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A Rare μ-Hydroxo-Bridged Species. Synthesis, Structure, and Properties of μ-Hydroxo(tetraphenylporphyrinatomanganese(III))(phthalocyaninato-(azido)chromium(III)), [(TPP)Mn–O(H)–CrPc(N_3)]

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A novel ditetrapyrrolic, heteroleptic, and heterometallic (Mn–Cr) μ-hydroxo-bridged complex has been prepared, and its structural and general properties have been studied. The species μ-hydroxo(tetraphenylporphyrinatomanganese(III))(phthalocyaninato(azido)chromium(III)), [(TPP)Mn–O(H)–CrPc(N_3)], isolated as a chloronaphthalene (ClNP) solvate, has been structurally characterized by single-crystal X-ray work. The two (TPP)Mn and CrPc(N_3) fragments are held together by the bridging μ-hydroxo ion with long Mn–O [1.993(5) Å] and Cr–O [1.976(5) Å] bond distances and a Mn–O(H)–Cr angle of 163.7(3)°. The five-coordinate Mn center in the (TPP)Mn fragment is displaced from the TPP rigorously planar central N_4 core by 0.128 Å, and the environment is typical of a Mn^{III} high-spin site. The six-coordinate Cr^{III} in the CrPc(N_3) moiety lies practically in the plane of the phthalocyanine macrocycle (displacement toward the azido group: 0.054 Å). The average Mn–N_{pyr} and Cr–N_{pyr} bond distances are 2.011(6) and 1.982(6) Å, respectively, and the Mn–Cr bond distance is 3.929(2) Å. The porphyrin and phthalocyanine rings are in an almost eclipsed position [5.16(2)°], and the mean planes of the two macrocycles form a dihedral angle of 5.79(4)°. Crystal data for [(TPP)Mn–O(H)–CrPc(N_3)]•2ClNP, $C_{76}H_{45}CrMnN_{15}O{\cdot}2C_{10}H_7Cl$: $a = 16.645(3)$ Å, $b = 17.692(4)$ Å, $c = 25.828(5)$ Å, $\alpha = 90°$, $\beta = 98.79(3)°$, $\gamma = 90°$, space group $P2_1/c$ (No. 14), $V = 7517(3)$ Å^3, $Z = 4$, R1 = 0.086, and wR2 = 0.267. IR and UV–vis–near-IR spectral and room temperature magnetic susceptibility data of the [Mn–Cr] species are also presented.

Introduction

Extensive research work has been conducted on single-atom-bridged dimetallic species having M−X−M′ trinuclear bond systems and mono- or multidentate ancillary ligands attached externally to the M and M′ metal centers with the formation of charged or neutral entities (in most cases M = M′).[1] Among the known classes of such compounds, the μ-O-bridged species (X = O) are largely prevalent[1] and are likely to be still intensively expanding. Numerous μ-O-bridged species, which have M = M′ (or M ≠ M′) incorporated into the cavities of tetrapyrrolic macrocycles such as porphyrins or phthalocyanines, with the formation of homo- or heteroleptic species are known, and reviews on these systems have fairly recently appeared.[2,3]

Far less numerous are the similar X-bridged dinuclear systems with X = N, C, S, Se, Te, or F.[1] Among the examples of μ-nitrido species (X = N) so far known, a restricted number of homometallic and homoleptic porphyrinato (Por), phthalocyaninato (Pc), and porphyrazinato (Pz) complexes were reported mainly responding to the basic

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formula [(L)M−N−M(L)] (L = Por, Pc, and Pz; M prevalently Fe) and derivatives therefrom.[4−7] First isolated and deeply studied were [(TPP)Fe−N−Fe(TPP)][4] (**I**) and its phthalocyanine analogue [PcFe−N−FePc] (**II**).[5] Both complexes were characterized as mixed-valence compounds carrying both Fe centers with oxidation states intermediate between +3 and +4, i.e., +3.5, owing to the rapid flow of electronic charge along the bridging essentially linear Fe−N−Fe bond system. Upon one-electron oxidation, species containing $Fe^{IV}-Fe^{IV}$ couples were obtained from **I**[4e,8] and **II**[5,9] and from the $[(TTP)Fe]_2N$ species, i.e., $\{[(TTP)Fe]_2N\}SbCl_6$, also reported.[10] Worth mentioning is [PcRu−N−RuPc],[7] to our knowledge the exclusive homonuclear and homoleptic [(L)M−N−M(L)] species so far known involving a second-row transition metal. Further work led later to the isolation and characterization of the unprecedented mixed-ligand dinuclear homometallic complex $[(TPP)Fe^{III1/2}-N-Fe^{III1/2}Pc]$[11] and heterometallic complexes $[(TPP)Mn^{IV}-N-Fe^{III}Pc]$[12] and $[(TPP)Fe^{IV}-N-Ru^{III}Pc]$[11b] and of the heterometallic OPTAP derivative [(OPTAP)Fe−N−Mn(OPTAP)], in which oxidation states for the two metal centers were not precisely established.[13] Metal-centered one-electron oxidation occurs for the first two species, and the cations of formula $[(THF)(TPP)M^{IV}-N-Fe^{IV}Pc(H_2O)]^+$ are formed (M = Fe^{IV} or Mn^{IV}), whereas the $[Fe^{IV}-Ru^{III}]$ species undergoes a ligand-centered oxidation to form the π-cation radical $[(TPP)Fe^{IV}-N-Ru^{III}Pc]^{\bullet+}$.[11b] The two cations $[(THF)(TPP)M^{IV}-N-Fe^{IV}Pc(H_2O)]^+$ are present in the neutral species of formula $[(THF)(TPP)M-N-Fe^{IV}Pc(H_2O)](I_5)\cdot 2THF$ (M = Fe^{IV} or Mn^{IV}), both of known structure based on single-crystal X-ray work.[11b,14] Undoubtedly, the achieved results in this area allowed characterization of new interesting dinuclear μ-N ditetrapyrrolic species, and the formation of stable complexes involving Fe centers in a high oxidation state (>3; i.e., $Fe^{III1/2}$ and Fe^{IV}) has often been observed.

