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A Structurally Characterized Nitrous Oxide Complex of Vanadium

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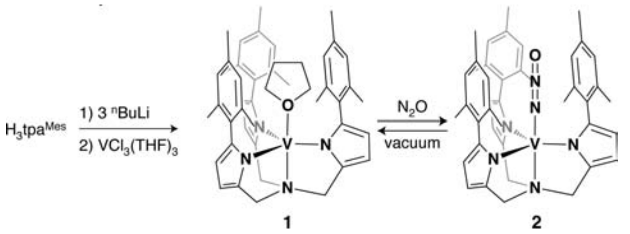
Supporting Information

ABSTRACT: Nitrous oxide (N_2O), a widespread greenhouse gas, is a thermodynamically potent and environmentally green oxidant that is an attractive target for activation by metal centers. However, N_2O remains underutilized owing to its high kinetic stability, and the poor ligand properties of this molecule have made well-characterized metal−N_2O complexes a rarity. We now report a vanadium−pyrrolide system that reversibly binds N_2O at room temperature and provide the first single-crystal X-ray structure of such a complex. Further characterization by vibrational spectroscopy and DFT calculations strongly favor assignment as a linear, N-bound metal−N_2O complex.

Nitrous oxide (N_2O) is a major greenhouse gas that is 300 times more powerful than CO_2 on a per molecule basis[1] and remains the number one emission contributing to ozone depletion in the 21st century.[2] This molecule is an appealing oxidant owing to its thermodynamic potency and environmentally friendly nature, as oxygen atom transfer (OAT) releases N_2 as the sole byproduct; however, efforts to utilize N_2O as an oxygen-transfer oxidant are hindered by its high kinetic stability.[3] Select transition and f-block metal complexes have been shown to activate N_2O toward OAT[4−10] or to insert N_2O into metal−ligand bonds[11] and, in one case, to cleave the N−N bond.[12] But while phosphine-activated N_2O adducts have been captured with various Lewis acids,[13] well-defined metal−N_2O complexes remain exceedingly rare owing to the poor ligand characteristics of this small molecule, including its low dipole moment and weak σ-donor and π-acceptor properties.[3b] Indeed, since Armor and Taube's initial report of the first metal−N_2O complex,[14] to our knowledge only one other discrete metal−N_2O compound has been reported,[15] and neither species has been characterized by single-crystal X-ray diffraction. We now report a three-fold symmetric vanadium−pyrrolide platform that reversibly binds N_2O at room temperature and the single-crystal X-ray structure of this well-defined vanadium−N_2O complex. Further studies support that N_2O binds this vanadium system in a linear, N-bound fashion.

Our strategy for promoting N_2O binding to a single metal site involves creating a Lewis acidic center with π-backbonding ability but only mild reducing character. In this context, we have been exploring complexes bearing pyrrolide ligands, which have relatively low basicity and poor π-donating abilities as compared to alkyl and amido congeners. Previous work from our laboratory described the activation of N_2O using Fe(II) centers supported by substituted tris(pyrrolylmethyl)amine (tpa) ligands,[6e] and we reasoned that early-metal analogues would afford more electron-deficient centers that might stabilize metal−N_2O adducts. To this end, we installed the trispyrrolide ligand $[\mathrm{tpa}^{\mathrm{Mes}}]^{3-}$ onto vanadium(III) by first treating $H_3\mathrm{tpa}^{\mathrm{Mes}}$ with 3.05 equiv of *n*-butyllithium in Et_2O and then adding a solution of the resulting $Li_3(\mathrm{tpa}^{\mathrm{Mes}})$ salt to a thawing, stirring suspension of $VCl_3(THF)_3$ in Et_2O (Scheme 1). This treatment results in a color change to orange-yellow, and after the mixture is warmed to room temperature and stirred for several hours, the LiCl is removed by successive extractions with Et_2O/*n*-pentane mixtures.[16] This procedure affords the THF adduct of $(\mathrm{tpa}^{\mathrm{Mes}})V$ as an orange powder in 70% yield. A single-crystal X-ray diffraction study reveals a trigonal bipyramidal coordination environment for $(\mathrm{tpa}^{\mathrm{Mes}})V(THF)$ (**1**), where THF is bound in the apical pocket supported by the three mesityl arms of the ligand (Supporting Information, Figure S1). At room temperature, complex **1** shows no distinguishable ^1H NMR signals and displays a μ_{eff} of 2.89(7) μ_B (Evans's method)[17] that is consistent with an $S = 1$ ground state, where the two unpaired electrons are expected to reside in the nonbonding, degenerate d_{xz} and d_{yz} orbitals in the C_3 field. The observation that THF binds to the metal center in **1** is noteworthy as it suggests a high degree of Lewis acidity at vanadium; in contrast, trigonal monopyramidal vanadium complexes of the type $V[(N(R)CH_2CH_2)_3N]$, bearing more electron-donating trisamidoamine ligands, do not appreciably coordinate THF.[6a]

