Synthesis and Characterization of Isostructural Metalloporphyrin Chalconitrosyl Complexes Ru(TTP)(NE)Cl (E = O, S) and a Remarkable Thionitrosyl/Nitrite → Nitrosyl/Thiazate Transformation

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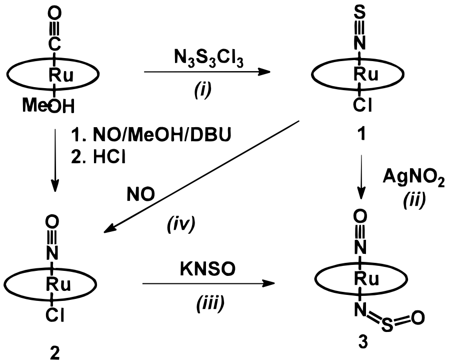
Although our understanding of the bonding in transition metal chalcocarbonyls, $L_nMC\equiv E$ (E = O, S, Se, Te), is well grounded in both experiment[1] and theory,[2] our knowledge of the bonding in the related family of chalconitrosyls, $L_nMN\equiv E$, is much more limited. For example, although numerous nitrosyl complexes have been characterized, and frequently reviewed,[3] the number of isostructural $L_nMN\equiv E$ complexes with E = O and S remains small, and there are no reported examples of stable isolable complexes with either a bent thionitrosyl or linear selenonitrosyl or telluronitrosyl ligand.[4] A thorough analysis of the bonding in $CpCr(CO)_2(NE)$ with Fenske−Hall calculations and vacuum UV photoelectron spectroscopy[5] indicates that for this metal fragment the stronger σ-donation of the thionitrosyl is complemented by stronger π interactions with both the filled high-energy π(NS) orbital and the empty π^*(NS). The net result is that the thionitrosyl removes more electron density than nitric oxide from the metal in the $CpCr(CO)_2$ fragment. Similar conclusions have been reached with CNDO/2 level calculations for $[LX_4M(NE)]$ (M = Ru, Os; E = O, S; X = Cl^-, NR_2^-; L = Cl^-, OH_2).[6,7] However, recent electrochemical and structural results for $[Tc(phen)_2X(NE)]^{n+}$ (phen = 1,10-phenanthroline; X = Cl, E = S, $n = 1$; X = NH_3, E = O, $n = 2$) complexes suggest that for this system there is stronger π-back-bonding to the nitrosyl ligand,[8] and there are similar trends for $OsCl_3(NE)(PPh_3)_2$.[9] These results suggest that when contrasting the relative interactions of nitrosyl and thionitrosyl ligands with transition metal centers, the fine balance of π-acceptance and donation needs to be carefully considered. In this communication we describe the following: (1) the synthesis and characterization by far-IR, UV−vis spectroscopy, differential scanning calorimetry, and cyclic voltammetry of a new isostructural pair of ruthenium porphyrin complexes Ru(TTP)(NE)Cl (E = O, S); (2) the remarkable transformation of a thionitrosyl/nitrite complex to a nitrosyl/thiazate complex; (3) the crystal structures of two of these derivatives. Together these results suggest that for complexes with strong axially symmetric high-field donor ligands, such as porphyrinato dianions, the nitrosyl ligand is the better π-acceptor.

Scheme 1. Synthesis and Reactions of Ru(TTP)(NE)Cl[a]



[a] Conditions: (i) CH_2Cl_2, 25 °C, 25 min; (ii) CH_2Cl_2, 1 h, 25 °C; (iii) CH_2Cl_2, 25 °C, 30 min; (iv) CH_2Cl_2, 25 °C, 2 min.