The presence of Cr atoms in the formation of μ-X-bridged dinuclear species is rare in general,[1] and only a few species are known of the μ-oxo type with chromium incorporated in tetrapyrrolic cavities. Examples of the type [(Por)Cr−O−Cr(Por)][15a] or [(Por)Cr−O−Fe(Por′)][15b] and the pyridine adduct [(py)(TPP)Cr−O−Fe(TMP)], having a partially elucidated structure, plus the species [(TPP)Cr−O−FePc], and Pc derivatives of formula $[(Y)PcCr-O-CrPc(Y)]^n$ [16,17] (Y = anions, $n = -2$;[16] Y = pyridine, $n = 0$[17]) were reported, but there appears to be so far only one μ-oxo Cr−Fe homoleptic porphyrin species, [(TPP)Fe−O−Cr(TPP)(pip)] with the structure fully elucidated by X-ray work.[18] No examples have appeared in the literature of μ-nitrido-bridged dinuclear species incorporating Cr as a metal center, with the exception of the cationic heterobimetallic diporphyrin species $[(OEP)Re-N-Cr(TPP)]^+$, postulated as an intermediate in N-atom-transfer reactions from (OEP)ReN.[19] Within this line of work, it was seen as interesting to involve chromium phthalocyanine, [PcCr], in the formation of a mixed-ligand (TPP, Pc) heterometallic μ-N-bridged system by reaction with $[(TPP)MnN_3]$, thus postulating the formation of the species $[(TPP)Mn^{IV}{=}N-Cr^{III}Pc]$.

Some unexpected evolution was verified by examining the reaction between $[(TPP)MnN_3]$ and [PcCr], and the results of this piece of research are presented here. As is shown, the reaction of $[(TPP)MnN_3]$ with [PcCr] affords a μ-hydroxo-bridged species, i.e., $[(TPP)Mn-O(H)-CrPc(N_3)]$, in which a hydroxyl group holds together (TPP)Mn and $CrPc(N_3)$ fragments through its oxygen atom. To our knowledge, the species so far reported having a single hydroxyl group bridging the two metal centers of the tetrapyrrolic macrocycles are homometallic and homoleptic diporphyrin cationic units of formula $[(L)M-O(H)-M(L)]^+$ (L = TPP, OEP; M = Fe, Mn).[20−22] The present [Mn−Cr] species is an unprecedented example of a μ-hydroxo-bridged ditetrapyrrolic system in that it is both heteroleptic and heterometallic and sees the presence of a Cr center incorporated in such

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species. Its structural and physicochemical properties are discussed here in comparison with those of structurally related species.

Experimental Section

Chemical reagents and solvents were commercial products. Chloronaphthalene (ClNP) was refluxed in the presence of CaH_2 and freshly distilled before use (111−113 °C, 5 mmHg). Benzene was made anhydrous by refluxing it over potassium. [PcCr] was prepared as described elsewhere.[23]

[(TPP)MnN$_3$]. As was noted before,[12,14] the synthesis of [(TPP)-MnN$_3$] from [(TPP)MnOAc] and NaN_3 in $CHCl_3$ followed by recrystallization from this solvent leads in most cases to the formation of [(TPP)MnN$_3$] in a mixture with the solvate [(TPP)-MnN$_3$]·0.5CHCl$_3$ of known structure.[14] This latter solvate can give a side reaction and unequivocally form [(TPP)MnCl] in ClNP, under conditions (120 °C) in which chlorine abstraction from the ClNP solvent only minimally takes place (see the Results and Discussion section). If prepared from methanol, [(TPP)MnN$_3$] was reported to give the solvate species [(TPP)Mn(N$_3$)(CH$_3$OH)]·CH$_3$OH.[24] In our direct experience, the reaction of [(TPP)MnOAc] with NaN_3 in CH_3-OH always led to the unsolvated [(TPP)MnN$_3$] which was used as such in the present work.

[(TPP)Mn−O(H)−CrPc(N$_3$)]·0.5ClNP. [(TPP)MnN$_3$] (128 mg, 0.17 mmol) was dissolved in ClNP (10 mL) freshly distilled over CaH_2. [PcCr] (50 mg, 0.09 mmol) was added to the solution in an inert atmosphere, and the reaction vessel was heated at 120 °C for 8 h. After cooling, filtration under N_2, and the addition of hexane (5 mL), the solution was kept in a refrigerator. Small crystals of the [Mn−Cr] complex eventually formed on the walls of the vessel were separated manually, and the rest of the suspension was filtered and the microcrystalline material was washed repeatedly to eliminate the excess of [(TPP)MnN$_3$], using small amounts of dry benzene to minimize loss of the [Mn−Cr] complex. The powdered material was brought to a constant weight under vacuum (10^{-2} mmHg) (ca. 70 mg; yield 60%). Calcd for [(TPP)Mn−O(H)−CrPc(N$_3$)]·0.5ClNP, $C_{81}H_{48.5}Cl_{0.5}CrMnN_{15}O$: C, 70.88; H, 3.56; N, 15.31. Found: C, 70.86; H, 3.50; N, 15.70%. UV−vis (nm, log ϵ): (CH_2Cl_2 solution) 342 (4.95), 365 (sh, 4.82), 395 (sh, 4.77), 474 (4.81), 595 (sh, 4.25), 619 (4.34), 689 (4.91), 869 (3.92), 989 (3.02), 1105 (2.76), 1197 (3.39). IR (KBr or CsI, cm^{-1}): 2040 vs (N_3^-), 1615 w (Pc), 1600 vw (ClNP), 1577 w, 1561 w, 1541 w, 1522 w, 1508 w, 1487 s (TPP, Pc), 1474 m, 1457 m−w, 1440 m−w, 1410 m−s (Pc), 1385 s, 1332 vs (TPP, Pc), 1284 m−s (Pc), 1224 vw (ClNP), 1201 w (Pc, TPP), 1184 vw, 1164 m−w (TPP, Pc), 1119 vs (Pc), 1083 vs (Pc), 1065 vs (TPP, Pc), 1009 vs (TPP), 948 w, 900 m−s (Pc), 872 w, 850 w, 835 w, 803 s (TPP, Pc), 777 m−w (Pc), 755 s (TPP, Pc), 731 vs (Pc), 712 w (TPP), 703 m (TPP), 680 m−w (ClNP), 621 w, 602 w, 569 w (Pc), 550 w, 510 w (Pc), 476 w, 455 w, 433 w, 420 m, 408 m−w, 375 w, 350 w, 325 w, 300 w, 280 w, 240 w.

