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# Synthesis and Structural Characterization of (Neopentyl)(octaethylporphyrinato)ruthenium Complexes, Including $[Ru(OEP)Np]_2(\mu\text{-}Li)_2$

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*Summary: Reaction of neopentyllithium (LiNp) with the octaethylporphyrin complex $Ru(OEP)Cl_2$ yields Ru(OEP)Np (1), which can be treated with further LiNp to give $[Ru(OEP)Np]_2(\mu\text{-}Li)_2$ (2). The structures of 1 (the first for an iron-group metalloporphyrin alkyl) and the more remarkable 2, revealing two Li atoms sandwiched between metalloporphyrin moieties, are determined.*

Research into the syntheses and properties of organoruthenium porphyrins (excluding carbonyl complexes) progresses steadily and is important in providing models to understand better certain aspects of the chemistry of cytochrome P-450 and vitamin $B_{12}$,[1] as well as in the development of unique organometallic chemistry.[1,2] Extensive organoruthenium porphyrin chemistry with derivatives in oxidation states II–IV has been developed using two general synthetic techniques: reactions of electrophiles with Ru(0) precursors[3] and treatment of $Ru(por)(halogen)_2$ or dimeric $[Ru(por)]_2^{2+}$ precursors[4] with Grignard or organolithium reagents.[5-7] For example, $Ru(por)R_n$ complexes ($n = 1, 2$; por = OEP, TPP; R = Ph, Me) have been prepared by typically using a 5-fold excess of LiR; the method yields a mixture of $Ru(por)R_2$ and Ru(por)R separable by column chromatography,[2c,5,6] while the latter can also be formed by the thermal decomposition of the former.[2e]

We describe here the two neopentyl complexes Ru(OEP)Np and $[Ru(OEP)Np]_2(\mu\text{-}Li)_2$, including their X-ray structures, which are the first reported for a metalloporphyrin alkyl of the iron group. The structure of the lithium-bridged dimer is of a unique and remarkable type.

A 3:1 mole ratio mixture of LiNp and $Ru(OEP)Cl_2$ reacts in benzene at RT to give a solution which, when added to an alumina (activity I) column, yields a red band containing Ru(OEP)Np (1); elution with benzene under Ar, followed by recrystallization from hexane, generates X-ray-quality crystals in 30% yield.[8] 1 is a paramagnetic ($S = {}^1/_2$), low-spin Ru(III) compound whose spectral and magnetic characteristics[9] correlate well with those of other monomeric $Ru^{III}(OEP)$ species.[2e,5,7,10]

The structure of 1 (Figure 1) is approximately square pyramidal with the Ru atom displaced 0.11 Å out of the mean porphyrin plane toward the Np ligand, comparable to the 0.12-Å displacement reported for Ru(OEP)Ph.[2e] The axial Np ligand is disordered, exhibiting two orientations with Ru–C bond lengths (2.069, 2.12 Å) considerably longer than the 2.005 Å found in Ru(OEP)Ph. This is consistent with the typically weaker $M\text{–}C_{sp^3}$ bond (vs $M\text{–}C_{sp^2}$),[2e,11] but steric effects in 1 also appear to contribute to elongation of the Ru–C bond. Thus, for either conformation the minimum N–Ru–C(Np) angle is appreciably <90° (81.1 and 78.1°), this bending relieving steric interaction between the porphyrin ring and the $\gamma$-H atoms of the Np. Indeed, this interaction produces substantial strain in the Np itself with the Ru–C(37 and 37A)–C(38) bond angles being 128.2 and 126.2°, much larger than the "expected" 109°. The Ru–C bonds are longer than those in hexakis(neopentyl)diruthenium(III) (2.023–2.051 Å), where there is no steric interaction.[12] The other bonds and angles in the metalloporphyrin moiety of 1, and the disorder in an ethyl group, are not unusual when compared to data reported for other Ru(OEP) structures.[2a,e,10,13]

Reduction of 1 with 1 equiv of LiNp in benzene forms quantitatively $[Ru(OEP)Np]_2(\mu\text{-}Li)_2$ (2) and 0.5 equiv of 2,2,5,5-tetramethylhexane (from the coupling of two Np•

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(4) Abbreviations used: por = porphyrin dianion; OEP = dianion of 2,3,7,8,12,13,17,18-octaethylporphyrin; TPP = dianion of 5,10,15,20-tetraphenylporphyrin; Np = neopentyl; RT = room temperature.

