Inorganic Chemistry

Article

pubs.acs.org/IC

Singlet–Triplet Gaps of Cobalt Nitrosyls: Insights from Tropocoronand Complexes

Kathrin H. Hopmann,[†,§] Jeanet Conradie,[†,‡,§] Espen Tangen,[†,§] Zachary J. Tonzetich,[⊥,∥,§] Stephen J. Lippard,*[,⊥] and Abhik Ghosh*[,†]

[†]Department of Chemistry and Center for Theoretical and Computational Chemistry, University of Tromsø, N-9037 Tromsø, Norway

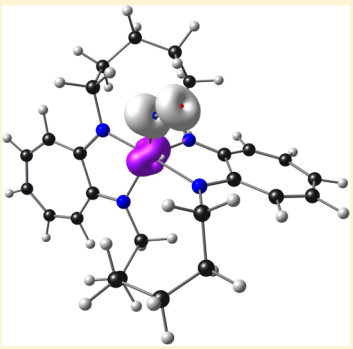
[‡]Department of Chemistry, University of the Free State, 9300 Bloemfontein, Republic of South Africa

[⊥]Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139-4307, United States

[∥]Department of Chemistry, University of Texas at San Antonio, San Antonio, Texas 78249, United States

Supporting Information

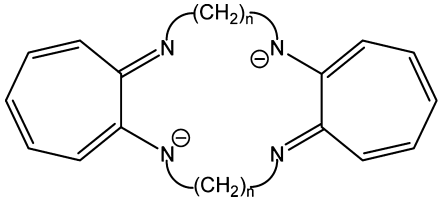
ABSTRACT: A density functional theory (DFT) study of {CoNO}^{8} cobalt nitrosyl complexes containing the [*n*,*n*]tropocoronand ligand (TC-*n*,*n*) has revealed a sharp reduction of singlet–triplet gaps as the structures change from near-square-pyramidal (for *n* = 3) to trigonal-bipyramidal with an equatorial NO (for *n* = 5, 6). An experimental reinvestigation of [Co(TC-3,3)(NO)] has confirmed that it is not paramagnetic, as originally reported, but diamagnetic, like all other {CoNO}^{8} complexes. Furthermore, DFT calculations indicate a substantial singlet–triplet gap of about half an eV or higher for this complex. At the other end of the series, low-energy, thermally accessible triplet states are predicted for [Co(TC-6,6)(NO)]. Enhanced triplet-state reactivity may well provide a partial explanation for the failure to isolate this compound as a stable species.



INTRODUCTION

Tropocoronand ligands ([TC-*n*,*n*]$^{2-}$; Scheme 1) provide sterically constrained coordination environments that, for five-coordinate complexes, vary from square-pyramidal (SQP) to trigonal-bipyramidal (TBP) as a function of the length of the alkylidene linkers. Several of these complexes have unusual geometric and electronic structures.[1] Among these are $S = {}^1/_2$ [Fe(TC-5,5)(NO)],[2] which has an unusual linear {FeNO}^{7} unit, and the unique $S = 1$ {MNO}^{6} complex [Mn(TC-5,5)(NO)].[3] The literature on {CoNO}^{8} tropocoronand complexes is also of interest. Whereas [Co(TC-3,3)(NO)] was reported to be paramagnetic,[4] the analogous TC-4,4 and TC-5,5 complexes are diamagnetic, a more common situation for {CoNO}^{8} complexes.[5] The hypothetical [Co(TC-6,6)(NO)] complex has thus far eluded isolation and characterization.[6]

Scheme 1. Dianion of a [TC-*n*,*n*] Ligand



In this study, density functional theory (DFT) calculations[7] were undertaken with the goal of contributing to our understanding of the divergent spin states and chemical behavior of {CoNO}^{8} tropocoronand complexes. The calculations showed that the essentially SQP [Co(TC-3,3)(NO)] complex is $S = 0$, like other {CoNO}^{8} species;[8] this result was confirmed by an experimental reinvestigation of the molecule. The calculations also revealed a decreasing singlet–triplet (S–T) gap and low-energy triplet states as the coordination geometry changed from the nearly SQP TC-3,3 complex to the TBP TC-5,5 and TC-6,6 complexes. Thermally accessible triplet states thus are a distinct possibility for [Co(TC-6,6)(NO)], which may partly explain its apparent instability.

