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Side-on Coordination in Isostructural Nitrous Oxide and Carbon

Dioxide Complexes of Nickel

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In memoriam: Professor Suning Wang

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Abstract: A nickel complex incorporating an N₂O ligand with a rare η^2 -*N*,*N'*-coordination mode was isolated and characterized by X-ray crystallography, as well as by IR and solid-state NMR augmented by ¹⁵N-labeling experiments. The isoelectronic nickel CO₂ complex reported for comparison features a very similar solid-state structure. Computational studies revealed that η^2 -N₂O binds to nickel slightly stronger than η^2 -CO₂ in this case, and comparably to or slightly stronger than η^2 -CO₂ to transition metals in general. Comparable transition state energies for the formation of isomeric η^2 -*N*,*N'*- and η^2 -*N*,O-complexes, and a negligible activation barrier for the decomposition of the latter likely account for the limited stability of the N₂O complex.

Among the numerous oxides of nitrogen, nitrous oxide (N₂O) is most intimately intertwined with modern human activities. It figures on the WHO's List of Essential Medicines for use in pain management,¹ and it also has a long history as a recreational drug dubbed "laughing gas".² It is used as an oxidant ("nitrous") in racing engines and is a suitable propellant in rockets,³ as well as in whipped cream and cooking oil canisters. Industrially, N₂O is an important by-product in nitric acid and adipic acid manufacturing.⁴ Although industrial pollutants are not to be neglected, natural, enzymatic denitrification processes⁵ are the main source of N₂O in the environment and for this reason the gas was proposed to be part of the biosignature of life on exoplanets.⁶ The widespread use of nitrogen fertilizers led to an enhancement of denitrification processes and N₂O rose to prominence as a greenhouse gas 300 times more potent than CO₂, and "the dominant ozone-depleting substance emitted in the 21st Century". ⁷ Although its decomposition into elements is thermodynamically favorable ($\Delta_{\rm f} {\rm H}^{\circ}_{\rm gas}$ 82.1 kJ mol⁻¹), the high activation barrier (250 kJ mol-1)8 associated with this process

means that N₂O persists in the atmosphere for an average of 117(8) years.⁹ Consequently, interest towards using N₂O as a synthon,¹⁰ as well as towards catalyzing its decomposition into elements has increased in recent years,¹¹ in turn prompting investigations meant to elucidate the interaction of this prominent small molecule with metals.



Figure 1. Transition metal complexes of N₂O.

N₂O reacts readily with numerous metal complexes and organic substrates, mostly as an oxidant but also as a nitrogen atom donor,^{4,10} and can be trapped by frustrated Lewis pairs¹² and N-heterocyclic carbenes (NHCs).¹³ Its reactivity involving insertion into M-C and M-H bonds is well documented.^{10,14} In contrast to its isoelectronic counterpart CO₂, however, which has a rich coordination chemistry,¹⁵ N₂O has been generally described as a poor, or exceedingly poor ligand due to its weak σ-donating and π-accepting properties, low polarity, and oxidizing character.^{8b,16}

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Extensive investigations of ruthenium derivative A (Figure 1), which remained for more than three decades the only known metal complex of nitrous oxide, revealed that N₂O coordinated in a linear fashion via the terminal nitrogen and was a poor ligand susceptible to reduction and displacement.¹⁷ These conclusions were supported by computational studies,^{17c,18} the spectroscopic characterization of complex B, 19 as well as the NMR characterization of surface-coordinated N2O.20 Confirmation of these findings was provided over the last decade by the comprehensive characterization of discrete, end-on bonded complexes C, D and E. (Figure 1).^{21,22,23} The rich coordination chemistry of CO₂ suggests that the isoelectronic N₂O molecule should also be able to adopt a bent, N,N'-side-on coordination mode, which had been probed computationally for surface binding.²⁴ Linear N₂O bound at the [4Cu:2S] active site of nitrous oxide reductase has been shown to display long, side-on Cu-N contacts.²⁵ Ultimately, the first $\eta^2 - N_1 N_2 O$ complex **F**, which was persistent below -25 °C, was recently characterized and the πbasicity of the metal was shown to be key to its isolation.²⁶



Scheme 1. Synthesis of compounds 1-3 and 5, and the postulated, fleeting $\eta^2\text{-}\textit{N},\text{O-isomer}$ 4. Dipp = 2,6-diisopropylphenyl.

