symmetry about the Re or Mn atoms and a trans configuration about the Pt center. The similar appearance of the spectra suggests that the two compounds are isostructural.

Collection of suitable ^{13}C NMR data was hampered by quadrupolar coupling (^{55}Mn, ^{185}Re, and ^{187}Re all have $I = {}^5/_2$) and the rather low solubility of the bimetallic compounds at low temperature. For $Re_2Pt(CO)_{12}$, two broad signals with half-widths of about 55 Hz were observed at room temperature. At -60 °C, these resonances narrowed to about 15 Hz and were centered at δ 190.3 ($\sim$8 C) and 183.7 ($\sim$2 C). These two resonances are presumably due to the eight equivalent equatorial and two equivalent axial carbonyl carbon atoms on rhenium.[25] Despite a careful search, the ^{13}CO resonance on Pt could not be observed. For $Mn_2Pt(CO)_{12}$ only a single, broad unresolved signal was observed at room temperature with a half-width of nearly 300 Hz. At -40 °C the signal was still quite broad ($w_{1/2} \sim 80$ Hz). Again, the ^{13}CO resonance on Pt was not observed.

It has recently been shown that binuclear reductive-elimination reactions between transition-metal alkyl and hydride complexes can occur by a variety of mechanistic routes.[27] Consequently, the organic ligand(s) may be eliminated as alkane(s) or aldehyde(s) depending on the nature of the reactants, the pathway(s), and the reaction conditions.[27b] In the reaction of $Me_2Pt(COD)$ with $HM(CO)_5$, spot tests for acetaldehyde[28] are negative.[29] Analysis of the gas above the reaction mixture by GC reveals that methane is formed in nearly quantitative yield. During the course of the reaction, substantial (approximately equimolar) amounts of $M_2(CO)_{10}$ are formed. Since $HM(CO)_5$ is stable in the presence of $M_2Pt(CO)_{12}$, this observation suggests that $M(CO)_5$ radicals are being generated, perhaps via a chain process.[30]

Conclusion. The binuclear reductive-elimination reaction of $Me_2Pt(COD)$ with excess $HM(CO)_5$ (M = Re, Mn) leads to the formation of the heterobimetallic carbonyls $M_2Pt(CO)_{12}$ in high yield with concomitant formation of $M_2(CO)_{10}$. A crystal structure determination for $Re_2Pt(CO)_{12}$ shows that the molecular ideally possesses D_{2h} symmetry with octahedral coordination about each rhenium atom and square-planar (trans) geometry about the platinum atom. The manganese analogue is probably isostructural.

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Note Added in Proof. The structure of $Mn_2Pt(CO)_{12}$ has been determined (Braunstein, P.; et al. *Nouv. J. Chim.*, in press).

Supplementary Material Available: Tables of the final thermal parameters (Table A) and final observed and calculated structure factor amplitudes (Table B) and figures showing the molecular ion multiplets (Figure S-1) and solution IR spectra (Figure S-2) (8 pages). Ordering information is given on any current masthead page.

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(25) At -60 °C the reported ^{13}C NMR spectrum (THF-d_8) of $Re_2(CO)_{10}$ is δ 192.8 [s, Re-CO(cis)] and 183.7 [s, Re-CO(trans)].[26]

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(30) The ability of $HM(CO)_5$ to undergo radical chain substitution is well documented. See: (a) Byers, B. H.; Brown, T. L. *J. Am. Chem. Soc.* **1977**, *99*, 2527. (b) Byers, B. H.; Brown, T. L. *Ibid.* **1975**, *97*, 947. (c) Byers, B. H.; Brown, T. L. *J. Organomet. Chem.* **1977**, *127*, 181.

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Synthesis and Structure of a Cobalt(I) *meso*-Tetraphenylporphyrin Complex, $[Co^I(TPP)][K\subset 222]_4Cl_3\cdot H_2O$

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Reduction of chlorocobalt(III) *meso*-tetraphenylporphyrin in chlorobenzene by an excess of 222 cryptated potassium 2-methyl-2-propanethiolate yields a cobalt(I) *meso*-tetraphenylporphyrin derivative, $[Co^I(TPP)][K\subset 222]_4Cl_3\cdot H_2O$ (**1**) of composition $C_{116}H_{174}N_{12}O_{25}Cl_3K_4Co$. The crystals of **1** are monoclinic, space group $C2/c$ with a = 15.190 (6) Å, b = 21.313 (8) Å, c = 40.763 (10) Å, β = 101.58 (2)°, V = 12928 Å^3, and Z = 4. The $(Co-N_p)_{av}$ bond distance in $[Co^ITPP]^-$ is 1.942 (3) Å. The porphyrin skeleton is quasi-planar although a few atoms deviate somewhat largely from their least-squares mean plane. When they are compared with the known Ni(II) porphyrin structures, the $(N-C_\alpha)_{av}$ bond distance appears somewhat lengthened and the $(C_\alpha-C_\beta)_{av}$ and $(C_\beta-C_\beta)_{av}$ bond lengths are slightly shortened. These small changes are most probably due to enhanced back-donation of the electron-rich cobalt(I) center toward the porphyrin π system.