RESULTS AND DISCUSSION

S–T Gaps. The lowest-energy singlet and triplet states of the [Co(TC-*n*,*n*)(NO)] complexes (*n* = 3–6) were optimized with the B3LYP, OLYP, and PW91 functionals and the 6-311G(d,p) basis set. In general, the hybrid functional B3LYP led to a broken-symmetry $M_S = 0$ solution as the ground state, whereas the pure functionals PW91 and OLYP led to closed-shell ground states. Interestingly, depending on the starting point of the optimizations, two distinct triplet states, denoted as T_1 and T_2 in the discussion below, could be obtained. The T_1

Received: April 21, 2015
Published: July 23, 2015

DOI: 10.1021/acs.inorgchem.5b00901
Inorg. Chem. 2015, 54, 7362–7367

Table 1. Energies (eV) of the Triplet States T_1 and T_2, Relative to the Lowest-Energy $M_S = 0$ State S_0[a]

	B3LYP/6-311G(d,p)		B3LYP-D3/6-311G(d,p)		OLYP/6-311G(d,p)		PW91/6-311G(d,p)	
complex	T_1	T_2	T_1	T_2	T_1	T_2	T_1	T_2
[Co(TC-3,3)(NO)]	0.43	0.61	0.45	0.65	1.03 (1.00)[b]	0.78	1.09	1.06
[Co(TC-4,4)(NO)]	0.38	0.23	0.40	0.29		0.36 (0.38)[b]	0.59	
[Co(TC-5,5)(NO)]	0.21	0.21	0.19	0.25	0.29	0.27 (0.28)[b]	0.35	
[Co(TC-6,6)(NO)]	0.27	0.15	0.18	0.20	0.40 (0.22)[b]	0.16 (0.17)[b]	0.30	

[a]The S_0 state corresponds to a broken-symmetry $M_S = 0$ calculation for B3LYP and B3LYP-D3 but to closed-shell $M_S = 0$ calculations for the pure functionals PW91 and OLYP. [b]These values were obtained with a STO-TZP basis set with the *ADF* program system.

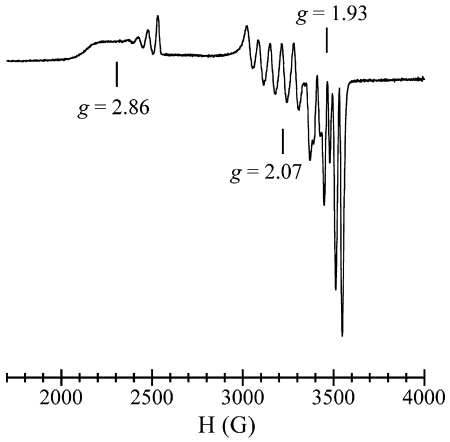


Figure 1. 9.335 GHz X-band EPR spectrum of [Co^{II}(TC-3,3)] recorded in a 2-MeTHF glass at 77 K. Instrument settings: 2.0 mW power, 100.0 kHz modulation frequency, 8.0 G modulation amplitude.

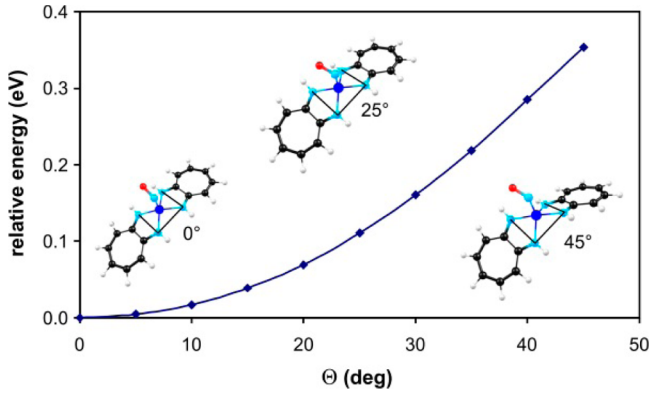


Figure 3. OLYP potential energy scan for TBP distortion (Θ) of the model complex [$Co(ATI)_2(NO)$], with all other internal coordinates separately optimized.

state may be described as low-spin $S = {}^1/_2$ cobalt(II) ferromagnetically coupled to a NO radical, whereas the T_2 state may be described as a high-spin $S = 2$ cobalt(III) antiferromagnetically coupled to an $S = 1$ NO^- anion. Table 1 lists the energies of the triplet states relative to the singlet ground state for the different functionals.

The energetics of the T_1 and T_2 states are qualitatively consistent across the three functionals. As noted elsewhere,[9] the classic pure functional PW91 may have a certain bias in favor of the singlet state, whereas the hybrid functional B3LYP may have a similar bias in favor of the triplet states. In certain applications involving transition-metal nitrosyls, OLYP was one of the least biased functionals vis-à-vis the issue of spin pairing.[8c] This generalization may also apply to the present study. It is significant in this context that the three functionals examined predict singlet ground states for all of the {CoNO}[8] complexes, with the highest S−T gap predicted for [Co(TC-3,3)(NO)], casting doubt on the original description of this compound as being paramagnetic.[4]

