N-Methyltetraphenylporphyrin Complexes. Crystal and Molecular Structure of Chloro-*N*-methyl-$\alpha,\beta,\gamma,\delta$-tetraphenylporphinatocobalt(II)

Sir:

In transition metal porphyrin chemistry, the transition metal complexes of the N-alkylated porphyrins may play a unique role as models for the "sitting-atop" complexes widely discussed as intermediates[1] in the metalation reactions of normal porphyrin systems. As part of our continuing systematic studies[2-4] of these novel five-coordinate systems, we have recently obtained x-ray crystallographic structural results for the high spin cobalt(II) compound, chloro-*N*-methyl-$\alpha,\beta,\gamma,\delta$-tetraphenylporphinatocobalt(II) (hereafter ClCo(N-CH$_3$TPP)). The results obtained and described here corroborate the expected five-coordinate nature of these complexes, and serve as an interesting contrast to the more usual low spin cobalt(II) porphyrin systems, in which the metal atom is only moderately out-of-plane.[5]

The title compound, ClCo(N-CH$_3$TPP), was prepared by combining a solution of 0.200 g of N-CH$_3$TPP[2] in 5 ml of dichloromethane, with a fivefold excess of CoCl$_2$·6H$_2$O in 20 ml of acetonitrile containing 100 μl of 2,6-di-*tert*-butylpyridine. The precipitate obtained on concentration of this reaction mixture was recrystallized from a 1:1 mixture of dichloromethane and acetonitrile, yielding dark purple crystals. Elemental analysis of the product[6] was satisfactory (calcd for ClCoC$_{45}$H$_{31}$N$_4$: C, 74.83; H, 4.33; N, 7.76; Cl, 4.91. Found: C, 74.68; H, 4.32; N, 7.96; Cl, 4.88). The magnetic moment, μ_{eff}, was found to be 4.9 ± 0.1 μ_{B} over the range 150-295 K (Faraday method), clearly indicating that the complex involves high spin cobalt(II), in strong contrast to nonalkylated Co(II) porphyrin systems, which are invariably low spin.[5]

X-Ray diffraction data from a large single crystal were collected on an Enraf-Nonius CAD-3 diffractometer employing Mo Kα radiation. The structure was solved by normal heavy atom methods, and refined using a model involving anisotropic thermal parameters for the cobalt(II) ion and atoms bound directly to the metal. Details of the preliminary crystal data and current refinement are as follows for ClCo(N$_4$C$_{45}$H$_{31}$): triclinic; with a = 7.484 (2), b = 14.972 (4), c = 17.398 (5) Å; α = 102.93 (1)°, β = 97.03 (1)°, γ = 94.13 (1)°; ρ_{calcd} = 1.28, ρ_{obsd} = 1.27 g cm^{-3}; Z = 2; space group $P\bar{1}$. For 2487 unique reflections ($F_o^2 > 3\sigma(F_o^2)$, $3° < \theta < 20°$), R = 0.068.

The five-coordinate geometry of the complex, as shown in Figure 1, is essentially as expected. The coordination geometry about the cobalt(II) ion, as seen in Figure 2, is derived from a square-based pyramid. The nitrogen atom bearing the methyl group is, however, much farther from the cobalt ion (Co-N1 2.380 (6) Å) than are the other three (Co-N2 2.063 (7), Co-N3 2.061 (6), Co-N4 2.015 (6) Å). These distances to N2, N3, and N4 are only slightly longer than normal Co-N(pyrrole) bond lengths in the low-spin cobalt(II) porphyrin derivatives known.[5] While the Co-N$_1$ bond is probably rather weak, it would seem to be significantly stronger here than the corresponding bond in the related *N*-ethylacetatooctaethylporphyrincobalt(II) complex, where the long bond was observed to be 2.455 (5) Å.[7] The chloride ion occupies the apical position of this distorted square pyramid, with the Co-Cl bond length (2.242 (3) Å) significantly shorter than that found (Co-Cl 2.271 (2) Å) in the related complex.[7] As in the octaethylporphyrin derivative, the cobalt(II) ion is shifted slightly toward the pyrrole nitrogen (N4) trans to the alkylated nitrogen (N1), while the chloride ion is tipped toward the N-alkylated pyrrole ring. The magnitude of this deviation is much less in the ClCo(N-CH$_3$TPP) structure, however, as the N1-Co-Cl angle is 97.0 (2)°, as compared to the 91.2 (1)° angle observed in the octaethylporphyrin derivative. Any access to the sixth coordination site of the cobalt(II) ion is strongly blocked by the methyl group attached to N1 (Co-C5 2.945 (9) Å, see Figure 2). Projection of hydrogen atoms of the methyl group into the sixth coordination site clearly restricts access to the cobalt(II) ion, as expected, and will preserve the five-coordinate geometry in complexes of other metal ions with this ligand.