Studies of model compounds and synthetic analogues for the active site of cobalt-substituted cytochrome P-450$_{CAM}$ have made chemical and structural investigations of mercaptocobalt porphyrins of interest.[1] In the course of such studies,[2] we have found that reduction of chlorocobalt(III) *meso*-tetraphenylporphyrin below the oxidation state II occurs by reaction with 222 cryptated potassium 2-methyl-2-propanethiolate in chlorobenzene. Reduction of cobalt(II) *meso*-tetraphenylporphyrin to the cobalt(I) derivative was first reported in 1965,[3] and other Co(I) porphyrins were obtained since.[4,5] However, to our knowledge no thiols or thiolates have been used as reducing agents although dielectronic cysteine reduction of vitamin B_{12} has been proposed in the enzymatic conversion of homocysteine to methionine.[6] We present here the structure of a compound,

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$[\mathrm{Co(TPP)}][\mathrm{K}\subset 222]_4\mathrm{Cl}_3\cdot\mathrm{H_2O}$, containing the $[\mathrm{Co^I(TPP)}]^-$ anion obtained by thiolate reduction of a cobalt(III) porphyrin derivative. Although the spectroscopic and chemical properties of $[\mathrm{Co^I(TPP)}]^-$ have been widely studied,[3-7] so far, no X-ray structure of such an anion has been established.

Experimental Section

General Procedures. All experiments were done under an inert atmosphere either by Schlenk techniques or in a Vacuum Atmospheres drybox. Solvents were rigorously purified and dried under argon. The free tetraphenylporphyrin $(\mathrm{TPP})\mathrm{H_2}$[8] and its cobalt(III) chloro[9] complex were prepared by using published methods.

Potassium 2-methyl-2-propanethiolate was prepared by reacting 2×10^{-4} mol of KOH with 2×10^{-3} mol of the thiol RSH in 20 mL of ethanol. It was precipitated by addition of diethyl ether; the resultant white powder was washed with pentane and dried under vacuum. Chlorobenzene solutions were obtained by addition of equivalent amounts of 222 cryptand.[10]

UV–visible spectra were obtained on a Cary 210 spectrometer.

Synthesis of $[\mathrm{Co(TPP)}][\mathrm{K}\subset 222]_4\mathrm{Cl}_3\cdot\mathrm{H_2O}$ (1). $\mathrm{Co^{III}(TPP)Cl}$ (20 mg) was dissolved in 50 mL of chlorobenzene. A large excess (180 mg) of 222 cryptand potassium 2-methyl-2-propanethiolate in 50 mL of chlorobenzene was added. Microcrystalline powders of $[\mathrm{Co(TPP)}][\mathrm{K}\subset 222]_4\mathrm{Cl}_3\cdot\mathrm{H_2O}$ were obtained by slow addition of pentane. Orange-colored single crystals suitable for X-ray studies were obtained by slow diffusion of a pentane layer into a chlorobenzene solution of $[\mathrm{Co(TPP)}][\mathrm{K}\subset 222]_4\mathrm{Cl}_3\cdot\mathrm{H_2O}$ at 25 °C.

Collection and Reduction of Intensity Data. A systematic search in reciprocal space using a Philips PW 1100/16 automatic diffractometer showed that crystals of **1** belong to the monoclinic system.

The unit-cell dimensions and their standard deviations were obtained and refined at room temperature with Cu K$\bar{\alpha}$ radiation ($\lambda = 1.5418$ Å) by using 25 carefully selected reflections and the standard Philips software. Final results: $\mathrm{C_{116}H_{174}N_{12}O_{25}Cl_3K_4Co}$, mol wt 2458, $a = 15.190$ (6) Å, $b = 21.313$ (8) Å, $c = 40.763$ (10) Å, $\beta = 101.58$ (2)°, $V = 12928$ Å^3, $Z = 4$, $d_{\mathrm{calcd}} = 1.26$ g cm^{-3}, $\mu = 34.08$ cm^{-1}, $F_{000} = 5232$, space group $C2/c$ or Cc.

A parallelepipedic crystal of 0.50 × 0.20 × 0.07 mm was sealed in a Lindemann glass capillary and mounted on a rotation-free goniometer head. All quantitative data were obtained from a Philips PW 1100/16 four-circle automatic diffractometer, controlled by a P852 computer, using graphite-monochromated radiation and standard software in bisecting mode. The vertical and horizontal apertures in front of the scintillation counter were adjusted so as to minimize the background counts without loss of net peak intensity at the 2σ level. The total scan width in the θ–2θ flying step-scan used as $\Delta\omega = 0.80 + (\mathrm{Cu\ K}\alpha_1,\alpha_2$ splitting)° with a step width of 0.05° and a scan speed of 0.024° s^{-1}. A total of 8751 reflections were recorded (5° < θ < 57°; $h,k,\pm l$). The resulting data set was transferred to a PDP 11/60 computer, and for all subsequent computations, the Enraf-Nonius SDP/V18 package was used,[11] with the exception of a local data reduction program.