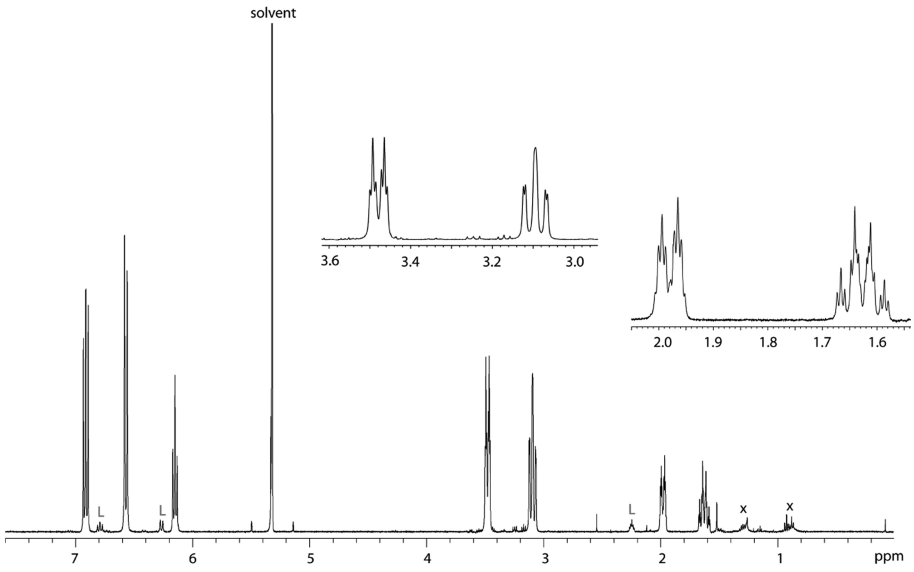


Figure 2. 500 MHz ^{1}H NMR spectrum of [$Co(TC-3,3)(NO)$] recorded in CD_2Cl_2. L represents peaks due to H_2(TC-3,3). The peaks marked X correspond to small amounts of pentane and ether used in purification.

DOI: 10.1021/acs.inorgchem.5b00901
Inorg. Chem. 2015, 54, 7362−7367

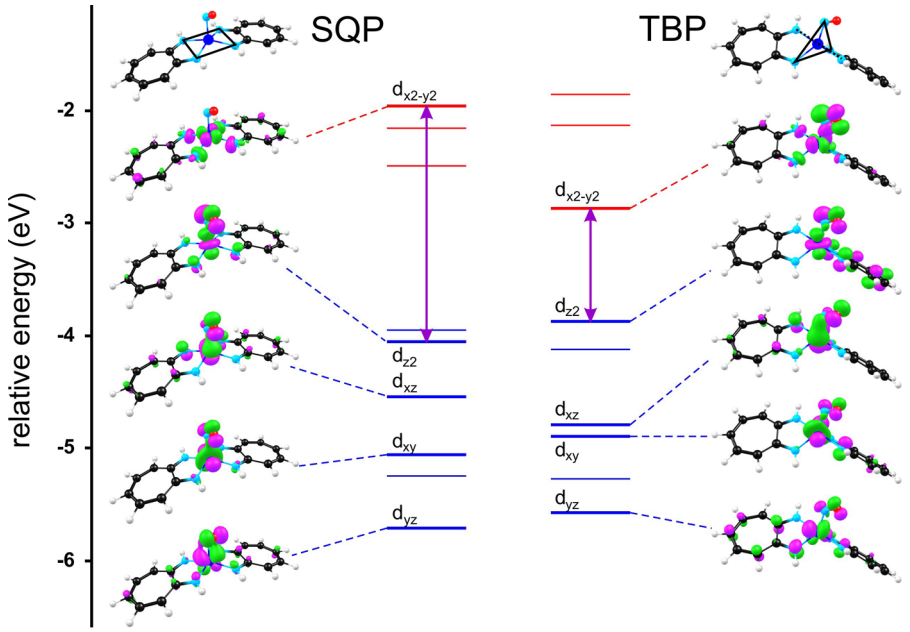


Figure 4. OLYP energy levels of the Co 3d-based MOs of limiting SQP and TBP forms of $[Co(ATI)_2(NO)]$. All internal coordinates were optimized except for Θ constrained to 45° in the TBP form of the complex.

