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[14] CD data from Figure 5. Wavelengths [nm], followed by molecular ellipticity [$\mathrm{cm^2\,dmol^{-1}}$]: 251.5 (-3.16×10^{-5}), 313.5 (7.69×10^{5}), 428.3 (-1.26×10^{-3}), 479.3 (1.73×10^{4}).

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Metalloporphyrins as Ligands: Synthesis and Characterization of $[(\eta^6\text{-cymene})\text{Ru}\{\eta^5\text{-Ni(OEP)}\}]^{2+}$[**]

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Arnold L. Rheingold, and Thomas B. Rauchfuss*

Interactions between transition metals and heterocycles are relevant to many areas of science and technology. This topic has elicited recent interest in the context of hydrotreating catalysis, the industrial process by which heteroatom-containing contaminants are removed from fossil fuels.[1] Studies to date have focused on two aspects of hydrotreating, hydrodesulfurization (HDS) and hydrodenitrification (HDN), which can be modeled through the study of thiophene–metal[2] and pyridine–metal interactions,[3] respectively.

Hydrotreating also encompasses hydrodemetalation (HDM), which primarily involves the removal of nickel and vanadium from crude oil stocks.[4] These metals are typically found in fossil fuels as metalloporphyrins.[5] Such species arise from the dehydrogenation and transmetalation of chlorophyll and related pigments present in fossil plants. Because HDS and HDN catalysts are poisoned by these metals, HDM reactors typically precede other petroleum processing steps. We have prepared what appear to be the first π–metal complexes of metalloporphyrins as models for the initial stages of HDM catalysis. Since metalloporphyrins are of widespread interest in catalysis,[6] energy conversion,[7] and supramolecular chemistry in general,[8] the new coordination mode may be more broadly applicable, especially as we show that the π complexation strongly affects the structural and spectroscopic properties of the porphyrin.

We have previously demonstrated that the reagent $[(\text{cymene})\text{Ru(OTf)}_2]$ **1** (cymene = *p*-isopropyltoluene; OTf = CF_3SO_3^-) is a potent arenophile, which rapidly forms π complexes with a variety of arenes and heterocycles.[9] We have now found that **1** reacts with octaethylporphyrinatonickel, [Ni(OEP)] **2**, to give the adduct $[(\eta^6\text{-cymene})\text{Ru}\{\eta^5\text{-Ni(OEP)}\}](\text{OTf})_2$ **3** [Eq. (a)].

$$[(\text{R})\text{M(OTf)}_2] + [\text{Ni(OEP)}] \longrightarrow [(\text{R})\text{M}\{\eta^5\text{-Ni(OEP)}\}](\text{OTf})_2 \qquad \text{(a)}$$

$$(\text{R})\text{M}^{n+} = (\text{cymene})\text{Ru}^{2+},\ (\text{cymene})\text{Os}^{2+},\ (\text{C}_5\text{Me}_5)\text{Ir}^{2+}$$

The reaction occurs readily at room temperature and is signaled by a conversion of the magenta color characteristic of the nickel porphyrin to deep green. Addition of hexanes to these solutions precipitates **3**, leaving unconverted **2** in solution. The new compound is air-stable and soluble in a variety of polar organic solvents. Coordinating solvents, such as MeCN, reverse the complexation to give free **2**.

The ^{1}H NMR spectrum of **3** illustrates that the complex lacks the D_{4h} symmetry of **2**. Two methyne singlets are observed at $\delta = 8.13$ and 8.72. These signals are shifted upfield relative to the methyne signal found in **2** at $\delta = 9.7$, indicating the reduced ring current of the metalloporphyrin upon complexation. Homonuclear decoupling experiments show that the methylene hydrogen atoms are diastereotopic, for example the overlapping doublet of quartets at $\delta = 3.83$ is coupled to the overlapping doublet of quartets at $\delta = 3.03$, consistent with C_s symmetry of the π complex. Typical for other π-arene complexes, it is assumed that the $\{\eta^5\text{-Ni(OEP)}\}$, as well as the η^6-cymene ligand, rotates freely about the metal–ring centroid axis. The ^{13}C NMR data are consistent with the ^{1}H NMR spectroscopic results. The lower symmetry of the complex may also be responsible for the broadening of the Soret band, which has shifted from 392 nm to 406 nm, and appearance of a band at 672 nm, which is similar to those exhibited by metallochlorins (Fig. 1).[10]

