co–O bond lengths of 2.256(4) Å. To the best of our knowledge, the only reported tetrapyrrolic macrocyclic analogues with the central metal axially ligating two DMSO molecules are the complexes [$TTDPzM(DMSO)_2$] (M = Fe^{II} and Mn^{II})[18] and the phthalocyanine Fe^{II} adduct [$PcFe(DMSO)_2$].[19] In the former case,[18] in which DMSO was established by its IR spectral behaviour also to be *O*-bonded, the M–O (DMSO) bond length (BL) is not known because of lack of X-ray studies. In the case of [$PcFe(DMSO)_2$], the elucidated structure[19] showed DMSO *S*- and not *O*-bonded to Fe^{II}. In a wider look at the literature, *O*-bonded DMSO is found in a number of six-coordinate Co^{II} species, very probably with the metal centres mostly in high-spin electronic configurations. Examples include a) the [$Co(DMSO)_6$]$^{2+}$ ion (BL = 2.08–2.10 Å),[20,21] b) CoO_6,[22–24] CoN_2O_4,[25–28] CoN_4O_2[29] or CoO_4S_2[30] bis-DMSO octahedrally distorted chromophores with the coordination environment completed by monodentate or bidentate O-, N-, O,N-, or O,S-donors (BL = 2.05–2.16 Å), and c) more complex environments in discrete molecular units or in polymeric, chained or multinuclear systems[31–38] (BL = 2.05–2.13 Å, with only one case of a Co–O bond length of ca. 2.24 Å, and other bond lengths in the same species of 2.05–2.10 Å). From these data it appears that the Co–O (DMSO) bond length in the [$Py_8TPyzPzCo(DMSO)_2$] complex [2.256(4) Å] is definitely longer than the observed values in practically all the examined six-coordinate species listed under points a), b) and c) above. This effect in the current low-spin (d^7) complex should probably be ascribed to more effective repulsion to DMSO ligation caused by the unpaired electron residing in the d_{z^2} orbital, more weakly expressed by the same type of electron for the mostly high-spin complexes under points a), b) and c) above.

The S–O bond length in axially ligated DMSO is 1.518(5) Å, in keeping with the data for metal–sulfoxide complexes reported in the literature[39] and longer than the S–O bond length in free DMSO [1.495(4) Å], as would be expected. The O–S–C angles [106.2(2)°, Table 1] are also average for corresponding angles retrieved from the literature for more than 400 related metal–sulfoxide complexes, and consistent with that found in free DMSO [105.7(2)°], as is the C–S–C bond angle [97.3(4)°] in relation to the corresponding value in free DMSO [98.6(2)°].[39]

The A and B and the Ai and Bi rings (Figure 5, Table 1) and their oppositely positioned pyridine rings, all of them essentially planar, form dihedral angles with the related pyrazine rings (C and Ci) in the 35–44° range, the values being slightly different if referred to those calculated for A, B, Ai and Bi in reference to the pyrazino-porphyrazine plane. The dihedral angles between the A and B rings and the Ai and Bi rings, also shown in Table 1, are 48.3(3)° and 54.5(3)°, respectively. Similar values for the corresponding dihedral pyridino–pyrazino and pyridino–pyridino angles were found in the dipyridino-pyrazine fragment present in the precursor, the 2,3-dicyano-5,6-di(2-pyridyl)-1,4-pyrazine [$(CN)_2Py_2Pyz$].[1]

Synthesis and Characterization of the Hydrated Co^{III} Species [$Py_8TPyzPzCo$]($SbCl_6$)

As stated above, one striking difference between the electrochemical behaviour of the Co^{II} complex [$Py_8TPyzPzCo$] in DMSO and that in pyridine is that a one-electron reversible oxidation is observed in DMSO at $E_{1/2}$ values of +0.67 V vs. SCE,[3b] whereas in pyridine no oxidation processes are seen up to +1.0 V vs. SCE.[2a] Similar behaviour has been observed for the Mn^{II} complex.[2a,3b] It is postulated that the stronger donor properties of the pyridine molecule with respect to DMSO make the redox potentials of the two metal complexes higher in pyridine, and so they remain unoxidized in this medium.