Reinvestigation of [Co(TC-3,3)(NO)]. In view of the DFT results arguing for a reassignment of the ground state of [Co(TC-3,3)(NO)], we chose to reinvestigate this compound. Published procedures for the synthesis of both [Co(TC-3,3)(NO)] and its precursor [Co(TC-3,3)] are low-yielding and afford only small quantities of the desired materials. New synthetic procedures were therefore sought to improve the yield and scale of the older preparations. Reaction in tetrahydrofuran (THF) of CoI_2 with Na_2[TC-3,3], prepared in situ by deprotonation of the free ligand with $NaN(SiMe_3)_2$, afforded [Co(TC-3,3)] in 69% yield after crystallization from toluene. The reported $S = {}^1/_2$ ground state of [Co(TC-3,3)] was confirmed by solution magnetic susceptibility measurements (Evan's method) and by electron paramagnetic resonance (EPR) spectroscopy (Figure 1).[1d] Preparation of [Co(TC-3,3)(NO)] from [Co^{II}(TC-3,3)] and NO gas proceeded smoothly in CH_2Cl_2 to afford the desired compound as brown microcrystals after precipitation at −30 °C. With this new synthetic procedure, [Co(TC-3,3)(NO)] could be obtained on scales of ca. 50 mg with reproducible yields exceeding 60%. Use of ^{15}NO gas afforded the ^{15}N-labeled analogue in an identical fashion. The ^{1}H NMR spectrum of [Co(TC-3,3)(NO)] clearly demonstrates that the nitrosyl compound is diamagnetic, with apparent C_{2v} symmetry in solution (Figure 2), consistent with the DFT results. The low solubility of the complex in common organic solvents hindered attempts to collect ^{13}C and ^{15}N NMR spectra, although a weak resonance was identified in the 50.7 MHz ^{15}N NMR spectrum of [Co(TC-3,3)(^{15}NO)] at 1040 ppm (vs NH_3). We tentatively assign this peak as the nitrosyl nitrogen atom based on its chemical shift, which is in the range commonly encountered for $\{CoNO\}^8$ species.[10]

Molecular Orbital (MO) Considerations. Perhaps the most interesting conclusion from Table 1 is that the S−T gap of the complexes decreases monotonically as the linker length *n* increases from 3 to 6. Because the coordination geometry of the cobalt changes from nearly SQP for *n* = 3 to TBP for *n* = 5, 6, we chose to examine the energetics of the linker-free model complex $[Co(ATI)_2(NO)]$ (ATI = dianion of aminotroponimine) as a function of the NNNN dihedral, Θ, defined as the dihedral angle between the two five-membered aminotroponiminate chelate rings, shown in Figure 3. The data displayed in Figure 3 strongly indicate that, in the absence of steric constraints such as those imposed by the polymethylene linkers in tropocoronand ligands, $\{CoNO\}^8$ complexes exhibit a distinct preference for SQP coordination.

Figure 4 compares the energy levels of the Co 3d-based MOs for the limiting SQP and TBP geometries of this complex. For TBP geometry, the orbital energy of the $d_{x^2-y^2}$ orbital is significantly lower than that of the SQP geometry, resulting in a lower HOMO−LUMO gap for the former structure. This MO picture thus provides a plausible explanation for decreasing S−T gaps with increasing linker lengths (*n* = 3−6) in CoNO tropocoronand complexes.

Although such qualitative correlations can be deceptive, it is tempting to propose a connection between the calculated S−T gap and the NO reactivity of the CoNO tropocoronand complexes. Thus, the high S−T gap of [Co(TC-3,3)(NO)] appears consistent with its observed lack of reactivity toward excess NO.[11] By contrast, the other [Co(TC-*n*,*n*)(NO)] (*n* > 3) complexes, with much lower S−T gaps, all form $\{Co(NO)_2\}^{10}$ complexes upon treatment with excess NO. [Co(TC-6,6)(NO)], which has the lowest S−T gap, appears not to exist as a stable molecule.[5]

Structural Considerations. As shown in Table 2, the calculations do a fair job of reproducing the experimentally observed CoNO geometric parameters of [Co(TC-*n*,*n*)(NO)] for *n* = 3−5. The hybrid functionals B3LYP and B3LYP-D3 overestimate the Co−N distance by up to 0.06 Å, whereas the pure functionals PW91 and OLYP underestimate this distance by up to 0.07 Å. For [Co(TC-5,5)(NO)], all the functionals appear to overestimate the CoNO angle by about 10°. Although these errors are slightly on the high side, they are still within acceptable limits, given that we have not made any attempt to model the solid-state environments of the molecules in question.

DOI: 10.1021/acs.inorgchem.5b00901
Inorg. Chem. 2015, 54, 7362−7367

Table 2. Selected Optimized and Experimental Distances (Å) and Angles (deg)

complex	Co–N					N–O					Co–N–O				
	B3LYP	B3LYP-D3	PW91	OLYP	exp	B3LYP	B3LYP-D3	PW91	OLYP	exp	B3LYP	B3LYP-D3	PW91	OLYP	exp
[Co(TC-3,3)(NO)]	1.844	1.836	1.722	1.778	1.785(6)	1.170	1.170	1.189	1.184	1.137(7)	122.2	121.5	122.9	123.4	127.3(6)
[Co(TC-4,4)(NO)]	1.824	1.821	1.747	1.746	1.779(6)	1.188	1.189	1.194	1.188	1.151(9)	132.3	131.9	131.6	133.0	128.9(6)
										1.18(2)					134.9(9)
[Co(TC-5,5)(NO)]	1.799	1.790	1.702	1.708	1.7856(17)	1.183	1.182	1.191	1.186	1.177(2)	137.5	137.6	140.7	139.5	129.48(13)
[Co(TC-6,6)(NO)]	1.804	1.796	1.709	1.708		1.185	1.184	1.191	1.186		137.0	137.3	139.3	139.6	

The twist angle Θ (defined in Figure 3) provides a measure of TBP distortion relative to a SQP base geometry. For the experimental [Co(TC-*n*,*n*)(NO)] structures, the Θ value is 0°, 34.4°, and 35.4° for n = 3, 4, and 5, respectively. For the B3LYP [Co(TC-*n*,*n*)(NO)] structures, Θ is 0°, 37.9°, 55.2°, and 53.5° for n = 3, 4, 5, and 6, respectively; the values obtained from all the other functionals are also very similar. Although the calculations do not reproduce the observed dihedrals quantitatively, the trend is correct and, as mentioned above, the S−T gaps correlate with the reactivity of the CoNO complexes.