We reported on a bis(NHC)₂Ni⁰–GeCl₂ complex incorporating a (NHC)₂Ni⁰ fragment with a bent L₂M geometry.²⁷ Computational studies indicated that this fragment featured the frontier orbitals necessary for efficient η^2 -interactions with π -acidic ligands.^{28,18c} Thus, we hypothesized that a bis(NHC)₂ supported Ni⁰ would be an excellent candidate for stabilizing side-on, η^2 -N₂O complexes, especially taking into account the immunity of NHC ligands to oxidation. Design of ligand **1**, incorporating a shorter silane linker, aimed to impose a narrow C_{NHC}-Ni-C_{NHC} angle and increase the π -basicity of the metal.²⁹ This allowed us to characterize analogous η^2 -bound Ni⁰ complexes of N₂O and CO₂ and to assess the relative binding ability of the two ligands for the first time.



Figure 2. ^{15}N CP-MAS NMR spectrum of 3 containing 33% $^{15}N_2O,$ the latter prepared using an original method (see Supporting Information).

Prepared by deprotonation of its bis(imidazolium) precursor, ligand **1** reacted with Ni(cod)₂ to yield (**1**)Ni(η^2 -cod), **2**. Solution ¹H NMR analysis of **2** revealed a broad, complex spectrum denoting C_1 symmetry, reflected in the ¹³C NMR spectrum by the presence of two resonances for the coordinated carbene carbons (200.4 and 208.4 ppm). Reduced conformational fluxionality in complexes containing bis(NHC)Ni fragments was shown to lead to broad, poorly resolved resonances in the solution NMR spectra, as well as lowering of the expected time-averaged symmetry.²⁷ An X-ray diffraction experiment on **2** confirmed chelation of the ligand to Ni in a bent geometry (C1-Ni1-C8 107.9(1)°) (Figure S30) and the η^2 -coordination of 1,5-cyclooctadiene.

Table 1	I. Selected	¹⁵ N NMR	resonances for	free ar	nd bound N ₂ O
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Cpd.	N ₂ O ²⁶	B ¹⁹	D ^{[a],22}	D ^{[b],22}	F ²⁶	3	3 [c]
Solv.	tol-d ₈	CD ₂ Cl ₂	DFB ^[d]	DFB ^[d]	tol-d ₈	solid	gas
δN_{term}	135	126	109	103	159	312	313
δN _{cent}	218		245	246	309	365	395

[a] $E = CH_2$. [b] E = O. [c] computed. [d] DFB = 1,2-F₂C₆H₄.

In solution, complex **2** reacted with 1 atm of N₂O at room temperature to yield **3**, which was isolated as a yellow crystalline solid (Scheme 1). The low solubility of **3** precluded its characterization in solution. As a solid, it can be stored for months at -78 °C and handled at room temperature in vacuum or under an inert atmosphere, but partial decomposition is apparent after 12 hours at room temperature (by IR). Heating to 70 °C in THF leads to dissolution upon N₂ development (Figure S3). The ¹³C CP-MAS NMR spectrum of **3** (Figure S19) features two resonances corresponding to the coordinated carbene carbons at 183.7 and 192.5 ppm, similar to the values measured in solution for **2**.



Figure 3. Overlaid FT-IR spectra for 3 and 3-($^{15}N_2)$ (99% isotopically enriched) with spectral difference bellow.

