# Molecular orbital analysis of the metal–hydrazide(2−) bonding in co-ordination chemistry †

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The bonding in mono- and bis-hydrazido metal complexes has been studied with the help of EHMO and *ab initio* calculations on various models as well as on free hydrazide. The theoretical results have been analysed together with a collection of structural data obtained through a Cambridge Data Base search covering 118 compounds. Although generally described as being a hydrazide(2−) ligand, its oxidation state is often closer −1 in early transition-metal complexes, corresponding to the following occupation of its frontier orbitals: $(\sigma_n)^2(\pi_{NN})^2(\pi_\sigma)^2(\pi^*_{NN})^1$. The occupied hydrazido $\pi_{NN}$ orbital, which does not interact significantly with the metal, is largely responsible for the significant double-bond character of the N−N bond. The partial population of the $\pi^*_{NN}$ level, which tends to reduce the N−N bond order, is partly balanced by depopulation of the somewhat antibonding $\pi_\sigma$ orbital. Assuming the traditional hydrazido(2−) formal charge, the ligand is a six-electron donor in mono-hydrazido metal species if co-ordinated linearly. If significantly bent, it is a four-electron donor. In the case of *cis* bis(hydrazido) species, the two formally hydrazide(2−) ligands act generally as a 10-electron donor system.

During the last two decades the chemistry of inorganic compounds containing transition metal–nitrogen multiple bonds has received considerable attention,[1] due mainly to the interest of these complexes as potential models for intermediates in biological nitrogen fixation. A particularly rich class among these compounds are those containing $NNR_2$ ligands. The bonding ability of this type of ligand, generally called hydrazide(2−), allows it to adopt a large variety of co-ordination modes, which may or may not involve the $\pi$ NN system. In this paper we analyse the terminal M−$NNR_2$ bonding, which is by far the most common.[2–90] The different ways a terminal $NNR_2$ ligand is *a priori* able to bind to a metal centre can be generated by starting from the two closed-shell representations of neutral isodiazene (**a**) and the hydrazido dianion (**b**) shown in Scheme 1. Depending on the electronic requirement of the metal, one, two or three ligand lone pairs can be involved in the complexation. This generates the $\mathbf{a_1}$, $\mathbf{a_2}$, $\mathbf{b_1}$, $\mathbf{b_2}$ and $\mathbf{b_3}$ co-ordination modes shown in Scheme 1. Note that the metal lone pair on $\mathbf{a_1}$ or $\mathbf{a_2}$ is unnecessary. It has been considered in order to keep all the formulae isoelectronic. Several variations of these formulae can be generated, depending on the dative or non-dative nature of each of the various M−$N_\alpha$ bonds. One should also notice that a bonding situation can sometimes be correctly described only if several canonical formulae are considered.

Table 1 lists the structurally characterized monohydrazido mononuclear (and related polynuclear) complexes, with some important structural data.[2–74] Table 2 lists similar information for the corresponding bis(hydrazido) species.[49,54,68,69,75–90] The bibliographic search, as well as the collection of some of the reported metric data, was made with the help of the Cambridge Data Base system.[91] One can see from these tables that most of the listed compounds are made of molybdenum or tungsten in a high oxidation state and lying in an octahedral environment.
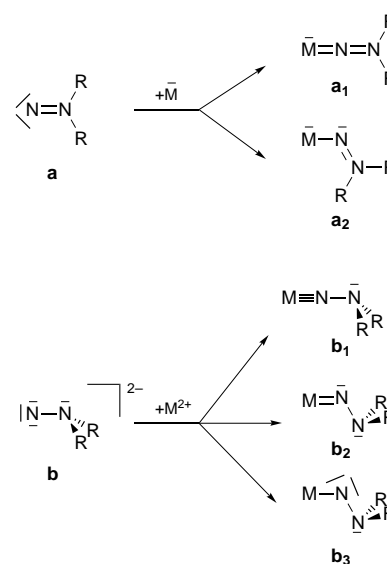
**Scheme 1**