Triplet States. Finally, a brief word is warranted on the open-shell states of the various complexes. Figure 5 depicts the B3LYP/6-311G(d,p) spin density profiles for the S_0 (broken-symmetry), T_1, and T_2 states of [Co(TC-6,6)(NO)], which we chose as a representative example, and Table 3 presents the Mulliken spin populations for the T_1 and T_2 states of all four CoNO complexes. We encourage the interested reader to verify that spin populations in Table 3 are consistent with the qualitative descriptions of the T_1 and T_2 states given above.

CONCLUSIONS

In summary, we have confirmed that [Co(TC-3,3)(NO)] is not paramagnetic, as originally stated, but diamagnetic and S = 0 like other {CoNO}^{8} species. Our calculations do, however, raise the possibility of low-energy S = 1 states for TBP {CoNO}^{8} complexes with an equatorial NO. For [Co(TC-6,6)(NO)], which has thus far eluded isolation, the S−T gap may be so low as to allow a thermally accessible triplet state. Such a state might then allow for reaction pathways that are energetically inaccessible for the other CoNO tropocoronand complexes.

EXPERIMENTAL SECTION

Computational Details. All calculations were carried out with the *Gaussian 09*[12] program system. Two pure functionals, PW91[13] and OLYP,[14,15] and the hybrid functionals B3LYP (20% Hartree−Fock exchange)[16] and the dispersion-corrected B3LYP-D3[17] were used, all with the 6-311G(d,p) basis set. Selected calculations were also repeated with STO-TZP basis sets using the *ADF 2012* program system. Fine meshes for numerical integration of matrix elements and tight criteria (opt = tight) for geometry optimizations were used throughout. All optimized geometries were confirmed as true minima by a frequency analysis. Furthermore, multiple starting geometries were examined for each molecule, and the reported structural parameters refer to the global minima; in no case did we find an alternate minimum of comparable energy.

General Comments. Manipulations of air- and moisture-sensitive materials were performed under an atmosphere of nitrogen gas using standard Schlenk techniques or in an MBraun glovebox under an atmosphere of purified nitrogen. Tetrahydrofuran (THF), pentane, dichloromethane, and toluene were purified by passage through activated alumina and then stored over 4-Å molecular sieves. 2-MeTHF was vacuum-distilled from sodium ketyl. Benzene-d_6 and dichloromethane-d_2 were dried over sodium ketyl and calcium hydride, respectively, and then vacuum-distilled prior to use.

Materials. The tropocoronand ligand H_2(TC-3,3) was prepared according to the published procedure.[18,19] CoI_2 and Na{N(SiMe$_3$)$_2$} were purchased from commercial suppliers and used as received. Nitric oxide (Matheson, 99%) was purified by passage through an Ascarite column (NaOH fused on silica gel) and a 6-ft coil filled with silica gel cooled to −78 °C. ^{15}N-labeled NO gas was purchased from Cambridge Isotope Laboratories and used as received. NO(g) and ^{15}NO(g) were stored and transferred under an inert atmosphere using standard gas storage bulbs and gastight syringes, respectively.

DOI: 10.1021/acs.inorgchem.5b00901
Inorg. Chem. 2015, 54, 7362−7367

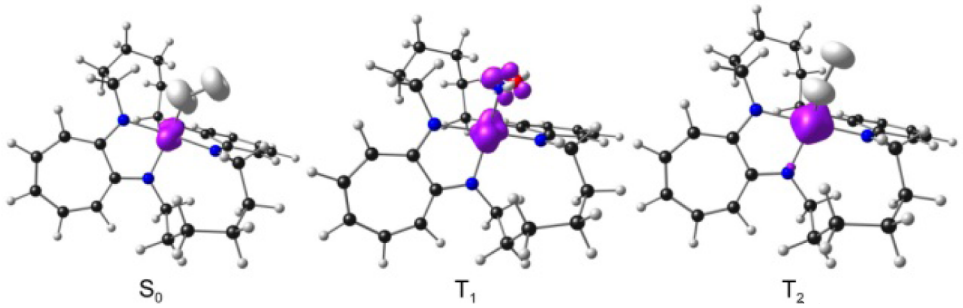


Figure 5. B3LYP/6-311G(d,p) spin density profiles (contour 0.03 e/Å^3) for the S_0 (broken-symmetry), T_1, and T_2 states of [Co(TC-6,6)(NO)].

