

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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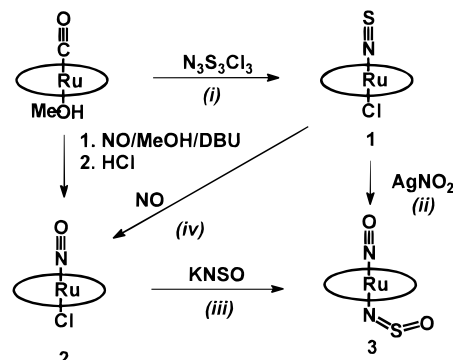
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Although our understanding of the bonding in transition metal chalcocarbonyls, $L_nMC\equiv E$ ($E = O, S, Se, Te$), is well grounded in both experiment¹ and theory,² our knowledge of the bonding in the related family of chalconitrosyls, $L_nMN\equiv E$, 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 spectroscopy⁵ 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 $\pi(NS)$ orbital and the empty $\pi^*(NS)$. 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.

When $Ru(TTP)(CO)(HOMe)$ is treated with trithiazyl trichloride at room temperature, there is rapid displacement of carbon

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.

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 complexes¹² and a typically short ruthenium–chloride bond length¹³ 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

- (10) All new compounds give satisfactory elemental analysis for C, H, and N. Additional characteristic data for **1–3** are as follows. ¹H 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, $p-CH_3$). ¹⁵N NMR ($CDCl_3$, δ in ppm referenced to nitric acid): **1**, 111.95 (s, NS).
- (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, $\beta = 92.56(3)^\circ$, $V = 6058(2)$ Å³, $Z = 6$, $D_c = 1.400$ Mg m⁻³, $\lambda = 0.71073$ Å, $\mu = 0.547$ mm⁻¹, $F(000) = 2616$, $T = 293$ K. Data were collected on a Siemens P4 diffractometer for $2 < \theta < 24^\circ$. The structure was solved by direct and Fourier methods and refined by least squares against F^2 to $R1 = 0.0509$ ($wR2 = 0.1002$) 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
- (14) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. J. *Chem. Soc., Dalton Trans.* **1989**, S1.

[†] University of Wyoming.

[‡] University of East Anglia.

- (1) Clark, G. R.; Marsden, K.; Rickard, C. E. F.; Roper, W. R. *Wright, L. J. J. Organomet. Chem.* **1988**, 338, 393.
- (2) Lichtenberger, D. L.; Fenske, R. F. *Inorg. Chem.* **1976**, 15, 2015.
- (3) Richter-Addo, G. B.; Legzdins, P. *Chem. Rev.* **1988**, 88, 991. Richter-Addo, G. B.; Legzdins, P. *Metal Nitrosyls*; Oxford University Press: Oxford, U.K., 1992.
- (4) For possible intermediary bent thionitrosyl and selenonitrosyl ligands see: Demant, U.; Willing, W.; Müller, U.; Dehnicke, K. Z. *Anorg. Allg. Chem.* **1986**, 532, 175. Vogler, S.; Massa, W.; Dehnicke, K. Z. *Naturforsch., B* **1991**, 46, 1625.
- (5) Lichtenberger, D. L.; Hubbard, J. L. *Inorg. Chem.* **1985**, 24, 3835.
- (6) Pandey, K. K.; Sharma, R. B.; Pandit, P. K. *Inorg. Chim. Acta* **1990**, 169, 207. Pandey, K. K. *J. Coord. Chem.* **1991**, 22, 307.
- (7) Pandey, K. K.; Massoudipour, M.; Palleria, V. *Ind. J. Chem.* **1990**, 29A, 260.
- (8) Lu, J.; Clarke, M. J. *J. Chem. Soc., Dalton Trans.* **1992**, 1243.
- (9) Roesky, H. W.; Pandey, K. K.; Clegg, W.; Noltemeyer, M.; Sheldrick, G. M. *J. Chem. Soc., Dalton Trans.* **1984**, 719.

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

E	X	no.	IR (cm ⁻¹) ^a	UV-vis (nm (log ϵ)) ^c			electrochemistry, $E_{1/2}$ ^d (mV)		thermochemistry: ^e $T_{\min}$ (°C), ΔH (kcal mol ⁻¹)
				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), ν (NSO) _{as} ; 1075 (1073) w, ν (NSO) _s ; 515 (509) w, δ (NSO) _s	416 (5.40)	572 (3.96), 606 sh				356, -25.28

^a Recorded in KBr pellets with ¹⁵N 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*-butyl)₄][PF₆] 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.

