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Group 7 'organohydrazide' chemistry: classification of ligand type based on crystal structural data†

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Group 7 organohydrazide complexes have been classified into eight monohapto structural types on the basis of crystal structural data. Classification on this basis provides a way for uniform identification of the ligand structural types present in a complex and for uniform assignment of oxidation states of the metal.

Transition metal organohydrazide complexes, which are defined as complexes containing a metal–nitrogen–nitrogen linkage, have received considerable attention as potential model systems for intermediates in biological nitrogen fixation. In the past, a variety of conventions have been used to describe the nature of the bonding of these ligands in metal complexes. In fact, some of the established conventions are contrary to the bond lengths and angles found in the crystal structural determinations of these complexes. This article proposes the use of crystal structural data to define the structural types and bonding modes of these ligands. The scope of this paper is limited to Group 7 mononuclear organohydrazide complexes. The convention that is adopted here assumes all electrons involved in the metal–nitrogen bonds have been donated by the highly reducing hydrazine precursor, accurately reflecting the chemistry observed. In cases where the diazo ligand is generated from the diazonium salt, this convention cannot necessarily be assumed because the reaction conditions have changed from reducing to oxidizing. The eight monohapto structural types of organohydrazide ligands are shown in Fig. 1. The structural types are the uninegative, linear, four-electron donor diazenido **A**; the uninegative, bent, two-electron donor diazenido **B**; the neutral, bent, two-electron donor diazene **Γ**; the zwitterionic, neutral, bent, four-electron donor isodiazene **Δ** the zwitterionic, neutral, bent, two-electron donor **E**; the uninegative, bent, two-electron donor **Z**; the unipositive, bent, two-electron donor **H**; and the neutral, bent, two-electron donor, hydrazino **Θ**. Not all of the structural types listed have been observed in Group 7 metal complexes as yet. It should be noted that within the eight structural types are the possibilities of *cis* and *trans* isomers.

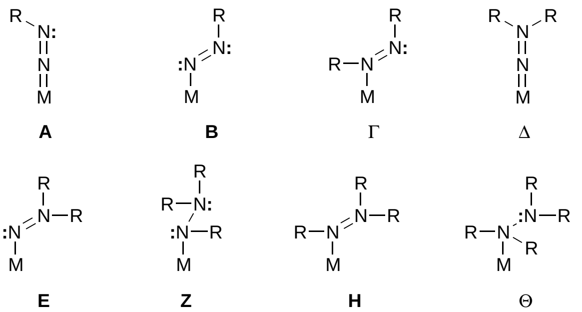

Fig. 1 The structural types of organohydrazide ligands. The uninegative, linear, four-electron donor diazenido **A**; the uninegative, bent, two-electron donor diazenido **B**; the neutral, bent, two-electron donor diazene **Γ**; the zwitterionic, neutral, bent, four-electron donor isodiazene **Δ**; the zwitterionic, neutral, bent, two-electron donor **E**; the uninegative, bent, two-electron donor **Z**; the unipositive, bent, two-electron donor **H**; the neutral, bent, two-electron donor, hydrazino **Θ**

Discussion

The diazenido ligand has two forms, the uninegative four-electron donor **A** and the uninegative two-electron donor **B**. Complexes containing structural type **A** (see Table 1) typically have metal–nitrogen bond lengths of 1.7 to 1.8 Å, indicative of multiple bonding, and nitrogen–nitrogen multiple bonding, which is evidenced by the bond lengths of 1.2 to 1.3 Å. The metal–nitrogen–nitrogen bond angle in this structural type is relatively linear. The chelating diazenido ligand form is an interesting case (see Table 2) because it has characteristics of **A**, as seen in the metal–nitrogen bond length, and characteristics of **B**, as seen by the bond angle, which is imposed by the additional constraint of the chelate. A crystal structural determination of a complex containing **B** has not been seen, and the chelating diazenido complexes are the closest example of this structural type. All of the structural examples of chelating diazenido complexes have an extended π system in the ring containing the metal, and as a result, the metal–nitrogen bond is shortened from what might be expected in **B**.