The addition of an excess of (phenox)$SbCl_6$ to a solution of the Co^{II} complex in THF (see Experimental Section) or DMSO leads to the formation of the oxidized species $[Py_8TPyzPzCo](SbCl_6)$. The one-electron oxidation forming the +1-charged species $[Py_8TPyzPzCo]^+$ is assumed to be metal-centred ($Co^{II} \rightarrow Co^{III}$) because no redox processes in the positive region (+1.0–0 V vs. SCE) have been observed in DMSO or pyridine either for the free-base ligand or for the electroinactive Mg^{II}, Cu^{II} and Zn^{II} derivatives.[3b] The UV/Vis spectral changes previously observed by spectroelectrochemistry[3b] in DMSO for the same $Co^{II} \rightarrow Co^{III}$ process are reproduced in Figure 6 (A). In the clear absence of intermediates, they show a slight shift and increase in intensity of the Q band and minor variations below 500 nm, all together indicative of low perturbation of the π-electron-delocalized macrocyclic system, consistently with findings also observed for the Co^{II}/Co^{III} redox processes in related porphyrin[40] and phthalocyanine macrocycles.[41] On chemical oxidation of $[Py_8TPyzPzCo]$ with (phenox)$SbCl_6$ in DMSO (Figure 6, B) quite similar spectral variations are observed in the 500–800 nm region, i.e., bathochromic shift (634 nm → 643 nm) and change of intensity of the Q band ($\log \varepsilon_{643} = 5.39$). Parallel behaviour is also observed in the region below 500 nm, although bands of the phenoxathiin fragment also contribute here. These results are substantially in keeping with the spectroelectrochemical behaviour described above and confirm the formation of the Co^{III} complex. It should be noted that slow dissolution accompanied by spontaneous reduction of the $[Py_8TPyzPzCo]^+$ cation in pure DMSO did not allow quantitative data to be obtained for the complete spectrum in the absence of excess of (phenox)$SbCl_6$.

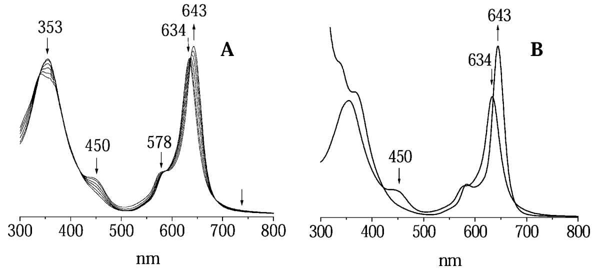

Figure 6. Spectral changes (in DMSO) observed during the one-electron oxidation of $[Py_8TPyzPzCo]$ by A) *spectroelectrochemical*[3b] and B) *chemical* pathways.

The brilliant green hydrated complex $[Py_8TPyzPzCo](SbCl_6)$ is stable under N_2 for months and also shows high stability in air. Its IR spectrum is practically identical to that of the corresponding unoxidized species, except for the presence of an absorption at 340 cm^{-1} assigned to the ν(Sb–Cl) mode. Room temperature magnetic susceptibility measurements give μ_{eff} values in the 0.6–1.0 BM range. This low paramagnetism, frequently encountered in diamagnetic phthalocyanine or porphyrazine materials, is most reasonably attributable to the presence of trace amounts of paramagnetic impurities, thus substantially confirming the low-spin diamagnetic state of the Co^{III} complex, in line with expectations.

Conclusions

A triad of Co^{I}, Co^{II} and Co^{III} derivatives of the macrocyclic ligand tetrakis[5,6-di(2-pyridyl)-2,3-pyrazino]porphyrazine, $[Py_8TPyzPzH_2]$, have been prepared and suitably characterized. Previous electrochemical work indicated that the Co^{II} complex $[Py_8TPyzPzCo]$, normally obtained as a hydrated species, can easily undergo a metal-centred one-electron reduction (–0.06 V vs. SCE in DMSO) with formation of the –1-charged species $[Py_8TPyzPzCo]^{1-}$. In this work the monoanion was obtained as a (hydrated) salt-like species of formula $Na[Py_8TPyzPzCo]$, stable under inert atmosphere and very slowly reoxidized in air. The available data confirm the presence of Co^{I} in the complex, which is believed to represent a unique reported example of a tetrapyrrolic porphyrin, phthalocyanine or porphyrazine macrocycle isolated and characterized as a solid material containing cobalt in the +1 oxidation state. Metal-centred reoxidation of $Na[Py_8TPyzPzCo]$, under precise experimental conditions, leads to the formation of the original Co^{II} complex in the form of the bis-DMSO adduct $[Py_8TPyzPzCo(DMSO)_2]$. Structurally elucidated by X-ray work, the adduct provides unprecedented information on the internal cavity of the pyrazino-porphyrazine macrocycle, the environment of the six-coordinate Co^{II} and the relative positioning of the external proximate pyridine rings and their orientation with respect to the porphyrazine macrocycle. The triad is completed by the synthesis and characterization of the air-stable Co^{III} complex $[Py_8TPyzPzCo](SbCl_6)$.