Table 3. Selected Mulliken Spin Populations

		Co				N				O			
complex	state	B3LYP	B3LYP-D3	PW91	OLYP	B3LYP	B3LYP-D3	PW91	OLYP	B3LYP	B3LYP-D3	PW91	OLYP
[Co(TC-3,3)(NO)]	T_1	0.935	0.922	0.832	0.890	0.761	0.768	0.964	0.755	0.401	0.408	0.394	0.378
	T_2	2.636	2.627	1.726	2.127	−0.581	−0.590	−0.117	−0.299	−0.511	−0.528	−0.147	−0.283
[Co(TC-4,4)(NO)]	T_1	1.334	1.335	1.295		0.349	0.343	0.165		0.143	0.139	0.077	
	T_2	2.615	2.601		1.960	−0.600	−0.596		−0.257	−0.510	−0.507		−0.240
[Co(TC5,5)(NO)]	T_1	0.910	0.766	1.113	1.468	0.580	0.660	0.318	0.112	0.380	0.466	0.213	0.048
	T_2	2.580	2.546		1.799	−0.583	−0.566		−0.088	−0.478	−0.463		−0.114
[Co(TC-6,6)(NO)]	T_1	1.520	1.456	1.171	1.550	0.219	0.254	0.286	0.067	0.076	0.102	0.186	0.022
	T_2	2.585	2.555		1.876	−0.570	−0.561		−0.134	−0.471	−0.461		−0.146

Caution! *Nitric oxide is a toxic gas that reacts rapidly with the ambient atmosphere. It must be handled under inert conditions in a properly ventilated area such as a glovebox or fume hood.*

Physical Measurements. ^{1}H NMR spectra were recorded on a Varian INOVA spectrometer operating at 500 MHz. Solution magnetic susceptibility measurements were determined by the Evans method without a solvent correction. Fourier transform infrared spectra were recorded with a ThermoNicolet Avatar 360 spectrophotometer running the *OMNIC* software; solid samples were pressed into KBr disks, and solution samples were prepared in CH_2Cl_2 in an airtight Graseby-Specac solution cell with CaF_2 windows and 0.1 mm spacers. UV−vis spectra were recorded on a Cary-50 spectrophotometer in airtight Teflon-capped quartz cells. X-band EPR spectra were recorded on a Bruker EMX spectrometer. Temperature control was maintained with a quartz finger dewar (77 K). Spectra were recorded in 4-mm-o.d. quartz EPR tubes capped with a tight-fitting rubber septum. Electrochemical measurements were performed at 25 °C on a VersaSTAT3 Princeton Applied Research potentiostat running the *V3-Studio* electrochemical analysis software. A three-electrode setup was employed comprising a glassy carbon working electrode, a platinum wire auxiliary electrode, and a silver wire quasi-reference electrode. Thrice-recrystallized Bu_4NPF_6 was used as the supporting electrolyte. All electrochemical data were referenced internally to the ferrocene/ferrocenium couple at 0.00 V. Elemental analyses were performed by Midwest Microlab, LLC, Indianapolis, IN.

[Co^{II}(TC-3,3)]. To a suspension of 0.883 g (2.75 mmol) of H_2(TC-3,3) in 20 mL of THF was added dropwise a solution of 1.112 g (6.06 mmol, 2.2 equiv) of $NaN(SiMe_3)_2$ in 20 mL of THF. Upon addition of the base, the initial yellow suspension became a homogeneous red-orange solution. This solution was allowed to stir for 10 min at ambient temperature before a suspension of 0.904 g (3.01 mmol, 1.1 equiv) of CoI_2 in 20 mL of THF was added. The resulting dark-green mixture was allowed to stir for an additional 60 min at ambient temperature. All volatiles were removed in vacuo, and the dark green-brown residue was extracted into 70 mL of warm (80 °C) toluene. While still warm, the solution was filtered to remove NaI. The solution volume was then reduced in vacuo to 25 mL, at which point a dark-green microcrystalline solid precipitated. The solid was collected by filtration and washed with toluene and pentane. Concentration of the mother liquor to ∼15 mL afforded a second crop of dark-green microcrystals. Total mass: 0.718 g (69%). UV−vis spectra of the material were identical with published values.[19] ^{1}H NMR (500 MHz, C_6D_6): δ 47.1, 29.8, −80.8, −116; μ_{eff} = 1.8 μ_B. CV (CH_2Cl_2, glassy carbon, 0.2 M Bu_4NPF_6): $E_{1/2}$ = −0.480 V. EPR (9.335 GHz, 2-MeTHF, 77 K): g_1 = 2.86, g_2 = 2.07, g_3 = 1.93.