The sum of the bond angles around $N_\beta$ ($\Sigma\alpha_i$) indicates invariably a planar (sp²) co-ordination for this atom (*i.e.* consistent with formulae $\mathbf{a_1}$ and $\mathbf{a_2}$), with the exception of eight compounds (**9**, **10**, **37**, **60**, **67**, **85**, **86** and **89**) in which the $N_\beta$ hybridization is found to be intermediate between sp³ and sp². Actually, the cases of **9**, **10** and **37** are irrelevant since their observed pyramidalization at $N_\beta$ is due to the existence of intermolecular hydrogen bonding.[9,13,36] In most of the listed compounds the M−$N_\alpha$−$N_\beta$ bond angle is close to 180°, indicating an sp hybridization for $N_\alpha$, while the $N_\alpha$−$N_\beta$ separation lies in the range between standard single and double bonds (1.47 and 1.25 Å, respectively).[92] The M−$N_\alpha$ distances are also generally indicative of some partial

**Table 1** Structurally characterized monohydrazido mononuclear and related polynuclear complexes

| Compound | Distance (Å) | | Angle (°) | Σα$_i$ | Co-ordin- | | | |
| | M−N$_\alpha$ | N$_\alpha$−N$_\beta$ | M−N$_\alpha$−N$_\beta$ | at N$_\beta$(°) | ation number | MVE | HVE | Ref. |
|---|---|---|---|---|---|---|---|---|
| **1** [W(NNH$_2$)Cl(dppe)$_2$]$^+$ | 1.73(1) | 1.37(2) | 171(1) | n.a. | 6 | 18 | 6 | 2 |
| **2** [Re(NNHPh)Cl$_2$(NH$_3$)(PMe$_2$Ph)$_2$]$^+$ | 1.750(2) | 1.28(2) | 172(1) | 358 | 6 | 18 | 6 | 3 |
| **3** [Mo(NNEtPh)(S$_2$CNCH$_2$CH$_2$CH$_2$CH$_2$CH$_2$)$_3$]$^+$ | 1.715(16) | 1.37(2) | 170(2) | 357 | 6 | 18 | 6 | 4 |
| **4** [W(NNHMe)Br(dppe)$_2$]$^+$ | 1.768(14) | 1.32(2) | 174(1) | n.a. | 6 | 18 | 6 | 4 |
| **5** [V(C$_5$H$_5$)$_2${NN(SiMe$_3$)$_2$}] | 1.666(6) | 1.369(9) | 180 | 360 | 7 | 19(17)$^a$ | 6(4)$^a$ | 5 |
| **6** [Mo(NNH$_2$)F(dppe)$_2$]$^+$ | 1.762(12) | 1.333(24) | 176.4(13) | 360 | 6 | 18 | 6 | 6 |
| **7** [Mo{NNH(C$_8$H$_{17}$)}I(dppe)$_2$]$^+$ | 1.801(11) | 1.259(14) | 174(1) | n.a. | 6 | 18 | 6 | 7 |
| **8** [W(C$_5$Me$_5$)Cl$_3$(NNPh$_2$)] | 1.769(2) | 1.296(3) | 173.8(2) | 360 | 7 | 18 | 6 | 8 |
| **9** [Mo(NNH$_2$)(quin)(PMe$_2$Ph)$_3$]$^+$ | 1.743(4) | 1.347(7) | 172.3(5) | 344 | 6 | 18 | 6 | 9,13 |