A third structural type is the neutral diazene **Γ** (see Table 3), which is a two-electron donor to the metal. Both the α-nitrogen and the β-nitrogen are substituted, and there is a double bond between the nitrogens. Electrons from the α-nitrogen are donated to the metal orbitals, and the charge on both nitrogens is neutral, resulting in an overall neutrally charged ligand. The metal–nitrogen bond lengths are about 1.9 Å, indicative of some multiple bonding, which results from the delocalization of the π system of the ligand. The nitrogen–nitrogen bond lengths are about 1.3 Å, which is demonstrative of multiple bonding. As would be expected, these bond lengths are longer than those found in diazenido complexes due to the change in hybridization of the α-nitrogen. Again, the chelating diazene ligands present an additional constraint to the system. The chelation forces **Γ** to have the substituents on the α- and the β-nitrogen atoms in a *trans* configuration, There is one example of a monodentate diazene complex, $[Tc(CO)_3(PPh_3)_2\{HNN(p\text{-}Bu^tC_6H_4)\}][PF_6]$.[22] This complex was synthesized from the diazonium salt, which inserts into a metal–hydride bond, instead of from the

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† This paper is dedicated to the late Sir Geoffrey Wilkinson. He profoundly influenced the direction of the senior author's life. In the first instance by accepting an unknown from South Wales into his research group, fostering him and then sending him to Harvard University as the first of a stream of his students that have had successful careers in the United States.

Table 1 Selected bond lengths (Å) and angles (°) for the diazenido **A** complexes

Complex	**M**=**N**NR	M**N**=**N**R	**M**=**N**=**N**R	Ref.
Re(NNPh)(PMe$_2$Ph)$_3$Cl$_2$	1.80	1.23	172	1, 2
[(η^5-C$_5$Me$_5$)Mn(*o*-N$_2$C$_6$H$_4$CF$_3$)(CO)$_2$][BF$_4$]	1.693(7)	1.211(8)	171.8(8)	3
Re(PPh$_3$)[S(CH$_2$)$_2$S(CH$_2$)$_3$S(CH$_2$)$_2$S](NNCOPh)	1.776(12)	1.267(17)	167.5(12)	4, 5
ReBr$_2$(**NNPh**)(NNHPh)(PPh$_3$)$_2$	1.793(11)	1.212(16)	172.4(10)	6
[NHEt$_3$][Re$_2$(NNPh)$_2$(SPh)$_7$]	1.81(2)	1.23(3)	170.0(18)	7
	1.81(2)	1.24(3)	171.4(19)	
ReCl$_2$(PPh$_3$)$_2$(NNCO$_2$Me)(O$_2$)	1.798(40)	1.108(56)	170.2(22)	8
Re(NNC$_6$H$_4$Br)$_2$(PPh$_3$)$_2$Cl	1.798(19)	1.241(29)	172.0(27)	9
Re(NNC$_6$H$_4$Br)$_2$(PPh$_3$)$_2$SC$_6$H$_3$Me$_2$-2,5	1.730(13)	1.324(17)	160.9(2)	9
	1.798(16)	1.249(23)	178.1(2)	
Tc(NNC$_6$H$_4$Br)$_2$(PPh$_3$)$_2$Cl	1.796(6)	1.229(9)	170.7(7)	10
ReCl$_2$(PPh$_3$)$_2$(NCMe)(NNCOPh)	1.756(7)	1.25(1)	172.1(6)	11
ReCl$_2$(PPh$_3$)$_2$(NNCO$_2$Ph)(C$_5$H$_5$N)	1.72(2)	1.28(2)	166.9(12)	11
ReCl$_2$(PPh$_3$)$_2$[**NNC(O)Ph**][H$_2$NNHC(S)Ph]	1.712(17)	1.267(24)	170.5(16)	12
ReCl$_2$(PPh$_3$)$_2$[**NNC(O)Ph**][H$_2$NNHC(O)SMe]	1.732(3)	1.248(5)	172.0(3)	12
[NEt$_4$][Re(NNPh)$_2$(O$_2$C$_6$H$_4$)$_2$]	1.825(11)	1.21(2)	163.9(9)	13
	1.809(9)	1.21(1)	170.0(9)	
[Re(HNNpy)(**NNpy**)(PMe$_2$Ph)$_2$Cl][Cl]*	1.802(7)	1.221(9)	172.0(9)	14
Re(**NNC$_4$H$_2$N$_2$CF$_3$**)(HNNC$_4$H$_2$N$_2$CF$_3$)(PPh$_3$)Cl$_2$	1.756(9)	1.267(12)	173.2(8)	18
Re(HNNpy)(**NNpy**)(PPh$_3$)Cl$_2$	1.778(14)	1.212(22)	172.8(13)	15
Re(HNNpy)(**NNpyH**)Cl$_3$	1.741(7)	1.253(12)	168.1(8)	16
[Re(*p*-NNC$_6$H$_4$Me)$_2$(Me$_2$PCH$_2$CH$_2$PMe$_2$)$_2$][PF$_6$]	1.909(2)	1.223(3)	162.7(2)	17