Experimental Section

General: Solvents and reagents were used as received, unless otherwise specified. The Co^{II} complex $[Py_8TPyzPzCo]\cdot xH_2O$ was obtained as previously reported (usually the amount of water retained depends on the batch of material prepared).[2a] Phenoxathiin hexachloroantimonate [(phenox)$SbCl_6$] was obtained by a reported procedure.[42]

Synthesis of $Na[Py_8TPyzPzCo]\cdot 7H_2O$: The complex $[Py_8TPyzPzCo]\cdot 6H_2O$ (74.0 mg, 0.057 mmol) was suspended in a solution of $NaBH_4$ (2.69 mg, 0.071 mmol) in freshly distilled DMSO (8 mL). The suspension was stirred for 2.5 h at room temperature under N_2, with the solution undergoing a colour change from green to deep purple during this time. A small amount of the reduced complex was already present as a solid at the end of the reaction, but most of it was then precipitated by addition of acetone. After filtration, the solid was washed abundantly with deairated (N_2) acetone and dried under vacuum (10^{-2} Torr) (60 mg, yield 78 %). IR (KBr): $\tilde{\nu}$ = 3400 [m (broad)], 1636 (w–m), 1585 (m–s), 1560 (s), 1524 (m–s), 1470 (m–s), 1439 (w), 1417 (vw), 1385 (vvw), 1358 (m), 1335 (vs), 1294 (vvw), 1242 (vs), 1184 (m–s), 1155 (s), 1094 (w–m), 1045 (w), 995 (m), 972 (m), 897 (vw), 826 (w), 787 (s), 750 (s), 714 (vs), 689 (vvw), 663 (w), 631 (w), 606 (vw), 557 (w), 507 (vw), 446 (w), 407 (vw), 350 (vvw), 240 (vw) cm^{-1}. Na[Py_8TPyzPzCo]·7 H_2O, $C_{64}H_{46}CoN_{24}NaO_7$: calcd. C 57.15, H 3.45, N 24.99; found C 57.25, H 2.96, N 24.52.

X-ray Crystal Structure of [Py_8TPyzPzCo(DMSO)$_2$]·6 DMSO: Crystal data were collected on an Oxford Diffraction Xcalibur Px diffractometer, fitted with a CCD area detector, focusing optics and sealed tube long fine focus with Cu anode and a Cryostream open-flow N_2 gas cryostat. A crystalline sample suitable for data collection was analysed at 100 K in order to minimize solvent escape, structural disorder and thermal motion effects and to increase the precision of the results. During data collection a reference frame was collected every 50 frames to monitor the stability of the crystal and no loss of intensities was observed. Intensities were corrected for Lorentz and polarization effects and for absorption. The structure was solved by direct methods by use of the program SIR97.[43] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms of the pyrazino-porphyrazine macrocycle and of all but two of the DMSO molecules were positioned with calculated geometries and refined isotropically with a riding model. Their thermal parameters were constrained to be 1.2 U_{eq} and 1.5 U_{eq} of the parent C atoms, respectively, by use of SHELX97.[44] Of the six clathrated DMSO molecules, four are disordered each over two positions, with approximately equal occupancies. Despite the solvent disorder and degradable small crystals, leading to weak diffraction, the experimental data were definitely sensitive enough to provide a reliable model at the level of the molecular structure. Crystal data, data collection and structure refinement details for the complex [Py_8TPyzPzCo(DMSO)$_2$]·6 DMSO are given in Table 2.

