

# INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

INORGANIC CHEMISTRY DIVISION

COMMISSION ON NOMENCLATURE OF INORGANIC CHEMISTRY\*

## NOMENCLATURE OF INORGANIC CHEMISTRY: II.2 THE NOMENCLATURE OF HYDRIDES OF NITROGEN AND DERIVED CATIONS, ANIONS, AND LIGANDS

(Recommendations 1981)

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NOMENCLATURE OF INORGANIC CHEMISTRY

II.2 THE NOMENCLATURE OF HYDRIDES OF NITROGEN AND DERIVED CATIONS,  
ANIONS, AND LIGANDS

(Recommendations 1981)

INTRODUCTION

These rules are concerned with hydrides of nitrogen containing one or two nitrogen atoms, hydrogen azide and their derivatives as specified in the title. Other compounds containing three or more contiguous nitrogen atoms are named according to NOC,C-9.4 (see Note a).

The nomenclature of hydrides of nitrogen and derived cations, anions, and ligands presents particularly difficult problems. The simple hydrides and many of their derivatives are commercial chemicals with well established non-systematic trivial and abbreviated names. The hydrides are inorganic but numerous derivatives are organic, and their nomenclature must be compatible with additive (inorganic) and substitutive (organic) nomenclature. It must also be in accord with present trends toward more systematic nomenclature.

These rules were formulated after some nine years of discussion and adjustment at annual meetings of the Commission on Nomenclature of Inorganic Chemistry together with a representative of the Commission on the Nomenclature of Organic Chemistry. They provide a compromise between existing names, future trends, and inorganic and organic nomenclature practices. Nothing stated in these rules alters the validity of NIC, 2.3; NIC, 3.15; or NIC, 3.221 (see Note a).

The systematic names are based on organic principles and the hydride name 'azane' where there is hydrogen to be substituted, and on the name 'nitrogen' where there is no hydrogen or only acidic hydrogen.

It is not proposed that these names should take precedence at present over the well established names for the common hydrides and common derivatives, but with the trend toward systematic nomenclature they may do so in the future. For this reason, the trivial names and non-systematically but well established derived names are described as "for the present use" or "preferred at the present time" rather than as "preferred." It is left to future usage to decide final preferences.

II.2.1 HYDRIDES

Systematic names for nitrogen hydrides are given in the first column of names in the table below and common names in the second column. Other names also used, are listed in the third column but are not preferred for naming derivatives. Ammonia and hydrazine recognized by NIC, 2.3, and hydrogen azide by NIC, 5.1 are exceptions to systematic hydride nomenclature. The names printed in capitals are the most widely accepted. They, and names derived from them by the following rules, are retained for present use.

	<u>Systematic name</u>	<u>Common name</u>	<u>Other names</u>
(a)	NH <sub>3</sub> azane	AMMONIA	
(b)	N <sub>2</sub> H <sub>4</sub> diazane	HYDRAZINE	
(c)	N <sub>2</sub> H <sub>2</sub> DIAZENE	diimide	diimine
(d)	HN <sub>3</sub> hydrogen trinitride	HYDROGEN AZIDE	hydrazoic acid

Note a. References are to numbered sections or rules in official IUPAC publications on nomenclature. Those with the initial II.2 are taken from this chapter. Those prefixed NIC are taken from Nomenclature of Inorganic Chemistry, 2nd Edn. Publ. Butterworths, London, 1970, but now available from Pergamon Press, Oxford. Those prefixed NOC,C are taken from Nomenclature of Organic Chemistry, Publ. Pergamon Press, Oxford, 1979 (Section C, pp. 85-322). Coordination compounds used as examples to illustrate the use of ligand names are named in accordance with the rules of Chapter 7 of Nomenclature of Inorganic Chemistry.

## II.2.2 CATIONS

Cations derived by the addition of one or more hydrogen ions to a nitrogen hydride or dinitrogen are named by adding 'ium' to the parent name (see Note b) with elision of the final 'e' of hydride names before 'i' (NIC, 3.153; NOC,C-816.2) except that  $\text{NH}_4^+$  is called 'ammonium' (NIC, 3.151). Systematic substitutive names are given in column (A), and names preferred for present use in column (B). One unit of charge need not be indicated in the name but if necessary it may be indicated by the Ewens-Bassett system (NIC, 2.252 and NIC, 3.17). Two units of charge must be indicated. This is done either by the addition of the Ewens-Bassett number or by the use of the infix 'di' between the hydride name and 'ium.'