* py = Pyridine.

Table 2 Selected bond lengths (Å) and angles (°) for the chelating diazenido complexes

Complex	**M**=**N**NR	M**N**=**N**R	**M**=**N**=**N**R	Ref.
ReCl$_2$(PPh$_3$)$_2$(NNCOPh)	1.769(8)	1.30(2)	133.8(7)	11
ReCl$_2$(PPh$_3$)$_2$(NNC$_8$H$_5$N$_2$)	1.79(2)	1.29(2)	136.4(9)	11
TcCl$_2$(PPh$_3$)$_2$(NNC$_8$H$_5$N$_2$)	1.767(12)	1.274(17)	138.6(7)	19
Re(NNpy)(PPh$_3$)$_2$Cl$_2$	1.815(8)	1.256(12)	137.3(7)	14
Tc(NNC$_4$H$_2$N$_2$CF$_3$)(PPh$_3$)$_2$Cl$_2$	1.810(8)	1.267(10)	138.0(6)	18

Table 3 Selected bond lengths (Å) and angles (°) for the diazene **Γ** complexes

Complex	**M**−**N**HNR	M−H**N**=**N**R	**M**−H**N**=**N**R	Ref.
Re[HNNC(S)Ph]$_3$·dmf[a]	2.003(13)	1.336(16)	127.8(8)	20
	1.994(12)	1.338(17)	N/A	
	2.002(9)	1.365(16)	N/A	
Re[HNNC(S)Ph]$_3$·OPPh$_3$	1.959(6)	1.333(8)	131.0(6)	20
ReO[**HNNC(S)Ph**][HNNHC(S)Ph]	2.022(9)	1.350(12)	124.2(6)	12
[Re{**HNNC(S)Ph**}{HNNHC(S)Ph}$_2$][Cl]	2.009(18)	1.347(21)	127.0(13)	20
HB(pz)$_3$ReO(HNNC$_8$H$_5$N$_2$)	1.935(7)	1.400(12)	121.0(6)	21
[Re(**HNNpy**)(NNpy)(PMe$_2$Ph)$_2$Cl][Cl]	1.949(9)	1.319(11)	126.4(7)	14
Re(NNC$_4$H$_2$N$_2$CF$_3$)(**HNNC$_4$H$_2$N$_2$CF$_3$**)(PPh$_3$)Cl$_2$	1.937(9)	1.322(13)	129.0(7)	18
Re(**HNNpy**)(NNpyH)Cl$_3$	1.936(10)	1.309(11)	127.1(8)	16
Re(**HNNpy**)(NNpy)(PPh$_3$)Cl$_2$	1.915(21)	1.340(26)	130.9(16)	15
[Tc(CO)$_3$(PPh$_3$)$_2${HNN(*p*-Bu^{t}C$_6$H$_4$)}][PF$_6$][b]	2.157(6)	1.243(8)	124.2(5)	22

[a] It is unclear whether all three of the organohydrazide ligands are protonated since the complex is paramagnetic. Dimethylformamide (dmf) is interacting with the organohydrazide ligand or ligands, which makes the placement of the proton or protons ambiguous. Molybdenum tris-(thiobenzoyl)diazene complexes were prepared, and a crystal structure was reported.[23] In this case, the dmf is not interacting with the diazene ligands.