[Co(TC-3,3)(NO)]. A flask containing a solution of 77.2 mg (0.205 mmol) of [Co^{II}(3,3-T,C)] in 20 mL of CH_2Cl_2 was sealed with a septum cap and treated with 15.0 mL (0.61 mmol, 3 equiv) of NO gas via syringe. The contents of the flask were mixed briefly by swirling the flask by hand. An immediate color change from dark green to brown occurred. The flask was allowed to stand at −30 °C for 20 h, during which time a brown microcrystalline solid precipitated. The solid was collected by filtration, washed with CH_2Cl_2, and dried in vacuo. Mass: 52.9 mg (63%). ^{1}H NMR (500 MHz, CD_2Cl_2): δ 6.91 (app t, 4H), 6.57 (d, 4H), 6.15 (t, 2H), 3.48 (dt, 4H), 3.09 (td, 4H), 1.98 (dp, 2H), 1.64 (qt, 2H). IR (KBr, cm^{-1}): 2918, 2825, 1597 (ν_{NO}), 1583, 1505, 1484, 1483, 1452, 1433, 1411, 1400, 1364, 1349, 1273, 1228, 1189, 1146, 1100, 1036, 1015, 987, 961, 887, 727, 505. IR (CH_2Cl_2, cm^{-1}): 1612 (ν_{NO}). UV−vis [CH_2Cl_2; λ_{max}, nm (ε, M^{-1} cm^{-1})]: 279 (43000), 346 (28000), 415 (22000), 676 (4000). CV (CH_2Cl_2, glassy carbon, 0.2 M Bu_4PF_6): $E_{1/2}$ = −0.258. Anal. Calcd for $C_{20}H_{22}CoN_5O$: C, 58.97; H, 5.44; N, 17.19. Found: C, 58.65; H, 5.46; N, 16.90.

[Co(3,3-T,C)(^{15}NO)] was prepared analogously as that above from ^{15}NO gas. IR (CH_2Cl_2, cm^{-1}): 1576 (ν_{NO}), $\Delta\nu_{NO}$ = 36 cm^{-1}. ^{15}N NMR (50.7 MHz, CH_2Cl_2): δ 1040 (vs NH_3).

■ ASSOCIATED CONTENT

Supporting Information

Additional spectra of [Co(TC-3,3)(NO] and optimized Cartesian coordinates of all cobalt nitrosyls. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b00901.

DOI: 10.1021/acs.inorgchem.5b00901
Inorg. Chem. 2015, 54, 7362−7367

AUTHOR INFORMATION

Corresponding Authors

*E-mail: lippard@mit.edu.
*E-mail: abhik@chem.uit.no.

Author Contributions

§These authors contributed equally to this work.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the Research Council of Norway (A.G.), the South African National Research Foundation (J.C.), the US National Science Foundation (S.J.L.), and an NIH postdoctoral fellowship (1 F32 GM082031-03 to Z.J.T.). We thank Mik Minier for helpful discussions.

REFERENCES

(1) Selected examples: (a) Zask, A.; Gonnella, N.; Nakanishi, K.; Turner, C. J.; Imajo, S.; Nozoe, T. *Inorg. Chem.* **1986**, *25*, 3400−3407. (b) Jaynes, B. S.; Ren, T.; Liu, S.; Lippard, S. J. *J. Am. Chem. Soc.* **1992**, *114*, 9670−9671. (c) Jaynes, B. S.; Ren, T.; Masschelein, A.; Lippard, S. J. *J. Am. Chem. Soc.* **1993**, *115*, 5589−5599. (d) Jaynes, B. S.; Doerrer, L. H.; Liu, S.; Lippard, S. J. *Inorg. Chem.* **1995**, *34*, 5735−5744. (e) Doerrer, L. H.; Bautista, M. T.; Lippard, S. J. *Inorg. Chem.* **1997**, *36*, 3578−3579. (f) Doerrer, L. H.; Lippard, S. J. *Inorg. Chem.* **1997**, *36*, 2554−2563. (g) Scott, M. J.; Lippard, S. J. *J. Am. Chem. Soc.* **1997**, *119*, 3411−3412. (h) Scott, M. J.; Lippard, S. J. *Organometallics* **1998**, *17*, 466−474.

(2) Selected examples: (a) Franz, K. J.; Lippard, S. J. *J. Am. Chem. Soc.* **1999**, *121*, 10504−10512; Addition/Correction: *J. Am. Chem. Soc.* **2001**, *123*, 1266−1266. (b) For a theoretical study, see: Tangen, E.; Conradie, J.; Ghosh, A. *Inorg. Chem.* **2005**, *44*, 8699−8706.

(3) Selected examples: (a) Franz, K. J.; Lippard, S. J. *J. Am. Chem. Soc.* **1998**, *120*, 9034−9040. (b) For a theoretical study, see: Tangen, E.; Conradie, J.; Franz, K. J.; Friedle, S.; Telser, J.; Lippard, S. J.; Ghosh, A. *Inorg. Chem.* **2010**, *49*, 2701−2705.