While **3** did not afford crystals, X-ray quality crystals of the tetrafluoroborate salt, $[(\eta^6\text{-cymene})\text{Ru}\{\eta^5\text{-Ni(OEP)}\}](\text{BF}_4)_2$, were obtained, although due to disorder in the anion and solvent, the structure is of limited quality. The crystallographic results confirm that **2** is indeed serving as a π ligand for the Ru dication (Fig. 2).[11] The pyrrolide and π arene deviate from parallel by only 4.13°. The Ni(OEP) ligand is strongly distorted, being folded along the C28-Ni-C46 axis. The planes defined by the pyrrolides containing N1, N3, and N4 are twisted 10°, 28°, and 27°, respectively, from the least-squares plane calculated

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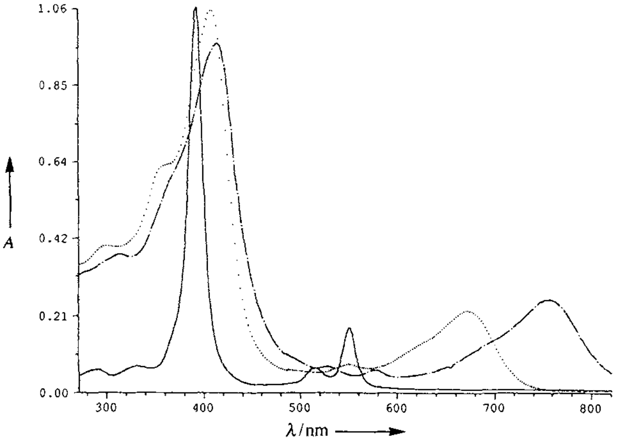

Fig. 1. Absorption spectra of [Ni(OEP)] (——), [(η^6-cymene)Ru{μ^5-Ni(OEP)}](BF$_4$)$_2$ (····), and [(η^6-cymene)Ru{η^5-Zn(OEP)}](OTf)$_2$ (–·–·–) in CH$_2$Cl$_2$. A = absorption.

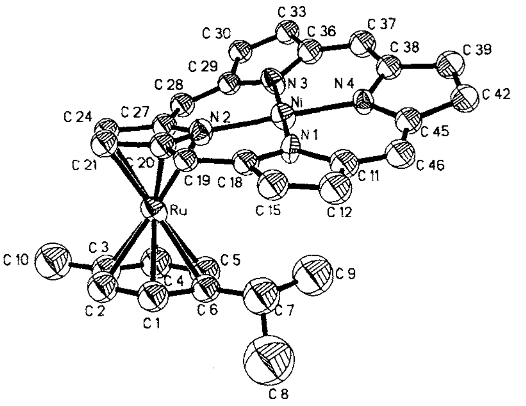

Fig. 2. Structure of the dication in [(η^6-cymene)Ru{η^5-Ni(OEP)}](BF$_4$)$_2$ with thermal ellipsoids drawn at the 50% probability level. (Ethyl groups omitted for clarity.) Selected bond lengths [Å]: Ru–N2 2.230, Ru–C20 2.169, Ru–C21 2.216, Ru–C24 2.237, Ru–C27 2.181, Ni–N1 1.922, Ni–N2 1.963, Ni–N3 1.945, Ni–N4 1.924.

for the π-complexed pyrrolide. The competition between Ni and Ru for electron density at N2 is also manifested in the structural data. The Ru–N2 distance is 0.081 Å longer than that in [(η^6-cymene)Ru(η^5-C$_4$Me$_4$N)](OTf)$_2$ (2.149 Å).[12] The Ni–N2 distance (1.963 Å) in **1** is only slightly longer than that found in the three known crystalline forms of **2**,[13–15] while the remaining three Ni–N bond lengths of the complex are either comparable or slightly shorter. It has been postulated[16] that 1.96 Å is the shortest metal–N bond length necessary to retain a planar macrocycle.[13] Thus, the somewhat shorter Ni–N1, Ni–N3, and Ni–N4 bond lengths are in accord with the severe nonplanarity of the Ni(OEP) ligand in **3**.

The new type of sandwich complex enjoys some the generality. ^{1}H NMR experiments confirm that both [(C$_5$Me$_5$)Ir(OTf)$_2$] and [(cymene)Os(OTf)$_2$] react with **2** in a manner analogous to **1**. The iridium adduct is deep blue, while the (cymene)Os derivative is green. We investigated the possibility that more than one metal could be attached to the porphyrin ring by treating **2** with an excess of **1**, but only the 1:1 adduct was isolated. We conclude that the first metalation diminishes the basicity of the entire porphyrin.