[b] This is the only non-chelating diazene structure, and as a result, the metal–nitrogen bond is elongated because the π system is not as extended as in the chelated examples.

organohydrazine. The lack of chelation will diminish the π system and lengthen the metal–nitrogen bond compared to the chelated examples.

Structural type **Δ** (see Table 4) displays multiple bonding between the metal and the α-nitrogen and between the two nitrogens. The β-nitrogen is disubstituted. Since there is multiple bonding present between the nitrogens, the charge on the β-nitrogen is positive. The α-nitrogen is unsubstituted, and its electrons are donated to the metal orbitals forming a double bond to the metal, which gives this nitrogen an overall negative charge. As a result of the negatively charged α-nitrogen and the positively charged β-nitrogen, this zwitterionic ligand form is neutral. Generally, these metal–nitrogen bond lengths are between 1.7 and 1.8 Å. The nitrogen–nitrogen bond shows multiple bond character with lengths of *ca.* 1.27 Å, and the geometry is nearly linear with metal–nitrogen–nitrogen bond angles ranging from 160 to 174°. This structural type is referred to as a hydrazido(2−) ligand in the literature, which causes confusion in the assignment of oxidation states. Another, perhaps more appropriate, name seen in the literature is the isodiazene ligand.

The metal–nitrogen–nitrogen bond angle of the unsubstituted α-nitrogen and disubstituted β-nitrogen ligand tends to vary from nearly linear as in **Δ** to relatively bent as in **E**. The variance in the metal–nitrogen bond lengths and the bond angles is indicative of the degree of metal–nitrogen multiple bonding and the residence of the lone pair of the α-nitrogen. In the neutral **E** (see Table 5), the ligand has a metal–nitrogen single bond and a nitrogen–nitrogen double bond. A lone pair resides on the α-nitrogen, which is demonstrated by the protonation chemistry at this site to generate ligand form H.[26,27] The metal–nitrogen bond is shortened due to conjugation of the π

Table 4 Selected bond lengths (Å) and angles (°) for the isodiazene **Δ** complexes

Complex	**M**=**N**=NR$_2$	M=**N**=**N**R$_2$	**M**=**N**=**N**R$_2$	Ref.
[ReCl$_2$(NH$_3$)(NNHPh)(PMe$_2$Ph)$_2$][Br]	1.750(12)	1.28(2)	172(1)	2
ReCl$_2$(PPh$_3$)$_2$(**NNHCOPh**)(HNNHCOPh)	1.730(7)	1.275(9)	174.3(6)	11, 24
ReCl$_2$(PPh$_3$)$_2$(**NNHCOPh**)(HNNHCOMe)	1.712(7)	1.27(1)	172.2(7)	11
[Re(NNMePh)$_2$(S$_2$CNMe$_2$)$_2$][BPh$_4$]	1.78(1)	1.29(1)	166.6(8)	25
	1.777(9)	1.30(1)	166.9(9)	
[NEt$_4$][Re(NNPh$_2$)$_2$(O$_2$C$_6$H$_4$)$_2$]	1.770(12)	1.33(2)	159.6(8)	13
	1.768(10)	1.32(2)	159.7(8)	