	(A)	(B)
(a) $\text{NH}_4^+$	azanium	ammonium
(b) $\text{N}_2\text{H}_5^+$	diazanium	hydrazinium
(c) $\text{N}_2\text{H}_6^{2+}$	diazanediium or diazanium(2+)	hydrazinium(2+) hydrazinediium
(d) $\text{N}_2\text{H}_3^+$	diazanium	diazanium
(e) $\text{N}_2\text{H}_4^{2+}$	diazanediium or diazenium(2+)	diazanium(2+) or diazenediium
(f) $\text{N}_2\text{H}^+$	diazynium	diazynium
(g) $\text{N}_2\text{H}_2^{2+}$	diazynediium or diazynium(2+)	diazynium(2+) or diazynediium

Examples

- $\text{NH}_4\text{Cl}$  ammonium chloride
- $[\text{N}_2\text{H}_5]_2\text{SO}_4$  hydrazinium sulfate
- $[\text{N}_2\text{H}_6]\text{Cl}_2$  hydrazinium(2+) chloride

## II.2.3 ANIONS

Anions derived by the loss of one or more hydrogen ions from the nitrogen hydrides are named as in the following table. Names derived consistently from the systematic hydride names, from the common trivial hydride names, or from 'nitrogen' are given in column (A), and commonly used names retained for present use are given in column (B).

The charge need not be shown when the anion contains only one nitrogen atom and obeys the octet rule or when it carries only one charge. Otherwise two or more units of charge must be indicated either by the Ewens-Bassett system or alternatively, when the anion contains replaceable hydrogen, by the insertion of numerical infixes 'di,' 'tri,' etc., between the hydride name and 'ide.'

	(A)	(B)
(a) $\text{NH}_2^-$	azanide	amide
(b) $\text{NH}^{2-}$	azanediide azanide(2-)	imide
(c) $\text{N}^{3-}$ (see Note c)	nitride	nitride
(d) $\text{N}_2\text{H}_3^-$	diazanide hydrazinide	hydrazide
(e) $\text{N}_2\text{H}_2^{2-}$	diazanediide or diazanide(2-) or hydrazinediide or hydrazinide(2-)	hydrazide(2-)
(f) $\text{N}_2\text{H}^{3-}$	diazanetriide or diazanide(3-) or hydrazinetriide or hydrazinide(3-)	hydrazide(3-)

Note b. The substitutive name 'diazyne' is used as the parent name for dinitrogen in names formed according to this rule.

(g) $\text{N}_2^{4-}$ (see Note c)	dinitride(4-)	dinitride(4-)
(h) $\text{N}_2\text{H}^-$	diazanide	diazanide
(i) $\text{N}_2^{2-}$ (see Note c)	dinitride(2-)	dinitride(2-)
(j) $\text{N}_3^-$ (see Note c)	trinitride(1-)	azide

Examples

1.  $\text{NaNH}_2$  sodium amide
2.  $\text{Hg}_2\text{I}(\text{NH})(\text{OH})$  dimercury hydroxide imide iodide
3.  $\text{Li}_3\text{N}$  lithium nitride
4.  $\text{Na}[\text{N}_2\text{H}_3]$  sodium hydrazide

## II.2.4 LIGANDS

There is generally no ambiguity or difficulty in naming ligands derived from the nitrogen hydrides when they occur in Main Group metal compounds where the bonding situation is well defined. In transition metal compounds the ligand is often intermediate between formal valence bond states, and the formal oxidation state of the metal is not defined. Thus the  $\text{N}_2\text{H}_3$  ligand may be regarded formally as  $\text{NH}_2\text{-NH}^-$  (carrying one negative charge) or  $\text{NH}=\text{NH}_2^+$  (carrying one positive charge). In Main Group element compounds, conventional ideas regarding valency or formal oxidation states normally lead to an unequivocal choice of names based on valence bond structures. In transition metal compounds no unequivocal choice may be possible and an arbitrary choice must be made for nomenclature purposes. It is important for indexing and information retrieval purposes that the ligand should always have the same name regardless of whether conventional oxidation state ideas dictate otherwise.

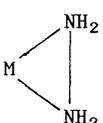
The following order of priorities is used to determine the ligand name.

- (1) If possible name the ligand as a neutral molecule which is not a zwitterion, nor a radical, nor a diradical.
- (2) If (1) is impossible, name it as an anionic ligand with the smallest possible formal charge.
- (3) If it cannot be named according to (1) or (2), name it as a zwitterionic ligand with a total formal charge of zero or, failing that, one with the smallest possible negative charge.
- (4) If none of the above is possible, name the ligand as a cationic ligand.