Scheme 1. Synthesis of 1 and Its Reaction with N_2O To Form 2



Addition of 1 atm of N_2O to an Et_2O solution of **1** triggers a prompt color change from the orange color of $(\mathrm{tpa}^{\mathrm{Mes}})V(THF)$ to yellow, along with precipitation of a yellow powder. This solid is isolated by filtration, and analysis by IR spectroscopy reveals a strong absorption at 2289 cm^{-1}, indicative of an NNO stretch (Figure 1). The new species is NMR silent, and measurement of its susceptibility by SQUID magnetometry confirmed that an $S = 1$ ground state is maintained. Accordingly, we assign this complex as the monometallic N_2O adduct $(\mathrm{tpa}^{\mathrm{Mes}})V(N_2O)$ (**2**, Scheme 1).

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In initial attempts to preparatively synthesize the vanadium—N_2O complex **2**, we noticed that application of vacuum to solutions of **2** returned the orange color of **1**. To further probe the potential reversibility of N_2O binding to the (tpa^{Mes})V platform, we turned to *in situ* solution IR spectroscopy measurements. Upon introduction of N_2O to a toluene solution of **1**, we observed a distinct IR absorption at 2295 cm^{-1}; when vacuum was applied to this solution, this absorption, along with the absorption for dissolved N_2O, diminished. Reintroduction of N_2O regenerated the peak associated with the formation of **2**, and reapplication of vacuum again caused this absorption to vanish (Supporting Information, Figure S2). In contrast, when solid samples of **2** were subjected to vacuum for *ca.* 18 h, the N_2O absorption at 2289 cm^{-1} remained prominent. These experiments establish that N_2O binding to the (tpa^{Mes})V system in solution is reversible at room temperature.

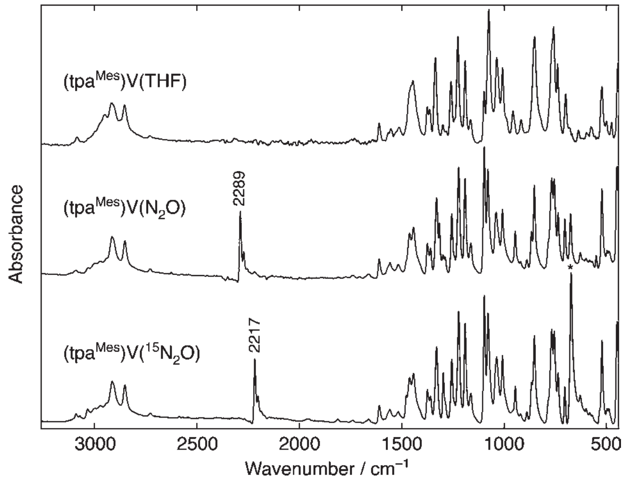

Figure 1. IR spectra of **1**, **2**, and **2**-^{15}N reveal the prominent NNO stretch of **2** that shifts upon ^{15}N-labeling (an asterisk indicates the position of residual benzene).

