Greenwood & Earnshaw

2^{nd} Edition

Chapter 11

Nitrogen

Dinitrogen

- **N≡N is chemically very unreactive, mp –210°C, bp –195.8°C its great bond strength, ΔH_{diss} = 945.41 kJ/mol, $d_{N\text{-}N}$ = 109.76 pm, and great thermodynamic stability causes many nitrogen compounds to be endothermic.**

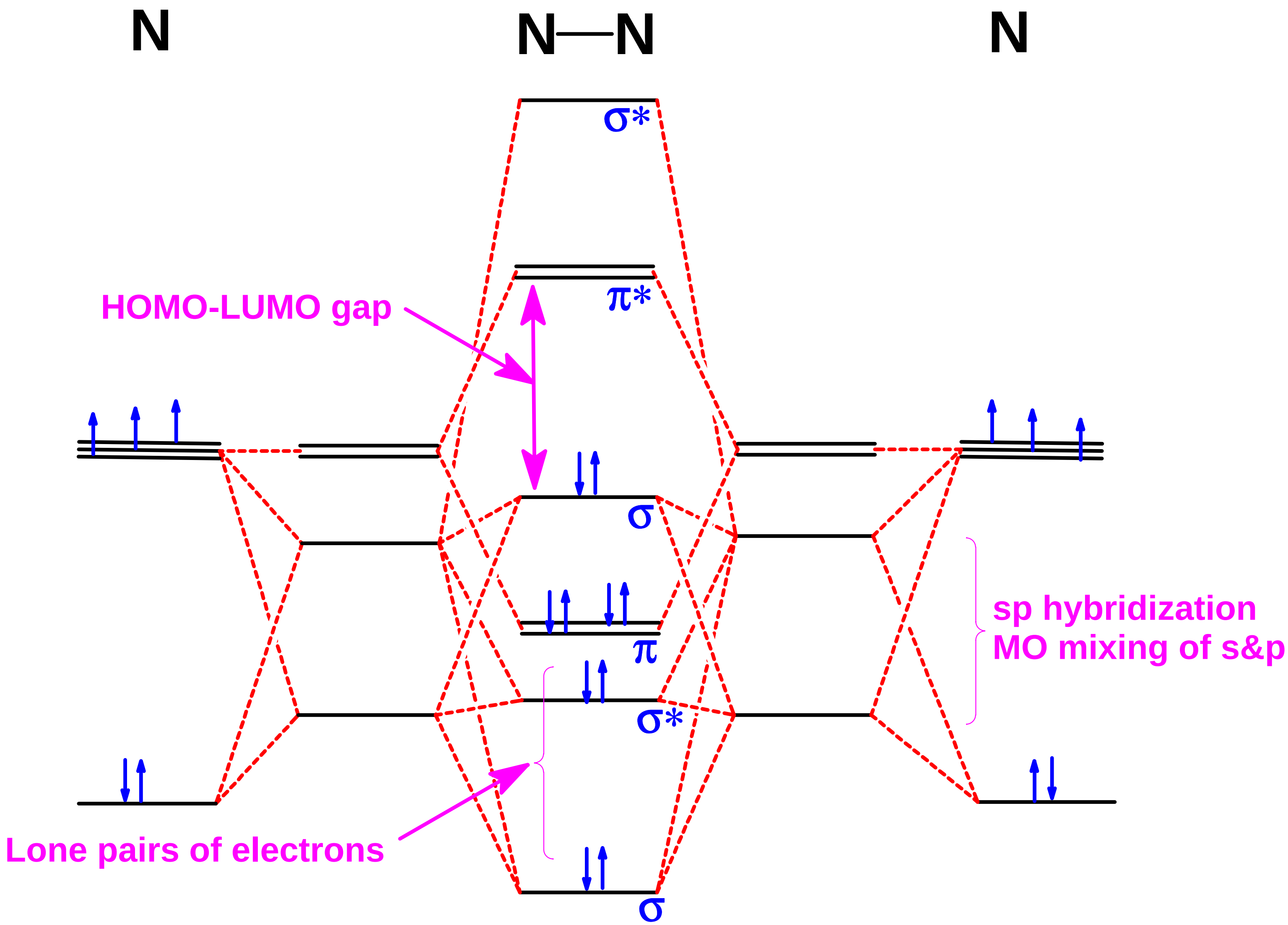
- **The N_2 lone pairs are very low in energy and are much less available for donation than the isoelectronic CO.**

- **The π* molecular orbitals are very high in energy (π bonds are very strong) and π-backbonding is less favored.**

- **A large HOMO-LUMO energy gap makes it hard to promote electrons or reduce dinitrogen.**

- **Dinitrogen is a non-polar molecule. isoelectronic with: CO, NO^+, CN^-, C_2^{2-}, and similar to HC_2^-, H_2C_2.**

Molecular Orbital Diagram - Dinitrogen



Note the two π-bonds are stronger than the σ-bond due to bond compression.

Reactions of Dinitrogen

Nitrides and nitrogen oxides:

$$6\,Li + N_2 \xrightarrow{25\,°C} 2\,Li_3N$$

Many small metals (Mg, Al, Ti) react with dinitrogen at elevated temperatures.

$$N_2 + O_2 \xrightarrow{\Delta,\ h\nu,\ \text{elec. dis.}} NO_x$$

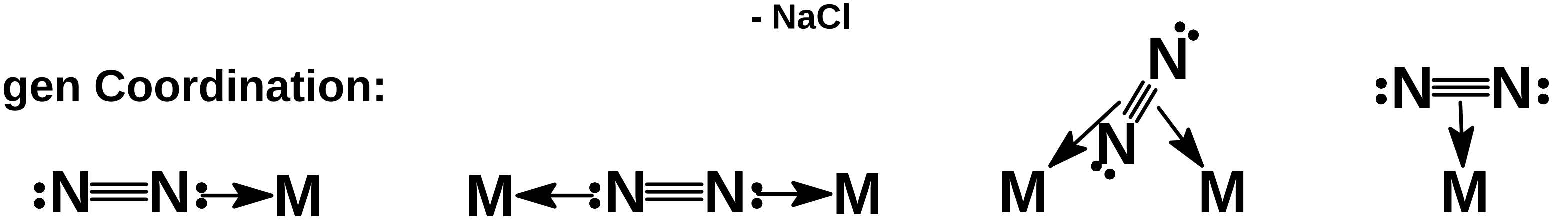
Dinitrogen "fixation" during electrical storms and high temperature combustion contributes to soil fertility & "acid rain."

