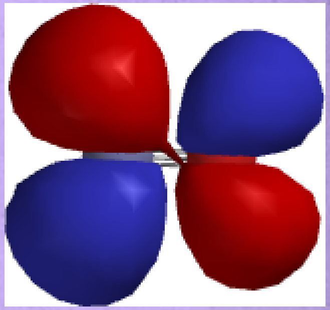
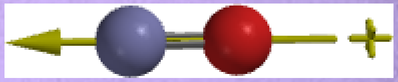
Iron Nitrosyl compounds

Nitric Oxide I

- Nitric oxide (NO) is a colorless gas that is thermodynamically unstable (ΔH_f= 90.2 kJ/mol).
- Due its odd number of electrons, the compound is paramagnetic. The unpaired electron is located in a π^*-orbital (HOMO orbital shown on the right)



- The molecule possesses a small dipole moment (μ=0.158 D) in which the nitrogen atom possesses a partial negative charge (60% spin density on nitrogen based on EPR).



- The N-O bond length (115 pm) corresponds with a bond order of about 2.5 (double bond: 118 pm, triple bond: 106 pm).

Nitric Oxide II

- Nitric oxide is a by-product of combustion of substances in the air (i.e., car engines, fossil fuel power plants). In both cases, it is quickly oxidized to form nitrogen dioxide, which is removed using a catalytic converter.
- Nitric oxide is also produced naturally during the electrical discharge of lightning. However, the direct reaction of nitrogen with oxygen requires temperatures in excess of 2000 ^oC, which is not practical for a large-scale synthesis.
- Industrially, the oxidation of ammonia at 850 ^oC with platinum as catalyst leads to the formation of nitric oxide.
- $4\ NH_3 + 5\ O_2 \longrightarrow 4\ NO + 6\ H_2O$
- Nitric oxide can be oxidized to form the nitrosonium ion (NO^+) or be reduced to form a nitroside ion (NO^-). The nitrosonium ion appears as the cation in nitrosyl salts NO^+X^- ($X=BF_4^-$, ClO_4^-, AsF_6^-, $SbCl_6^-$, OsF_6^-, HSO_4^-, $PtCl_6^{2-}$).
- Nitrosyl chloride is formed in a mixture of hydrochloric acid and nitric acid also known as *aqua regia*.
- $HNO_3 + 3\ HCl \longrightarrow ClNO + Cl_2 + 2\ H_2O$
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Metal Nitrosyl Complexes I

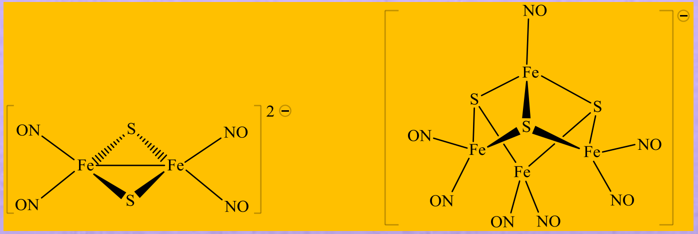
- Metal nitrosyl complexes, have gained significant interest in the past twenty years because of the important role nitric oxide displays as signaling molecule in biological systems.
- Louis Ignarro, a professor in the pharmacology department at UCLA, received the Noble Prize in Physiology and Medicine in 1998 for his discovery about the signaling properties of nitric oxide.
- Iron dithiocarbamates are used as model compounds for NO spin trapping
- The first nitrosyl complex was discovered in 1790 by J. Priestley ($[Fe(H_2O)_5(NO)]^{2+}$). This complex is also formed in the qualitative test for nitrate with ferrous sulfate and sulfuric acid (“brown ring test”).