Table 1. Comparison of Experimental and Calculated Structures and Vibrational Energies^a for 2 and Free N_2O

	2 (exptl)	**2** (calcd)	N_2O (exptl)
r(V—N)/Å	2.139(1)	2.14	—
r(N—N)/Å	1.119(2)	1.13	1.128
r(N—O)/Å	1.187(2)	1.18	1.184
∠(V—N—N)/°	176.7(1)	179.8	—
ν_1/cm^{-1}	1315 (1297)^b	1313 (1297)^b	1286 (1266)^{b,c}
ν_3/cm^{-1}	2289 (2217)^b	2335 (2261)^b	2224 (2156)^{b,c}
ν_2/cm^{-1}	551 (534)^b	536 (520)^b	589 (572)^{b,c}

[a] All vibrational energies output from calculations have been scaled by a factor of 0.96. [b] Values in parentheses are those for the $^{15}N_2O$ isotopomer [c] Values are taken from ref 21.

To provide additional support for the assignment of **2** as a metal—N_2O complex, we conducted a more detailed vibrational analysis. Specifically, we synthesized the isotopically labeled $^{15}N_2O$ complex (tpa^{Mes})V($^{15}N_2O$) (**2**-^{15}N) in a manner similar to that used for the unlabeled species and acquired IR spectra on solid samples of both **2** and **2**-^{15}N. Upon ^{15}N incorporation, the ν_3 vibration of the N_2O ligand in **2** shifts from 2289 to 2217 cm^{-1} (Figure 1). Comparison of the two sets of data also allowed us to assign the ν_1 vibration of the NNO oscillator to an absorption at 1315 cm^{-1} in **2** that shifts to 1297 cm^{-1} for **2**-^{15}N (Supporting Information, Figure S3). The magnitudes of the isotopic shifts establish that the higher energy band is predominantly N—N in character, whereas the lower energy band is largely N—O in character. The energies of the N_2O modes for these complexes and for free N_2O are collected in Table 1. Interestingly, we observe that both the ν_1 and ν_3 vibrations of N_2O shift to higher energies upon metal binding, which is counter to expectations that π-backbonding might reduce the energy of at least one of these modes, as seen for Taube's $[(H_3N)_5Ru(N_2O)]^{2+}$ complex.[14] However, N_2O adsorbed onto zeolites is reported to raise the energy of both modes when the molecule binds through its nitrogen atom.[18] In addition, the ν_2 N_2O bending mode was also identified from the labeling study, and its energies are listed in Table 1.

We next confirmed that **2** is a well-defined metal—N_2O complex by single-crystal X-ray analysis. Single crystals of **2** suitable for X-ray diffraction were grown under an atmosphere of N_2O by vapor diffusion of diisopropyl ether into a toluene solution of **2**. The structure of the (tpa^{Mes})V(N_2O) complex **2** confirms that the NNO ligand coordinates in a linear fashion within the apical pocket of the (tpa^{Mes})V platform (Figure 2a). Lehnert and Bottomley both refer to the linear coordination mode of the NNO ligand as a signature of an N-bound isomer.[19] We also assign the coordination mode of N_2O as N-bound to the metal on the basis of the observed interatomic distances and supporting DFT calculations (*vide infra*). Moreover, as the IR data do not reflect marked activation of the N_2O molecule, the N—N linkage is expected to be the shorter of the two interatomic