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(8) Crystal data for 1: $C_{41}H_{55}N_4Ru$, fw 704.98, dimensions 0.25 × 0.30 × 0.40 mm, triclinic, space group $P\bar{1}$ (No. 2), $a = 13.044(2)$ Å, $b = 14.270(2)$ Å, $c = 12.500(2)$ Å, $\alpha = 115.83(1)°$, $\beta = 110.76(1)°$, $\gamma = 95.92(1)°$, $V = 1864.2$ Å$^3$, $\mu = 4.43$ cm$^{-1}$, $D_c = 1.256$ g cm$^{-3}$, $Z = 2$; 11 331 reflections collected with $2\theta < 60°$ on a Rigaku AFC6S diffractometer at 21 °C using graphite-monochromatized Mo K$\alpha$ radiation. Symmetry-equivalent data were averaged ($R_{int} = 0.04$) to give a data set of 10 848 reflections, corrected for absorption, Lorentz, and polarization effects. The structure was solved by the Patterson method, least squares, using TEXSAN and teXsan structure analysis packages (Molecular Structure Corp., 1985 and 1992). Residuals $R = 0.036$ ($R_w = 0.032$) and goodness of fit 1.73, for 4980 observed reflections ($I > 3.0\sigma(I)$).

(9) $^1H$ NMR ($\delta$, $C_6D_6$, 294 K, all broad singlets): 13.48 (8H, $CH_a$ of Et), 6.08 (8H, $CH_b$ of Et), 5.78 (9H, $CH_3$ of Np), 2.15 (4H, meso), −1.40 (24H, $CH_3$ of Et). The isotropic shifts, using Ru(OEP)(CO) as the diamagnetic reference, obey the Curie law from −30 to +50 °C; the Ru–$CH_2$ protons are not observed, as with other paramagnetic Ru(por)(alkyl) species.[2e,7] UV/vis (toluene, RT; $\lambda_{max}$, nm (log $\epsilon$)): 504 (4.19), 392 (4.99), 362 (4.84). $\mu_{eff} = 2.4\ \mu_B$ (solution, Evans method).

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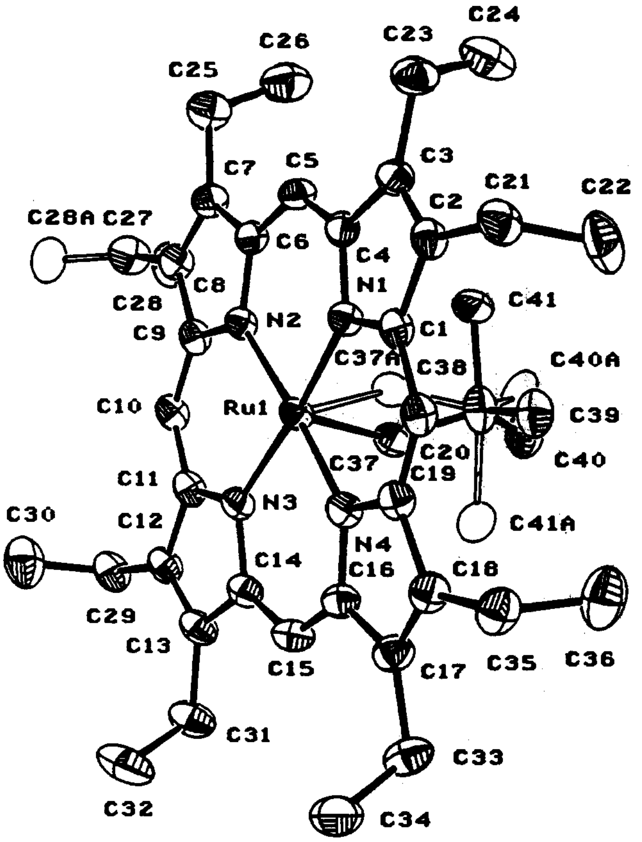