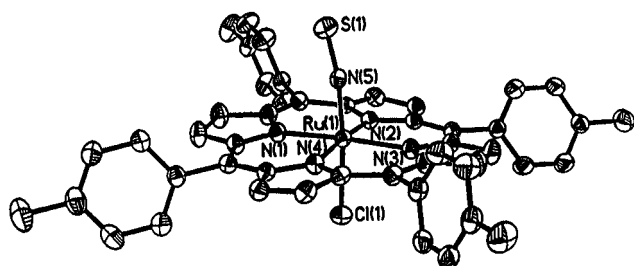


Figure 1. Molecular structure of Ru(TTP)(NS)Cl for the nondisordered molecule A. Hydrogen atoms are omitted for clarity. Important bond lengths (Å) and angles (deg): Ru(1)–N(1–4) 2.046–2.050(4); Ru(1)–N(5) 1.768(4); N(5)–S(1) 1.489(5); Ru(1)–Cl(1) 2.356(2); Ru(1)–N(5)–S(1) 169.1(3); N(5)–Ru(1)–Cl(1)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

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)(PMe₃)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, ¹⁵NO 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

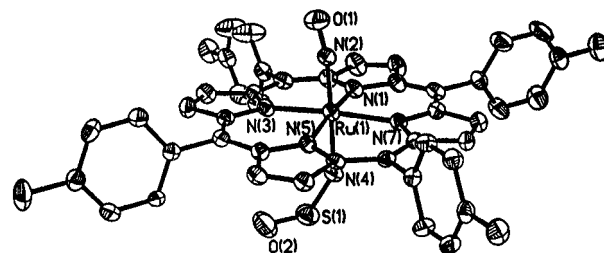


Figure 2. Molecular structure of Ru(TTP)(NO)(NSO) with view as per Figure 1: Ru(1)–N(1,3,5,7) 2.052–2.064(5); Ru(1)–N(2) 1.737(5); N(2)–O(1) 1.164(6); Ru(1)–N(4) 2.022(5); N(4)–S(1) 1.467(5); S(1)–O(2) 1.458(6); Ru(1)–N(4)–S(1) 140.8(3); N(4)–S(1)–O(2) 122.8(3); Ru(1)–N(2)–O(1) 170.2(5).

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, Figure 2, by IR spectroscopy, and an independent synthesis by treating **2** with potassium thiazate, Scheme 1.¹⁹ Although a similar thionitrosyl $\rightarrow$ thiazate transformation has been observed for the oxygenation of IrCl₂(NS)(PPh₃)₂,²⁰ the transformation of the most likely intermediate, Ru(TTP)(NS)(NO₂) 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.

(16) Bohle, D. S.; Goodson, P. A.; Smith, B. D. *Polyhedron* **1996**, *15*, 3147.

(17) Buchler, J. W.; Smith, P. D. *Chem. Ber.* **1976**, *109*, 1465.

(18) Crystal data for **3**: Ru(TTP)(NO)(NSO), C₄₈H₃₆N₆O₂RuS·2C₆H₆, *M* = 1018.17, monoclinic, space group C2/c, *a* = 40.918(16) Å, *b* = 9.012(4) Å, *c* = 24.965(11) Å, β = 96.666(4)°, *V* = 9144(7) Å³, *Z* = 8, *D*_c = 1.479 Mg m⁻³, λ = 0.710 69 Å, μ = 0.428 mm⁻¹, *F*(000) = 3472, *T* = 293 K. Data were collected on a Molecular Structure Corp. rotating anode diffractometer for 1.64 < θ < 23°. The structure was solved by direct and Fourier methods and refined by least squares against *F*² to *R*1 = 0.0450 (*wR*2 = 0.1155) and *S*_{goof} = 1.029 for 6352 unique intensity data with *I* > 2 σ (*I*). In the latter stages of refinement two benzene solvate molecules were located, one disordered and the other not.

(19) Armitage, D. A.; Brand, J. C. *J. Chem. Soc., Chem. Commun.* **1979**, 1078.

(20) Pandey, K. K.; Agarwala, U. C. *Indian J. Chem.* **1981**, *20*, 906.

(21) Griffith, W. P. *The Chemistry of the Rarer Platinum Metals*; Wiley-Interscience: New York, 1967; p 174.