The ¹⁵N CP-MAS NMR resonances for bound N₂O in an isotopically enriched sample of **3** were observed at 365 and 312 ppm (Figure 2), corresponding to the central and terminal nitrogen atoms in N₂O, respectively (vs. the gas phase computed values of 395 and 313 ppm). These values are significantly deshielded compared to those observed in the κ^1 -*N*- and the η^2 -*N*,*N'*-N₂O complexes, as well as those for free N₂O (Table 1). Resonances

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corresponding to the naturally abundant nitrogen atoms in the imidazole rings appear between 187.5-190.4 ppm, matching literature data for NHC ligands.³⁰ Infrared spectroscopy suggests that N₂O is side-on, η^2 -*N*,*N*'-coordinated in **3**. The observed v_{NN} stretching and v_{NNO} bending vibrations (Figure 3) at 1533 and 1138 cm⁻¹, respectively (vs. the gas phase computed values of 1725 and 1243 cm⁻¹, and the experimental values for **F** of 1624 and 1131 cm⁻¹) shift to lower frequencies (1495 and 1121 cm⁻¹) in ¹⁵N-enriched samples of **3**. The v_{NN} stretching vibration measured in **3** is the lowest value observed in N₂O metal complexes, both κ^1 -*N* (2234-2303 cm⁻¹ for v_{NN} and 1150-1337 cm⁻¹ for v_{NNO} in **A** – **E**) and η^2 -*N*,*N'*-N₂O (1624 cm⁻¹ for v_{NN} and 1131 cm⁻¹ for v_{NNO} in **F**), in agreement with the high π -basicity of the (**1**)Ni⁰ fragment and its strong interaction with the π^* system of N₂O.

X-ray crystallography revealed for **3** the expected, bent (**1**)Ni fragment (C-N-C 104.47(13)°) with the side-on, η^2 -*N*,*N*⁻ coordinated N₂O ligand completing the coordination sphere of nickel (Figure 4). The metric parameters characterizing the N₂O moiety (N5-N6 1.225(4) Å and N5-O1 1.276(4) Å) are consistent with the calculated values and compare well with the N-N bond length measured in **F** (1.212(8) Å). The nickel substituents are coplanar, with the plane of the N₂O ligand forming an angle of 8.4(3)° with the C_{NHC}NiC_{NHC} plane.

the energies are even greater, at 129 (74) kJ mol⁻¹. Furthermore, an energy decomposition analysis with ETS-NOCV revealed that the instantaneous interaction energies of L in (1)Ni(L) follow a similar trend, largely owing to the significantly stronger orbital interactions (in parathesis): -401 (-643) and -415 (-709) kJ mol⁻¹ for $L = CO_2$ and N_2O_1 , respectively. The total orbital interaction term can further be decomposed using NOCV, showing a dominant contribution (83 % for 3 and 84 % for 5) involving donation from the metal to the π^* system of the ligand. Taken as a whole, the results of the DFT calculations indicate that N₂O binds to (1)Ni⁰ slightly stronger than CO₂ due to stronger orbital interactions in 3. To probe whether the observed energetic trend is more general, the equilibrium TM-CO₂ + N₂O \Rightarrow TM-N₂O + CO₂ (TM = transition metal fragment) was analyzed computationally for 12 crystallographically characterized n²-C,O-CO₂ complexes and their hypothetical N₂O analogues. The data (Table S2) showed stronger binding for N₂O in 9 systems (up to 26 kJ mol⁻¹) demonstrating that when bound in η^2 -fashion, N₂O is a comparable or slightly better π -acceptor than CO₂. However, it needs to be stressed that N2O is oxidizing whereas CO2 is not, for which reason the increased binding energy in the hypothetical N₂O systems considered above is unlikely to stabilize n²-N.N-N₂O complexes over metal or ligand oxidation.



Figure 4. Solid-state structure of one of the two independent molecules of 3 with 50% thermal ellipsoids, and hydrogen atoms omitted. Selected bond lengths (Å) and angles (°) with [calculated values]: N5-N6 1.225(4) [1.210], N5-O1 1.276(4) [1.239], Ni1-N5 1.803(3) [1.821], Ni-N6 1.926(3) [1.910], Ni1-C1 1.901(3) [1.934], Ni1-C8 1.893(3) [1.919], N5-N6-O1 134.7(3) [138.4], C1-Ni1-C8 104.47(13) [107.7].