When Ru(TTP)(CO)(HOMe) is treated with trithiazyl trichloride at room temperature, there is rapid displacement of carbon monoxide and incorporation of both thionitrosyl and chloride to give **1**, Scheme 1, in 85% yield.[10] An ORTEP view for the structure of **1** as determined by X-ray diffraction is shown in Figure 1.[11] Important metrical parameters for this complex include a significantly shorter nitrogen−sulfur bond length than is found in most thionitrosyl complexes[12] and a typically short ruthenium−chloride bond length[13] as is frequently found for chloride ligands bound *trans* to nitric oxide. These data suggest diminished Ru−NS interaction with relatively weak Ru(d)−NS(π^*) back-bonding. In addition, the porphyrin exhibits a very slight S_4-ruffling with the ruthenium displaced 0.101 Å toward the thionitrosyl ligand.

The spectroscopic results for Ru(TTP)(NE)Cl in Table 1 allow for a comparison of the bonding of a thionitrosyl versus a nitrosyl group in an isosteric and isoelectronic environment. In

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(10) All new compounds give satisfactory elemental analysis for C, H, and N. Additional characteristic data for **1**−**3** are as follows. ^{1}H NMR (δ in ppm and coupling constants in Hz): **1** (in $CDCl_3$), 8.92 (s, 8H, H_β), 8.10 (d, $^3J_{HH} = 6.8$, 4H, H_m), 8.05 (d, $^3J_{HH} = 6.8$, 4H, $H_{m'}$), 7.48 (t, $^3J_{HH} = 7.7$, 8H, H_o, $H_{o'}$), 2.63 (s, 12H, p-CH_3); **2** (in C_6D_6), 9.16 (s, 8H, H_β), 8.11 (d, $^3J_{HH} = 7.1$, 4H, H_m), 7.91 (d, $^3J_{HH} = 7.7$, 4H, $H_{m'}$), 7.16 (H_o, $H_{o'}$ obscured by solvent), 2.39 (s, 12H, p-CH_3); **3** (in $CDCl_3$), 8.90 (s, 8H, H_β), 8.07 (d, $^3J_{HH} = 7.7$, 4H, H_m), 8.00 (d, $^3J_{HH} = 8.6$, 4H, $H_{m'}$), 7.48 (t, $^3J_{HH} = 9.0$, 8H, H_o, $H_{o'}$), 2.62 (s, 12H, p-CH_3). ^{15}N NMR ($CDCl_3$, δ in ppm referenced to nitric acid): **1**, 111.95 (s, *N*S).

(11) Crystal data for **1**: Ru(TTP)(NS)Cl, $C_{48}H_{36}ClN_5RuS$, $M = 851.43$, monoclinic, space group $P2_1/n$, $a = 11.309(2)$ Å, $b = 27.633(6)$ Å, $c = 19.404(4)$ Å, $\beta = 92.56(3)°$, $V = 6058(2)$ Å^3, $Z = 6$, $D_c = 1.400$ Mg m^{-3}, $\lambda = 0.710\ 73$ Å, $\mu = 0.547$ mm^{-1}, $F(000) = 2616$, $T = 293$ K. Data were collected on a Siemens P4 diffractometer for $2 < \theta < 24°$. The structure was solved by direct and Fourier methods and refined by least squares against F^2 to $R1 = 0.0509$ (w$R2 = 0.1002$) and $S_{goof} = 1.123$ for 9476 unique intensity data with $I > 2\sigma(I)$. There are two independent molecules in the unit cell with a nondisordered molecule lying on a general position, shown in Figure 1, and the second disordered molecule lying on an inversion center. For molecule B axial ligand NS/Cl disorder prevents meaningful interpretation of the metric parameters for these ligands, but the final least-squares refinement of this fragment was unconstrained and included half-occupancies of nitrogen, sulfur, and chlorine on both sides of the porphyrin.

(12) Typical range of MN−S bond lengths is 1.49(2)−1.592(11) Å.