| **10** [W(NNH$_2$)(quin)(PMe$_2$Ph)$_3$]$^+$ | 1.753(10) | 1.360(17) | 174.7(9) | 351 | 6 | 18 | 6 | 9,13 |
| **11** [MoO(NNMe$_2$)(S$_2$CNMe$_2$)$_2$] | 1.708(6) | 1.288(10) | 168.0(7) | 360 | 6 | 18 | 6 | 10 |
| **12** [Mo(NNMePh)(NHNMePh)(S$_2$CNMe$_2$)$_2$]$^+$ | 1.752(10) | 1.285(14) | 169.6(7) | 360 | 6 | 18 | 6 | 11 |
| **13**$^b$ [W(NNHPh)Cl$_3$(PMe$_2$Ph)$_2$] | 1.737(5) | 1.325(8) | 174.4(5) | 359 | | | | |
| | 1.739(5) | 1.316(8) | 170.5(6) | 359 | 6 | 17 | 6 | 12 |
| **14** [Mo(NNH$_2$)(quin)(PMe$_2$Ph)$_3$]$^+$ | 1.735(8) | 1.344(14) | 168.3(8) | 360 | 6 | 18 | 6 | 13 |
| **15** [W(NNCOCH$_2$CH$_2$CO)F(dppe)$_2$]$^+$ | n.a. | n.a. | 174.2 | 360 | 6 | 18 | 6 | 14 |
| **16** [MoO(NNMe$_2$)(SPh)$_3$]$^+$ | 1.821(9) | 1.292(14) | 152.5(10) | 360 | 5 | 14 | 6 | 15 |
| **17** [W(NNH$_2$)Cl$_3$(PMe$_2$Ph)$_2$] | 1.752(10) | 1.300(17) | 178.7(9) | 360 | 6 | 17 | 6 | 16 |
| **18** [MoO(NNPh$_2$){SCH$_2$CH$_2$N(Me)CH$_2$CH$_2$-N(Me)CH$_2$CH$_2$S}] | 1.778(3) | 1.309(4) | 172.9(2) | 360 | 6 | 18 | 6 | 17 |
| **19** [MoO(NNMe$_2$)(quin)$_2$] | 1.800(9) | 1.28(1) | 155.5(9) | 360 | 6 | 18 | 6 | 18 |
| **20** [W(NNH$_2$)(OMe)(dppe)$_2$][FeCo$_3$(CO)$_{12}$] | 2.00(2) | 1.25(3) | 174.7 | n.a. | 6 | 18 | 6 | 19 |
| **21** [Re(C$_5$H$_5$){NNMe(C$_6$H$_4$OMe-$p$)}(CO)$_2$] | 1.937(7) | 1.283(10) | 138.1(6) | 360 | 6 | 18 | 4 | 20 |
| **22** [W(C$_5$H$_5$)$_2${NNH(C$_6$H$_4$F-$p$)}H]$^+$ | 1.837(7) | 1.315(9) | 146.4(5) | n.a. | 8 | 18 | 4 | 21 |
| **23** [MoO(NNHPh){O(CH$_2$CH$_2$S)$_2$}] | 1.766(17) | n.a. | 173.2(6) | n.a. | 5 | 14 | 6 | 22 |
| **24** [Fe(tcpp)(NNC$_9$H$_{18}$)] | 1.809(4) | 1.232(5) | 180 | 360 | 5 | 16 | 6 | 23 |
| **25** [W{NNH(SiMe$_3$)}I$_2$(PMe$_2$Ph)$_3$] | 1.777(17) | 1.325(28) | 171.4(16) | n.a. | 6 | 18 | 6 | 24,25 |
| **26** [Re{NNH(COPh)}{NHNH(COPh)}Cl$_2$(PPh$_3$)$_2$] | 1.728(7) | 1.27(1) | 174.7(7) | n.a. | 6 | 18 | 6 | 26,34 |
| **27** [Re(NNHPh)(NNPh)Br$_2$(PPh$_3$)$_2$] | 1.922(11) | 1.287(15) | 131.2(10) | 358 | 6 | 18 | 4 | 27 |
| **28** [Mo(NNMe$_2$){PhP(CH$_2$CH$_2$S)$_2$}$_2$] | 1.775(6) | 1.265(9) | 178.3(5) | 360 | 7 | 18 | 6 | 22,28 |
| **29** [Mo(NNH$_2$)Cl{PhP(CH$_2$CH$_2$PPh$_2$)$_2$}(PPh$_3$)]$^+$ | 1.694(12) | 1.34(2) | 172.2(11) | 356 | 6 | 18 | 6 | 29,41 |