Aiming to provide a comparison for **3**, its CO₂ analog **5** was prepared by reaction of **2** with 1 atm of CO₂ in THF. The product was stable under an inert atmosphere and did not dissolve in hydrocarbon and ethereal solvents. The solid-state ¹³C NMR spectrum of **5** (Figure S21) is very similar to the spectrum of **3**, featuring two carbene resonances (188.2 and 192.2 ppm) and a resonance corresponding to the CO₂ ligand (167.3 ppm). A characteristic v_{CO} stretching vibration is observed in the IR spectrum of **5** at 1695 cm⁻¹ (*vs.* the gas phase computed value of 1855 cm⁻¹). The solid-state structure of **5** is very similar to that of **3** (Figure 5). The bond angles in the coordinated CO₂ and N₂O match closely (∠NNO 134.7(3) in **3** *vs.* ∠OCO 135.0(2)° in **5**) but differences are apparent in the bond distances to their terminal atoms (N5-O1 1.275(3) Å in **3** *vs.* C35-O2 1.217(3) Å in **5**).

A DFT computational comparison of the binding energies of L in (1)Ni(L) (with ΔG° in parenthesis) yielded values of 87 (33) and 110 (56) kJ mol⁻¹ for L = CO₂ and N₂O, respectively, while for a hypothetical complex of (1)Ni with the classic π -acceptor ethylene,



Figure 5. Solid-state structure of 5 with 50% thermal ellipsoids, and hydrogen atoms omitted. Selected bond lengths (Å) and angles (°) with [calculated values]: O1-C35 1.283(4) [1.264], C35-O2 1.218(4) [1.206], Ni1-O1 1.949(2) [1.937], Ni-C35 1.828(3) [1.839], Ni1-C1 1.973(3) [1.964], Ni1-C8 1.866(2) [1.856], O1-C35-O2 134.6(3) [137.5], C1-Ni1-C8 106.95(10) [109.4].

The energy landscape for the formation of **3** from (**1**)Ni⁰ and N₂O was also probed with computational methods (Figure S33). The results revealed that the formation of 3 involves a modest barrier $(\Delta G^{\ddagger} = 38 \text{ kJ mol}^{-1})$, with $\Delta G^{\circ} = -56 \text{ kJ mol}^{-1}$. The formation of the η^2 -O,N-N₂O isomer, 4, though not observed experimentally, was found to involve a greater barrier (ΔG^{\ddagger} = 70 kJ mol⁻¹) and a minute ΔG° of -2 kJ mol⁻¹. However, **4** appears to be a metastable species and readily converts to (1)NiO(N₂) almost without a barrier. Barrierless decomposition of η^2 -O,N-N₂O bound to iron has been investigated computationally and matched experimental observations.³¹ Thus, at a relative energy of -63 kJ mol⁻¹, $(1)NiO(N_2)$ represents the lowest energy point on the potential energy surface and confirms that metal-oxo formation is thermodynamically favored over η^2 -*N*,*N*-N₂O complex formation, albeit only by 7 kJ mol⁻¹. As suggested by the calculated energy landscape, 3, unlike 5, is a kinetic, not a thermodynamic, product, in agreement with its limited stability. Similarly, decomposition of F was reported to proceed via formation of a reactive metal-oxo species and transfer of oxygen to the ancillary isocyanide ligand.²⁶

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To summarize, employing the π -basic fragment (1)Ni, we isolated **3** by reaction of **2** with N₂O. The rare n^2 -*N*,*N*'-coordination mode of the N₂O ligand in 3 was proved by single-crystal X-ray crystallography, as well as ¹⁵N CP-MAS NMR and IR spectroscopy aided by ¹⁵N isotopic enrichment. The isostructural, n^2 -CO₂ complex **5** was also synthesized, allowing a direct comparison of the metal binding properties of the two isoelectronic small molecules of environmental relevance. Computational studies indicate that π -acceptance is the main contributor to N₂O binding in **3**, and place the η^2 -N,N'-metal binding ability of this ligand to the (1)Ni fragment in-between that of CO₂ and ethylene. In general, the n^2 -N,N'-binding ability of N₂O to transition metals is found to be comparable to, or slightly better than that of CO_2 . This demonstrates that the need for a strongly π -basic metal fragment comes not so much from the frequently invoked "poor σ -donating and π -accepting properties" of N₂O, but from the need to stabilize η^2 -N,N'-coordination over the thermodynamically more favorable metal-oxo formation. The wellknown oxidizing character of N₂O may be mostly, if not entirely responsible for the scarcity of n²-metal complexes employing this ligand, and more of such complexes are expected to be in reach in complex designs featuring the right balance of π -basicity and resilience to oxidation at the metal center and associated ligands.