Dinitrogen coordinates to some metal complexes:

$$[Ru(NH_3)_5(H_2O)]^{2+} + N_2 \longrightarrow [Ru(NH_3)_5(N_2)]^{2+} + H_2O$$

$$[MoCl_4(PMe_2Ph)_2] + 2\,N_2 \xrightarrow[\text{PMe}_2\text{Ph},\ -\text{NaCl}]{\text{toluene, Na/Hg}} \textit{cis-}[Mo(N_2)_2(PMe_2Ph)_2]$$

Dinitrogen Coordination:



η^1 most common

bis-η^1 impt in fixation

μ-bis-η^2

η^2 rare

Nitrides – Nitrido Complexes

^{14}N 99.634%, I = 1 ^{15}N 0.366%, I = $^{1}/_{2}$

Ionic: $3\ Ca + N_2 \longrightarrow Ca_3N_2$ also Li, Mg, Zn, Ti other small cations.

$Al_2O_3 + N_2 + C_x \longrightarrow 2AlN + 3\ CO$

Covalent: Si_3N_4 Network covalent - with alumina in hi tech ceramics.

S_4N_4

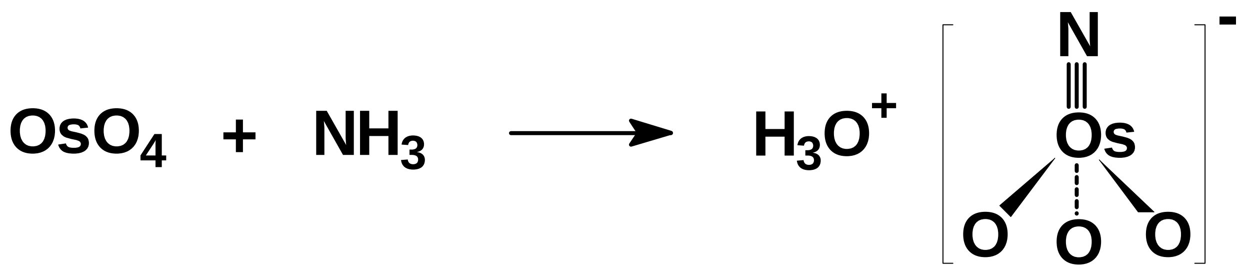
P_3N_5

Molecular, all have some type of dπ-pπ bonding.

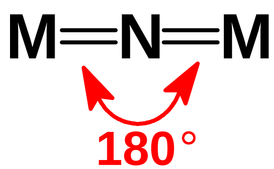
Metallic: Transition metals (Zr, Ti, Cr) in cubic and hexagonal close packed littices, N fits into octahedral sites.

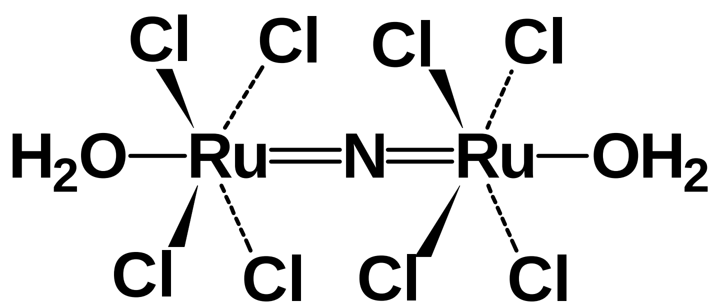
Nitrides – Nitrido Complexes

Nitrido:

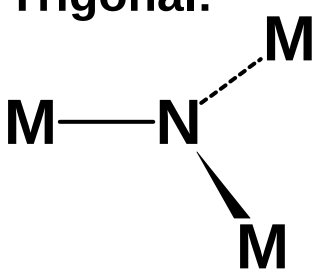


Linear:



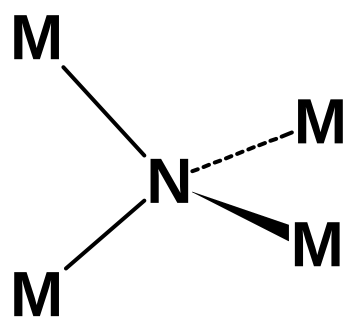


Trigonal:



$[NIr_3(SO_4)_6(H_2O)_3]^{4-}$

Tetrahedral:

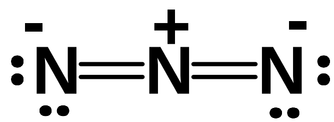


$[N(HgMe)_4]^+$

Azides – Azido Compounds

Ionic Azides:

N_3^-



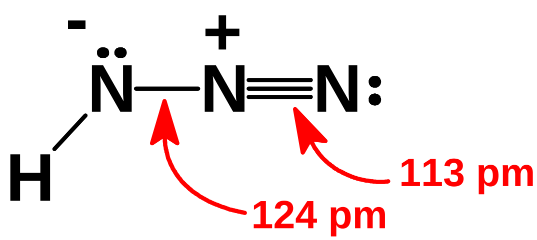
isoelectronic with O=C=O

$d_{N=N}$ = 116 pm

Ionic azides are stable, the ion is symmetrical, the alkali metal salts are commercially available.

Covalent Azides:

HN_3, RN_3, $Pb(N_3)_2$, HgN_3



Hydrazoic acid, pKa = 4.77, pungent, revolting odor, very toxic. Concentated and anhydrous acids are explosive.

ΔH_f° = 269.5 kJ/mol ΔG_f° = 327.2 kJ/mol

A very energetic molecule, heavy metal salts are used as detonators for explosives, not hygroscopic, reliable.

Hydrides

Ammonia: NH_3 $K_b = 1.8 \times 10^{-5}$ NH_4^+

Largest industrial commodity on a molar basis.

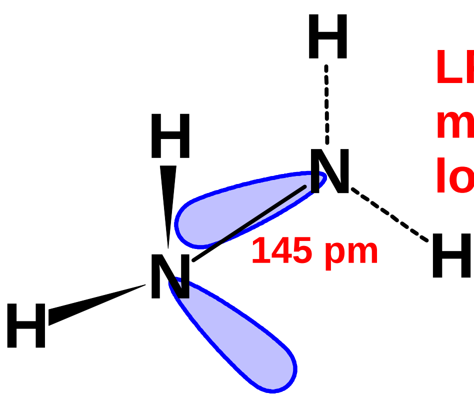
$$RBr + NH_3 \longrightarrow RNH_3^+\,Br^- \xrightarrow{OH^-} \xrightarrow{RBr} \xrightarrow{OH^-} \xrightarrow{RBr} \xrightarrow{OH^-} \xrightarrow{RBr} R_4N^+\,Br^-$$

$$R_4N^+\,Br^- \xrightarrow{Ag_2O.H_2O} R_4N^+\,OH^-$$

Ammonia and amines are weak bases ammonium ions are weak acids. Tetraalkylammonium hydroxide is a strong base.