Three standard reflections measured every hour during the entire data collection period showed no significant trend.

The raw step-scan data were converted to intensities by using the Lehmann–Larson method[12] and then corrected for Lorentz, polarization, and absorption factors, the latter computed by the numerical integration method of Busing and Levy[13] (transmission factors between 0.44 and 0.79). No extinction corrections were applied. A unique data set of 4811 reflections having $I > 3\sigma(I)$ was used for determining and refining the structure. A Nz cumulative test and the statistics of normalized structure factors showed that the most probable space group was $C2/c$, which was assumed.

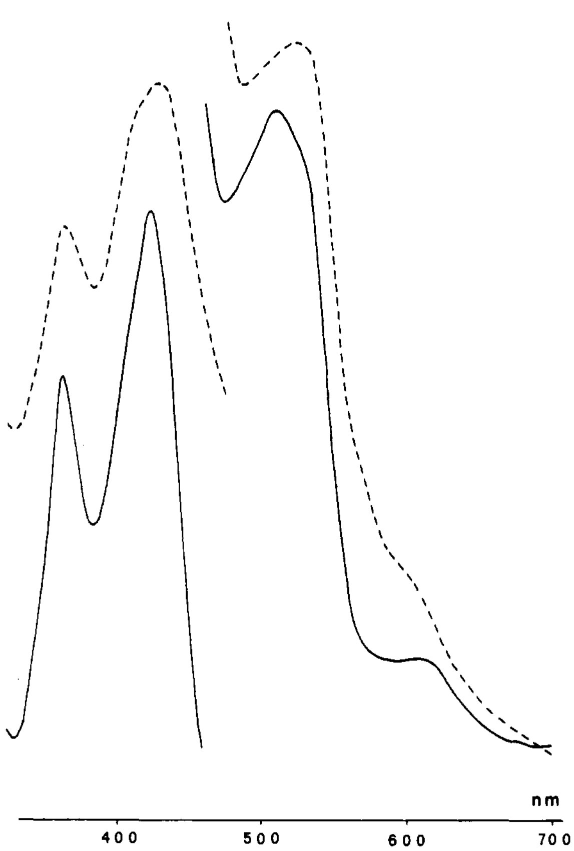

Figure 1. UV–visible spectra at 25 °C of $[\mathrm{Co(TPP)}][\mathrm{K}\subset 222]_4\mathrm{Cl}_3\cdot\mathrm{H_2O}$: solid (broken line); solution in $\mathrm{C_6H_5Cl}$ (solid line).

MULTAN failed to give a correct solution; therefore, the structure was solved using the heavy-atom method. After refinement of the heavy atoms, a difference-Fourier map revealed maximas of residual electronic density close to the positions expected for carbon-bonded hydrogen atoms; they were introduced in structure factor calculations by their computed coordinates (C–H = 0.95 Å) and isotropic temperature factors of 10 Å^2 but not refined. The hydrogen atoms of the water molecule could not be located. Full least-squares refinement converged to $R(F) = 0.068$ and $R_w(F) = 0.094$ ($\sigma(F^2) = (\sigma_{\mathrm{count}}^2 + (pI)^2)^{1/2}$). The unit weight observation was 1.90 for $p = 0.08$. A final difference map revealed no significant maxima.

Table I lists the atomic positional parameters for all non-hydrogen atoms with the estimated standard deviations.

Results and Discussion

Reduction of cobalt(II) *meso*-tetraphenylporphyrin below the cobalt(II) oxidation state by various reducing agents has been reported.[3-7] The spectroscopic properties of the diamagnetic complex obtained by these methods indicate that the electron furnished by the reducing agent is mainly trapped by the central cobalt atom.[7] The UV–visible spectrum of $|\mathrm{Co^I(TPP)}|^-$, which is of the d hyperporphyrin type, thus atypical for a cobalt porphyrin,[14] could be reproduced by taking into account enhanced back-donation from the Π system of the cobalt(I) center toward the Π system of the porphyrin.[7]

The complex, $[\mathrm{Co(TPP)}][\mathrm{K}\subset 222]_4\mathrm{Cl}_3\cdot\mathrm{H_2O}$ (**1**), obtained by 222 cryptated potassium 2-methyl-2-propanethiolate reduction of $\mathrm{Co^{III}Cl(TPP)}$ in chlorobenzene is also diamagnetic and presents UV–vis spectral properties very similar to those reported for $[\mathrm{Co^I(TPP)}]^-$ [3-5] (Figure 1).