X-ray Crystallography for [(TPP)Mn−O(H)−CrPc(N$_3$)]·2ClNP. Data were collected on single crystals of the [Mn−Cr] complex on a MAR345 IPDS image plate at 143 K using Mo Kα radiation. A total of 60 images were collected with a $\Delta\varphi$ of 3° and an exposition time of 3 min. Solution and refinement were carried out using the programs *SHELXS97* and *SHELXL97*.[25] The H atoms were assigned to idealized positions and refined as riding, with isotropic thermal parameters equal to 1.2 times of the thermal parameter of the atom to which they were attached. One Cl atom of a ClNP molecule was found to be disordered over two positions, with site occupation factors of 0.75 and 0.25 for the major and minor contributors, respectively. The details of the X-ray data collection, structure solution, and refinement are given in the Supporting Information.[26]

Other Physical Measurements. UV−vis−near-IR (NIR) spectra were taken with a Varian Cary 5E spectrophotometer. IR spectra were recorded on a Perkin-Elmer 783 spectrophotometer in the range of 4000−200 cm^{-1} by using KBr pellets or CsI disks (Nujol mulls). Thermogravimetric analyses were performed on a Stanton Redcroft model STA-781 analyzer under a N_2 atmosphere (0.5 L/min). The room-temperature magnetic moment of the Mn−Cr species was measured on the MSB-MK1 instrument (Sherwood Scientific Ltd.). The diamagnetic contributions of the TPP and Pc macrocycles were taken as -386×10^{-6} and -430×10^{-6} cgsu/mol, respectively; additional corrections for the azide and bridging OH groups and the two metal centers (Mn and Cr) were calculated from Pascal's constants. 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.

Results and Discussion

Synthetic Aspects and General Properties. Accurate work has been directed to identify the precise reaction conditions for the prevalent formation of the [Mn−Cr] complex, preventing the formation of undesired materials. Thus, the molar ratio of the reactants, [(TPP)MnN$_3$]/[PcCr], was fixed at 2:1, and the reaction was carried out in ClNP at 120 °C for 8 h. It was verified that the use of lower ratio values of the reactants (1:1 or little higher) and shorter reaction times depress the yield of the dinuclear complex and leave residual amounts of unreacted [PcCr], which can, in turn, generate undesired products possibly formed from it during manipulation for purification of the ground material. The 2:1 molar ratio minimizes the amount of unreacted [PcCr] and leaves an excess of [(TPP)MnN$_3$], which can be easily washed out from the [Mn−Cr] complex. It was separately observed that [(TPP)MnN$_3$], kept alone in ClNP under identical experimental conditions (120 °C, 8 h), remains substantially unchanged, with only a minimum amount being converted into the chloride [(TPP)MnCl], which is evidently formed upon release of the azide group by [(TPP)MnN$_3$], followed by "chlorine abstraction" operated by the [(TPP)Mn] fragment from ClNP. Something similar was also observed in the reaction of [PcFe] with I_2 in ClNP.[27] Upon chlorine abstraction, [PcFeCl] was formed, and the species [PcFeCl·I$_2$·ClFePc] was isolated and identified crystallographically.

The jumping of the azide group from [(TPP)MnN$_3$] to [PcCr] with the formation of the PcCrN$_3$ fragment in the

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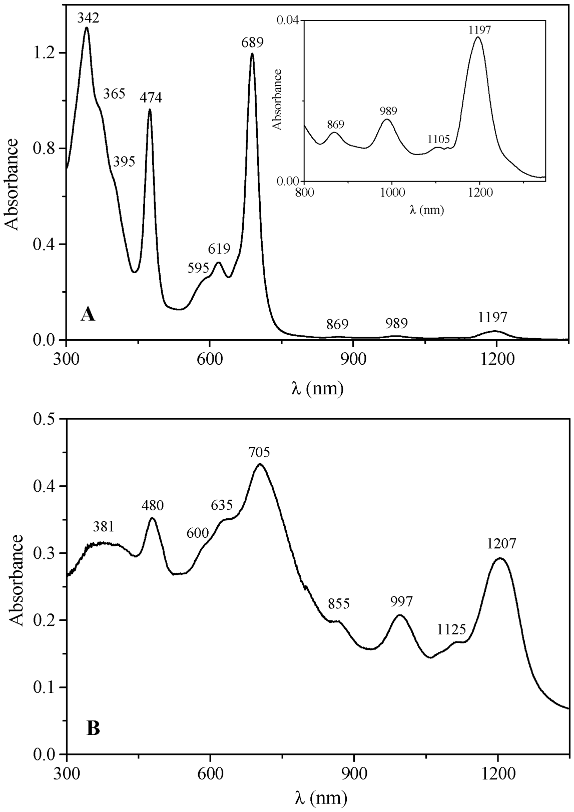

Figure 1. (A) UV−vis−NIR spectrum in CH_2Cl_2 ($c = 1.48 \times 10^{-5}$ M) and (B) reflectance spectrum of [(TPP)Mn−O(H)−CrPc(N_3)].