Hydrazine: H_2NNH_2 $K_b = 8.5 \times 10^{-7}$ $H_2NNH_3^+$

$K_b = 8.9 \times 10^{-16}$ $^+H_3NNH_3^+$ A strong acid



LP-LP repulsions make the N-N bond long and weak.

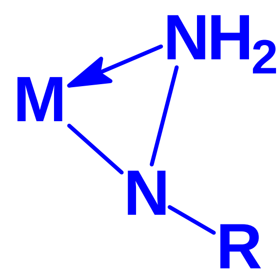
gauche conformation
torsion angle 90°-95°

1e,2e,4e reducing agent, stronger in base than acid.

1e $E°_{red}$ = -1.74 V acid

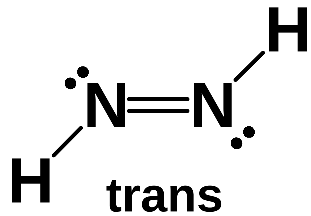
1e $E°_{red}$ = -2.42 V base

Hydrazide Ligand:

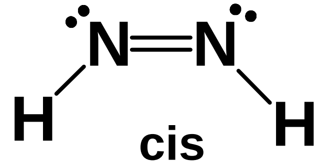


Less Common Binary Hydrides

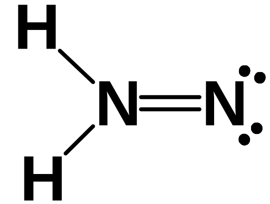
Diazine: HNNH



trans
more stable



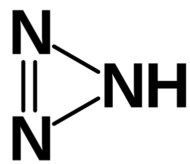
cis
not stable
Ligand important in nitrogen fixation.



1,1-isomer

Cyclotriazene:

(triaziridine)



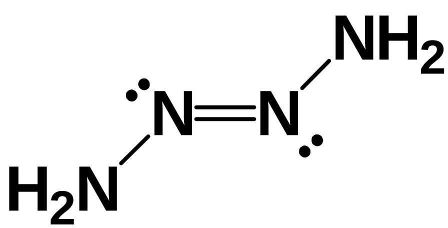
Triazane: H_2NNHNH_2

(aminohydrazine)

Tetrazane: $H_2NNHNHNH_2$

(diaminohydrazine)

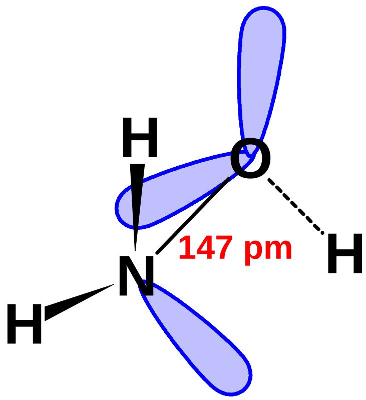
***trans*-2-tetrazene**



Several "binary hydrides" can be made such as ammonium and hydrazinium azide salts; dimers and trimers of hydrazoic acid or triaziridine.

Hydroxylamine & Nitrogen Fixation

Hydroxylamine: H_2NOH $K_b = 6.6 \times 10^{-9}$ $H_3\overset{+}{N}OH$

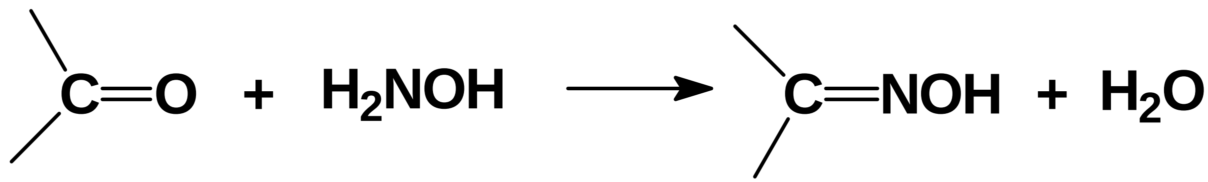


Trans conformation in the crystal

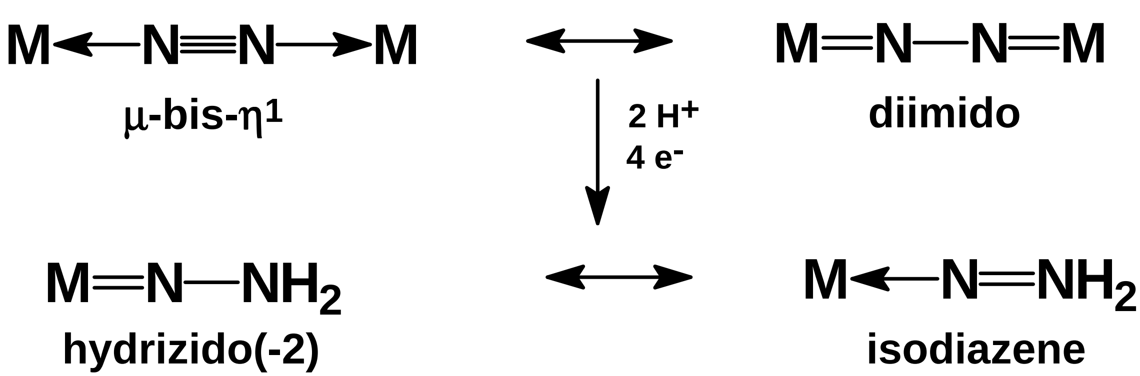
Made by the reduction of ammonium nitrite in a gel using aqueous bisulfate/sulfur dioxide, Raschig Synthesis.

Industrially used as reducing agent, absorbent for nitrogen oxides.