(13) For example the average Ru−Cl bond length in octahedral complexes of 102 structures is 2.409(40) Å.[14]

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Table 1. Summary of Characteristic Data for Ru(TTP)(NE)X Complexes

compd				UV−vis (nm (log ϵ))[c]			electrochemistry, $E_{1/2}$[d] (mV)		thermochemistry:[e] T_{min} (°C), ΔH (kcal mol^{-1})
E	X	no.	IR (cm^{-1})[a]	Soret	Q-bands	MLCT	oxidn	redn	
S	Cl	**1**	1271 (1235), ν(NS); 298 m, ν(RuCl)	424 (5.44)	514 (4.26), 538 sh	658 (3.32)	940 (178), 1410(174)	−655	384, −5.25
O	Cl	**2**	1845 (1830), ν(NO);[b] 323 m, ν(RuCl)	414 (5.28)	562 (3.94), 600 sh		1021 (126), 1489 (120)	−789	stable to 480
O	NSO	**3**	1829 (1793), ν(NO); 1255 (1232), $\nu(NSO)_a$; 1075 (1073) w, $\nu(NSO)_s$; 515 (509) w, $\delta(NSO)_s$	416 (5.40)	572 (3.96), 606 sh				356, −25.28

[a] Recorded in KBr pellets with ^{15}N labeled bands given in parentheses. All bands are strong unless otherwise noted. [b] Solid-state splitting as confirmed by solution IR. [c] Measured in dichloromethane. [d] Potentials listed in mV *vs* Ag^+/Ag in dichloromethane solution with 0.1 M $[N(n\text{-}butyl)_4][PF_6]$ as supporting electrolyte on a platinum button working electrode. Peak separation at a 100 mV s^{-1} scan speed in the cyclic voltammetric experiment given in parentheses for reversible processes; all other potentials are for quasi-reversible processes. [e] As determined by differential scanning calorimetry with a 10 °C/min scan rate under a flow of nitrogen.

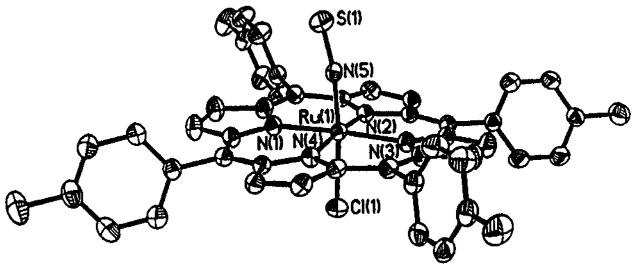

Figure 1. Molecular structure of Ru(TTP)(NS)Cl for the nondisordered molecule A. Hydrogen atoms are omitted for clarity. Important bond lengths (Å) and angles (deg): Ru(1)−N(1−4) 2.046−2.050(4); Ru(1)−N(5) 1.768(4); N(5)−S(1) 1.489(5); Ru(1)−Cl(1) 2.356(2); Ru(1)−N(5)−S(1) 169.1(3); N(5)−Ru(1)−Cl(1) 174.3(1).

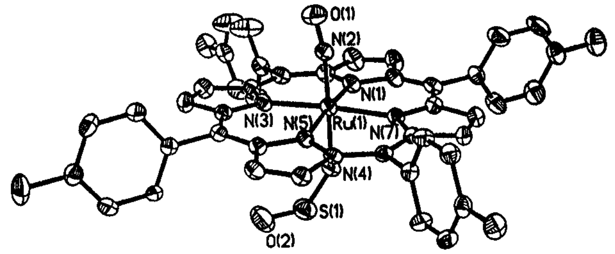

Figure 2. Molecular structure of Ru(TTP)(NO)(NSO) with view as per Figure 1: Ru(1)−N(1,3,5,7) 2.052−2.064(5); Ru(1)−N(2) 1.737(5); N(2)−O(1) 1.164(6); Ru(1)−N(4) 2.022(5); N(4)−S(1) 1.467(5); S(1)−O(2) 1.458(6); Ru(1)−N(4)−S(1) 140.8(3); N(4)−S(1)−O(2) 122.8(3); Ru(1)−N(2)−O(1) 170.2(5).