[Mn−Cr] complex is in itself not surprising. In fact, a similar process was observed[11b] in the reaction of [(TPP)FeN_3] with [PcFe]. In this reaction, the dinuclear mixed-ligand species [(TPP)Fe−N−FePc] is mainly produced, but the Pc species [PcFe−N−FePc] is also formed as a contaminant. The latter is undoubtedly formed by thermal decomposition of the intermediate azide [PcFeN_3], with this, in turn, obtained upon transfer of the azide group from [(TPP)FeN_3] to [PcFe].

If more elevated temperatures (150−180 °C) are used in the synthesis of the [Mn−Cr] complex, the formation of [PcCrN_3], easily detectable by IR spectra, definitely prevails, but concomitant decomposition of this chromium azide takes place with the formation of a material that has not been further investigated.

It has been observed that the amount of ClNP incorporated by the solid [Mn−Cr] complex is variable from preparation to preparation and is fixed in a precise molar ratio [Mn−Cr]:ClNP = 1:2 only in the single crystals formed and suitable for structure elucidation. The complex is practically indefinitely stable in air as a solid crystalline material. Single crystals used for X-ray work were used again after 2 years, allowing collection of data and structure refinement once again. The IR spectrum of the complex shows specific absorptions belonging to both the TPP and Pc macrocycles (see Figure S1 in the Supporting Information) and the narrow intense absorption of the azide group (2040 cm^{-1}). Absorptions due to the ClNP molecule can be found in the region 700−1600 cm^{-1}, more or less evident depending on the type of sample examined.

Table 1. X-ray Data on the Crystalline [Mn−Cr] Complex [(TPP)Mn−O(H)−CrPc(N_3)]·2ClNP

formula	$C_{76}H_{45}CrMnN_{15}O \cdot 2C_{10}H_7Cl$
a, Å	16.645(3)
b, Å	17.692(4)
c, Å	25.828(5)
α, deg	90
β, deg	98.79(3)
γ, deg	90
V, $Å^3$	7517(3)
Z	4
fw	1616.5
space group	$P2_1/c$ (No. 14)
T, °C	143
λ, Å	0.710 73
ρ_{calc}, g cm^{-3}	1.428
μ, cm^{-1}	4.48
transm coeff	0.980−1.000
R1[a]	0.086
wR2	0.267
GOF	1.083
no. of obsd[b]	6394
no. of independent[c]	10 470
no. of refinement[d]	10 470
variables	1002

[a] Calculated on the observed reflections having $I > 2\sigma(I)$. [b] "no. of obsd" is the total number of the independent reflections having $I > 2\sigma(I)$. [c] "no. of independent" is the number of independent reflections. [d] "no. of refinement" is the number of reflections used in the refinement.

The present [Mn−Cr] species cannot be purified by column chromatography in a variety of conditions, owing very likely to decomposition and probably implying the rupture of the Mn−O(H)−Cr bridge. The complex is stable enough in non donor solvents (CH_2Cl_2, $CHCl_3$, toluene). The UV−vis−NIR spectrum in CH_2Cl_2 (Figure 1A; quantitative data in the Experimental Section) shows only slight variations of the relative intensity of the peaks over a period of 24−48 h, very likely due to some aggregation initially present and disappearing with time. Similar spectra and variations for comparable times are also seen for solutions of the complex in $CHCl_3$ and benzene. At longer times (benzene, days), slow precipitation leads to a solid phthalocyanine material probably consisting mainly of the [PcCrN_3] fragment. In keeping with this, the IR spectrum of the solid shows only peaks of the phthalocyanine macrocycle and an absorption at 2040 cm^{-1} attributable to the N_3^- group. The UV−vis spectrum of the same residue in a pyridine solution shows exclusively the peaks expected for the Pc macrocycle in the Soret (300−400 nm) and Q-band regions (600−700 nm) due to the $\pi-\pi^*$ transitions of the Pc macrocycle, in the absence of peaks attributable to the porphyrin ring. The porphyrin fragment present in solution is also easily identified by its UV−vis spectrum as well as by the IR spectrum of the residue obtained after evaporation of the solvent (not further investigated).

X-ray Crystal Structure of [(TPP)Mn−O(H)−CrPc(N_3)]·2ClNP

Isolation of single crystals has allowed elucidation of the structure of the [Mn−Cr] complex. Crystal data are listed in Table 1. Selected bond distances and angles are quoted in Table 2. Its formula is proposed here as [(TPP)Mn−X−CrPc(N_3)] (hereafter neglecting ClNP) for the appropriate discussion. In fact, although in the correct formulation of

Table 2. Selected Bond Distances (Å) and Angles (deg) for the Complex [(TPP)Mn−O(H)−CrPc(N_3)]·2ClNP

Mn1−N1	2.018(6)	Cr1−N9	1.974(6)
Mn1−N2	2.012(5)	Cr1−N11	1.984(5)
Mn1−N3	2.002(6)	Cr1−N13	2.004(7)
Mn1−N4	2.010(5)	Cr1−O1	1.976(5)
Mn1−O1	1.993(5)	N13−N14	1.184(10)
Cr1−N5	1.989(6)	N14−N15	1.186(10)
Cr1−N7	1.979(5)		
O1−Mn1−N1	90.8(2)	O1−Cr1−N13	177.7(3)
O1−Mn1−N2	99.3(2)	N5−Cr1−N7	89.8(2)
O1−Mn1−N3	99.7(2)	N5−Cr1−N9	177.2(2)
O1−Mn1−N4	91.0(2)	N5−Cr1−N11	90.2(2)
N1−Mn1−N2	89.7(2)	N5−Cr1−N13	92.0(2)
N1−Mn1−N3	169.5(2)	N7−Cr1−N9	90.4(2)
N1−Mn1−N4	89.4(2)	N7−Cr1−N11	176.6(2)
N2−Mn1−N3	89.5(2)	N7−Cr1−N13	91.0(2)
N2−Mn1−N4	169.7(2)	N9−Cr1−N11	89.4(2)
N3−Mn1−N4	89.5(2)	N9−Cr1−N13	90.8(3)
O1−Cr1−N5	85.8(2)	N11−Cr1−N13	92.4(2)
O1−Cr1−N7	88.5(2)	Mn1−O1−Cr1	163.7(3)
O1−Cr1−N9	91.5(2)	Cr1−N13−N14	121.7(6)
O1−Cr1−N11	88.1(2)	N13−N14−N15	177.1(8)