Interestingly, H$_2$(OEP) itself does not form a complex with **1**. Stable π complexes derived from pyrroles typically feature the deprotonated heterocycle.[17] We reason that the greater coordinating power of **2** relative to H$_2$(OEP) reflects the electron-releasing tendency of the electropositive Ni center. Consistent with this view, [Zn(OEP)] forms a very stable adduct with Ru(cymene)$^{2+}$ ions but [VO(OEP)] does not appear to bind at all. Spectroscopic and microanalytical data for [(cymene)Ru{Zn(OEP)}](OTf)$_2$ (**4**) suggest that this olive green species adopts a structure similar to that of the cation of **3** [Eq. (b)]. In

$$[(\mathrm{R})\mathrm{Ru(OTf)_2}] + [\mathrm{Zn(OEP)}] \longrightarrow [(\mathrm{R})\mathrm{M}\{\eta^5\text{-}\mathrm{Zn(OEP)}\}](\mathrm{OTf})_2 \qquad \text{(b)}$$
$$(\mathrm{R})\mathrm{M}^{n+} = (\mathrm{cymene})\mathrm{Ru}^{2+},\ (\mathrm{C_5Me_5})\mathrm{Ir}^{2+}$$

contrast to Zn(OEP),[18] whose photophysical properties have been widely studied, neither [(cymene)Ru{Zn(OEP)}]$^{2+}$ nor [(C$_5$Me$_5$)Ir{Zn(OEP)}]$^{2+}$ fluoresces.

The results define a new mode for metal–porphyrin interactions potentially relevant to catalyst–metalloporphyrin interactions in the hydrodemetalation process. The π-complexation strongly perturbs the electronic and structural properties of this important family of heterocycles. This new coordination mode presents new opportunities for the design of metal–metalloporphyrin superstructures.

Experimental Procedure

All preparative operations were conducted under purified nitrogen unless otherwise stated.

[(cymene)Ru{Ni(OEP)}](BF$_4$)$_2$: In a 100 mL Schlenk flask [(cymene)RuCl$_2$]$_2$ (0.078 g, 0.127 mmol) and AgBF$_4$ (0.098 g, 0.507 mmol) were combined and CH$_2$Cl$_2$ (10 mL) was added. After the mixture had been stirred for 2 h at room temperature, the orange solution was filtered to remove AgCl. The solution of [(cymene)Ru(BF$_4$)$_2$] was treated with **2** (0.158 g, 0.267 mmol). After about 16 h, the dark purple solution was reduced in volume to about 10 mL and diluted with hexane. The green solid precipitate was washed with hexane until the filtrate was colorless. The green powder was collected and dried under vacuum. Yield: 0.150 g (60%). Single crystals were obtained from a THF/hexane solvent system. ([(η^6-cymene)Ru{η^5-Ni(OEP)}][OTf]$_2$ was prepared analously using AgOTf, but no crystals were isolated.) Anal. calcd for C$_{46}$H$_{58}$N$_4$B$_2$F$_8$NiRu·0.6 THF (found): C 55.70 (54.60), H 6.07 (6.18), N 5.37 (4.48). ^{1}H NMR (CD$_2$Cl$_2$): δ = 0.54 (d, 6H), 1.39 (t, 6H), 1.52 (m, 18H), 1.60 (m, 1H), 2.00 (s, 3H), 3.03 (m, 2H), 3.25 (m, 10H), 3.57 (m, 2H), 3.83 (m, 2H), 5.52 (d, 2H), 6.10 (d, 2H), 8.13 (s, 2H), 8.72 (s, 2H). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ = 16.0, 16.3, 16.7, 17.1, 17.8, 18.6, 18.7, 19.0, 19.2, 21.8, 31.0, 86.0, 89.8, 97.3, 102.9, 103.0, 106.2, 106.7, 112.5, 145.9, 148.5, 148.8, 151.1, 154.6, 159.2. FAB-MS: *m/z*: 826.3 ([cymene)Ru{Ni(OEP)}]$^{2+}$). UV/Vis (CH$_2$Cl$_2$): λ [nm] (ε[M^{-1}cm^{-1}]) 300 (20500), 360 (32400), 406 (55000), 490 (2800), 550 (3700), 624 (6700), 672 (11600).