Forms Oximes with aldehydes and ketones:



Nitrogen Fixation:



Nitrogen Halides

$NH_4^+HFH^-_{(l)}$ electrolysis → NF_3

$NH_4^+Cl^-_{(aq)}$ electrolysis, pH4 → NCl_3

$(Me_3Si)_2NBr$ + 2 BrCl, pentane, -87°C → NBr_3

NH_3 + I_3^- aqueous → $NI_3 \cdot NH_3$

	NF_3	NCl_3
mp	-206.8°	-40°
bp	-129.0°	+71°

NCl_3: $\rho_{20°}$ = 1.65 g/cc

NF_3: Stable, ΔG° = -83.3 kJ/mol., colorless, low dipole moment (0.234 D), ∠ 102°, pyramidal, low reactivity.

NBr_3: decomposes at -60°C, and very reactive

$NI_3 \cdot NH_3$: a layer lattice, NI_4 tetrahedra linked in infinite chains of -N-I-N-I-, connected into sheets by I-I interactions and sheets linked by I-NH_3 interactions.

all are shock sensitive and explosive

NCl_3 → (H_2O,air) → NH_3 & 3 HOCl used commercially to sterilize and bleach flour.

N_2F_4 → (SbF_5) → $N_2F_3^+$ SbF_6^-

N_2F_4 ⇌ 2 NF_2

N_2F_4: mp -165.5°C, bp -73°C

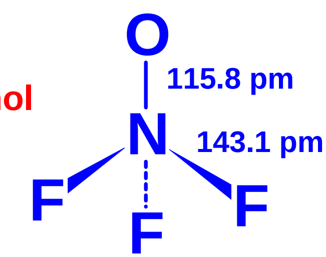
2 NF_2: DHdiss = 83.2 kJ/mol

NF_3 → (Δ, Cu) → N_2F_4

NF_3 → (2 F_2 + SbF_3, 200°C, 100 atm) → $[NF_4]^+$ $[SbF_6]^-$

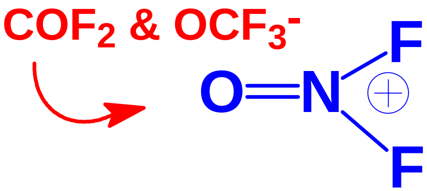
Many salts known, oxidizer for chemical lasers.

NF_3 → (O_2, -196°C, electric discharge) → ONF_3

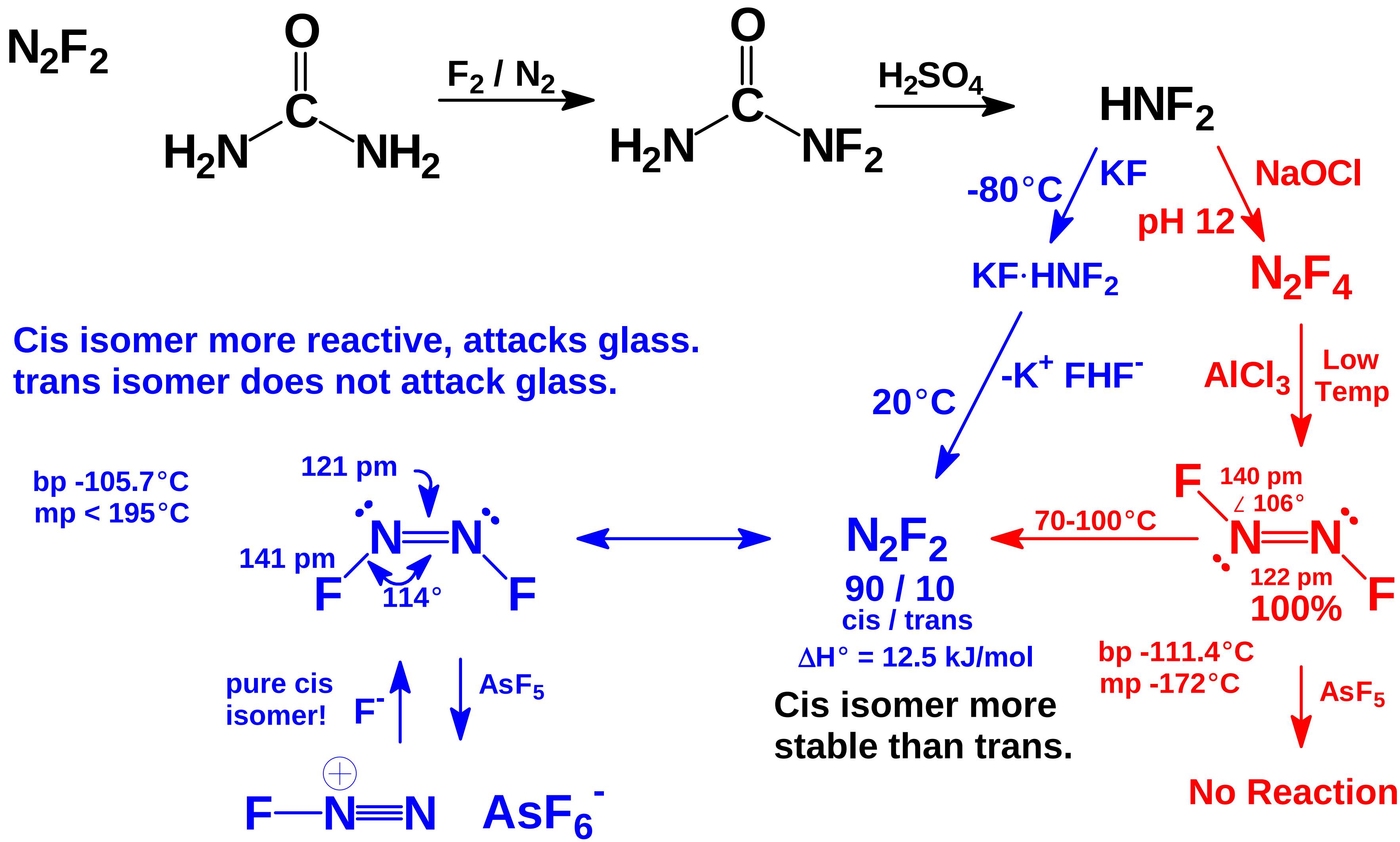


ONF_3 → (BF_3) → $[ONF_2]^+$ $[BF_4]^-$

cf. COF_2 & OCF_3^-

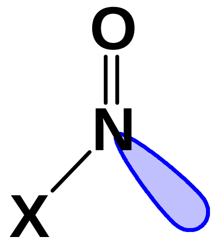


Nitrogen Halides



Nitrosyl & Nitryl Halides

Nitrosyl halides: XNO



X	F	Cl	Br
mp °C	-132.5	-59.6	-56
bp °C	-59.9	-6.4	~0
∠XNO	110	113	117
ΔH°f kJ/mol	-66.5	+51.7	+82.2

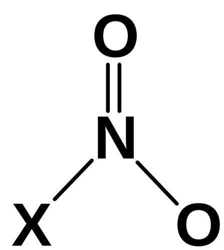
BF_3, AsF_5, $AlCl_3$ → $:N{\equiv}O:^{\oplus}$ (106 pm) BF_4^-, AsF_6^-, $AlCl_4^-$

H_2O → {HOX, HNO} → HX + HNO_2

$$3\ HNO_2 \longrightarrow HNO_3 + 2\ NO + H_2O$$

Potent solvents for dissolving metals.