the far-IR, the ν(Ru−Cl) is *ca.* 25 cm^{-1} lower in energy for the thionitrosyl complex **1**, and this is consistent with a stronger *trans* influence due to better σ-donation by the NS ligand. Both the UV−vis and electrochemical results in Table 1 suggest that there is greater electron density on the Ru(TTP) moiety in **1**; the oxidation potentials are significantly lower and the separation of the Soret and *Q*-bands is less for **1** than for **2**. An unusual relatively weak and broad band at 658 nm is observed in the UV−vis spectrum of **1**. On this basis, we have assigned this band as resulting from an MLCT transition from the ruthenium to the low-lying π^*(NS) and note that we have not observed a similar band for any of the series Ru(TTP)(NO)X.[15,16]

Most notably though, the reactions of **1** are indicative of a markedly more labile thionitrosyl ligand than is the nitric oxide ligand in **2**. For example, when **1** is treated with trimethylphosphine at room temperature, there is rapid loss of both the NS and Cl ligands; $Ru(TTP)(PMe_3)_2$ is formed quantitatively. When **1** is treated with a stream of nitric oxide at room temperature and atmospheric pressure, there is rapid substitution of the thionitrosyl to give **2**. In contrast, ^{15}NO exchange in Ru(TTP)(NO)Cl is slow and requires forcing conditions of temperature and pressure,[16] and prolonged exposure of **2** to excess tertiary phosphines results in little appreciable loss of nitric oxide.

The best comparison of the relative bonding of NO versus NS would be their presence mutually *trans* in a single complex with identical steric effects. However, a mutually *trans* arrangement of two nitrosyl ligands is very rare, with $Os(OEP)(NO)_2$ being the only reported stable example;[17] a similar complex with *trans* NO/NS ligands has not been described. In an attempt to prepare such a complex, **1** was treated with silver nitrite, which instead of returning the anticipated methathesis product, Ru(TTP)(NS)(ONO), as is known for its reaction with **2**,[16] resulted in the formation of a nitrosyl thiazate complex, Ru(TTP)(NO)(NSO), **3**. The identity of this complex has been confirmed by X-ray crystallography,[18] Figure 2, by IR spectroscopy, and an independent synthesis by treating **2** with potassium thiazate, Scheme 1.[19] Although a similar thionitrosyl → thiazate transformation has been observed for the oxygenation of $IrCl_2(NS)(PPh_3)_2$,[20] the transformation of the most likely intermediate, $Ru(TTP)(NS)(NO_2)$ to **3** represents a remarkable case of an oxo transfer reaction to give a thiazate/nitrosyl complex and illustrates the propensity for the formation of ruthenium nitrosyl complexes.[21] We are currently using Fenske−Hall level theory to dissect the relative Ru-NE bonding interactions and will describe these results in the future.

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Supporting Information Available: Listings of crystallographic and structural data and ORTEP diagrams for **1** and **3** (23 pages). Ordering information is given on any current masthead page.

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(15) The UV and near-IR spectra for all reported complexes have been measured between 200 and 1700 nm.

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(18) Crystal data for **3**: Ru(TTP)(NO)(NSO), $C_{48}H_{36}N_6O_2RuS\cdot 2C_6H_6$, $M = 1018.17$, monoclinic, space group *C*2/*c*, $a = 40.918(16)$ Å, $b = 9.012(4)$ Å, $c = 24.965(11)$ Å, $\beta = 96.666(4)°$, $V = 9144(7)$ Å^3, $Z = 8$, $D_c = 1.479$ Mg m^{-3}, $\lambda = 0.710\ 69$ Å, $\mu = 0.428$ mm^{-1}, $F(000) = 3472$, $T = 293$ K. Data were collected on a Molecular Structure Corp. rotating anode diffractometer for $1.64 < \theta < 23°$. The structure was solved by direct and Fourier methods and refined by least squares against F^2 to $R1 = 0.0450$ ($wR2 = 0.1155$) and $S_{goof} = 1.029$ for 6352 unique intensity data with $I > 2\sigma(I)$. In the latter stages of refinement two benzene solvate molecules were located, one disordered and the other not.

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