- World Health Organization. World Health Organization model list of essential medicines: 21st list 2019. 2019 Geneva: World Health Organization.
- [2] M. Laing, S. Afr. J. Sci. 2003, 99, 109-114.
- [3] V. Zakirov, M. Sweeting, T. Lawrence, J. Sellers, Acta Astronautica, 2001, 48, 353–362.
- [4] V. N. Parmon, G. I. Panov, A. Uriarte, A. S. Noskov, *Catal. Today* 2005, 100, 115–131.
- [5] a) N. Lehnert, H. T. Dong, J. B. Harland, A. P. Hunt, C. J. White, *Nat. Rev. Chem.* 2018, 2, 278–289.
- [6] a) J. L. Grenfell, *Phys. Rep.* **2017**, *713*, 1-17.
- [7] A. R. Ravishankara, J. S. Daniel, R. W. Portmann, Science 2009, 326, 123–125.
- [8] a) A. H. H. Chang, D. R. Yarkony, J. Chem. Phys. 1993, 99, 6824-6831;
 b) W. C. Trogler, Coord. Chem. Rev. 1999, 187, 303-327.
- [9] M. J. Prather, J. Hsu, N. M. DeLuca, C. H. Jackman, L. D. Oman, A. R. Douglass, E. L. Fleming, S. E. Strahan, S. D. Steenrod, O. A. Søvde, I. S. A. Isaksen, L. Froidevaux, B. Funke, *J. Geophys. Res. Atmos.* 2015, 120, 5693–5705.
- [10] K. Severin, Chem. Soc. Rev. 2015, 44, 6375-6386.
- [11] M. Konsolakis, ACS Catal. 2015, 5, 6397–6421.
- a) E. Otten, R. C. Neu, D. W. Stephan, J. Am. Chem. Soc. 2009, 131, 9918–9919; b) R. C. Neu, E. Otten, A. Lough, D. W. Stephan, Chem. Sci. 2011, 2, 170–176; c) M. J. Kelly, J. Gilbert, R. Tirfoin, S. Aldridge, Angew. Chem., Int. Ed. 2013, 52, 14094–14097.
- [13] a) A. G. Tskhovrebov, E. Solari, M. D. Wodrich, R. Scopelliti, K. Severin, Angew. Chem. Int. Ed. 2012, 51, 232–234; b) A. G. Tskhovrebov, B. Vuichoud, E. Solari, R. Scopelliti, K. Severin, J. Am. Chem. Soc. 2013, 135, 9486–9492.
- a) G. A. Vaughan, P. B. Rupert, G. L. Hillhouse, J. Am. Chem. Soc. 1987, 109, 5538–5539; b) G. A. Vaughan, C. D. Sofield, G. L. Hillhouse, A. L. Rheingold, J. Am. Chem. Soc. 1989, 111, 5491–5493.
- [15] a) A. Pastor, A. Montilla, F. Galindo, Adv. Organomet. Chem. 2017, 68, 1-91; b) A. Paparo, J. Okuda, Coord. Chem. Rev. 2017, 334, 136-149.
- [16] W. B. Tolman, Angew. Chem. Int. Ed. 2010, 49, 1018-1024.
- [17] a) J. N. Armor, H. Taube, J. Am. Chem. Soc. **1969**, *91*, 6874-6876; b) F. Bottomley, W. V. F. Brooks, *Inorg. Chem.* **1977**, *16*, 501-502; c) F. Paulat,

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Conflict of interest

The authors declare no conflict of interest.