the [Mn−Cr] complex X is a hydroxyl group (see below), the alternative possibilities of X either being (i) an N atom, i.e., the complex is postulated as a μ-nitrido-bridged species, [(TPP)Mn−N−CrPc(N_3)], or (ii) an O atom, i.e., the complex is a μ-oxo-bridged species, [(TPP)Mn−O−CrPc(N_3)], are also briefly preliminarily considered; this is believed to help in finalizing the structural and other physicochemical information available on the [Mn−Cr] complex to the unequivocal identification of its molecular structure.

The hypothesis of X = N is easily excluded on the basis of the crystal data and electroneutrality of the [Mn−Cr] complex (see also the Supporting Information for FAB spectra). As can be seen from the data in Table 2, partly quoted also in Table 3 (top), the Mn−O(H)−Cr bond angle [163.7(3)°] for the [Mn−Cr] complex is far from being linear, as is practically instead the case for all of the μ-nitrido ditetrapyrrolic analogues listed in Table 3 (177−180°). Moreover, the Mn−O and Cr−O bond distances, 1.993(5) and 1.976(5) Å, respectively, are definitely too far away from the values of the observed M−N distances of the other μ-nitrido structures (1.62−1.68 Å). As to the electroneutrality of the complex, neutralization of the 8− total charge (4− for the two macrocyclic rings, 3− for the bridging N atom, and 1− for the azide group) would require for the two metal centers formation of one of the couples Mn^{V}−Cr^{III}, Mn^{III}−Cr^{V}, or Mn^{IV}−Cr^{IV}. Each one of these couples implies too high oxidation states (IV or V) for at least one of the two metal centers, which is seen as hardly accessible owing to the inert atmosphere of the reaction (N_2) and a substantially reducing reaction medium determined by the presence of [PcCr] (this latter easily undergoes oxidation to Cr^{III} species in air or in the presence of oxidizing agents). Moreover, the presence of a couple of the type Mn^{III}−Cr^{III} is strongly supported by structural (Mn) and UV−vis−NIR spectral data (Cr) (see below). In conclusion, therefore, there appears to be convincing evidence that the [Mn−Cr] species cannot be a μ-nitrido species.

The hypothesis of the occurrence of a μ-oxo species, i.e., [(TPP)Mn−O−CrPc(N_3)], neglecting at this point the implied problems of electroneutrality, necessarily brings up the

Table 3. Crystal Data on the [Mn−Cr] Complex and Related Species

compound	M−X (Å)[a]	$M-N_{pyr}$ (Å),[b] average value	$M-Y_a$ (Å)[c]	$M-C_t$[d] (Å)	M−X−M angle (deg)	twist angle (deg)	ref
[(TPP)Mn−O(H)−CrPc(N_3)]	(Mn) 1.993(5), (Cr) 1.976(5)	2.011(6), 1.982(6)		(Mn) 0.182(1), (Cr) 0.054(1)	163.7(3)	−5.16(2)	this work
[(THF)(TPP)Fe_1−N−Fe_2Pc(H_2O)]$^+$	(Fe_1) 1.625(2), (Fe_2) 1.655(2)	2.00(5), 1.949(45)	2.078(13), 2.159(40)	0.11	179.0(6)	eclipsed	11b
[(THF)(TPP)Mn−N−FePc(H_2O)]$^+$	(Fe) 1.683(12), (Mn) 1.669(12)	1.972(13), 2.018(13)	2.116(9), 2.200(10)	0.097, 0.138	178.6(7)	eclipsed	14
[(TPP)Fe]$_2$N	1.6605(7)	1.991(3)		0.32	180	31.7	4b
{[(TTP)Fe]$_2$N}($SbCl_6$)	1.6280(7)	1.979(5)		0.34	180	30.3	10
[(Br)PcFe]$_2$N	1.639(2)	1.945(9)	2.495(3)	0	180	39	9d
{[(N_3)PcFe]$_2$N}$^-$	1.650(1)	1.947(5)	2.152(7)	0.08	177.4(4)	38.5	9c
[(TPP)Fe]$_2$O	1.763(1)	2.087(5)		0.50	174.5	35.4	28
[(OEP)Fe]$_2$O	(tri) 1.756(3), (mono) 1.755(10)	2.077(3), 2.080(5)		0.50,[e] 0.54[e]	172.2(2), 176.21(23)	17.0, 16.8	29
[(1-meim)PcFe]$_2$O	1.749(1)	1.92(3)	2.039(7)	0.02	175.1	45	30
{[(py)PcMn]$_2$O}·2py	1.71(1)	1.97	2.15	0.02	178	41	31
[(N_3)(TPP)Mn]$_2$O	1.743(4), 1.794(4)	2.014	1.97	0.09	180	28.5	32
[(TPP)Fe−O−Cr(TPP)(pip)]	(Fe) 1.751(4),[c] (Cr) 1.775(4)[d]		2.288(7)[e]		177.7(3)		18
[Cp(dppe)Fe−CN−(Pc)−Mn]$_2$O	1.71(1)		2.05(1)		177.9(5)		33
{[(py)PcCr]$_2$O}·2py	1.752/1.767	1.984/1.981	2.192/2.199	Cr1 in plane; Cr2 out of plane (0.04 Å) toward O	178.8	40.1	17, 34, 35
{[(TPP)Mn]$_2$OH}$^+$	2.041(5), 2.015(5)	2.008(8)		0.21, 0.22	160.4(8)	29.9	20a
{[(OEP)Mn]$_2$OH}$^+$	1.998(2), 2.024(2)	2.006(5)		0.19, 023[e]	152.73(11)	4.3	20b