**Figure 1.** Molecular structure of Ru(OEP)Np (1). Thermal ellipsoids are drawn at the 33% probability level. Selected bond lengths (Å) and angles (deg): Ru–N = 2.021(3)–2.033(2), Ru–C(37) = 2.069(7), Ru–C(37A) = 2.12(1), C(37A)–C(38) = 1.46(1), C(37)–C(38) = 1.483(8), C(38)–C(40) = 1.45(2), C(38)–C(40A) = 1.51(2), C(38)–C(41) = 1.674(7), C(38)–C(41A) = 1.81(1); N–Ru–C(37) = 81.1(2)–106.2(2), N–Ru–C(37A) = 78.1(3)–107.9(3), Ru–C(37)–C(38) = 128.2(4), Ru–C(37A)–C(38) = 126.2(6), angles at C(38) 91.8(4)–125.1(5).

radicals), as judged by $^1$H NMR when $C_6D_6$ is used; 2 can also be made from $[Ru(OEP)]_2$[13b] and 2 equiv of LiNp in benzene, and indeed crystals for X-ray analysis were obtained from such a solution by slow evaporation.[14]

The remarkable structure of 2 (Figure 2) reveals a centrosymmetric dimer in which two monomeric units of 1 (but now nondisordered) are bridged via two Li atoms. Each Li is bonded to 12 atoms and is sandwiched between two 6-membered rings, one on each metalloporphyrin moiety; within each of these, the Ru and N(4) atoms are common to both Li atoms, with C(19), C(20), C(1), and N(1) completing one 6-membered ring and C(16), C(15), C(14), and N(3) completing the other. Although there is no dramatic effect on the geometry of the metalloporphyrin core, compared to that in 1, the N(4) atom is displaced 0.165 Å out of the mean porphyrin plane toward the two Li atoms, while the Ru atoms are pulled more toward the porphyrin plane (now only 0.0135 Å out of the mean plane toward the Np ligand). The Ru–C(37) distance is 2.100 Å, the minimum N–Ru–C(37) angle is 79.75°, and the Ru–C(37)–C(38) angle is 124.2°, and thus the steric constraints observed in 1 are still evident. The two porphyrin moieties are stacked in a somewhat staggered, rather than eclipsed, manner.

The Li–C bond distances (2.309–2.408 Å) lie within the 2.26–2.66-Å range reported for π-bonded Li atoms in analogous sandwich compounds involving aromatic or nonaromatic hydrocarbon residues;[15] the Li–N bond lengths (2.359–2.441 Å) are much longer than the typical 2.10–2.25-Å values noted for Li–N σ bonds,[15] reflecting the weaker nature of the Li–N π-bond, for which we can find no precedent. In a recent structural study of $Na_2(THF)_4(OEP)$ revealing two $Na(THF)_2$ moieties symmetrically bound to all four nitrogens, one on each face of the porphyrin ring, the Na–N distances (containing the larger Na) were in the 2.452–2.508-Å range;[16] a corresponding Li compound crystallized as $[Li(THF)_4^+][Li(OEP)^-]$.[16] The Ru–Li bonds in 2 (2.777–2.837 Å) are the longest within the π-interactions; the values are at the higher end of a range of Li–transition-metal bond lengths (2.38–2.92 Å) noted in mixed-metal organolithium compounds.[15]