The asymmetric unit of the crystals of **1** contains half of a porphyrin anion located on a crystallographic inversion

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Table I. Positional Parameters and Their Estimated Standard Deviations

atom	x	y	z	B,[a] Å^2	atom	x	y	z	B,[a] Å^2
Co	−0.250	0.250	0.500	2.86 (3)	C41	0.4122 (5)	0.6235 (4)	0.6450 (2)	7.2 (2)
N1	−0.1614 (3)	0.1846 (2)	0.5133 (1)	3.3 (1)	C42	0.4224 (5)	0.6208 (4)	0.6822 (2)	7.1 (2)
C2	−0.1732 (4)	0.1196 (3)	0.5108 (2)	3.6 (1)	C43	0.4114 (6)	0.5104 (4)	0.6915 (2)	8.2 (3)
C3	−0.0902 (5)	0.0878 (3)	0.5218 (2)	4.7 (2)	C44	0.3528 (6)	0.4549 (4)	0.6942 (2)	8.2 (3)
C4	−0.0260 (4)	0.1303 (3)	0.5315 (2)	4.7 (2)	O45	0.2810 (4)	0.4540 (2)	0.6656 (1)	7.3 (2)
C5	−0.0695 (4)	0.1912 (3)	0.5266 (2)	3.7 (1)	C46	0.2240 (7)	0.4023 (4)	0.6672 (3)	8.9 (3)
C6	−0.0242 (4)	0.2471 (3)	0.5339 (1)	3.5 (1)	C47	0.1535 (8)	0.3989 (4)	0.6378 (3)	9.9 (3)
C7	−0.0653 (4)	0.3042 (3)	0.5258 (2)	3.5 (1)	O48	0.0950 (4)	0.4523 (2)	0.6355 (1)	7.1 (1)
C8	−0.0193 (4)	0.3629 (3)	0.5314 (2)	4.5 (2)	C49	0.0279 (6)	0.4508 (4)	0.6064 (2)	8.4 (3)
C9	−0.0801 (4)	0.4081 (3)	0.5210 (2)	4.6 (2)	C50	−0.0372 (6)	0.5012 (4)	0.6073 (2)	7.7 (2)
C10	−0.1656 (4)	0.3783 (3)	0.5097 (2)	3.7 (1)	N51	0.0172 (5)	−0.1098 (3)	0.5962 (2)	7.4 (2)
N11	−0.1568 (3)	0.3133 (2)	0.5119 (1)	3.3 (1)	C52	0.0099 (8)	−0.0515 (5)	0.5784 (3)	11.5 (3)
C12	−0.2553 (4)	0.0899 (3)	0.5007 (2)	4.1 (1)	C53	0.051 (1)	−0.0007 (5)	0.5949 (3)	14.5 (4)
C13	−0.2561 (4)	0.0196 (3)	0.5013 (2)	4.5 (2)	O54	0.1148 (5)	0.0055 (3)	0.6180 (2)	14.4 (2)
C14	−0.2386 (5)	−0.0130 (3)	0.4739 (2)	6.3 (2)	C55	0.152 (1)	0.0585 (5)	0.6329 (4)	16.6 (5)
C15	−0.2354 (6)	−0.0794 (3)	0.4747 (2)	7.6 (2)	C56	0.1915 (9)	0.0646 (5)	0.6632 (4)	14.3 (5)
C16	−0.2511 (6)	−0.1102 (4)	0.5024 (2)	7.9 (3)	O57	0.2244 (6)	0.0137 (3)	0.6820 (2)	13.9 (2)
C17	−0.2706 (6)	−0.0775 (3)	0.5293 (2)	7.3 (2)	C58	0.2980 (8)	0.0186 (5)	0.7047 (3)	10.3 (3)
C18	−0.2732 (5)	−0.0130 (3)	0.5287 (2)	5.9 (2)	C59	0.3293 (9)	−0.0326 (5)	0.7255 (3)	12.1 (4)
C19	0.0716 (4)	0.2448 (3)	0.5513 (2)	3.9 (1)	N60	0.3324 (4)	−0.0939 (3)	0.7110 (2)	6.7 (2)
C20	0.0915 (5)	0.2382 (4)	0.5860 (2)	6.0 (2)	C61	0.4132 (6)	−0.1039 (6)	0.6992 (2)	9.7 (3)
C21	0.1791 (6)	0.2344 (4)	0.6036 (2)	7.1 (2)	C62	0.4126 (6)	−0.1536 (5)	0.6754 (3)	10.5 (3)
C22	0.2465 (5)	0.2389 (3)	0.5868 (2)	7.4 (2)	O63	0.3491 (4)	−0.1390 (3)	0.6448 (1)	7.3 (1)
C23	0.2292 (5)	0.2461 (4)	0.5525 (2)	7.0 (2)	C64	0.3450 (6)	−0.1852 (5)	0.6194 (3)	9.9 (3)
C24	0.1421 (5)	0.2486 (3)	0.5349 (2)	5.6 (2)	C65	0.2805 (7)	−0.1676 (5)	0.5895 (2)	10.0 (3)
N25	0.3688 (4)	0.5711 (3)	0.6944 (1)	6.0 (2)	O66	0.1920 (4)	−0.1683 (3)	0.5957 (1)	8.5 (2)
C26	0.3603 (5)	0.5851 (4)	0.7289 (2)	6.5 (2)	C67	0.1257 (9)	−0.1620 (5)	0.5661 (2)	11.0 (4)
C27	0.2938 (6)	0.6336 (4)	0.7318 (2)	6.9 (2)	C68	0.0365 (8)	−0.1613 (6)	0.5745 (2)	10.9 (3)
O28	0.2069 (3)	0.6105 (2)	0.7179 (1)	6.1 (1)	C69	−0.0625 (7)	−0.1239 (5)	0.6091 (3)	9.7 (3)
C29	0.1389 (6)	0.6542 (4)	0.7218 (2)	7.2 (2)	C70	−0.0516 (7)	−0.1714 (5)	0.6355 (3)	9.8 (3)
C30	0.0477 (6)	0.6303 (5)	0.7073 (2)	7.6 (2)	O71	0.0115 (4)	−0.1519 (3)	0.6639 (1)	6.9 (1)
O31	0.0400 (3)	0.6264 (3)	0.6718 (1)	6.4 (1)	C72	0.0214 (6)	−0.1970 (5)	0.6894 (3)	9.2 (3)
C32	−0.0483 (5)	0.6098 (4)	0.6556 (2)	7.7 (2)	C73	0.0811 (6)	−0.1755 (5)	0.7194 (2)	8.4 (3)
C33	−0.0579 (5)	0.6101 (4)	0.6184 (2)	7.1 (2)	O74	0.1677 (4)	−0.1668 (3)	0.7126 (1)	7.3 (1)
N34	−0.0015 (4)	0.5647 (3)	0.6055 (2)	5.9 (2)	C75	0.2299 (8)	−0.1532 (6)	0.7410 (2)	10.5 (3)
C35	0.0060 (6)	0.5790 (4)	0.5717 (2)	7.3 (2)	C76	0.3215 (6)	−0.1422 (5)	0.7348 (2)	8.7 (3)
C36	0.0680 (6)	0.6344 (4)	0.5693 (2)	7.5 (2)	K1	0.1850 (1)	0.56865 (7)	0.65098 (4)	4.72 (3)
O37	0.1563 (3)	0.6172 (2)	0.5848 (1)	6.0 (1)	K2	0.1775 (1)	−0.10410 (7)	0.65373 (4)	5.25 (4)
C38	0.2176 (6)	0.6659 (4)	0.5813 (2)	6.8 (2)	Cl1	0.1937 (1)	0.27412 (8)	0.30865 (4)	4.19 (4)
C39	0.3097 (6)	0.6446 (4)	0.5946 (2)	6.7 (2)	Cl2	0.500	0.2633 (1)	0.250	5.35 (6)
O40	0.3230 (3)	0.6386 (2)	0.6303 (1)	6.1 (1)	O77	0.4115 (5)	0.2595 (5)	0.3174 (2)	13.6 (3)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Table II. Selected Bond Lengths (Å), Angles (deg), and Averages with Their Estimated Standard Deviations for $[Co(TPP)]^-$