Synthesis of [Py_8TPyzPzCo](SbCl$_6$)·8 H_2O: The complex [Py_8TPyzPzCo]·6 H_2O (95.1 mg, 0.073 mmol) was added to a solution of (phenox)SbCl$_6$ (213.3 mg, 0.40 mmol) in THF (200 mL). The suspension was stirred at room temperature for 30 h. The solid material obtained was suspended in hot THF (50 °C) and stirred for 1.5 h. It was then separated by filtration and brought to constant weight under vacuum (10^{-2} Torr) (98 mg, yield 80%). IR (KBr): $\tilde{\nu}$ = 3400 [m (broad)], 1614 (m), 1584 (w), 1560 (m), 1526 (m–s), 1468 (w–m), 1435 (w), 1385 (vvw), 1358 (s), 1344 (s), 1296 (w–m), 1250 (s), 1196 (m), 1167 (vvw), 1126 (s), 1107 (m–s), 1099 (m–s), 1045 (w), 995 (m), 970 (s), 878 (w), 826 (w), 785 (s), 752 (s), 708 (vs), 687 (vvw), 660 (m), 621 (w–m), 606 (vvw), 577 (vvw), 555 (m), 527 (vvw), 505 (w), 446 (m), 409 (vw), 350 [(m), ν(Sb–Cl)] cm^{-1}. [Py_8TPyzPzCo](SbCl$_6$)·8 H_2O, $C_{64}H_{48}Cl_6CoN_{24}O_8Sb$: calcd. C 45.90, H 2.89, N 20.07, Cl 12.70; found C 45.65, H 2.64, N 19.71, Cl 12.58.

Other Physical Measurements: IR spectra were taken with Perkin–Elmer 1760 X and 783 spectrophotometers in the 4000–200 cm^{-1} range with use of KBr pellets. UV/Vis solution spectra were recorded with a Varian Cary 5E spectrometer. Thermogravimetric analyses (TGA) were performed on a Stanton Redcroft model STA-781 analyzer under N_2 (0.05 L min^{-1}). Elemental analyses for C, H and N were provided by the “Servizio di Microanalisi” at the Dipartimento di Chimica, Università “La Sapienza” (Rome) on an EA 1110 CHNS-O instrument. Elemental analyses for chlorine were obtained from Analytische Laboratorien (Lindlar, Germany). EPR spectra at 77 K were recorded on a Varian V 4502–4 spectrometer at the Dipartimento di Chimica, Università “La Sapienza”.

CCDC-704400 contains the supplementary crystallographic data for {[Py_8TPyzPzCo(DMSO)$_2$]·6 DMSO}. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 2. Crystal data, data collection and structure refinement details for [Py_8TPyzPzCo(DMSO)$_2$]·6 DMSO.

Crystal data	
Empirical formula	$C_{80}H_{68}CoN_{24}O_8S_8$[a]
M_r	1809.07
Crystal system	triclinic
Space group	$P\bar{1}$
T (K)	100 (2)
a [Å]	9.819 (1)
b [Å]	15.290 (10)
c [Å]	16.590 (2)
α [°]	115.88 (1)
β [°]	94.67 (1)
γ [°]	102.88 (1)
V [Å^3]	2138.7 (15)
Z	1
D_x [$Mg\,m^{-3}$]	1.405
Radiation type	Cu-K_α
μ [mm^{-1}]	3.97
Crystal form, colour	tablets, purple
Crystal size [mm]	0.12 × 0.10 × 0.10
Data collection	
Diffractometer	Oxford Diffraction Xcalibur Px CCD
Data collection method	ω and ϕ
Absorption correction	multi-scan (based on symmetry-related measurements)
T_{min}	0.662
T_{max}	0.675
Measured reflections	6488
Independent reflections	6467
Observed reflections	4299
Criterion for obsd. refl.	$I > 2\sigma(I)$
R_{int}	0.05
θ_{max} [°]	62.1
Refinement	
Refinement on	F^2
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$	0.071, 0.220
S	1.09
No. of reflections	6467
No. of parameters	573
H-atom treatment	constrained to parent site
Weighting scheme	calculated $w = 1/[\sigma^2(F_o^2) + (0.0702\,P)^2 + 11.0945\,P]$, $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	<0.0001
$\Delta\rho_{max}$, $\Delta\rho_{min}$ [e Å^{-3}]	0.49, –0.48

[a] It should be noted that although the formula weight of the complex [Py_8TPyzPzCo(DMSO)$_2$]·6 DMSO, $C_{80}H_{80}CoN_{24}O_8S_8$, is 1821.16, the actual data in the Table reflect the lack of twelve hydrogen atoms of two disordered DMSO molecules in the crystallographic model.

Acknowledgments

Financial support by the University of Rome “La Sapienza” and the Ministero dell’Università e della Ricerca Scientifica (MIUR) (PRIN 2007XWBRR4) is gratefully acknowledged. E. V. was partly financed by the Consorzio Interuniversitario di Ricerca in Chimica dei Metalli nei Sistemi Biologici (CIRCMSB) for a grant during her doctoral work. Thanks are expressed to Prof. F. Monacelli for useful discussions and Dr. M. Occhiuzzi for help with EPR measurements.

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Received: January 12, 2009