Metal Nitrosyl Complexes II

- The second compound, an iron cyano complex ($[Fe(CN)_5(NO)]^{2-}$), was described about 60 years later by K. L. Playfair.
  - The dark-red sodium nitroprusside $Na_2[Fe(CN)_5(NO)]*2\ H_2O$ is obtained from potassium ferrocyanide and concentrated nitric acid
  - It is a potent vasodilator (SNP, *Nitropress*).
  - This compound is also used in *Simon's test* in the detection of methamphetamine (blue) and as reagent to detect sulfide ions as $[Fe(CN)_5(NOS)]^{4-}$, which is purple.
- Roussin's salts (red: $K_2[Fe_2S_2(NO)_4]$, black: $Na[Fe_4S_3(NO)_7]$) are both iron sulfur nitrosyl complexes that were discovered in 1858.
- The esters of the Roussin's Red salt are being investigated as nitric oxide donors because photolysis of the compounds causes the release of NO.

Metal Nitrosyl Complexes III

- The nitric oxide donated by Roussin’s Black salt has proven to be toxic to some melanoma cancer cells.
- The same salt demonstrates antibacterial activity in some food processing applications as well.
- The structure of the red salt displays an edge-shared bitetrahedron: four nitrosyl ligands are terminal and two sulfide ligands are located in the bridge.
- The black salt forms an incomplete cubane structure, which is missing one corner (4 Fe and 3 S).



Metal Nitrosyl Complexes IV

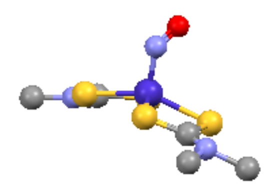
- The nitrosyl ligand can act as a one-electron or a three-electron donor.
- The nitrosyl cation ($:N{\equiv}O:^+$) can use its lone pair on the nitrogen atom to form a bond to the metal atom like its isoelectronic counterparts the carbonyl ($:C{\equiv}O:$) and the cyanide ($:C{\equiv}N:^-$).
- As carbonyl ligands, various degrees of π-back bonding are observed (NO^+ is a stronger π-acceptor than CO):

Metal Nitrosyl Complexes V

$$\mathrm{M{-}N{\equiv}O} \longleftrightarrow \mathrm{M{=}N{=}O} \longleftrightarrow \mathrm{M{\equiv}N{-}O}$$

(I) (II) (III)

- Increasing strength of the π-back bond strengthens the M-N bond and weakens the N-O bond.
- In extreme cases, both bonds can be characterized as double bonds (II). In cases in which the M-N-O angle is close to 180°, the M-N bond is usually relatively short.
- If the backbonding effect is weak, the angle decreases significantly (< (M-N-O)= ~120 °) and the ligand can be described as “NO$^-$“ as it is observed in the cobalt complexes below
- The Enemark-Feltham notation is used to describe the number of *d-type* electrons present in a given metal nitrosyl complex. Complexes with "d+π^*-electrons" in excess of six often tend to have bent NO ligands i.e., Co(NO)dtc$_2$ (7 e,127°).



Metal Nitrosyl Complexes VI

- **Examples**

Compound	***(M-N-O)***	***d(M-N)***	***d(N-O)***
$[Fe(CN)_5(NO)]^{2-}$	173.9°	164.3 pm	114.5 pm
$[Mn(CN)_5(NO)]^{3-}$	177.0°	165.1 pm	117.4 pm
$[Co(NH_3)_5(NO)]^{2+}$	119.0°	187.1 pm	115.4 pm
trans-$[Co(en)_2(NO)Cl]^{+}$	124.4°	182.0 pm	104.3 pm
$[Cr(CN)_5(NO)]^{3-}$	176.0°	171.0 pm	121.1 pm
$Ir(NO)(P(C_6H_5)_3)_3$	180.0°	166.6 pm	124.4 pm

- Infrared spectroscopy and EPR spectroscopy can be used to distinguish between different bond modes.
- Linear M-N-O groups (N-O triple bond) absorb in the range 1650–1900 cm^{-1} (i.e., $[Fe(CN)_5(NO)]^{2-}$: 1939 cm^{-1}, $[Mn(CN)_5(NO)]^{3-}$: 1700 cm^{-1})
- Bent nitrosyl groups (N-O double bond) absorb in the range 1525–1690 cm^{-1} (i.e., $[Co(NH_3)_5(NO)]^{2+}$: 1620 cm^{-1}).