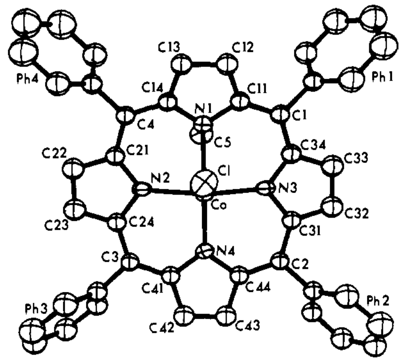

Figure 1. ClCo(N-CH$_3$TPP) viewed from above the main complex plane, to show the outline of the ligand. The chloride ion is above (and partially obscuring) the cobalt(II) ion, and the methyl group (C5) is partially obscured by the nitrogen (N1) to which it is attached.

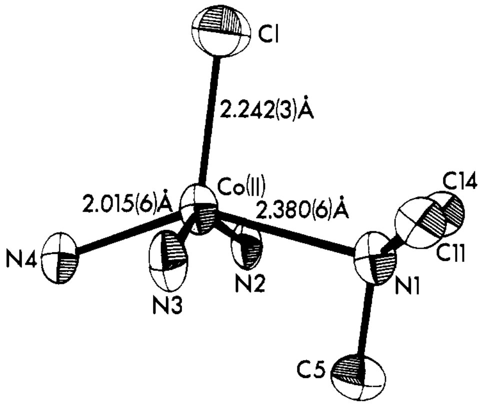

Figure 2. A side view of the coordination geometry immediately about the cobalt(II) ion, indicating the square pyramidal nature of the coordination and the close proximity of the methyl group (C5) to the metal ion below the main complex plane.

The cobalt(II) ion is raised significantly above the mean plane of the *N*-methylporphyrin ligand. The cobalt ion is 0.558 Å above the plane of N2, N3, and N4 (cf. 0.613 Å in the octaethylporphyrin derivative). The displacement of cobalt(II) from the mean planes of the individual pyrrole rings, however, is not as large (0.282, 0.219, and 0.316 Å above the N2, N3, and N4 rings, respectively), indicating the strong degree of overall distortion of the macrocyclic ligand induced by introduction of the methyl group at N1. The deviation from the mean plane of the ligand is extreme for the N-alkylated pyrrole ring, which is tilted at an angle of 32° to the plane of nitrogen atoms N2, N3, and N4 (cf. corresponding angles of 8°, 10°, and 7° for the pyrrole rings of N2, N3, and N4). The extent of this deviation from planarity, necessary to bring the lone pair of the now essentially sp^3 hybridized N1 atom into bonding orientation with the cobalt(II) ion, is illustrated by the positions of atoms C11 and C14 of the N-methylated pyrrole ring in Figure 2.

Thus, the N-methylation of tetraphenylporphine affords a ligand at which five-coordinate geometry is highly likely, with a strong out-of-plane position and concomitant spin state alterations for the metal ions. Synthetic, mechanistic, and structural work on several other derivatives of N-methylated porphyrins are underway in these laboratories.

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References and Notes

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Laser Photodissociation Spectrum of Gas-Phase 1,3,5-Hexatriene Radical Cation

Sir:

Photodissociation spectroscopy of gas-phase ions[1] is a convenient and widely applicable approach to obtaining optical spectroscopic information about such ions. Spectra of a number of ions have been published[1-6] with an optical resolution of the order of 10–20 nm, and the spectra have been found to be highly informative in regard to both the structures of the ions and the properties of their excited electronic states. It has been recognized that spectra of higher resolution showing resolved vibrational or rotational structure would greatly increase the amount and usefulness of the information obtained about an ionic species, and following this path, at least two groups of researchers have used tunable laser techniques to obtain high-resolution spectra.[3,6] The results of these efforts have been disappointing in that, although spectra of good quality were obtained, there was no apparent resolved vibrational structure in the ions studied. The present communication describes the laser photodissociation of the first cation to display prominent resolved vibrational structure, the *trans*-1,3,5-hexatriene cation; the partial analysis of this spectrum so far achieved confirms the expectation that this approach yields high quality information about the vibrational frequencies and vibronic transitions of the ion.