The $^1$H NMR spectrum for 2[17] shows the *meso*-, $CH_2$, and $CH_3$ protons at shifts typical of diamagnetic $Ru^{II}$(OEP) systems,[2b,3a,5,13a-c] and all the Np protons are detected, not unexpectedly,[3,5] upfield of TMS. 2 almost certainly remains dimeric in benzene, as judged by the extent of separation of the diastereotopic methylene resonances (δ 3.531, 3.365; multiplets at 300 MHz) of the $ABX_3$ splitting pattern of the ethyl groups which results from magnetic inequivalence of the two sides of the porphyrin plane; for the monomeric Na[Ru(OEP)R] (R = Ph, Me) species,[2b,5] the corresponding AB part of the $ABX_3$ pattern (again in $C_6D_6$ at up to 300 MHz) appears as a single multiplet (δ 3.70 and 3.60, respectively, for the two species). The more significant separations observed for 2 are similar to those noted for diamagnetic dimers such as $[Ru^{III}(OEP)]_2^{2+}$ and $[Ru(OEP)L]_2(\mu\text{-}O)$ (L= halide, hydroxy, alkoxy, phenyl),[2c,18-20] where the proximity of two porphyrin rings results in sufficient shielding to resolve better the anisotropic magnetic environments. In the absence of structural data for the Na[Ru(OEP)R] complexes, the possibility of these being dimeric in the solid state (akin to 2) cannot, however, be ruled out completely. The relative simplicity of the $^1$H NMR spectrum for 2 (e.g. only a single resonance for the *meso*protons) implies the presence of a fluxionality, presumably between two staggered structures, where the two Li atoms move in parallel to alternative bonding positions on the porphyrin (e.g. with Li(1) switching to bind at Ru(1), N(2), C(6), C(5), C(4), and N(1)). The $^7$Li{$^1$H} NMR signal (δ −14.85 vs aqueous LiBr) is a broad

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(14) Crystal data for 2: $C_{82}H_{110}Li_2N_8Ru_2$, fw 1423.84, dimensions 0.25 × 0.30 × 0.40 mm, triclinic, space group $P\bar{1}$ (No. 2), $a$ = 13.824(3) Å, $b$ = 14.025(2) Å, $c$ = 11.943(3) Å, $\alpha$ = 106.80(2)°, $\beta$ = 114.78(2)°, $\gamma$ = 99.53(2)°, $V$ = 1900.0 Å, $\mu$ = 4.45 cm$^{-1}$, $D_c$ = 1.244 g cm$^{-3}$, $Z$ = 1; 14 234 reflections collected with $2\theta < 65°$ using diffractometer and radiation as for 1; 13 721 unique reflections ($R_{int}$ = 0.041), corrected for absorption, Lorentz, and polarization effects. The structure was solved by the Patterson method (SHELXS86) and expanded using Fourier techniques (DIRDIF92). Residuals $R$ = 0.038 ($R_w$ = 0.039) and goodness of fit 1.82, for 7455 observed reflections ($I > 3.0\sigma(I)$).

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(17) $^1$H NMR (δ, $C_6D_6$, 294 K): 8.003 (singlet s, 8H, meso), 3.531 (multiplet m, 16H, $CH_a$ of Et), 3.365 (m, 16H, $CH_b$ of Et), 1.65 (triplet, 48H, $CH_3$ of Et), −2.284 (s, 18H, $CH_3$ of Np), −7.447 (s, 4H, $CH_2$ of Np). $^{13}$C NMR (δ, $C_6D_6$, 294 K, assigned using HMQC): 141.73 (N–*C*), 141.63 (N–C–*C*), 101.77 ($C_{meso}$), 27.41 ($CH_3$ of Np), 22.04 ($CH_2$ of Np), 19.48 ($CH_3$ of Et), 17.84 ($CH_2$ of Et). $^7$Li NMR (δ, $C_6D_6$, 294 K): −14.85 (s) upfield from aqueous LiBr. UV/vis (benzene, RT; $\lambda_{max}$, nm): 510, 382.