Nitryl halides: XNO_2



X	F	Cl
mp °C	-166	-145
bp °C	-72.5	-15.9
∠XNO	118	115
ΔH°f kJ/mol	-80	+13

AsF_5 → $O{=}N^{\oplus}{=}O$ (115 pm) AsF_6^-

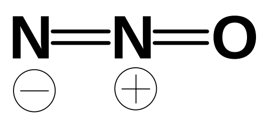
H_2O → {HOX, HNO_2} → HX + HNO_2

Oxides of Nitrogen

Dinitrogen Monoxide:

(Nitrous Oxide)

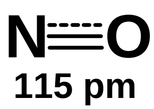
N_2O



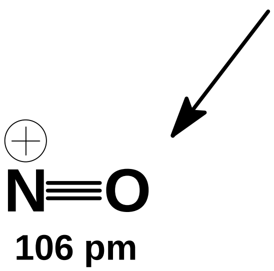
Isoelectronic with carbon dioxide & NO_2^+. Very unreactive, very stable gas, anesthetic (laughing gas), greenhouse gas $t_{1/2}$ = 115 year "lifetime." Natural source, microbial degradation of NH_4NO_3.

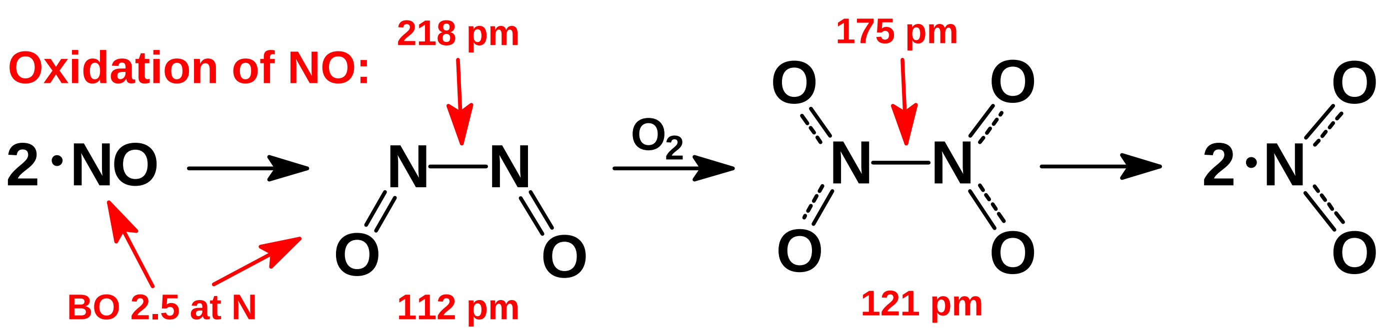
Nitrogen Monoxide:

(Nitric Oxide)



A stable free radical, paramagnetic, colorless, bp - 151.8°C, little tendency to dimerize. Oxidation to NO_2 has a negative temperature coefficient.



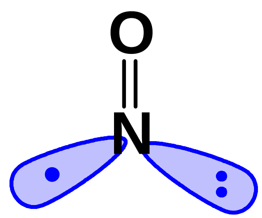


Nitric Oxide as a Ligand – Bent Nitrosyls

Linear: NO^+ **A 3 electron donor, 2 NO's will replace 3 CO's in an EAN complex.**

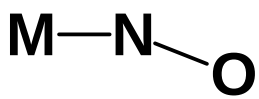
∠ 170-180°

νNO = 1650-1900 cm^{-1}. Common with early transition metals and middle transition metals in higher oxidation states.



Bent:

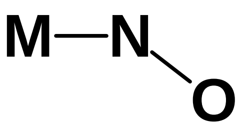
Gp A: **(2 electron donor)**



∠ 140-170°

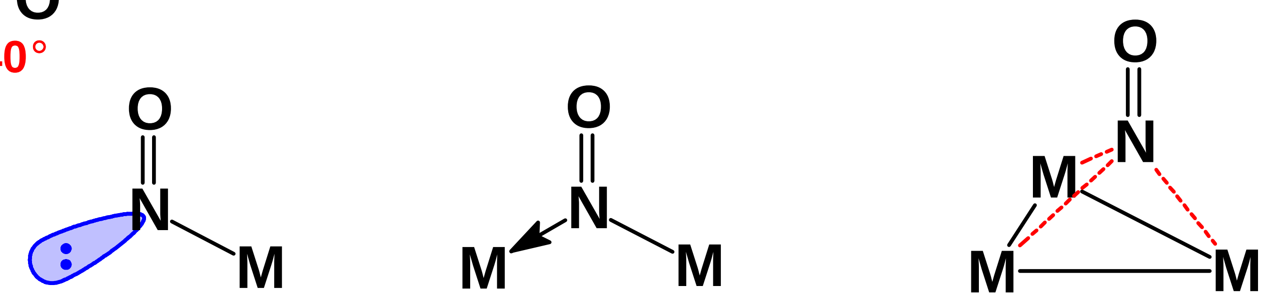
νNO = 1500-1690 cm^{-1}. Common with late transition metals and middle transition metals in lower oxidation states.