The spectrum at 1 nm (or ~0.003 eV) resolution is shown in Figure 1, and was obtained using conventional steady-state ICR photodissociation methods (11 eV ionizing energy, $\sim 5 \times 10^{-8}$ Torr pressure), with a Coherent Radiation Model 490 CW tunable dye laser pumped by a Model CR-12 argon-ion laser as light source. Dyes used were sodium fluorescein (530–570 nm), rhodamine 6-G (570–645 nm), and rhodamine B (635–670 nm). Because of temporal and spatial variations of laser output for tuning over a wide range, the spectrum was pieced together from segments of varying width, as indicated by the different symbols in Figure 1; except for the interface at 570 nm, where the dyes overlap at only one wavelength, all segment-matching was based on overlap at several wavelengths. Each data series was taken at constant light intensity, removing the uncertainty associated with correcting steady-state ICR photodissociation data for varying light intensity.[7] Ir analysis[8] showed the sample to be a roughly 4:1 mixture of trans and cis isomers. Wavelength was calibrated against a Schoeffel monochromator, and is believed accurate within 1 nm. The laser bandwidth is given as less than 0.1 nm by the manufacturer.

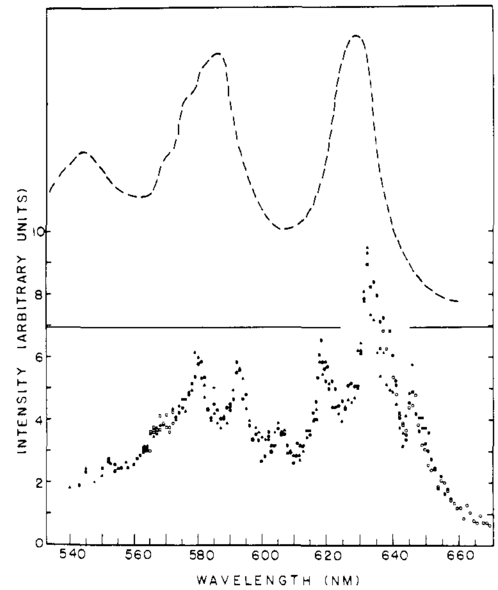

Figure 1. Laser photodissociation spectrum (lower curve) and photoelectron spectrum[9] (upper curve) of 1,3,5-hexatriene radical cation. The photoelectron spectrum is adjusted to put the energy zero at the ion ground state, and plotted in wavelength units. (The photoelectronbaseline is the line at ~7 intensity units.)

Plotted for comparison in Figure 1 is the photoelectron spectrum of *trans*-1,3,5-hexatriene for this energy region,[9] with the zero of energy shifted to the position of the ion ground state. The electronic transition in question here is a $\pi \rightarrow \pi^*$ transition of the cation which promotes an electron from the second-highest occupied π orbital into the highest occupied orbital;[10] therefore the excited state involved is a single-electron excitation from the neutral molecule, and as such is expected to be observed in both photoelectron and photodissociation spectra.[2] As has been discussed,[11] the connection between the photoelectron and photodissociation spectra for such a state is direct, and the two curves in Figure 1 should agree except to the extent that the Franck–Condon factors for photoelectron (initial neutral molecule) and photodissociation (initial ion ground state) differ.

The photodissociation spectrum clearly shows the same vibrational progression at about 1200 cm^{-1} as the photoelectron spectrum; in addition, the higher resolution clearly reveals another clear progression at 350 ± 10 cm^{-1}. The series of three peaks at 632.5, 617, and 605 nm is most probably a typical short vibrational progression corresponding to a 350 cm^{-1} normal mode, and the 0–0 transition is assigned at 632.5 nm; a hot band corresponding to the $1 \rightarrow 0$ transition of the low-energy 350 cm^{-1} vibration is expected to have significant intensity at 646.0 nm, and definitely must account for some or all of the peak at this position. The position of the 0–0 transition for the cis isomer is not certain (assuming it to retain its structural identity) and could be taken to account for some of the intensity at 646.0 nm; however, photoelectron data[8] suggest that it should be of the order of 5 nm to the red of trans, and indeed the photodissociation spectrum does give some indication of a shoulder on the low-energy side of the 632.5-nm peak.

Definitive analysis of this spectrum will definitely require separate spectra of the cis and trans isomers, which are now being obtained. It may be noted for now, however, that a satisfactory fit to the observed 646–605-nm region is possible on the assumption of equal Franck–Condon factors for all the $n \rightarrow n \pm 1$ transitions of the 350-cm^{-1} vibration, if the effective temperature of the 350-cm^{-1} normal mode is near 1000 K. In the process of obtaining this fit it was found that the assumed shoulder due to the cis isomer has the effect of shifting the