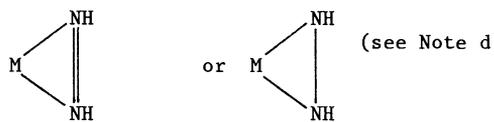
Some ligands derived from the dinitrogen skeleton have as many as three systematic names depending on the parent chosen for their derivation. Application of the above rules limits the choice to one parent for each  $\text{N}_2\text{H}_x$  ( $x = 0$  to 5) ligand as listed in Table 1. The preferred names for the derivation of ligand names are given in capital letters.

## II.2.41 NITROGEN HYDRIDES AND THEIR CATIONS AS LIGANDS

The ligand names are the same as those of the hydrides and cations from which they are derived except that 'ammonia' gives the ligand name 'ammine' (NIC, 7.322). The points of attachment of the ligand are indicated by suffixing the italicised symbol(s) of the ligand atom or atoms to the name of the ligand (NIC, 7.33). Ligands in their different bonding situations are given below (M = metal).

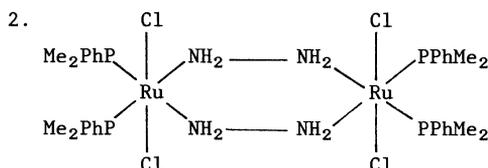
<u>Bound ligand</u>	<u>Ligand name</u>
(a) $\text{M-NH}_3$	ammine
(b) $\text{M-NH}_2\text{-NH}_2$	hydrazine- <u>N</u>
(c) 	hydrazine- <u>N,N'</u>

Note c. Because these anions contain no replaceable hydrogen, substitutive names are not needed, and those derived from the name of the element are preferred. The substitutive names would be: (c) azanetriide, (g) diazanettriide, and (i) diazenediide; (j) has no approved substitutive name.

- (d)  $M-NH_2-NH_3^+$  hydrazinium  
 (e)  $M-NH=NH$  diazene-N  
 (f)  (see Note d) diazene-N,N'  
 (g)  $M-NH_2-NH_2-M$   $\mu$ -hydrazine-N,N'  
 (h)  $M-NH=NH-M$   $\mu$ -diazene-N,N'  
 (i)  $M-N_3H$  (hydrogen azide)

Examples

1.  $[Cu(NH_3)_4]SO_4$  tetraamminecopper(II) sulfate



cdgh-tetrachloro-abij-tetrakis(dimethylphenylphosphine)-ef-di( $\mu$ -hydrazine-N,N')diruthenium(II) (see Note e)

di( $\mu$ -hydrazine-N,N')-bis[dichlorobis(dimethylphenylphosphine)ruthenium(II)]

3.  $[WBr_2(NH=NH)(Ph_2PCH_2CH_2PPh_2)_2]$   
 dibromo(diazene-N)bis[ethylenebis(diphenylphosphine)]tungsten(II)  
 (see Note f)

4.  $[\eta-(C_5H_5)(CO)_2Mn-NH=NH-Mn(CO)_2\eta-(C_5H_5)]$   
 tetracarbonylbis( $\eta$ -cyclopentadienyl)- $\mu$ -diazene-N,N'-dimanganese(I)  
 $\mu$ -diazene-N,N'-bis[dicarbonyl-( $\eta$ -cyclopentadienyl)manganese(I)]

### II.2.42 LIGANDS FORMALLY DERIVED FROM THE NITROGEN HYDRIDES BY THE LOSS OF ONE OR MORE HYDROGEN IONS

These ligands have the same formulae as the corresponding anions. Their names are systematically derived from those of the corresponding anions by replacing the final 'e' of the anion name by 'o.' The point of attachment of the ligand to the metal is indicated according to NIC, 7.33 and NIC, 7.34. When alternative derivations are possible make a choice according to II.2.4.

<u>Bound ligand</u> (see Note g)	<u>Ligand name</u>
(A) From ammonia	
(a) $M-NH_2$	amido
(b) $M=NH$	imido
(c) $M\equiv N$	nitrido
(d) $M-NH_2-M$	$\mu$ -amido
(e) $M-NH-M$	$\mu$ -imido
(f) $M-N=M$	$\mu$ -nitrido
(g) 	$\mu_3$ -imido
(h) 	$\mu_3$ -nitrido
(i) 	$\mu_4$ -nitrido

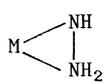
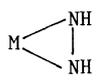
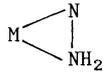
Note d. According to II.2.4 these two valence bond structures are given the same name.

Note e. Locant designators a, b, c, etc., have been assigned according to assignment 4 of NIC, 7.613.