Gp B: **(1 electron donor)** NO^-

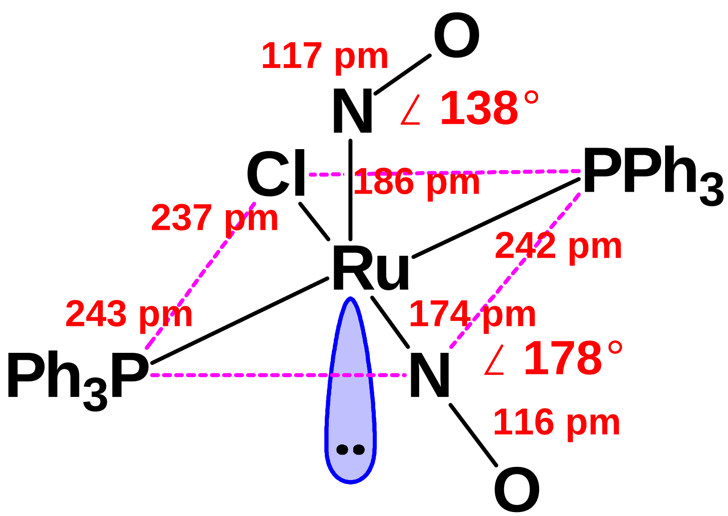


∠ 120-140°

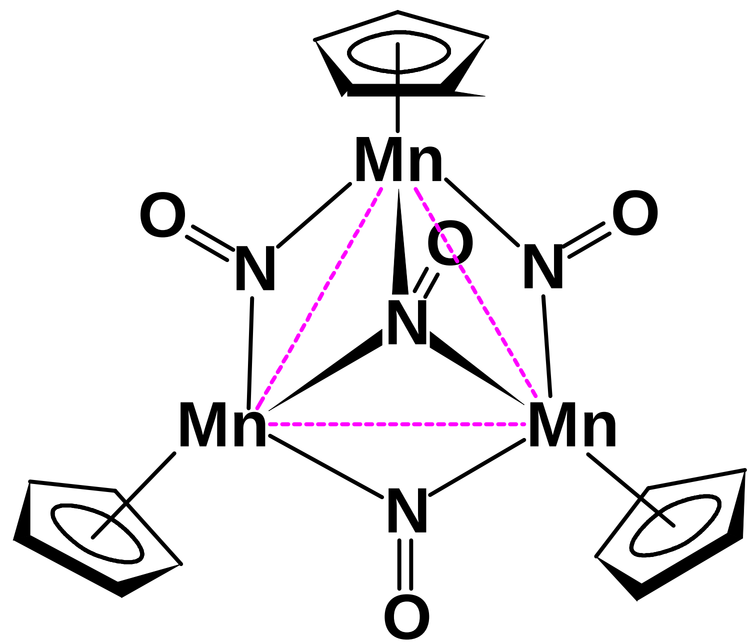
Bonding Modes of NO:



Nitric Oxide as a Ligand



$[RuCl(NO)_2(PPh_3)_2]^+$



$[\{(\eta^5\text{-}C_5H_5)Mn\}_3(\mu_2\text{-}NO)_3(\mu_3\text{-}NO)]$

Oxides of Nitrogen

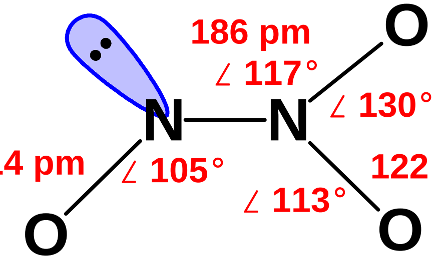
Dinitrogen Trioxide:

$N_2O_3 \rightleftharpoons NO + NO_2$

NO: colorless; NO_2: red-brown

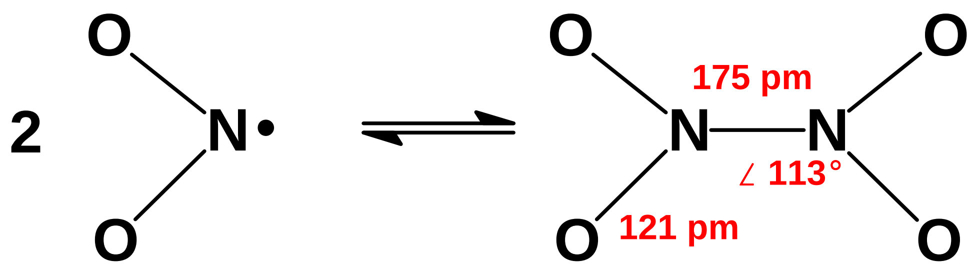
mp -100.1°C

mixed dimer



Light blue solid, intense blue liquid, turns green as NO_2 dissociates, color becomes less intense.

Nitrogen Dioxide & Dinitrogen Tetroxide



ΔH_{diss} = +57.20 kJ/mol

ΔG_{diss} = +4.77 kJ/mol

$\Delta S°$ = 175.7 J/K·mol

Isoelectronic with B_2F_4 & $C_2O_4^{2-}$ whose C-C and B-B bonds are of normal length. Does not autoionize, but ionic intermediates form in high dielectric solvents. An intermediate in the production of nitric acid.

Nitric Acid:

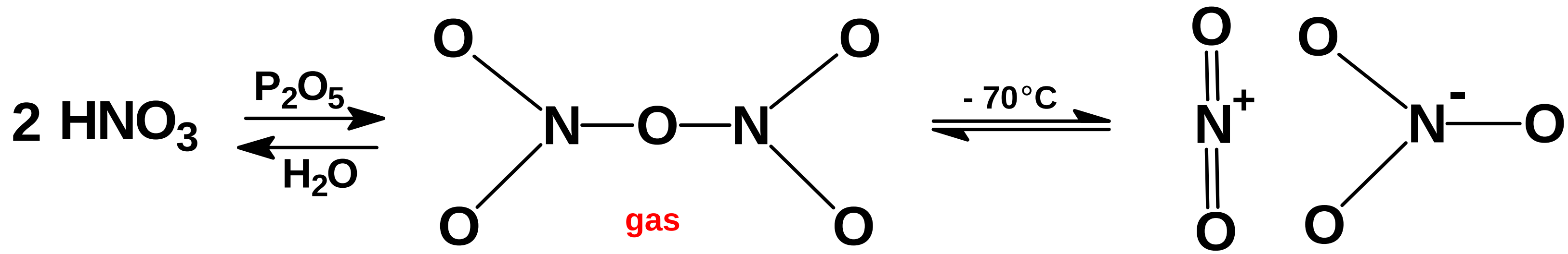
$$NH_3 \xrightarrow[O_2]{Pt} NO \xrightarrow{O_2} N_2O_4 \xrightarrow{H_2O} HNO_3 + HNO_2$$

$$3\ HNO_2 \longrightarrow H_3O^+\ NO_3^- + 2\ NO$$

to be recycled

Oxides of Nitrogen

Dinitrogen Pentoxide:



Structure poorly understood

Ionic solid

Oxoacids – Oxoanions:

Hyponitrous Acid - Hyponitrite

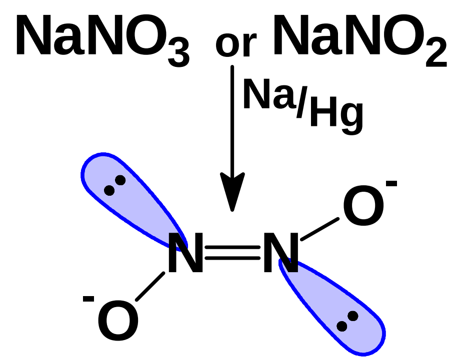
HON=NOH

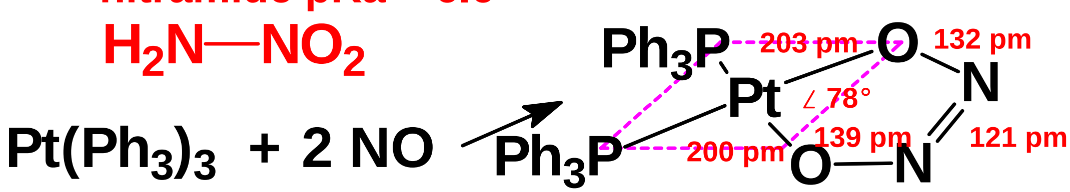
pKa = 6.9 ; 11.6

Isomeric with nitramide pKa = 6.6

$H_2N—NO_2$

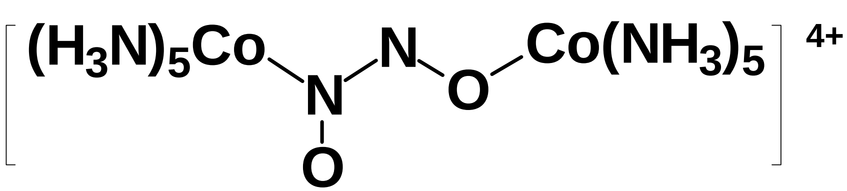
Weak dibasic acid of unknown structure. Stable for weeks in acidic solution, decomposes at pH > 4.





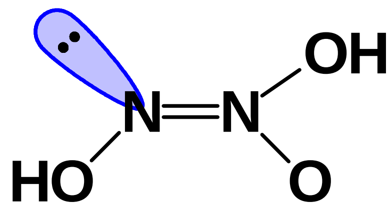
Salts are stable, reducing, *"trans"* by vibrational spect. *"Cis"* ion known as a ligand. Many "non-EAN" nitrosyls are *cis*-hyponitrites.

also:

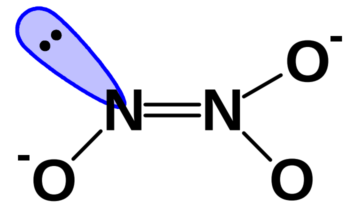


Oxoacids – Oxoanions

Hyponitric Acid - Hyponitrates:



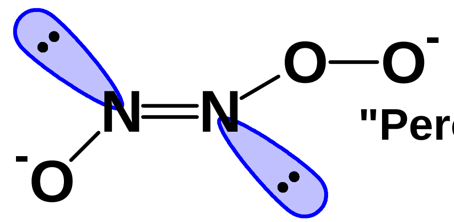
α form



$Na_2N_2O_3$
Angeli's Salt

Acid is known only in solution and is explosive.

β form



"Peroxohyponitrite"

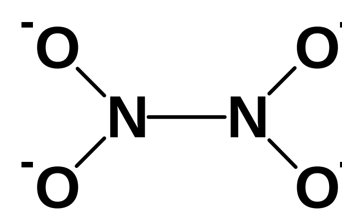
$$Na_2N_2O_2 \xrightarrow[\text{fast}]{N_2O_{4(l)}} \beta\text{-}N_2O_3^{2-} \xrightarrow{\text{slow}} N_2O_5^{2-} \xrightarrow[100\,^{\circ}C]{\text{slow}} N_2O_6^{2-}$$

$$\alpha\text{-}N_2O_3^{2-} \longrightarrow N_2O_4^{2-} \longrightarrow N_2O_6^{2-}$$

Nitroxylic (Hydronitrous) Acid - Nitroxolate Anion:

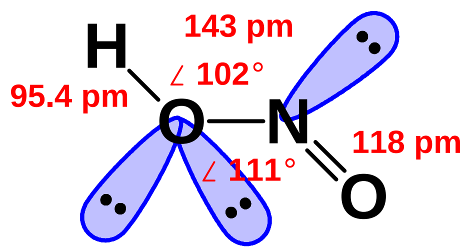
"Acid Explosive"

$$2\ NaNO_2 \ + \ 2\ Na \xrightarrow[NH_{3(l)}]{}$$

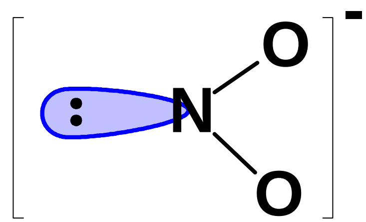


Oxoacids – Oxoanions

Nitrous Acid - Nitrites

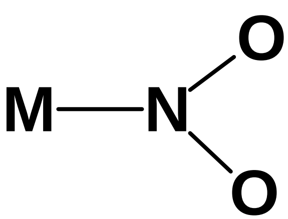


planar

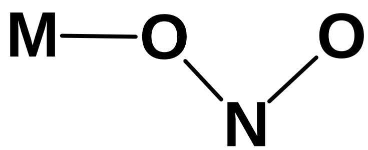


45 kJ/mol barrier to rotation

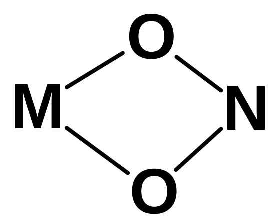
nitrite is a very versatile ligand



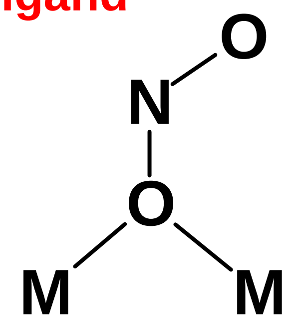
nitro



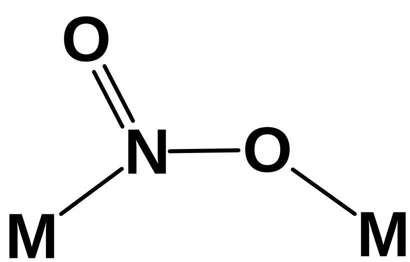
nitrito



chelating

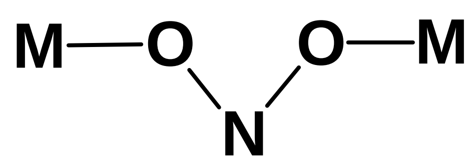


O-bridging



cis-unsymmetrical

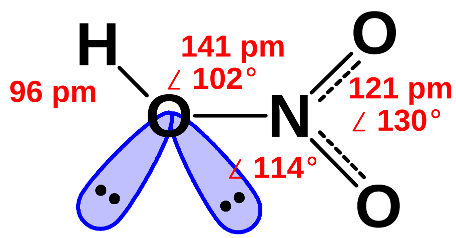
N,O bridging -- *trans*??