Experiment (Theory)

- In the lab, an iron nitrosyl complex will be synthesized by the reaction of ferrous sulfate with nitrous acid in the presence of a dithiocarbamate ligand.
- The reaction of the nitrite with sulfuric acid generates the nitrous acid (HNO_2) *in-situ*, which is reduced by Fe^{2+} to yield nitric oxide, which reacts with the iron aquo complex to form $[Fe(H_2O)_5(NO)]^{2+}$.
- The addition of the dithiocarbamate ion leads to the formation of the dark-green $Fe(NO)dtc_2$.
- In the second part, the product of the first reaction is reacted with iodine to yield the brown $FeI(NO)dtc_2$.
- The structures of both compounds are investigated using infrared spectroscopy, EPR and NMR spectroscopy.

Experiment I

- Safety
  - The first experiment has to be performed under a well-ventilated hood because nitrogen dioxide (NO_2) is formed as a byproduct in this reaction.
  - Chloroform is classified as selected carcinogen and should only be handled in the hood.
  - Petroleum ether is flammable. Keep away from any ignition sources.

Experiment II

- **Bis(diethyldithiocarbamato)nitrosyl iron (Fe(NO)dtc$_2$)**
  - Ferrous sulfate ($FeSO_4$* 7 H_2O) and sodium nitrite ($NaNO_2$) are dissolved in 0.5 M sulfuric acid (student most likely has to prepare this solution).
  - A aqueous solution of of sodium (*N,N*-diethyldithiocarbamate) ($Na(S_2CNEt_2)$*3 H_2O) is added immediately.
  - The dark reaction mixture is stirred vigorously for 5 minutes before being transferred into a separatory funnel (without the spin bar).
  - The reaction mixture is extracted several times with chloroform (it could be a difficult to see the phase separation here).
  - The combined organic layers are dried over anhydrous magnesium sulfate before the volume of the solution is reduced using the rotary evaporator.
  - Petroleum ether is added to the solution to precipitate the dark green solid.
  - If the solid does not crystallize at 0 ^oC, some of the chloroform is removed by careful evaporation using the rotary evaporator (do not use heat here!).
  - The crystals are isolated by filtration, are washed with petroleum ether and are dried in vacuum.

Experiment III

- **Bis(diethyldithiocarbamato)(iodo)nitrosyl iron**
  - Bis(diethyldithiocarbamato)nitrosyl iron is suspended in absolute ethanol.
  - A solution of iodine in absolute ethanol is added drop wise over a period of 15 minutes.
  - The resulting mixture is stirred for one hour at room temperature during which a brown precipitate forms.
  - The precipitate is removed by filtration, washed with 95% ethanol and dried in vacuum.

Characterization I

- **Infrared spectroscopy**
  - Fe(NO)dtc$_2$
    - ν(NO)= 1685 cm^{-1}
  - FeI(NO)dtc$_2$
    - ν(NO)= 1805 cm^{-1}
    - Increased stretching frequency due to reduced π-backbonding due to the higher oxidation state

- **NMR spectroscopy**
  - FeI(NO)dtc$_2$
    - Complex multiplet at δ=3.63 ppm (8 lines) and δ=1.24 ppm (8 lines)

Characterization II

- Fe(NO)dtc$_2$
  - The nitrosyl group has an unpaired electron ($<$(Fe-N-O)= 174^{o})
  - The electron is located at the nitrogen atom and therefore couples with the nucleus (^{14}N: 99.638% abundance, I=1)
  - A three line spectrum is observed for this compound (=2*1+1)