(4) Franz, K. J.; Doerrer, L. H.; Spingler, B.; Lippard, S. J. *Inorg. Chem.* **2001**, *40*, 3774−3780.

(5) CoNO porphyrins are diamagnetic, with no indication of a thermally accessible paramagnetic state: (a) Ellison, M. K.; Scheidt, W. R. *Inorg. Chem.* **1998**, *37*, 382−383. (b) Jaworska, M. *Chem. Phys.* **2007**, *332*, 203−210.

(6) Selected examples: (a) Kozhukh, J.; Lippard, S. J. *J. Am. Chem. Soc.* **2012**, *134*, 11120−11123. (b) Kozhukh, J.; Lippard, S. J. *Inorg. Chem.* **2012**, *51*, 9416−9422.

(7) Reviews on quantum-chemical studies on nitrosyls: (a) Enemark, J. H.; Feltham, R. D. *Coord. Chem. Rev.* **1974**, *13*, 339−406. (b) Ghosh, A.; Hopmann, K. H.; Conradie, J. In *Computational Inorganic and Bioinorganic Chemistry*; Solomon, E. I., Scott, R. A., King, R. B., Eds.; John Wiley & Sons Ltd: Chichester, U.K., 2009; pp 389− 410. (c) Goodrich, L. E.; Paulat, F.; Praneeth, V. K. K.; Lehnert, N. *Inorg. Chem.* **2010**, *49*, 6293−6316.

(8) Selected examples: (a) Richter-Addo, G. B.; Legzdins, P. *Metal Nitrosyls*; Oxford University Press, New York, 1992; pp 353−384. (b) Wyllie, G. R. A.; Scheidt, W. R. *Chem. Rev.* **2002**, *102*, 1067−1090. (c) Huie, B. T.; Brant, P.; Feltham, R. D. *Inorg. Chim. Acta* **1978**, *29*, L221−L222.

(9) Representative comparative studies of functionals: (a) Reiher, M.; Salomon, O.; Artur Hess, B. *Theor. Chem. Acc.* **2001**, *107*, 48−55. (b) Salomon, O.; Reiher, M.; Hess, B. A. *J. Chem. Phys.* **2002**, *117*, 4729−4737. (c) Ghosh, A.; Taylor, P. R. *Curr. Opin. Chem. Biol.* **2003**, *7*, 113−124. (d) Conradie, J.; Swarts, J. C.; Ghosh, A. *J. Phys. Chem. B* **2004**, *108*, 452−456. (e) Swart, M.; Ehlers, A. W.; Lammertsma, K. *Mol. Phys.* **2004**, *102*, 2467−2474. (f) Conradie, J.; Ghosh, A. *J. Phys. Chem. B* **2007**, *111*, 12621−12624. (g) Hopmann, K. H.; Conradie, J.; Ghosh, A. *J. Phys. Chem. B* **2009**, *113*, 10540−10547. (h) Conradie, M. M.; Conradie, J.; Ghosh, A. *J. Inorg. Biochem.* **2011**, *105*, 84−91.

(10) Duffin, P. A.; Larkworthy, L. F.; Mason, J.; Stephens, A. N.; Thompson, R. M. *Inorg. Chem.* **1987**, *26*, 2034−2040.

(11) The B3LYP and B3LYP-D3 S−T gaps for [Co(TC-3,3)(NO)] are very similar to those calculated for the porphyrin complex [Co(Por)(NO)] (0.40 for B3LYP and 0.42 for B3LYP-D3), which is understandable, given that both are SQP, essentially C_s complexes.

(12) Frisch, M. J.; et al. *Gaussian 09*, revision C.01; Gaussian, Inc.: Wallingford, CT, 2010.

(13) (a) Perdew, J. P.; Chevary, J. A.; Vosko, S. H.; Jackson, K. A.; Pederson, M. R.; Singh, D. J.; Fiolhais, C. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1992**, *46*, 6671−6687. Erratum: Perdew, J. P.; Chevary, J. A.; Vosko, S. H.; Jackson, K. A.; Pederson, M. R.; Singh, D. J.; Fiolhais, C. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1993**, *48*, 4978.

(14) The OPTX exchange functional: Handy, N. C.; Cohen, A. *Mol. Phys.* **2001**, *99*, 403−412.

(15) The LYP correlation functional: Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1988**, *37*, 785−789.

(16) Stephens, J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623−11627.

(17) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. *J. Chem. Phys.* **2010**, *132*, 154104.

(18) Zask, A.; Gonnella, N.; Nakanishi, K.; Turner, C. J.; Imajo, S.; Nozoe, T. *Inorg. Chem.* **1986**, *25*, 3400−3407.

(19) Jaynes, B. S.; Doerrer, L. H.; Liu, S.; Lippard, S. J. *Inorg. Chem.* **1995**, *34*, 5735−5744.

DOI: 10.1021/acs.inorgchem.5b00901
Inorg. Chem. 2015, 54, 7362−7367