[a] X: atom bridging the two metal centers. [b] $M-N_{pyr}$: average value of the bond distances in the MN_4 core. [c] Y_a: external axial ligand. [d] C_t: center of the inner pyrrole N_4 core. [e] Displacement of M from the respective porphyrinato 24-atom mean plane.

question of which might be the source of the O atom. It is believed that it might come from subtle amounts of H_2O present in ClNP rather than from improbable traces of O_2 present in the reaction medium. A number of structurally elucidated μ-oxo tetrapyrrolic homo- or heterometallic complexes are known. Examples are listed in Table 3, i.e., $[(TPP)Fe]_2O$,[28] $[(OEP)Fe]_2O$,[29] $[(1\text{-meim})PcFe]_2O]$,[30] $\{[(py)PcMn]_2O\}\cdot 2py$,[31] $[(N_3)(TPP)Mn]_2O$,[32] $[(Cp)(dppe)Fe-CN-(Pc)-Mn]_2O$,[33] and $[(TPP)Fe-O-Cr(TPP)(pip)]$.[18] All of these μ-oxo species exhibit practically linear M−O−M or M−O−M′ bond angles (172−180°) and M−O bond distances in the range of 1.71−1.78 Å. These data are again quite distant from those observed for the present [Mn−Cr] species (Table 2). It is briefly noticed here that some similarity exists between the [Mn−Cr] complex and the only so far fully structurally elucidated ditetrapyrrolic μ-oxo dinuclear complex containing Cr, i.e., $[(TPP)Fe-O-Cr(TPP)(pip)]$[18] (Table 3). This latter shows an Fe^{III} center in a five-coordinate (TPP)Fe fragment and a six-coordinate Cr^{III} on the other side of the bridging oxygen atom. Nevertheless, substantial differences are seen in the bond system Fe−O−Cr, practically linear (177.3°), and in the bond distances Fe−O (1.75 Å) and Cr−O (1.775 Å), much shorter than those in the present [Mn−Cr] complex. Mentioned should also be the phthalocyanine derivative $\{[(py)PcCr]_2O\}\cdot 2py$,[17] isomorphous with the corresponding Mn^{III} analogue[31] and for which preliminary X-ray data have been reported.[34] In this $[Cr^{III}-Cr^{III}]$ species, the Cr−O−Cr bond angle is nearly linear and the Cr−O bond distance is also definitely shorter[35] than that in the [Mn−Cr] complex (Table 3). Thus, it can be confidently concluded that the present [Mn−Cr] complex cannot be a μ-oxo species of formula $[(TPP)Mn-O-CrPc(N_3)]$ (see also a short discussion of FAB spectra in the Supporting Information).

As we shall see here, unequivocal support to the identification of the [Mn−Cr] complex as a $Mn^{III}-Cr^{III}$ μ-hydroxo-bridged species is given by its structural features, in keeping with information derived from its physicochemical behavior. Side and top views of the complex are shown in Figures 2 and 3, respectively.

(TPP)Mn Fragment. The conformation of the TPP macrocycle is essentially planar (Figure 2). The average transannular torsion angle $(C_\alpha N_{pyr} N_{pyr} C_\alpha)_{op}$ is 2.0(7)°, and the average out-of-plane displacement of the C_{meso} atoms from the 24-atom mean plane is 0.051(7) Å. The moderate ruffling of the porphyrin system is indicated also by the minimum and maximum out-of-plane displacements, which are −0.120(8) and 0.067(8) Å for C18 and C3, respectively. The mean absolute perpendicular displacements from the 24-atom mean plane of the N_{pyr}, C_α, and C_β atoms are 0.027(5), 0.032(7), and 0.058(8) Å, respectively.

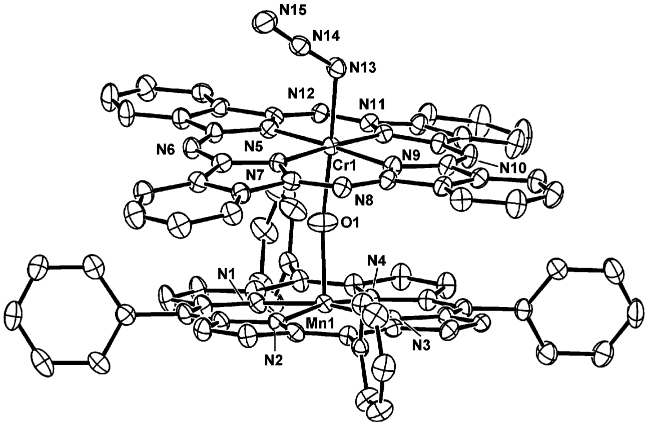

Figure 2. ORTEP side view of the [Mn−Cr] complex (30% probability ellipsoids). H atoms are omitted for clarity. The Mn−O(H)−Cr bridge is in the plane of the paper.

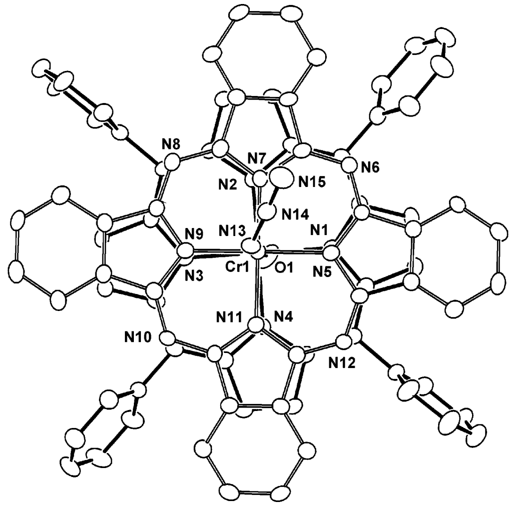

Figure 3. ORTEP top view of the [Mn−Cr] complex (30% probability ellipsoids). H atoms are omitted for clarity. The Mn−Cr axis is perpendicular to the plane of the paper.