Co–N1	1.939 (3)	1.942 (3)	N1–Co–N11	89.9 (1)	
Co–N11	1.946 (3)		N1–Co–N11′	90.0 (1)	
N1–C2	1.397 (5)	1.397 (3)	C2–N1–C5	103.4 (3)	103.5 (3)
N1–C5	1.398 (6)		C7–N11–C10	103.7 (3)	
N11–C7	1.404 (6)		N1–C2–C3	110.8 (4)	110.7 (2)
N11–C10	1.392 (6)		N1–C5–C4	110.7 (4)	
C2–C3	1.422 (7)	1.434 (3)	N11–C7–C8	110.9 (4)	
C4–C5	1.454 (7)		N11–C10–C9	110.5 (4)	
C7–C8	1.427 (6)		C2–C3–C4	108.7 (4)	107.4 (2)
C9–C10	1.436 (7)		C3–C4–C5	106.2 (4)	
C3–C4	1.332 (7)	1.337 (7)	C7–C8–C9	107.1 (4)	
C8–C9	1.343 (7)		C8–C9–C10	107.7 (4)	
C2–C12	1.386 (6)	1.380 (3)	C5–C6–C7	121.9 (4)	122.4 (4)
C5–C6	1.378 (6)		C2–C12–C10′	123.0 (4)	
C6–C7	1.378 (6)		Co–N1–C2	128.3 (3)	128.1 (2)
C6–C19	1.486 (7)	1.484 (7)	Co–N1–C5	128.1 (3)	
C12–C13	1.498 (7)		Co–N11–C7	128.0 (3)	
mean C$\underset{\cdot\cdot}{-}$C (phenyl)	1.379 (3)		Co–N11–C10	128.1 (3)	
			mean C–C–C (phenyl)	119.9 (2)	