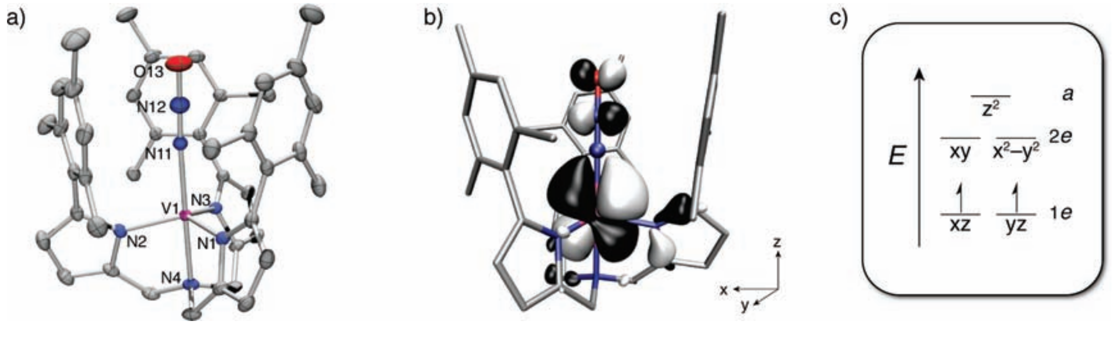

Figure 2. (a) Single-crystal X-ray structure of **2** with thermal ellipsoids plotted at 50% and hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): V1—N11, 2.1389(10); N11—N12, 1.1191(16); N12—O13, 1.1869(17); V1—N4, 2.1165(10); V1—N11—N12, 176.73(11). (b) One of the two degenerate SOMOs calculated for **2**, plotted at an isovalue of 0.02. (c) A d-orbital splitting diagram for the three-fold symmetric (tpa^{Mes})V platform, showing the half-filled, π-backbonding d_{xz}/d_{yz} orbitals in the C_3 field.

distances, as observed in free N_2O. The two other reported examples of well-characterized monometallic N_2O complexes, both on ruthenium, have been assigned as N-bound isomers.[15,19] The N-bound nature of the ligand and the steric protection of the ligand "pickets" are likely contributing factors in preventing vanadium(V)−oxo formation.

As a further probe into the binding mode of N_2O in complex **2**, we carried out DFT calculations using the crystallographically determined structure as a basis for geometry optimization.[20] When the N-bound isomer was utilized as a starting point, the structure converged on a geometry that agreed well with the input (Table 1). However, when the binding of N_2O to the vanadium center was switched to O-bound *in silico*, the N_2O ligand took on a significant bend at the oxygen atom (144°), and the bond lengths converged on a structure in which the N−O and N−N distances again resemble those in free N_2O and are not consistent with the observed crystallographic data (Supporting Information, Table S2).

The calculated vibrational frequencies for each isomer alone are inconclusive, but when free N_2O is calculated using the same computational method, the picture becomes clearer. The differences between the experimental and calculated values for free N_2O are nearly identical to the differences between the experimental data on **2** and those calculated for the N-bound isomer (Table S2). Therefore, we assign these deviations to a systematic error in the calculation and continue to favor an N-bound assignment based on all available experimental and computational data. Finally, from the DFT calculations, we confirmed the electronic structure of **2** and visualized the critical bonding orbitals. In the three-fold symmetric field provided by the $(\text{tpa}^{\text{Mes}})$V platform, the d_{xz} and d_{yz} orbitals of vanadium hold the two unpaired electrons of **2**, which backbond weakly into the degenerate π^* orbitals of the N_2O ligand (Figure 2b,c). The lone pair of N_2O contributes to the bonding combination of all nitrogen lone pairs around the metal into d_{z^2} that falls as the HOMO−4. We suggest that the three-fold symmetric environment provides a key factor in stabilizing the putative d^2 metal−N_2O adduct, as distortions to lower symmetries will weaken these π-accepting interactions.

In conclusion, we have presented the synthesis of a unique vanadium complex that reversibly binds N_2O at room temperature, the single-crystal X-ray structure of this well-defined monometallic N_2O complex, and vibrational and DFT studies to support its assignment as an N-bound metal−N_2O adduct. Efforts to use $(\text{tpa}^{\text{Mes}})$V($N_2O$) and related species as a source of activated N_2O in stoichiometric and catalytic oxidation reactions are currently underway.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental details, details on DFT calculations, supporting figures, and complete ref 20; X-ray structure information in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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