| **30** [Mo(NNH$_2$)Cl{PhP(CH$_2$CH$_2$PPh$_2$)$_2$}(PMePh$_2$)]$^+$ | 1.778(18) | 1.31(2) | 178.1(15) | 360 | 6 | 18 | 6 | 29,41 |
| **31** [W{NNHC(Me)CHC(O)Me}(acac)(PMe$_2$Ph)$_3$]$^+$ | 1.793(13) | 1.375(29) | 176.4(16) | n.a. | 6 | 18 | 6 | 30 |
| **32** [MoO(NNMePh){(SCH$_2$CH$_2$)$_2$NCH$_2$CH$_2$NMe$_2$}] | 1.787(8) | 1.30(1) | 164.8(7) | n.a. | 5 | 14 | 6 | 31 |
| **33** [V(NNMePh)Cl$_2$(H$_2$NNMePh)$_2$]$^+$ | 1.696(24) | 1.295(17) | 174.4(19) | 360 | 7 | 18 | 6 | 32 |
| **34** [ReO(NNMePh)(SPh)$_3$] | 1.858(9) | 1.255(15) | 145.6(10) | 360 | 5 | 14 | 6 | 33 |
| **35** [Re{NNH(COPh)}{NHNH(CO$_2$Me)}Cl$_2$(PPh$_3$)$_2$] | 1.712(7) | 1.27(1) | 172.2(7) | n.a. | 6 | 18 | 6 | 34 |
| **36** [{MoO(NNMePh)(μ-OMe)(μ-MoO$_4$)}$_2$]$^{2-}$ | 1.71(1) | 1.34(2) | 170.0(13) | 360 | 6 | 18 | 6 | 35 |
| **37**$^b$ [W(NNH$_2$)Br(depe)$_2$]$^+$ | 1.739(15) | 1.325(26) | 175.1(13) | 359 | | | | |
| | 1.773(11) | 1.340(18) | 177.2(12) | 350 | 6 | 18 | 6 | 36 |
| **38** [W(NNCH$_2$CH$_2$CH$_2$)Br(dtpe)$_2$]$^+$ | 1.72(6) | 1.42(6) | 171.4(46) | 359 | 6 | 18 | 6 | 37 |
| **39** [Mo$_6$O$_{18}$(NNMePh)]$^{2-}$ | 1.769(6) | 1.318(10) | 173.9(6) | 360 | 6 | 18 | 6 | 38 |
| **40**$^c$ [Mo$_2$(NNHPh)(NNPh)(SCH$_2$CH$_2$S)$_3$-(SCH$_2$CH$_2$SH)]$^{2-}$ | 1.782(12) | 1.272(17) | 164.3(10) | n.a. | | | | |
| | 1.775(12) | 1.310(17) | 159.2(11) | n.a. | | | | |
| | 1.779(13) | 1.271(20) | 167.0(10) | n.a. | 6 | 18 | 6 | 39 |
| **41** [Mo$_2$O$_4$(NNPh$_2$)(Me$_2$NCH$_2$CH$_2$NHCH$_2$CH$_2$S)$_2$] | 1.808(4) | 1.314(5) | 169.3(3) | n.a. | 6 | 18 | 6 | 40 |
| **42** [W(NNSiMe$_2$CH$_2$CH$_2$SiMe$_2$)I$_2$(PMe$_2$Ph)$_3$] | 1.76(8) | 1.36(1) | 174.3(7) | 360 | 6 | 18 | 6 | 42,53 |
| **43** [MoO(NNPh$_2$){PhC(S)N(Me)O}$_2$] | 1.779(13) | 1.309(4) | 176.2(3) | 360 | 6 | 18 | 6 | 43 |
| **44**$^b$ [MoO(NNPh$_2$){PhC(O)N(Me)O}$_2$] | 1.781(6) | 1.314(8) | 169.4(6) | 359 | | | | |
| | 1.763(6) | 1.315(8) | 172.2(5) | 360 | 6 | 18 | 6 | 43 |
| **45** [W(NNH$_2$)F(depe)$_2$]$^+$ | 1.771(12) | 1.355(13) | 174.9 | n.a. | 6 | 18 | 6 | 44 |
| **46** [Mo$_2$(NNMePh)$_2$Cl{PhCH(S)SiMe$_2$CH(S)Ph}$_3$]$^-$ | 1.748(9) | 1.329(11) | 171.7(10) | 359 | | | | |