center, half of a Cl^- anion located on a crystallographic twofold axis along with one Cl^-, two $[K\subset 222]^+$ cations, and one water molecule located in general positions of space group $C2/c$. Table II gives selected bond distances and angles found within $[Co(TPP)]^-$ present in **1**. Figure 2 shows the structure of the centrosymmetric $[Co(TPP)]^-$ anion. The cobalt and the four porphyrinato nitrogens form a square necessarily planar entity with a $(Co–N_p)_{av}$ bond distance of 1.942 (3) Å and a $(Np–Co–Np)_{av}$ bond angle of 89.9 (1)°. The porphyrin is not strictly planar although the cobalt is centered in the 24-atom core mean plane of the porphyrin ring. The deviations found from the 24-atom core mean plane (Figure 3) show that the porphyrin skeleton is slightly puckered. The mean displacement of the atoms belonging to the macrocycle with respect to their mean plane is 0.037 (6) Å, and the largest deviation from this mean plane is 0.092 (6) Å (meso carbon C6).

However, despite the slight puckering of the ring the individual pyrrole rings are as usual planar and the dihedral

Table III. Average Bond Lengths (Å) of Various Metalloporphyrins[a]

	$[Co^I(TPP)]^-$ [b]	$[Co^{II}(Pip)_2(TPP)]$ [c]	[Ni(OEP)] [d]	[Ni(DEUT)] [e]	$[Fe^I(TPP)]^-$ [f]	$[Fe^{II}(L)_2(TPP)]$ [g]
M-N	1.942 (3)	1.987 (2)	1.958 (2)	1.960 (14)	1.980 (6)	2.002 (5)
$N-C_\alpha$	1.397 (3)	1.380 (2)	1.376 (6)	1.382 (19)	1.401 (6)	1.385 (3)
$C_\alpha-C_\beta$	1.434 (3)	1.444 (3)	1.443 (3)	1.447 (15)	1.429 (12)	1.438 (4)
$C_\beta-C_\beta$	1.337 (7)	1.344 (3)	1.346 (2)	1.350 (19)	1.338 (1)	1.340 (5)
$C_\alpha-C_m$	1.380 (3)	1.393 (2)	1.371 (4)	1.374 (25)	1.385 (5)	1.397 (5)

[a] Figures in parentheses are the rms standard deviations of the average when there is more than one contribution to the average; otherwise, the esd is given. [b] Present work. [c] Reference 20. [d] Reference 15. [e] Reference 18. [f] References 21 and 22. [g] Average values for $Fe(Pip)_2(TPP)$[23] and $Fe(THT)_2(TPP)\cdot THT$.[24]

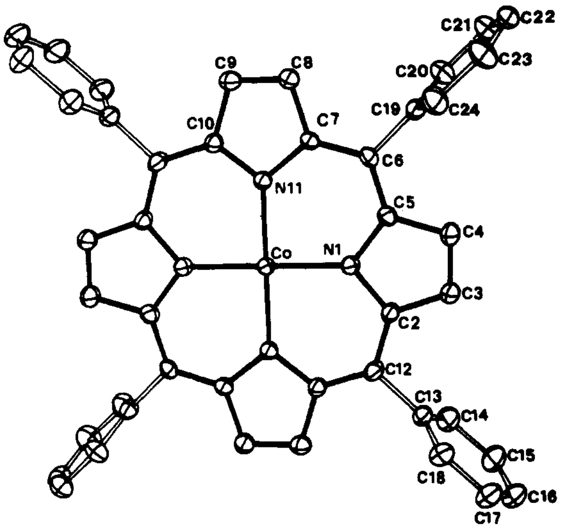

Figure 2. ORTEP plot of the porphyrin unit with the labeling scheme used. Ellipsoids are scaled to enclose 40% of the electronic density. Hydrogen atoms are omitted. Principal mean bond lengths (Å): $N-C_\alpha = 1.397$ (3), $C_\alpha-C_\beta = 1.434$ (3), $C_\alpha-C_m = 1.380$ (3), $C_m-C_p = 1.492$ (6), $Co-C_m = 3.422$ (4), $Co-C_\alpha = 3.014$ (4). Principal mean bond angles (deg): $Co-N-C_\alpha = 128.1$ (2), $C_\alpha-N-C_\alpha = 103.5$ (3), $N-C_\alpha-C_\beta = 110.7$ (2), $N-C_\alpha-C_m = 125.4$ (4), $C_\beta-C_\alpha-C_m = 123.8$ (4), $C_\alpha-C_\beta-C_\beta = 107.4$ (2), $C_\alpha-C_m-C_\alpha = 122.4$ (4).