Table 5 Selected bond lengths (Å) and angles (°) for **E**-type complexes

Complex	**M**–**N**=NR$_2$	M–**N**=**N**R$_2$	**M**–**N**=**N**R$_2$	Ref.
(η^5-C$_5$H$_5$)Re(CO)$_2$[*p*-NN(CH$_3$)C$_6$H$_4$OMe]	1.937(7)	1.283(10)	138.1(6)	26
ReBr$_2$(NNPh)(**NNHPh**)(PPh$_3$)$_2$	1.922(11)	1.287(15)	131.2(10)*	6
ReO(NNMePh)(SPh)$_3$	1.858(9)	1.255(15)	145.6(10)	9
[ReOCl(NNMePh)(PPh$_3$)$_2$][PF$_6$]$_2$	1.845(6)	1.261(8)	146.3(4)	25

* There is hydrogen bonding between a bromine and the β-nitrogen proton, which causes the bond angle to be decreased.

Table 6 Selected bond lengths (Å) and angles (°) for the **Z**-type complexes

Complex	**M**–**N**R–NR$_2$	M–**N**R–**N**R$_2$	**M**–**N**R–**N**R$_2$	Ref.
ReCl$_2$(PPh$_3$)$_2$(NNHCOPh)(**HNNHCOPh**)	2.212(8)	1.44(1)	119.5(4)	11, 24
ReCl$_2$(PPh$_3$)$_2$(NNHCOPh)(**HNNHCOMe**)	2.206(8)	1.441(9)	121.3(5)	11

Table 7 Selected bond lengths (Å) and angles (°) for the **H**-type complexes

Complex	**M**–**N**R=NR$_2$	M–**N**R=**N**R$_2$	**M**–**N**R=**N**R$_2$	Ref.
[(η^5-C$_5$H$_5$)Re(CO)$_2${*p*-HNN(CH$_3$)C$_6$H$_4$Me}][BF$_4$]	1.949(9)	1.32(1)	139.1(7)	27
ReO[HNNC(S)Ph][**HNNHC(S)Ph**]	2.054(7)	1.379(9)	122.3(5)	12
[Re{NHNC(S)Ph}{**HNNHC(S)Ph**}$_2$][Cl]	1.965(18)	1.397(21)	127.3(12)	20
	1.989(15)	1.376(20)	123.0(12)	

Table 8 Selected bond lengths (Å) and angles (°) for the hydrazino **Θ** complexes

Complex	**M**–**N**R$_2$–NR$_2$	M–**N**R$_2$–**N**R$_2$	**M**–**N**R$_2$–**N**R$_2$	Ref.
ReCl$_2$(PPh$_3$)$_2$[NNC(O)Ph][**H$_2$NNHC(S)Ph**]	2.224(17)	1.427(20)	119.9(11)	12
ReCl$_2$(PPh$_3$)$_2$[NNC(O)Ph][**H$_2$NNHC(O)SMe**]	2.192(4)	1.421(5)	119.6(3)	12

system throughout the ligand. A typical metal–nitrogen bond length is 1.9 Å, and a typical nitrogen–nitrogen bond length is approximately 1.2 Å. The ligand is bent, with typical metal–nitrogen–nitrogen bond angles in the 130 to 146° range, indicative of the sp^2 hybridization of the α-nitrogen. As expected, this structural type has longer metal–nitrogen bond lengths than **Δ** since it is more bent; however, the nitrogen–nitrogen bond length does not seem to vary as greatly from those of **Δ**.

Structural type **Z** (see Table 6) has a metal–nitrogen single bond and a nitrogen–nitrogen single bond. Complexes with this uninegative ligand have metal–nitrogen bond lengths of about 2.2 Å and nitrogen–nitrogen bonds of about 1.4 Å. The metal–nitrogen–nitrogen bond angle is approximately 120°, indicative of the sp^3 hybridization of the nitrogens. Structural type **Z** is appropriately referred to as a uninegative ligand in the literature.

Structural type **H** (see Table 7) can be considered as a substituted form of the neutral diazene **Γ**. Since the β-nitrogen is disubstituted, the overall ligand charge is unipositive. The metal–nitrogen bond length is between 1.9 and 2.0 Å, and the nitrogen–nitrogen bond length is approximately 1.3 Å. The metal–nitrogen bond is slightly shorter than a typical single bond due to some delocalization of the π system of the ligand. The nitrogen–nitrogen bond length is indicative of multiple bonding. The metal–nitrogen–nitrogen bond angle is bent, ranging from 123 to 139°.