| | 1.768(10) | 1.326(15) | 168.4(6) | 360 | 6 | 18 | 6 | 45 |
| **47** [W{NNH(SiMePh$_2$)}(OH)(dppe)$_2$][Co(CO)$_4$] | n.a. | 1.36(2) | 169.3(9) | n.a. | 6 | 18 | 6 | 46 |
| **48** [{MoO(NNPh$_2$)(acac)(μ-OEt)}$_2$] | 1.784(1) | 1.298(2) | 169.5(1) | 360 | 6 | 18 | 6 | 47 |
| **49** [MoO(NNMePh){2-SC$_5$H$_3$N(SiMe$_3$)-3}$_2$] | 1.787(3) | 1.298(4) | 173.5(3) | 360 | 6 | 18 | 6 | 48 |
| **50** [Mo(NNMePh)Cl$_2${2-SC$_5$H$_3$N(SiMe$_3$)-3}$_2$] | 1.75(1) | 1.30(2) | 171.3(11) | n.a. | 7 | 18 | 6 | 49 |
| **51** [Mo(NNMePh){PhP(C$_6$H$_4$S)$_2$}$_2$] | 1.782(4) | 1.290(5) | 172.1(4) | n.a. | 7 | 18 | 6 | 49 |
| **52** [MoO(NNMePh)(acac)$_2$] | 1.789(3) | 1.281(4) | 175.6(2) | 360 | 6 | 18 | 6 | 50 |
| **53** [{MoO(NNMePh)(acac)(μ-OPr)}$_2$] | 1.780(4) | 1.292(6) | 165.5(4) | 360 | 6 | 18 | 6 | 50 |
| **54** [W(NNMe$_2$)(CO)$_3$dppe] | 2.12(1) | 1.21(2) | 139(1) | 360 | 6 | 18 | 4 | 51 |
| **55** [W{NNH(COCHPh$_2$)}Cl$_2$(PMe$_2$Ph)$_3$] | 1.70(3) | 1.37(5) | 167(3) | n.a. | 6 | 18 | 6 | 52 |
| **56** [W{NNH(COCHPh$_2$)}Cl(py)(PMe$_2$Ph)$_3$]$^+$ | 1.753(8) | 1.344(11) | 170.5(7) | 357 | 6 | 18 | 6 | 52 |
| **57** [W(NNSiMe$_2$CH$_2$CH$_2$SiMe$_2$)I$_2${$p$-MeC(O)-C$_6$H$_4$CN}(PMe$_2$Ph)$_2$] | 1.77(1) | 1.29(2) | 172.1(16) | 360 | 6 | 17 | 6 | 53 |
| **58** [W(NNSiMe$_2$CH$_2$CH$_2$SiMe$_2$)Cl$_3$(PMe$_2$Ph)$_2$] | 1.76(1) | 1.33(2) | 175.9(14) | n.a. | 6 | 17 | 6 | 53 |
| **59** [ReO(NNMePh)Cl(PPh$_3$)$_2$]$^{2+}$ | 1.845(6) | 1.261(8) | 146.3(4) | 360 | 5 | 14 | 6 | 54 |
| **60** [W(NNMe$_2$)Cl$_2$(PMe$_2$Ph)$_3$] | 1.851(5) | 1.385(8) | 173.8(4) | 348 | 6 | 18 | 6 | 55 |
| **61** [W(NNPh$_2$)Cl$_2$(PMe$_2$Ph)$_3$] | 1.761(8) | 1.36(1) | 178.0(6) | 360 | 6 | 18 | 6 | 55 |
| **62** [Mo(NNH$_2$)Br$_3$(dppe)] | 1.79(2) | 1.28(3) | 173(2) | 360 | 6 | 17 | 6 | 56 |
| **63** [ReN(NNPh$_2$)Cl$_2$(PPh$_3$)] | 1.837(5) | 1.280(6) | 142.9(4) | 360 | 5 | 14 | 6 | 57 |
| **64**$^d$ [Os(NNEt$_2$)(bpy)(tpy)]$^{2+}$ | 1.89(1) | 1.25(2) | 137 | 360 | | | | |
| | 1.85(2) | 1.40(2) | 137 | n.a. | 6 | 18 | 4 | 58,73 |
| **65**$^b$ [Mo(NNH$_2$)F(dippe)$_2$]$^+$ | 1.743(4) | 1.332(5) | 174.7(4) | 359 | | | | |
| | 1.742(4) | 1.340(6) | 175.3 | 360 | 6 | 18 | 6 | 59 |