angle between the adjacent pyrroles is only 4.2°. As most of the so-called planar porphyrins have angles between adjacent pyrroles lying between 3 and 5°,[15] one can admit that $[Co(TPP)]^-$ also belongs to this category. The minimal radius of the cavity in an undistorted metalloporphyrin has been estimated by Hoard to be 1.96 Å.[16] In order to accommodate an ion that is undersized with respect to the size of the cavity, the porphinato core has to contract and must distort from planarity presumably by a ruffling of the ring. Hoard's work is in total agreement with the structures known for all the metalloporphyrins[17] in which the metal is undersized with respect to the cavity size, especially with the structures of several nickel(II) porphyrins.[15,18,19]

However, no ruffling of the 24-atom core appears in $[Co(TPP)]^-$ although the $(Co-N_p)_{av}$ bond distance of 1.942 (3) Å is significantly shorter than 1.96 Å (by 6 esd). Instead of the ruffling, a larger puckering of the ring appears when compared to the quasi-planar triclinic form of Ni(OEP) in which the $(Ni-N_p)_{av}$ bond distance of 1.958 (2) Å is not significantly different from Hoard's value of 1.96 Å.[16] As seen above, the largest deviation from the plane defined by the macrocyclic of $[Co(TPP)]^-$ is 0.092 Å whereas only a 0.02-Å deviation is observed in triclinic Ni(OEP).[15]

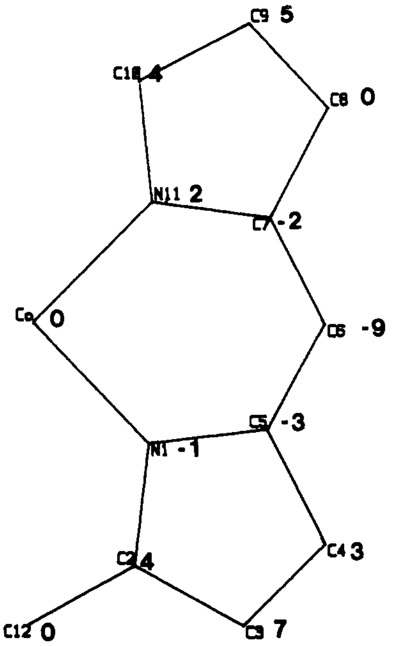

Figure 3. Stick model of the independent half of the porphyrin core. The dark numbers are the deviations in 0.01-Å unit of the atoms from the porphyrin core mean plane.

Table IV. Selected Bond Lengths (Å), Angles (deg), and Average Values with Their Estimated Standard Deviations for the $[K\subset 222]^+$ Cations

K1-O28	2.824 (4)	K2-O63	2.804 (5)
O31	2.799 (4)	O66	2.783 (5)
O45	2.846 (4)	O57	2.794 (5)
O48	2.841 (4)	O54	2.815 (6)
O37	2.839 (4)	O71	2.826 (5)
O40	2.834 (4)	O74	2.777 (4)
N25	2.990 (5)	N51	3.026 (5)
N34	3.060 (5)	N60	2.972 (5)

K-O: 2.777→2.846 d:[a] 2.81→2.74
K-N: 2.972→2.846 α:[a] 11.7

[a] See ref 25 for the definitions of d and α.

With C_α and C_β denoting the respective α- and β-carbon atoms of a pyrrole ring, C_m a methine carbon, and C_p a phenyl carbon that is bonded to the core, the average bond lengths and angles in the porphyrin skeleton are reported in the caption of Figure 2.

Some bond lengths found in the cobalt compound are slightly different from those present in the quasi-planar six-coordinate cobalt(II) porphyrins[20] and the quasi-planar nickel(II) porphyrins[15,18] that are isoelectronic with $[Co^I(TPP)]^-$ (Table III). Especially, the $(N-C_\alpha)_{av}$ bond distance appears to be somewhat longer, and the $(C_\beta-C_\beta)_{av}$ and $(C_\alpha-C_\beta)_{av}$ bond lengths are slightly shortened. These bond distances are very close to those present in $[Fe^I(TPP)]^-$[21,22]

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in which small differences appear when compared with low-spin six-coordinate iron(II) porphyrins such as $Fe(Pip)_2(TPP)$[23] and $Fe(THT)_2(TPP)\cdot THT$[24] (Table IV). These small changes that appear in the core of $[Fe(TPP)]^-$ have been interpreted as being due to a small contribution of a spin-coupled iron(II) porphyrin radical anion, $[Fe^{II}(TPP)]^-$.[22] A minor contribution of a spin-coupled cobalt(II) porphyrin radical anion could also be present in $[Co(TPP)]^-$ by occupation of the lowest unoccupied molecular orbital (LUMO) of e_g symmetry. The porphyrin LUMO is antibonding with respect to $N-C_\alpha$ and bonding relative to $C_\alpha-C_\beta$ and $C_\beta-C_\beta$. However, in such a spin-coupled cobalt(II) radical porphyrin anion the orbital containing the unpaired electron present in the low-spin cobalt(II) center should have the same symmetry as the porphyrin LUMO. Or, this is in conflict with the well-known $(d_{z^2})^1$ configuration of low-spin cobalt(II) in cobalt(II) porphyrins. Consequently, it is more reasonable to assume that the small changes that appear in the $(N-C_\alpha)_{av}$, $(C_\alpha-C_\beta)_{av}$, and $(C_\beta-C_\beta)_{av}$ bond lengths are due to enhanced back-donation of the electron-rich Co(I) center toward the porphyrin Π system when compared with the back-donation of the nickel center in Nickel(II) porphyrins. In this case, the occupied $(d_{xz})^2$ and $(d_{yz})^2$ cobalt orbitals have the symmetry of the porphyrin LUMO. Furthermore, this enhanced back-donation with the comcomitant changes in some bond lengths of the porphyrin skeleton is most probably also indirectly responsible for the nonobservation of HOARD's rule in $[Co(TPP)]^-$.[16] In summary, the structure of $[Co(TPP)]^-$ is consistent with a cobalt(I) porphyrin formulation, $[Co^I(TPP)]^-$, with a strong back-donation from the metal into the porphyrin Π system.