Structural type **Θ** (see Table 8), appropriately referred to as hydrazino, is a fully substituted, neutral organohydrazine behaving as a neutral donor ligand such as an amine ligand. Typical bond lengths are about 2.2 Å for the metal–nitrogen bond and 1.4 Å for the nitrogen–nitrogen bond. The metal–nitrogen–nitrogen bond angle is bent at approximately 120°, indicative of the sp^3 hybridization of the nitrogens.

There are some ambiguities with respect to the designation of a structural type in a complex if sufficient spectroscopic data do not exist. For example, if the substituent on the α- or the β-nitrogen atom is hydrogen which is not found crystallographically, then simple examination of the bond lengths and angles will not suffice to determine the ligand type. Comparison of the bond lengths and angles of the diazenido, **A**, with the isodiazene, **Δ**, shows that there is no way to discern between the two types on this basis. A case in point is the complex ReCl$_2$(PPh$_3$)$_2$[NNHC(O)Ph][HNNHC(O)Ph].[11,24] In the report of this complex, the formulation is of the types **Δ** and **Z**, which places a hydrogen on the β-nitrogen (**Δ**) and hydrogens on the α- and β-nitrogens (**Z**). However, in the absence of sufficient spectroscopic data, the argument for the complex containing ligands **A** and **Θ** can be made, placing all three hydrogens on one of the organohydrazide ligands.[12] As is the case with **A** and **Δ**, the bond lengths and angles of **Z** and **Θ** do not allow for differentiation between the two. The similar complex ReCl$_2$(PPh$_3$)$_2$[NNC(O)Ph][H$_2$NNHC(S)Ph][12] has been reported as consisting of organohydrazide types **A** and **Θ**. Since in both of the above mentioned complexes there are insufficient data to determine conclusively which structural types are present, this paper classifies the complexes as they appear in the literature.

Additionally, an ambiguity can exist in the classification of types **Γ** and **E** by crystal data when the substituents on the nitrogens are hydrogens and no additional spectroscopic data exist. An example of this dilemma is found in the complex [HB(pz)$_3$]ReO(HNNC$_8$H$_5$N$_2$) (pz = pyrazol-1-yl).[21] In the report of this complex, the hydrogen is not placed definitively on the α- or the β-nitrogen. The only spectroscopic evidence given for this hydrogen is a resonance in the ^{1}H NMR spectrum at δ 12. The bond lengths and angles of the two possible types, **Γ** and **E**, do not allow for an assignment to be made; however, the oxidation state assignment of the metal in either case should be rhenium(III) instead of rhenium(V) since both **Γ** and **E** are neutral. In some complexes, the placement of the hydrogen can be made using ^{1}H NMR data. In the case of [Re(HNNpy)(NNpy)(PMe$_2$Ph)$_2$Cl][Cl],[14] the resonance for the α-nitrogen proton is found at δ 19, which indicates that this proton is deshielded and resides close to the metal. In addition, a correlation spectroscopy NMR experiment shows no coupling to this resonance.

Many of the problems in assigning the charge of some types of the organohydrazide ligand can be attributed to treating the organohydrazine as a redox inactive species. Since the reaction of the organohydrazine with a metal complex is a redox reaction, the loss of hydrogens from the hydrazine to form the hydrazide cannot be considered as a simple deprotonation, and therefore, the charge on the organohydrazide ligand cannot be assigned simply as a function of the number of hydrogens lost. The assignment of the charge by counting the number of hydrogens lost from the organohydrazine to form the organohydrazide accounts for much of the confusion in the charge assignment for many of the organohydrazide ligand forms shown in Fig. 1. Since organohydrazines are reducing, all of the electrons forming the metal–nitrogen bond can be considered to be derived from the organohydrazine. In addition, the nitrogen is more electronegative than the metal, and when considering the charge assignments of the ligands, the electrons, by definition, should be assigned to the more electronegative element. Some additional examples and inconsistencies found in the literature are given below.