# Table 1 (*Contd.*)

| Compound | Distance (Å) M−N$_\alpha$ | N$_\alpha$−N$_\beta$ | Angle (°) M−N$_\alpha$−N$_\beta$ | Σα$_i$ at N$_\beta$(°) | Co-ordination number | MVE | HVE | Ref. |
|---|---|---|---|---|---|---|---|---|
| **66** [W{N(NC$_4$H$_4$)}F(dppe)$_2$]$^+$ | 1.761(5) | 1.362(7) | 174.4(5) | 360 | 6 | 18 | 6 | 60,65 |
| **67** [MoO(NNMe$_2$){S$_2$CN(CH$_2$CHMe$_2$)$_2$}$_2$] | 1.841(18) | 1.390(18) | 162.6(16) | 344 | 6 | 18 | 6 | 61 |
| **68** [Mo(NNPh$_2$)(NHNPh$_2$)(acac)Cl$_2$] | 1.750(4) | 1.301(3) | 171.9(4) | 359 | 6 | 18 | 6 | 62 |
| **69** [Mo(NNMePh)(NHNMePh)(acac)Cl$_2$] | 1.750(2) | 1.301(3) | 173.8(2) | 360 | 6 | 18 | 6 | 62 |
| **70** [Mo(NNMe$_2$){OC$_6$H$_4$NC(Me)C$_6$H$_4$O}- (OC$_6$H$_4$NH)] | 1.771(6) | 1.296(8) | 152.9(5) | 360 | 6 | 18 | 6 | 63 |
| **71** [MoO(NNPh$_2$)(SC$_6$H$_4$CO$_2$)$_2$]$^{2-}$ | 1.774(2) | 1.310(3) | 176.1(2) | 360 | 6 | 18 | 6 | 64 |
| **72** [W{N(NC$_4$H$_4$)}Br$_2$(PMe$_2$Ph)$_3$] | 1.743(4) | 1.365(4) | 177.9(3) | 360 | 6 | 18 | 6 | 65 |
| **73** [W{N(NC$_4$H$_3$Br-3)}F(dppe)$_2$]$^+$ | 1.73(1) | 1.37(1) | 178.2(7) | 360 | 6 | 18 | 6 | 65 |
| **74** [W{N(NC$_4$H$_2$Cl$_2$-2,5)}F(dppe)$_2$]$^+$ | 1.764(6) | 1.336(8) | 176.6(5) | 360 | 6 | 18 | 6 | 65 |
| **75** [W{N(NC$_4$H$_3$[C(O)C$_6$H$_4$Me-*p*]-3)}Cl(dppe)$_2$]$^+$ | 1.778(5) | 1.352(6) | 176.7(5) | 360 | 6 | 18 | 6 | 65 |
| **76** [Re(NNHPh)(NNPh){2-SC$_5$H$_3$N(SiMe$_3$-3)}- (PPh$_3$)$_2$]$^+$ | 1.860(3) | 1.288(4) | 137.4(3) | 360 | 6 | 18 | 4 | 66 |
| **77** [W(NNCH$_2$C$_6$H$_4$CO)Cl$_2$(PMe$_2$Ph)$_3$] | 1.734(9) | 1.35(1) | 179.0(8) | 359 | 6 | 18 | 6 | 67 |
| **78** [W(NNCHCHCH$_2$CO)F(dppe)$_2$]$^+$ | 1.746(6) | 1.356(6) | 172.2(6) | 360 | 6 | 18 | 6 | 67 |
| **79** [W(NNCH$_2$CHCHCO)F(dppe)$_2$]$^+$ | 1.769(4) | 1.346(5) | 172.4(4) | 360 | 6 | 18 | 6 | 67 |
| **80** [W{NNCH(OMe)CHCBrCO}F(dppe)$_2$]$^+$ | 1.728(6) | 1.360(7) | 173.6(5) | 357 | 6 | 18 | 6 | 67 |
| **81** [MoO(NNPh$_2$)Cl$_2$(bpy)] | 1.792(4) | 1.296(3) | 172.4(3) | 360 | 6 | 18 | 6 | 68 |
| **82** [MoO(NNPh$_2$)Cl$_2$(phen)] | 1.791(4) | 1.276(5) | 173.1(2) | 360 | 6 | 18 | 6 | 68 |
| **83** [Mo(NNPh$_2$)(NHNPh$_2$)Cl$_4$] | 1.748(2) | 1.304(3) | 174.2(2) | 360 | 6 | 17 | 6 | 69 |
| **84** [{Nb(C$_5$H$_5$)(NNMe$_2$)Cl$_2$}$_2$] | 1.67(2) | 1.38(2) | 168.7(17) | 359 | 7 | 18 | 6 | 70 |
| **85** [Nb(C$_5$H$_5$)(NNMe$_2$)Cl$_2${P(OMe)$_3$}] | 1.789(2) | 1.338(2) | 170.4(2) | 340 | 7 | 18 | 6 | 70 |
| **86** [W(NNMe$_2$)(py)(OPr$^i$)$_4$] | 1.765(14) | 1.355(25) | 171.0(16) | 350 | 6 | 18$^e$ | 6 | 71 |
| **87** [Co(NNMe$_2$){MeC(CH$_2$PPh$_2$)$_3$}]$^+$ | 1.668(9) | 1.296(11) | 176.3(7) | n.a. | 4 | 18 | 6 | 72 |
| **88** [Os{NN(CH$_2$CH$_2$)$_2$O}(bpy)(tpy)]$^{2+}$ | 1.849(16) | 1.405(24) | 137.1(12) | 359 | 6 | 18 | 4 | 73 |
| **89** [Nb($\eta^5$-C$_5$H$_4$Me)$_2$(NNMe$_2$)Cl] | 1.794(2) | 1.340(3) | 178.8(2) | 342 | 8 | 20(18)$^a$ | 6(4)$^a$ | 74 |