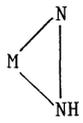
Note f. The ditertiary phosphine ligand may also be named 1,2-bis(diphenylphosphino)ethane.

Note g. Only the simplest formal structures are shown here. Generally in transition metal compounds the M-N and even N-N bond orders will be higher than shown.

## (B) From hydrazine

- (j)  $M-NH-NH_2$  hydrazido-N
- (k)  hydrazido-N,N'
- (l)  $M=N-NH_2$  hydrazido(2-)-N
- (m)  diazene-N,N' (see Note h)
- (n)  hydrazido(2-)-N,N' (see Note h)
- (o)  $M-NH-NH_2-M$   $\mu$ -hydrazido-N,N'
- (p)  $M-NH-NH-M$   $\mu$ -diazene-N,N' (see Note h)
- (q)  $M=N-NH_2-M$   $\mu$ -hydrazido(2-)-N,N'
- (r)   $\mu$ -hydrazido-N
- (s)   $\mu$ -hydrazido(2-)-N

## (C) From diazene (see Note i)

- (t)  $M-N=N-H$  diazenido-N
- (u)  diazenido-N,N'
- (v)   $\mu$ -diazenido-N
- (w)  $M-N=NH-M$   $\mu$ -diazenido-N,N'

The ligand obtained by stripping all the hydrogen atoms from hydrazine or diazene may be called dinitrogen, dinitride(2-), or dinitride(4-) according to its formal charge. In the absence of firm evidence otherwise the name dinitrogen is used (II.2.4).

Examples

- $[MoCl(NH)(Ph_2PCH_2CH_2PPh_2)_2]$   
chlorobis[ethylenebis(diphenylphosphine)]imidomolybdenum(III)
- $K_2[OsCl_5N]$   
potassium pentachloronitridoosmate(2-)
- $[Mo(NNH_2)O(S_2CNMe_2)_2]$   
hydrazido(2-)oxobis(N,N-dimethyldithiocarbamato)molybdenum(VI)
- $[Ir_3(\mu_3-N)(SO_4)_6(H_2O)_3]^{3-}$   
 $\mu_3$ -nitridotris[aquabis(sulfato)iridate](3-)
- $[CoH(N_2)(PPh_3)_3]$   
hydrido(dinitrogen-N)tris(triphenylphosphine)cobalt(I)

## II.2.43 LIGANDS DERIVED FROM THE NITROGEN HYDRIDE MONO-CATIONS BY LOSS OF ONE OR MORE HYDROGEN IONS FROM THE UNCHARGED NITROGEN CENTRE

These are named by adding the suffix 'ido' to the cation name. The Ewens-Bassett system is used to indicate the total formal charge on the ligand, including zero and one unit of negative charge.

Note h. Symmetrical hydrazido(2-) and all hydrazido(3-) ligands are named as derived from diazene [II.2.4 (see, e.g., ligand (f) II.2.41)].

Note i. See also ligands (m), (n), and (p) of II.2.42.

<u>Bound ligand</u>	<u>Ligand name</u>
(a) $M-NH-NH_3^+$	hydraziniumido(0)
(b) $M=N-NH_3^+$	hydraziniumido(1-)
(c) $\begin{array}{c} NH_3^+ \\   \\ M-NH-M \end{array}$	$\mu$ -hydraziniumido(0)
(d) $\begin{array}{c} NH_3^+ \\   \\ M-N-M \end{array}$	$\mu$ -hydraziniumido(1-)
(e) $\begin{array}{c} NH_3^+ \\   \\ M-N-M \\   \\ M \end{array}$	$\mu_3$ -hydraziniumido(1-)
(f) $M-N=NH_2^+$	hydrazido(2-)- $\underline{N}$ or diazeniumido(0) (see Note j)

### II.2.5 ORGANIC DERIVATIVES OF THE NITROGEN HYDRIDE LIGANDS

These are named as substitution products of parents whose names are set out in II.2.1 to II.2.43. When the compound contains two contiguous nitrogen atoms they are designated by  $N^1$  and  $N^2$  or by  $\underline{N}$  and  $\underline{N}'$ . In ligands where both nitrogen atoms carry no formal charge or when the nitrogen atoms carry equal formal charges the number 1 or unprimed  $\underline{N}$  is assigned to the nitrogen atom carrying most substituents, or when each nitrogen atom is also equally substituted, to that carrying the substituent coming first in alphabetical order of substituents. The metal does not count as a substituent for these purposes. In ligands which contain formally negatively charged nitrogen by the application of II.2.4, as well as neutral or positively charged nitrogen the anionic nitrogen is designated by the number 1 or unprimed  $\underline{N}$ . If both nitrogen atoms carry formal negative charges, that carrying the greater negative charge has priority for number 1 or the unprimed  $\underline{N}$ . For more complex substitutions see NOC, C8 and C9.