Structural type **A** is found in a number of complexes in the literature (see Table 1). An early example is the rhenium diazenido complex, Re(NNPh)(PMe$_2$Ph)$_3$Cl$_2$,[1,2] which is formed from the reaction of Re(PMe$_2$Ph)$_3$Cl$_3$ with phenylhydrazine. The diazenido complex is correctly assigned as rhenium(III), and the metal–nitrogen bond is described as having a σ- and π-donation to the metal center. This assignment is based on the crystal structural determination, which found that the rhenium–nitrogen bond length is 1.80 Å, consistent with π-orbital interaction between the nitrogen and the metal orbitals.[28] The nitrogen–nitrogen bond length of 1.23 Å is consistent with a double bond.

Starting from ReOCl$_3$(PPh$_3$)$_2$, trigonal bipyramidal complexes, Re(NNC$_6$H$_4$Br)$_2$(PPh$_3$)$_2$L (L = Cl or SR) with two uninegative diazenido ligands have been made.[9] The rhenium–nitrogen bond lengths are 1.798(19) Å and 1.730(13) Å, and the nitrogen–nitrogen bond lengths are 1.241(29) Å and 1.324(17) Å, respectively. As a result, the formal oxidation state of rhenium in these complexes should be assigned as +3. The analogous Tc(NNC$_6$H$_4$Br)$_2$(PPh$_3$)$_2$Cl has also been synthesized and assigned as technetium(I) by Nicholson *et al.*[10] The technetium–nitrogen bond length is 1.796(6) Å, and the nitrogen–nitrogen bond length is 1.229(9) Å. The bond lengths of all of these complexes demonstrate multiple bonding character throughout the diazenido unit. The formal oxidation state of the metal should be assigned as +3, as is the assignment made by Dilworth *et al.*[29] of Tc^{III}(NNC$_6$H$_4$Cl)$_2$(PPh$_3$)$_2$Cl.

Similar octahedral complexes can also be made using potentially chelating organohydrazines (see Table 2). An example is ReCl$_2$(PPh$_3$)$_2$(NNC$_8$H$_5$N$_2$), which has been assigned in its report as rhenium(V) due to the designation of the diazenido unit as a 3− ligand.[11] Instead, the designation of the diazenido ligand as a 1− ligand makes the formal oxidation state of the complex rhenium(III). The rhenium–nitrogen bond length in this complex is 1.79(2) Å, and the nitrogen–nitrogen bond length is 1.29(2) Å. These lengths demonstrate the multiple bond character of the metal–nitrogen bond and the multiple bond character of the nitrogen–nitrogen bond. The chelating diazenido forms an extended π system with the metal center, and complexes of this type have non-contact shifted NMR spectra.[14,18]

Conclusion

Crystal structural data have been applied in the classification of the structural forms found in the Group 7 organohydrazide complexes. The degree of substitution and the degree of multiple bonding between the metal and the α-nitrogen and the α- and the β-nitrogen, in most cases, can be determined from the structural data. The organization of these complexes on this basis creates a uniform way of characterizing and discussing this class of compounds. Although not all instances have been addressed by this survey, a rational basis for discussion of this chemistry has been presented.