$^a$ See text. $^b$ Two independent molecules. $^c$ Three independent molecules. $^d$ Two crystalline varieties. $^e$ Assuming that the four (OPr$^i$) ligands are donating 10 electrons (four σ-type pairs + one π-type pair). n.a. = not available. dppe = 1,2-Bis(diphenylphosphino)ethane; quin = quinolin-8-olate; py = pyridine; phen = 1,10-phenanthroline; acac = acetylacetonate; depe = 1,2-bis(diethylphosphino)ethane; dtpe = 1,2-bis(di-*p*-tolylphosphino)-ethane; bpy = 2,2′-bipyridine; tpy = 2,2′:6′,2″-terpyridine; dippe = 1,2-bis(diisopropylphosphino)ethane; H$_2$tcpp = *meso*-5,10,15,20-tetra-*p*-chloro-phenylporphyrin.

double bonding. Clearly, the co-ordination chemistry of the NNR$_2$ ligand needs a deeper description than that using the simple Lewis structures depicted in Scheme 1. On the other hand, theoretical data on transition metal hydrazido complexes are particularly scarce,[63,93] contrarily to imido [1b,94,95] and other related [96–100] complexes. In this paper we analyse the electronic factors governing the structure, bonding and stability of the NNR$_2$ complexes with the help of *ab initio* and extended-Hückel molecular orbital (EHMO) calculations on the free (neutral and anionic) NNH$_2$ ligand, as well as on different model complexes. The question of the NNR$_2$ oxidation state (−2, −1 or 0), and accordingly that of the metal, will be discussed. The details of the calculations are given below.

## Computational Details

### (a) EHMO calculations

All the calculations were carried out within the standard extended-Hückel formalism [101] using the modified Wolfsberg–Helmholz formula.[102] The CACAO package developed by Mealli and Proserpio [103] was used. Standard atomic parameters were taken for H, C and O.[93] The exponents (ζ) and the valence shell ionization potential ($H_{ii}$ in eV) used for Mo are the standard CACAO parameters,[103] *i.e.* 1.956, −8.34 for 5s, 1.921, −5.24 for 5p. The $H_{ii}$ value for 4d was −10.50. A linear combination of two Slater-type orbitals ($\zeta_1 = 4.54$, $c_1 = 0.5899$; $\zeta_2 = 1.900$, $c_2 = 0.5899$) was used to represent the atomic 4d orbitals. It has been checked that a reasonable variation of the molybdenum parameters does not modify the qualitative conclusions of this study. Unless specified in the text, the following bond distances (Å) and angles (°) were considered: Mo−H 1.600, Mo−N 1.781, N−N 1.310, N−H 1.010, Mo−S$_{bridging}$ 2.242, Mo−S$_{terminal}$ 2.161, Mo−C(C$_5$H$_5$) 2.340, C(C$_5$H$_5$)−C(C$_5$H$_5$) 1.420 and C−H 1.080; N−N−H, H−N−H 120 and Cp−H−Cp 126.

### (b) *Ab initio* calculations

The GAUSSIAN 94 system was used.[104] All the results reported here have been obtained by using the 6-31+G** basis set.[105] The presence of diffuse functions on the non-hydrogen atoms was found to be necessary in order to prevent dissociation during geometry optimization of some of the considered anions. In the case of the other anionic and neutral species, the results were essentially the same whether the diffuse functions were added or not. The NNH$_2^q$ ($q = 0$, −1 or −2) models have been optimized assuming a non-planar $C_s$ symmetry. The XNNH$_2^q$ (X = H or Li) ($q = +1$, 0 or −1) models have been optimized assuming a $C_1$ symmetry. Under these conditions, the geometries were fully optimized both at the Hartree–Fock (HF) and second-order Møller-Plesset [106] (MP2) levels. All the stationary points were characterized as energy wells by calculating the eigenvalues of the Hessian matrix. Since the HF and MP2 calculations lead to similar results, only the MP2 results are reported and discussed here. They are summarized in Table 3. In all the XNNH$_2^q$ ($q = −1$, 0 or +1) models, X was found to be bonded in a $\eta^1$ fashion to the ligand, except for [Li(NNH$_2$)]$^-$ where two minima, corresponding to $\eta^1$ and $\eta^2$ bonding, respectively, were found.‡