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T. Kuschel, C. Näther, V. K. K. Praneeth, O. Sander, N. Lehnert, *Inorg. Chem.* 2004, 43, 6979–6994.

- [18] a) D. F.-T. Tuan, R. Hoffmann, *Inorg. Chem.* 1985, 24, 871–876; b) H.
 Yu, G. Jia, Z. Lin, *Organometallics* 2008, 27, 3825–3833; c) J. G. Andino,
 K. G. Caulton, *J. Am. Chem. Soc.* 2011, 133, 12576-12576.
- [19] C. B. Pamplin, E. S. F. Ma, N. Safari, S. J. Rettig, B. R. James, J. Am. Chem. Soc. 2001, 123, 8596–8597.
- a) S. Hu, T. M. Apple, J. Catal. 1996, 158, 199-204; b) V. M. Mastikhin,
 I. L. Mudrakovsky, S. V. Filimonova, Chem. Phys. Lett. 1988, 149, 175-179; c) V. M. Mastikhin, I. L. Mudrakovsky, S. V. Filimonova, Zeolites 1990, 10, 593-597.
- [21] N. A. Piro, M. F. Lichterman, W. H. Harman, C. J. Chang, J. Am. Chem. Soc. 2011, 133, 2108–2111.
- [22] M. R. Gyton, B. Leforestier, A. B. Chaplin, *Angew. Chem. Int. Ed.* 2019, 58, 15295-15298.
- [23] V. Zhuravlev, P. J. Malinowski, Angew. Chem. Int. Ed. 2018, 57, 11697– 11700.
- [24] b) A. Heyden, B. Peters, A. T. Bell, F. J. Keil, J. Phys. Chem. B 2005, 109, 1857–1873; a) C.-L. Hu, Y. Chen, J.-Q. Li, Y.-F. Zhang, Chem. Phys. Lett. 2007, 438, 213–217.
- [25] A. Pomowski, W. G. Zumft, P. M. H. Kroneck, O. Einsle, *Nature* 2011, 477, 234–237.
- [26] C. C. Mokhtarzadeh, C. Chan, C. E. Moore, A. L. Rheingold, J. S. Figueroa, J. Am. Chem. Soc. 2019, 141, 15003–15007.
- [27] C. Gendy, A. Mansikkamäki, J. Valjus, J. Heidebrecht, P. C.-Y. Hui, G. M. Bernard, H. M. Tuononen, R. E. Wasylishen, V. K. Michaelis, R. Roesler, *Angew. Chem. Int. Ed.* **2019**, *58*, 154–158.
- [28] a) T. Ziegler, *Inorg. Chem.* **1985**, 24, 1547-1552; b) L. P. Wolters, F. M. Bickelhaupt in *Structure and Bonding* (Eds.: O. Eisenstein, S. Macgregor), Springer, Berlin, **2014**.
- [29] a) C. Massera, G. Frenking, *Organometallics* 2003, *22*, 2758-2765; b) F.
 Hering, J. Nitsch, U. Paul, A. Steffen, F. M. Bickelhaupt, U. Radius, *Chem. Sci.* 2015, *6*, 1426–1432.
- [30] A. J. Arduengo, R. L. Harlow, M. Kline, J. Am. Chem. Soc. 1991, 113, 361–363.
- a) P. B. Armentrout, L. F. Halle, J. L. Beauchamp, *J. Chem. Phys.* **1982**, 76, 2449–2457; b) L. Zhao, Y. Wang, W. Guo, H. Shan, X. Lu, T. Yang, *J. Phys. Chem. A* **2008**, *112*, 5676–5683.

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The characterization of η^2 -*N*,*N'*-N₂O and CO₂ complexes of nickel and the associated computational study reveal that the bonding ability of N₂O to nickel is intermediate between that of CO₂ and that of H₂C=CH₂. It is shown that in general, N₂O η^2 -binds to metals comparably to, or stronger than CO₂, indicating that the rarity of η^2 -N₂O metal complexes is due mostly to its oxidizing character and not to its weak σ -donating and π -accepting properties.

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