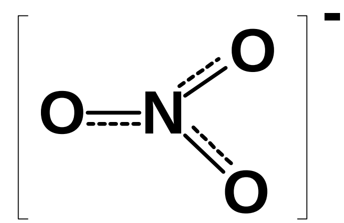


not definitely established

Oxoacids – Oxoanions

Nitric Acid - Nitrates





Almost planar gas, $\angle_{HON}$ torsion 2°
bp 82.6°C. Nitric Acid will form H-bonded complexes with nitrate.

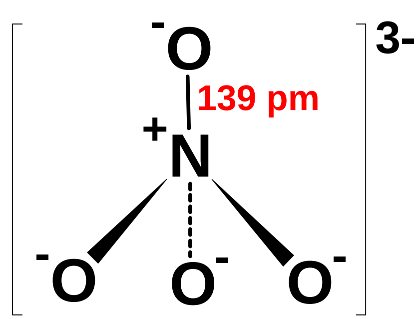
The nitrate ligand may coordinate in a manner similar to nitrite and may use all three oxygen atoms.

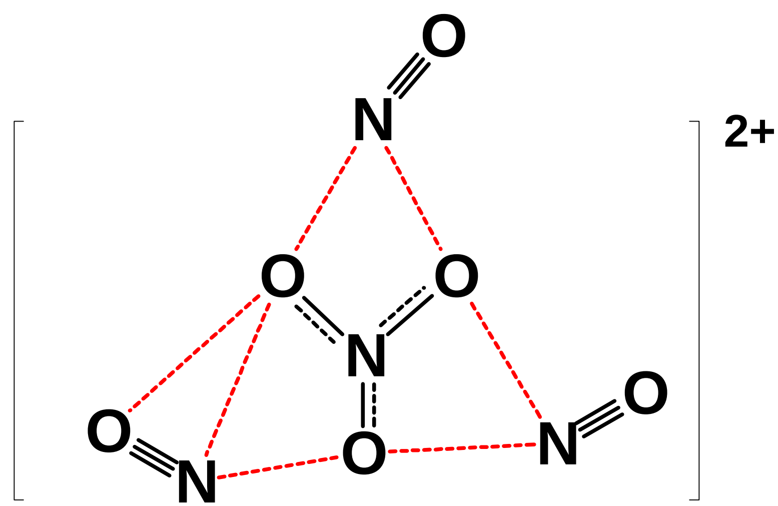
Orthonitrate: H_3NO_4 unknown

$[N_4O_6]^{2+} \leftarrow NO_3^- + 3\ NO^+$

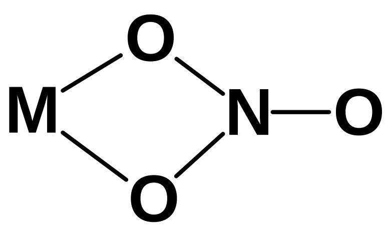
$Na_2O + NaNO_3 \xrightarrow{\text{fuse}} Na_3NO_4$

Tetrahedral anion, very short N-O bond due to strong polar interactions.

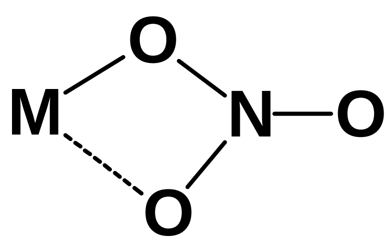




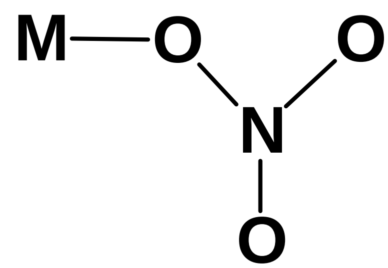
Coordination Modes of Nitrate Ligand



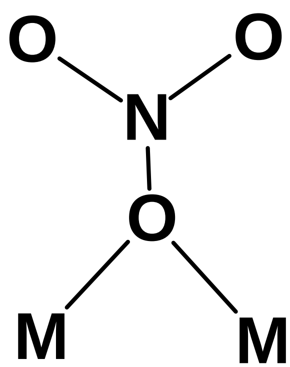
sym bidentate



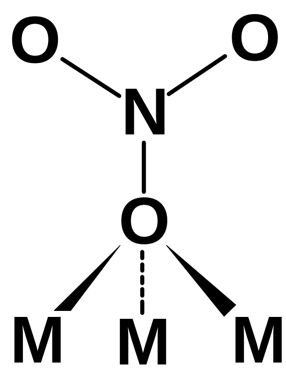
unsym bidentate



unidentate

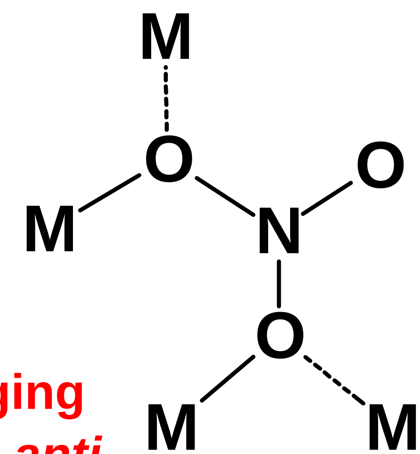


μ_2-O-bridging



μ_3-O-bridging

bis-μ_2-O-bridging
syn-syn ; *anti-anti*



Many metal nitrates melt at "low" temperatures without decomposition
$LiNO_3$ (255°C); $CsNO_3$ (419°C); $AgNO_3$ (212°C).