#### Examples of linkage:

(a) $M-N=N-C_6H_5$	2-phenyldiazenido- $\underline{N}^1$
(b) $M=N-N(CH_3)_2$	2,2-dimethylhydrazido(2-)- $\underline{N}^1$
(c) $M-N(CH_3)=N(C_2H_5)$	1-ethyl-2-methyldiazene- $\underline{N}^2$
(d) $M-N(CH_3)-N(C_2H_5)(C_3H_7)$	2-ethyl-1-methyl-2-propylhydrazido- $\underline{N}^1$
(e) $M-N(CH_3)-N(CH_3)_2H^+$	1,2,2-trimethylhydraziniumido(0)- $\underline{N}^1$
(f) $M-NHCH_3-N(CH_3)_2$	1,1,2-trimethylhydrazine- $\underline{N}^2$
(g) $M-NH=N(CH_3)-M$	$\mu$ -1-methyldiazene- $\underline{N}^1, \underline{N}^2$

#### Examples

- $$\begin{array}{c} P(CH_2H_5)_3 \\ | \\ Cl-Pt-N=N-Ph \\ | \\ P(C_2H_5)_3 \end{array}$$
trans-chloro(2-phenyldiazenido- $\underline{N}^1$ )-bis(triethylphosphine)platinum(II)
- $$\left[ \begin{array}{c} P(CH_2H_5)_3 \\ | \\ Cl-Pt-NH=NPh \\ | \\ P(C_2H_5)_3 \end{array} \right] Cl$$
trans-chloro(1-phenyldiazene- $\underline{N}^2$ )-bis(triethylphosphine)platinum(II) chloride
- $$[WBr_2\{=N-N(CH_3)_2\}\{(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2\}_2]$$
dibromo[(2,2-dimethylhydrazido(2-)- $\underline{N}^1$ )]bis[ethylenebis(diphenylphosphine)] tungsten(IV)

Note j. The ligand  $-N=NH_2^+$  and other diazenium ligands are normally named as hydrazine derivatives according to II.2.4 [see ligand (1) of II.2.42].

TABLE 1. Names of nitrogen hydrides, neutral molecules, cations, anions, and zwitterions derived from the N-N skeleton (see Note k)

<u>Stoichiometric Formula</u>	<u>Parent Molecule Hydrazine</u>		<u>Parent Molecule Diazene</u>	<u>Parent Molecule Dinitrogen</u> (Common name nitrogen)
$N_2H_6$	$NH_3^+ - NH_3^+$ hydrazinium(2+) hydrazinedium			
$N_2H_5$	$NH_2^+ - NH_3^+$ HYDRAZINIUM			
$N_2H_4$	$NH^- - NH_3^+$ HYDRAZINIUMIDE(0)			
$N_2H_3$	$N^{2-} - NH_3^+$ HYDRAZINIUMIDE(1-)			
$N_2H_4$	$NH_2 - NH_2$ HYDRAZINE		$NH_2^+ = NH_2^+$ diazanium(2+) diazenedium	
$N_2H_3$	$NH^- - NH_2$ HYDRAZIDE hydrazinide		$NH = NH_2^+$ diazanium	
$N_2H_2$	$N^{2-} - NH_2$ HYDRAZIDE(2-) hydrazinediide		$N^- = NH_2^+$ diazaniumide(0)	
$N_2H_2$	$NH^- - NH^-$ hydrazide(2-) hydrazinediide		$NH = NH$ DIAZENE	$NH \equiv NH^+$ diazynedium diazynium(2+)
$N_2H$	$N^{2-} - NH^-$ hydrazide(3-) hydrazinetriide		$N^- = NH$ DIAZENIDE	$N \equiv NH^+$ diazynium (see Note l)
$N_2$	$N^{2-} - N^{2-}$ dinitride(4-)		$N^- = N^-$ dinitride(2-)	$N \equiv N$ DINITROGEN

Note k. The ligand name is derived from the form given in capitals (see II.2.4).

Note l. This species is systematically named diazynium. The apparent alternative, diazonium, from organic nomenclature is not the name of  $N_2H^+$ . Diazonium is a suffix used with the name of the organic parent substance as in benzenediazonium,  $PhN_2^+$  (NOC, C 931.1). The substitutive name of that ion would be phenyldiazynium. The inorganic name of the ion  $N_2H^+$  would be hydrodinitrogen(1+) but is not recommended for present use.