[Cp*Ir{Ni(OEP)}](OTf)$_2$: The synthesis was carried out as for [(cymene)-Ru{Ni(OEP)}](BF$_4$)$_2$ by using [Cp*IrCl$_2$]$_2$ (0.038 g, 0.048 mmol), AgOTf (0.051 g, 0.198 mmol), and [Ni(OEP)] (0.060 g, 0.101 mmol). A blue powder was isolated. Yield: 0.070 g (60%). ^{1}H NMR (CD$_2$Cl$_2$): δ = 1.26 (s, 5H), 1.58 (m, 24H), 3.16 (m, 2H), 3.37 (m, 10H), 3.60 (m, 2H), 3.84 (m, 2H), 8.36 (s, 2H), 8.64 (s, 2H). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ = 8.4, 15.9, 16.7, 16.9, 17.1, 17.5, 19.1, 19.2, 19.4, 96.7, 96.9, 100.4, 106.0, 108.6, 147.4, 149.7, 150.0, 152.0, 155.7, 159.3. FAB-MS: *m/z*: 918.4 ([Cp*Ir{Ni(OEP)}]$^{2+}$). UV/Vis (CD$_2$Cl$_2$): λ [nm] (ε [M^{-1}cm^{-1}]) 312 (16000), 394 (39000), 410 (49000), 550 (6000), 582 (7000), 636 (10000).

4: A solution of **1**, generated from [(cymene)RuCl$_2$]$_2$ (0.026 g, 0.042 mmol) and AgOTf (0.044 g, 0.170 mmol) in CH$_2$Cl$_2$ (10 mL) was treated with [Zn(OEP)] (0.075 g, 0.125 mmol). The slurry was refluxed at 65 °C for about 16 h. After the mixture had been cooled to room temperature, the dark purple solution was filtered (in air) to remove the unconverted, solid [Zn(OEP)]. The remaining [Zn(OEP)] was removed by first precipitating the complex with diethyl ether and washing with this solvent until the filtrate was colorless. The complex was recrystallized from a CH$_2$Cl$_2$/hexane solvent system to give olive green microcrystals. Yield: 0.065 g (67%). Anal. calcd for C$_{48}$H$_{58}$N$_4$F$_6$O$_6$RuS$_2$Zn (found): C 50.95 (50.83), H 5.17 (5.50), N 4.95 (4.39). ^{1}H NMR (CD$_2$Cl$_2$): δ = 0.92 (d, 6H), 1.29 (m, 6H), 1.54 (m, 18H), 2.09 (s, 3H), 2.43 (m, 1H), 3.30 (m, 14H), 3.44 (m, 2H), 5.7 (dd, 4H), 7.89 (s, 1H), 8.05 (s, 1H). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ = 15.89, 16.51, 16.90, 17.34, 18.67, 18.70, 18.91, 18.92, 19.02, 22.18, 31.40, 86.10, 88.37, 96.63, 102.07, 102.56, 104.98, 108.78, 111.96, 145.81, 147.11, 147.34, 155.78, 163.80, 167.24. FAB-MS: *m/z*: 832.3 ([(cymene)Ru{Zn(OEP)}]$^{2+}$). UV/Vis (CH$_2$Cl$_2$): λ [nm] (ε [M^{-1}cm^{-1}]) 274 (22000), 312 (25000), 370 (41000), 412 (65000), 528 (4000), 576 (3500), 692 (8500), 754 (17000).

[Cp*Ir{Zn(OEP)}](OTf)$_2$: [Cp*Ir(OTf)$_2$] was generated from [Cp*IrCl$_2$]$_2$ (0.033 g, 0.042 mmol) and AgOTf (0.043 g, 0.166 mmol) in CH$_2$Cl$_2$ (10 mL). To this solution, [Zn(OEP)] (0.075 g, 0.125 mmol) was added as a solid. The reaction mixture was heated to reflux for about 16 hours. After cooling to room temperature, the reaction mixture was filtered (in air) to remove the unconverted [Zn(OEP)]. The crude product was repeatedly precipitated from a thf/hexane solvent system until the washings were colorless. A green powder was recovered. Yield: 0.065 g (64%). Anal. calcd for $C_{48}H_{59}N_4F_6IrO_6S_2Zn$ (found): C 47.11 (47.20), H 4.86 (4.97), N 4.58 (4.50). ^1H NMR (CD_2Cl_2): $\delta = 0.88$ (s, 15H), 1.60 (m, 18H), 1.70 (t, 6H), 3.19 (m, 2H), 3.38 (m, 12H), 3.49 (m, 2H), 8.14 (s, 2H), 8.27 (s, 2H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): $\delta = 8.04$, 15.90, 16.83, 17.05, 17.43, 17.85, 19.03, 19.05, 19.14, 94.53, 95.94, 98.87, 107.09, 108.94, 145.83, 147.32, 148.14, 155.65, 163.59, 166.68. FAB-MS: m/z: 924.2 ($[Cp^*Ir\{Zn(OEP)\}]^{2+}$). UV/Vis (CH_2Cl_2): λ [nm] (ε [$M^{-1}cm^{-1}$]) 334 (29000), 404 (51000), 420 (71000), 526 (4400), 572 (5000), 712 (19000).