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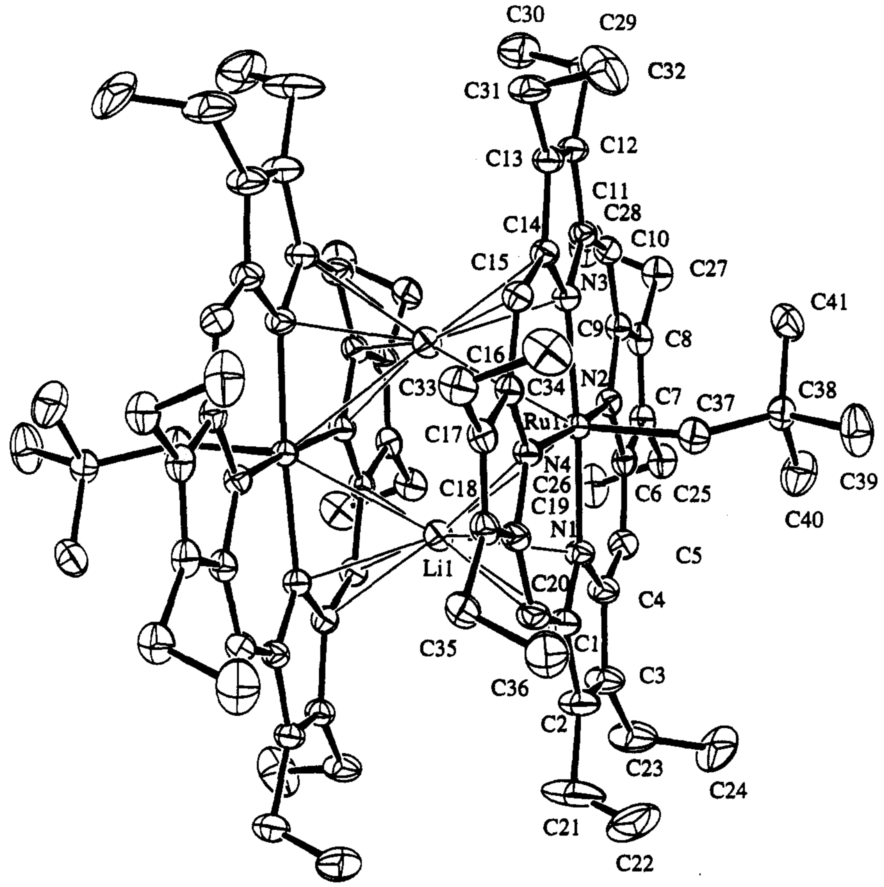

**Figure 2.** Molecular structure of $[Ru(OEP)Np]_2(\mu\text{-}Li)_2$ (**2**). Thermal ellipsoids are drawn at the 33% probability level. Selected bond lengths (Å) and angles (deg): Ru–N = 2.012(2)–2.048(2), Ru–C(37) = 2.100(3), C(38)–C = 1.492(4)–1.556(5), Ru–Li = 2.777(5), Ru–Li* = 2.837(5), Li–C = 2.323(6)–2.364(6), Li*–C = 2.309(6)–2.408(6), Li–N(1 or 4) = 2.369(5), Li*–N(3) = 2.359(5), Li*–N(4) = 2.441(5); N–Ru–C(37) = 79.75(10)–107.06(10), Ru–C(37)–C(38) = 124.2(2), angles at C(38) 106.1(3)–114.0(3), Ru–Li–Ru* = 115.0(2), N(2)–Ru–Li = 56.6(1), N(4)–Ru–Li = 56.4(1), Li–Ru–Li* = 65.0(2), Ru–N(4)–Li = 77.5(1), Ru–N(1)–Li = 78.0(1), C(37)–Ru–Li = 122.2(1), C(37)–Ru–Li* = 122.4(1).

singlet, shifted upfield because of the porphyrin ring current, and is similar to those signals recently reported for $Li_2(THF)_4(OEP)$ species.[16]

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**Supplementary Material Available:** Text giving a full description of the structure analyses and tables of crystallographic data, positional and thermal parameters, interatomic distances and angles, torsion angles, nonbonded distances, and least-squares planes for 1 and 2 (38 pages). Ordering information is given on any current masthead page.

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