The pyrrole rings are strictly planar; the dihedral angles that they form with the porphyrin mean plane are 0.69(19), 2.18(18), 1.55(18), and 4.7(2)° for N1/C1···C4, N2/C6···C9, N3/C11···C14, and N4/C16···C19, respectively. The dihedral angles formed by the opposite N1/C1···C4, N3/C11···C14 and N2/C6···C9, N4/C16···C19 rings are 1.5(3) and 5.7(3)°, respectively. The C21···C26, C27···C32, C33···C38, and C39···C44 *meso*-phenyl substituents are twisted with respect to the porphyrin mean plane by 67.88(17), 87.00(16), 68.78(18), and 79.58(19)°, respectively.

The inner N_4 core is rigorously planar, with the Mn atom displaced by 0.182(1) Å from it toward the hydroxo group [0.156(1) Å with respect to the mean plane through the 24-atom porphyrin macrocycle]. The $Mn-N_{pyr}$ bond distances [average value 2.011(6) Å] are not significantly different.

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The Mn out-of-plane displacement and the Mn$-$N$_{pyr}$ bond distances typically identify the five-coordinate environment usually observed for Mn^{III} in a high-spin state (refs 20a and 20b and references therein).

PcCrN$_3$ Fragment. The Pc macrocycle assumes a significant ruffled (twisted) nonplanar conformation, mainly due to some vertical tilt of isoindole moieties associated with a small sideways tilt.

The ruffling of the isoindole rings is described by the average value of the transannular torsion angles (C$_\alpha$N$_{pyr}$-N$_{pyr}$C$_\alpha$)$_{op}$ [4.3(7)°] and the average out-of-plane displacement of the N$_{meso}$ atoms from the phthalocyanine mean plane [0.047(6) Å]. The minimum and maximum out-of-plane displacements are $-$0.117(6) and 0.718(10) Å for C64 and C72, respectively. The mean absolute perpendicular displacements from the phthalocyanine mean plane of the N$_{pyrrole}$, C$_\alpha$, and C$_\beta$ atoms and the ortho and meta C atoms of the benzo rings are 0.046(6), 0.059(7), 0.146(7), 0.253(8), and 0.365(9) Å, respectively.

The indole rings are not strictly planar, as indicated by the out-of-plane distances falling in the range $-$0.038(8)/0.025(7), $-$0.042(7)/0.044(8), $-$0.011(8)/0.012(8), and $-$0.016(7)/0.029(10) Å for N5/C45$\cdots$C52, N7/C53$\cdots$C60, N9/C61$\cdots$C68, and N11/C69$\cdots$C76, respectively. The dihedral angles that they form with the phthalocyanine mean plane are 0.54(10), 7.83(8), 2.10(10), and 9.04(11)°, respectively. The opposite N5/C45$\cdots$C52, N9/C61$\cdots$C68 and N7/C53$\cdots$C60, N11/C69$\cdots$C76 form dihedral angles of 1.76(14) and 16.85(14)°, respectively.

The N$_4$ core is planar within experimental error [maximum deviation from the planarity 0.008(6) Å], with the Cr atom being displaced by 0.054(1) Å toward the azide group from the least-squares plane through it [0.171(1) Å with respect to the mean plane through the phthalocyanine macrocycle]. The Cr$-$N$_{pyr}$ bond distances are not significantly different from one another [average value 1.982(6) Å]. The presence of Cr^{III} is strongly suggested by the NIR spectrum. As can be seen from the solution spectrum in CH$_2$Cl$_2$ (Figure 1A), the [Mn$-$Cr] complex shows low-intensity absorptions in the region 950$-$1250 nm. The number, shape, and relative intensity of these absorptions in CH$_2$Cl$_2$ are perfectly in keeping with the findings for a number of Cr^{III} phthalocyanine species[36] and are assigned as triplet$-$quartet (LMCT) transitions. The reflectance spectrum shows quite similar features, although the UV$-$vis and NIR absorptions appear to be of comparable intensity (Figure 1B).

Inter-ring Contacts and the Mn$-$O(H)$-$Cr Bridging System. The TPP and Pc macrocycles within the entire dinuclear unit adopt a nearly eclipsed orientation (Figure 3), with an average N$-$Mn$\cdots$Cr$-$N torsion angle of $-$5.16(2)°. The separation of the two macrocycles is indicated by the distance between the centroids of overlapping pyrrole rings, which ranges from 3.726(10) Å (for the pyrrole rings associated with N3 and N9) to 4.402(10) Å (for the opposite pyrrole rings containing N1 and N5). The mean planes through the two macrocycles form a dihedral angle of 5.79(4)°. The separation between the metal centers is 3.929(2) Å. For both macrocycles, the C$-$N and C$-$C bond distances and angles are as expected and consistent with a complete delocalization of the π-bonding system.