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[11] Crystal data of $[(\eta^6\text{-cymene})Ru\{\eta^5\text{-Ni(OEP)}\}](BF_4)_2 \cdot 0.5THF$: $C_{48}H_{62}B_2F_8N_4NiO_{0.5}Ru$ crystals were grown from a THF/hexane solution, $M_r = 1036.42$, monoclinic, space group $P2_1/n$, $a = 13.413(3)$, $b = 17.017(3)$, $c = 22.516(5)$ Å, $\beta = 101.93(3)°$; $V = 5028(2)$; $Z = 4$; $\rho_{calcd} = 1.369$ Mg m^{-3}, $F(000) = 2144$, $\lambda = 0.71073$ Å, $T = 247(2)$ K, $\mu(Mo_{K\alpha}) = 0.741$ mm^{-1}, reflections were collected on a $0.2 \times 0.1 \times 0.1$ mm^3 crystal using a Siemens diffractometer, of a total of 6415 reflections, 5392 were independent, largest peak and hole: 0.806 and -0.549 e^{-3}, $R1(I > 2\sigma(I)) = 0.721$ and $wR2 = 0.1703$ (final data) with $R1 = \Sigma||F_0| - |F_c||/\Sigma||F_0|$ and $wR2 = (\Sigma w(F_o^2 - F_o^2)^2/\Sigma w(F_o^2)^2)^{0.5}$. The structure was solved with direct methods (SHLETXL version 5.03) and refined by full-matrix least squares based on F^2. A riding model was applied to refine the hydrogen atom positions. The uncoordinated disordered thf molecules were refined at half occupancy. Crystallographic data (excluding structure factors) for the structure(s) reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-179-53. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: Int. code +(1223) 336-033; e-mail: teched@chemcrys.cam.ac.uk).

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DNA Cleavage by a Nine-Membered Masked Enediyne, an Analogue of the Kedarcidin and C-1027 Chromophores**

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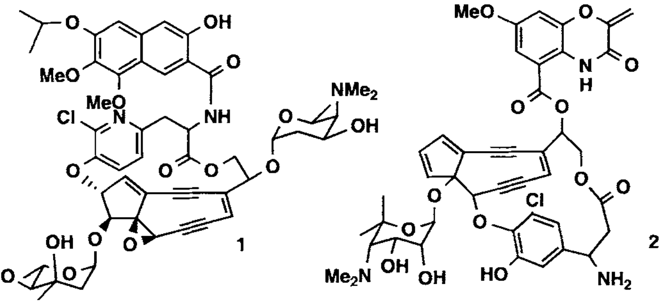
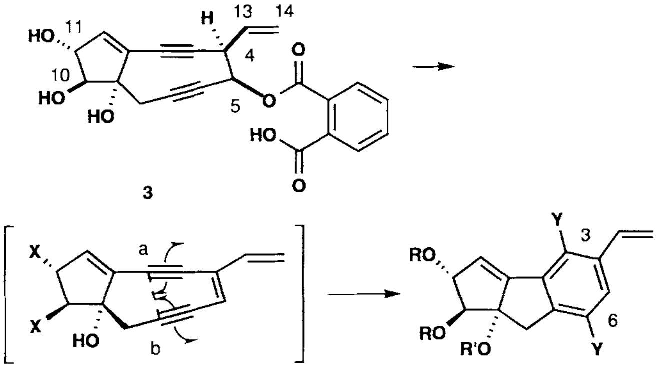
Kedarcidin (KD)[1] and C-1027[2] belong to a new class of chromoprotein antitumor antibiotics consisting of a 1:1 complex of apoproteins and cytotoxic nonprotein chromophores. Their chromophores, KD-chr (**1**) and C-1027-chr (**2**), possess a common nine-membered enediyne core structure. Their biological activities are associated with their ability to cause strong DNA cleavage. The proposed mechanism of the DNA cleavage is that biradical species generated from the highly strained nine-membered enediyne chromophores abstract hydrogens from deoxyribose.[1d,2d] Unlike other enediynes, C-1027 shows predominant DNA-cleaving activity even in the absence of thiols or reducing agents, a valuable implication for its application as a potent cancer chemotherapeutic agent.[3]



1 **2**

The design and synthesis of DNA-cleaving molecules has been a subject of recent synthetic and biochemical investigations.[4,5] We have already reported an approach to the enediyne **4a** (Scheme 1) as a nine-membered esperamicin–calicheamicin



3

4a: X=H
4b: X=OH

5a: R=R'=H, Y= •
5b: R=R'=OAc,Y=H
5c: R=TBS, R'=TMS, Y=D

Scheme 1. Mechanism of enediyne and biradical generation from **3**.

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