References

1 V. F. Duckworth, P. G. Douglas, R. Mason and B. L. Shaw, *Chem. Commun.*, 1970, 1083.
2 R. Mason, K. M. Thomas, J. A. Zubieta, P. G. Douglas, A. R. Galbraith and B. L. Shaw, *J. Am. Chem. Soc.*, 1974, **96**, 260.
3 C. F. Barrientos-Penna, F. W. B. Einstein, D. Sutton and A. C. Willis, *Inorg. Chem.*, 1980, **19**, 2740.
4 T. Nicholson, N. Shaikh and J. Zubieta, *Inorg. Chim. Acta*, 1985, **99**, L45.
5 T. Nicholson and J. Zubieta, *Inorg. Chem.*, 1987, **26**, 2094.
6 J. R. Dilworth, S. A. Harrison, D. R. M. Walton and E. Schweda, *Inorg. Chem.*, 1985, **24**, 2594.
7 T. Nicholson and J. Zubieta, *Inorg. Chim. Acta*, 1985, **100**, L35.
8 T. Nicholson and J. Zubieta, *Inorg. Chim. Acta*, 1987, **134**, 191.
9 T. Nicholson, P. Lombardi and J. Zubieta, *Polyhedron*, 1987, **6**, 1577.
10 T. Nicholson, N. De Vries, A. Davison and A. G. Jones, *Inorg. Chem.*, 1989, **28**, 3813.
11 T. Nicholson and J. Zubieta, *Polyhedron*, 1988, **7**, 171.
12 A. Moehlenkamp and R. Mattes, *Z. Naturforsch., B: Chem. Sci.*, 1992, **47**, 969.
13 P. B. Kettler, Y.-D. Chang and J. Zubieta, *Inorg. Chem*, 1994, **33**, 5864.
14 M. Hirsch-Kuchma, T. Nicholson, A. Davison, W. M. Davis and A. G. Jones, *Inorg. Chem.*, 1997, **36**, 3237.
15 T. L. Nicholson, J. Cook, A. Davison, J. A. Zubieta and A. G. Jones, *Inorg. Chim. Acta*, 1996, **252**, 427.
16 T. L. Nicholson, J. Cook, A. Davison, J. A. Zubieta and A. G. Jones, *Inorg. Chim. Acta*, 1996, **252**, 421.
17 B. Coutinho, J. Dilworth, P. Jobanputra, R. M. Thompson, S. Schmid, J. Strähle and C. M. Archer, *J. Chem. Soc., Dalton Trans.*, 1995, 1663.
18 M. Hirsch-Kuchma, T. Nicholson, A. Davison, W. M. Davis and A. G. Jones, *J. Chem. Soc., Dalton Trans.*, 1997, **18**, 3185.
19 M. J. Abrams, S. K. Larsen, S. N. Shaikh and J. Zubieta, *Inorg. Chim. Acta*, 1991, **185**, 7.
20 A. Moehlenkamp and R. Mattes, *Z. Naturforsch., Teil B*, 1990, **45**, 1167.
21 P. B. Kettler, Y.-D. Chang, Q. Chen, J. Zubieta, M. J. Abrams and S. K. Larsen, *Inorg. Chim. Acta*, 1995, **231**, 13.
22 J. Cook, A. Davison, W. M. Davis and A. G. Jones, *Organometallics*, 1995, **14**, 650.
23 J. R. Dilworth, J. Hyde, P. Lyford, P. Vella, K. Ventatasubramaman and J. A. Zubieta, *Inorg. Chem.*, 1979, **18**, 268.
24 T. Nicholson and J. Zubieta, *J. Chem. Soc., Chem. Commun.*, 1985, 367.
25 J. R. Dilworth, P. Jobanputra, S. J. Parrott, R. M. Thompson, D. C. Povey and J. A. Zubieta, *Polyhedron*, 1992, **11**, 147.
26 C. F. Barrientos-Penna, F. W. B. Einstein, T. Jones and D. Sutton, *Inorg. Chem.*, 1982, **21**, 2578.
27 C. F. Barrientos-Penna, C. F. Campana, F. W. B. Einstein, T. Jones, D. Sutton and A. S. Tracey, *Inorg. Chem.*, 1984, **23**, 363.
28 G. W. Parshall, *J. Am. Chem. Soc.*, 1965, **87**, 2133.
29 J. R. Dilworth, P. Jobanputra, T. M. Thompson, D. C. Povey, C. M. Archer and J. D. Kelly, *J. Chem. Soc., Dalton Trans.*, 1994, 1251.

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