Table IV gives the average bond distances and angles found within the complex cations, $[K\subset 222]^+$. As usual, the potassium ion is completely enclosed by the macrobicyclic ligand. The average K–O and K–N distances are similar to those found elsewhere.[25] The Cl^- anions and the water molecule present in the asymmetric unit are arranged in centrosymmetric, Cl--HOH--Cl′--HOH--Cl units in which three chloride ions are linked together via two hydrogen-bonded water molecules. The two Cl--O and Cl′--O distances are 3.29 and 3.27 Å, respectively, and the $Cl--OH_2--Cl'$ angle is 118°. All the Co--Cl and $Co--OH_2$ separations are larger than 8.75 and 10.14 Å, respectively.

Registry No. 1, 91209-58-4; $Co^{III}(TPP)Cl$, 60166-10-1; $[K\subset 222]$ 2-methyl-2-propanethiolate, 91209-59-5.

Supplementary Material Available: Listings of least-squares planes, H atom positional parameters, general temperature factors of all anisotropic atoms, and observed and calculated structure factors (30 pages). Ordering information is given on any current masthead page.

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Synthesis and Characterization of Technetium(V) 8-Quinolinolates. X-ray Crystal Structure of *cis*-Chlorobis(2-methyl-8-quinolinolato)oxotechnetium(V)

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Technetium(V) complexes of 8-quinolinolates of the form $TcOL_2X$ (L = 8-quinolinolate and its 5,7-dichloro, 5,7-dibromo, 5-nitro, and 2-methyl derivatives; X = Cl, Br) have been synthesized and characterized. These neutral species precipitate from methanol after reaction of the quinolinolate ligand with $TcOX_4^-$. HPLC analyses of the complexes show that the halide ligand of *cis*-$TcO(8\text{-quinolinolate})_2X$ is susceptible to solvolysis in methanol, forming what is believed to be $TcOL_2(OCH_3)$; when X is Cl, the specific first-order rate constant governing this process is $1 \times 10^{-4}\ s^{-1}$ (25 °C, no ionic strength, in methanol). A single-crystal X-ray structure determination shows that the chlorobis(2-methyl-8-quinolinolato)oxotechnetium(V) complex, $TcO(CH_3C_9H_5NO)_2Cl$, formula weight 467, has a distorted-octahedral coordination geometry, with the chloro and oxo ligands in a cis configuration. A oxo-induced structural trans effect characteristic of M═O moieties is manifested in a lengthening of the Tc–O bond trans to the yl oxygen and a displacement of the Tc atom out of the mean equatorial plane. This complex crystallizes in the triclinic centrosymmetric space group $P\bar{1}$ with $a = 7.693$ (2) Å, $b = 9.337$ (2) Å, $c = 12.739$ (3) Å, $\alpha = 86.52$ (2)°, $\beta = 85.99$ (2)°, $\gamma = 84.12$ (2)°, and $V = 907$ (2) Å^3, with $Z = 2$, for 2882 observed reflections with $I_o \geq 2\sigma(I)$. Structural aspects of metal complexes containing 8-quinolinolate ligands are discussed.

Introduction

Complexes formed from the short-lived isotope ^{99m}Tc ($t_{1/2} = 6$ h) are widely used in nuclear medicine as imaging agents because of the ideal nuclear properties of ^{99m}Tc.[3] Adducts of 8-quinolinol and technetium-99m have been reported to have high brain uptake in laboratory animals,[4] but the chemical identities of the moieties leading to this uptake are not known. In order to obtain information about the possible composition and nature of these ^{99m}Tc moieties, we have undertaken a study of 8-quinolinol technetium complexes using macroscopic amounts of the relatively stable isotope ^{99}Tc ($t_{1/2} = 2.1 \times 10^5$ years). It is hoped that this study will eventually lead to the development and in vivo evaluation of well-characterized 8-quinolinol ^{99m}Tc imaging agents.

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