The most striking feature of the structure is the presence of an OH$^-$ group bridging the (TPP)Mn^{III} and PcCr^{III}N$_3$ units through its oxygen atom. Despite of the fact that the hydrogen atom of the OH$^-$ group could not be directly located from a difference Fourier map, the existence of a μ-hydroxo group is unequivocally supported by a number of crystal data related to the geometry of the Mn$-$O(H)$-$Cr moiety, as well as by the electroneutrality of the complex and other data. It is extremely interesting to compare the structural data of the [Mn$-$Cr] complex (Table 2) with those of the two related structurally elucidated porphyrin systems having a single μ-hydroxo ligand bridging two metalloporphyrin fragments, i.e., the two [Mn^{III}$-$Mn^{III}] monocations [(TPP)Mn$-$O(H)$-$Mn(TPP)]$^{+}$ [20a] and [(OEP)Mn$-$O(H)$-$Mn(OEP)]$^{+}$ [20b] (Table 3, bottom). It can be seen from the data reported that the five-coordinate environment for the (TPP)Mn$-$O(H) fragment in the [Mn$-$Cr] complex shows that the average M$-$N$_e$ bond distance [2.011(6) Å] is practically coincident with those of the TPP and OEP μ-hydroxo [Mn^{III}$-$Mn^{III}] cations [2.008(8) and 2.006(5) Å, respectively] and the out-of-plane displacement of Mn from the mean plane of the central N$_4$ core (0.182 Å) is quite well comparable to the corresponding values measured for the same cations (0.19$-$0.23 Å). More interestingly, the Mn$-$O bond distance in the [Mn$-$Cr] complex [1.993(5) Å] very closely approaches those of the cited cations [(TPP)Mn$-$O(H)$-$Mn(TPP)]$^{+}$ [20a] [average value 2.026(15) Å] and [(OEP)Mn$-$O(H)$-$Mn(OEP)]$^{+}$ [20b] [average value 2.011(13) Å]. Also, the angle Mn$-$O(H)$-$Cr [163.7(3) Å], far from linearity although larger than that of the latter charged species [152.73(11) Å],[20b] is very close to that of the TPP analogue [160.4(8) Å].[20a]

Consideration of the six-coordinate environment around Cr^{III} in the (H)OPcCrN$_3$ fragment of the present species is also highly informative, especially if comparison is made with similar environments in μ-hydroxo and μ-oxo analogues. As shown in Table 3, the Cr$-$O(H) bond distance [1.976(5) Å] in the [Mn$-$Cr] complex is very close to the Mn$-$O bond distances observed in the same species [1.993(5) Å] and those given for the just mentioned μ-hydroxo TPP and OEP cations.[20] As was already noticed, instead, the much shorter Cr$-$O bond distances (1.752/1.767 Å) and linearity of the trinuclear O-bridged moiety (178.8°) found in the [Cr^{III}$-$Cr^{III}] μ-oxo species {[(py)PcCr]$_2$O}·2py[17,34,35] and the Cr$-$O bond distance in the μ-oxo [Fe^{III}$-$Cr^{III}] complex [(TPP)Fe$-$O$-$Cr(TPP)(pip)][18] (1.775 Å, Table 3) again indicate that a bridging trinuclear μ-oxo moiety, i.e., Mn$-$O$-$Cr, in the [Mn$-$Cr] complex must be definitely discarded. In conclusion, then these data and the overall available structural information identify the present [Mn$-$Cr] unit as the μ-hydroxo species of formula [(TPP)Mn$-$O(H)$-$CrPc(N$_3$)]. The observed Cr$-$N13 bond distance [2.004(7) Å] and the angle Cr$-$N13$-$N14 [121.7(6)°] in the Cr$-$N$_3$ moiety are

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in the normal range expected for such types of M$-$N$_3$ terminal moieties (Mn$-$N$_3$[14,24,32] and Cr$-$N$_3$[37]).

Finally, despite the lack of magnetic data for a range of temperatures, the room-temperature magnetic moment of the [Mn$-$Cr] complex is of some interest. The measured value of $\mu_{\mathrm{eff}} = 6.31 \pm 0.12\ \mu_{\mathrm{B}}$ (diamagnetic corrections in the Experimental Section) is not too far from the spin-only value of 7.94 μ_{B} calculated for the seven unpaired electrons present in the d^4$-$d^3 dinuclear system. The observed value indicates that spin coupling between the two metal centers is scarcely effective. This finds adequate explanation in the long Mn$-$O and Cr$-$O bond lengths (1.98$-$1.99 Å) and the long enough Mn$-$Cr separation (3.93 Å). Such long distances cannot allow the occurrence of significant antiferromagnetic coupling either through a superexchange mechanism or by direct metal$-$metal orbital contact. These data are obviously in keeping with the established presence of a μ-hydroxo-bridged Mn$-$O(H)$-$Cr moiety in the [Mn$-$Cr] complex.

Conclusions. The reaction of [(TPP)MnN$_3$] with [PcCr] in ClNP leads unexpectedly to the formation of a μ-hydroxo species of formula [(TPP)Mn$-$O(H)$-$CrPc(N$_3$)] containing a high-spin five-coordinate Mn$^{\mathrm{III}}$ (d^4) and a six-coordinate Cr$^{\mathrm{III}}$ (d^3). The [Mn$-$Cr] complex is an unprecedented example of a mixed-ligand heterometallic ditetrapyrrolic species. Cr is included for the first time in such a type of dinuclear entity. Long Mn$-$O and Cr$-$O bond distances are very close to those found for rare porphyrin Mn$-$Mn analogues, whereas they appear to be definitely incompatible with the presence of a single N or O atom bridging the two metal centers in μ-nitrido- or μ-oxo-bridged species. The overall structural data, electroneutrality, and additional information (IR and UV$-$vis$-$NIR spectra and room-temperature magnetic moment) of the [Mn$-$Cr] complex are in keeping with the proposed μ-hydroxo-bridged formulation. Studies concerning the chemical and electrochemical behavior of the [Mn$-$Cr] complex are currently in progress.

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Supporting Information Available: IR spectrum of the [Mn$-$Cr] complex (Figure S1), FAB spectra of the [Mn$-$Cr] and the μ-nitrido species [(TPP)Mn$-$N$-$FePc] (Figure S2) with an associated discussion, two ORTEP drawings of the TPP and Pc fragments (Figures S3 and S4), and X-ray crystallographic data in CIF format for the [Mn$-$Cr] complex. This material is available free of charge via the Internet at http://pubs.acs.org.

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