## Results and Discussion

### Electronic structure of free NNH$_2$, [NNH$_2$]$^-$ and [NNH$_2$]$^{2-}$

(*a*) *Qualitative EHMO analysis of the NNH$_2$ frontier orbitals.* The frontier molecular orbital (FMO) diagram of a planar NNH$_2$ unit of symmetry $C_{2v}$ is shown on the left side of Fig. 1. The electron occupation is fully arbitrary and corresponds to a

‡ In the case of [Li(NNH$_2$)]$^-$ the lowest minimum was found to be a dissymmetrical $\eta^2$ co-ordination (Li−N$_\alpha$ 1.78, Li−N$_\beta$ = 2.03 Å) of $C_s$ symmetry. The $\eta^1$ minimum is 13 kcal mol$^{-1}$ less stable.

**Table 2** Structurally characterized dihydrazido mononuclear and related polynuclear complexes

| Compound | Distance (Å) | | Angle (°) | $\Sigma\alpha_i$ | Co-ordin- | | | |
| | M–N$_\alpha$ | N$_\alpha$–N$_\beta$ | M–N$_\alpha$–N$_\beta$ | at N$_\beta$(°) | ation number | MVE | HVE | Ref. |
|---|---|---|---|---|---|---|---|---|
| **90** [Mo(NNPh$_2$)$_2$(S$_2$CNMe$_2$)$_2$] | 1.790(8) | 1.31(1) | 169.9(8) | 360 | 6 | 18 | 10 | 75,79 |
| **91** [Mo(NNMe$_2$)$_2$Cl(PPh$_3$)$_2$]$^+$ | 1.752(5) | 1.291(7) | 173.4(4) | 360 | 5 | 16 | 10 | 76,79 |
| | 1.763(4) | 1.276(8) | 163.8(4) | 360 | | | | |
| **92** [S$_2$Mo($\mu$-S)$_2$Mo(NNMe$_2$)$_2$(PPh$_3$)] | 1.78(3) | 1.30(4) | 165.0(30) | 360 | 5 | 16 | 10 | 77 |
| | 1.85(3) | 1.27(4) | 178.2(30) | 360 | | | | |
| **93** [S$_2$Mo($\mu$-S)$_2$Mo(NNMe$_2$)$_2$($\mu$-S)$_2$MoS$_2$]$^{2-}$ | 2.13(1) | 1.16(2) | 165.9(16) | 355 | 6 | 16 | 8 | 78 |
| **94** [Mo(NNMePh)$_2$(S$_2$CNMe$_2$)$_2$] | 1.790(9) | 1.30(1) | 172.6(8) | 355 | 6 | 18 | 10 | 79 |
| **95** [Mo(NNMe$_2$)$_2$(bpy)$_2$]$^{2+}$ | 1.80(1) | 1.27(2) | 168.2(7) | 360 | 6 | 18 | 10 | 79 |
| | 1.79(1) | 1.28(2) | 173.5(8) | 360 | | | | |
| **96** [S$_2$W($\mu$-S)$_2$W(NNMe$_2$)$_2$(PPh$_3$)] | 1.84(2) | 1.25(3) | 173.6(20) | 358 | 5 | 16 | 10 | 80 |
| | 1.72(2) | 1.35(4) | 166.4(20) | 360 | | | | |
| **97** [{Fe(CO)$_3$($\mu_3$-S)}$_2$Mo(NNMe$_2$)$_2$(PPh$_3$)] | 1.825(15) | 1.30(2) | 159.4(14) | 360 | 5 | 14 | 10 | 81 |
| | 1.758(17) | 1.34(3) | 178.2(15) | 360 | | | | |
| **98** [Mo(NNMePh)$_2${2-SC$_5$H$_3$N(SiMe$_3$)-3}$_2$] | 1.782(4) | 1.310(5) | 172.3(3) | n.a. | 6 | 18 | 10 | 49 |
| **99** [Re(NNMePh)$_2$(S$_2$CNMe$_2$)$_2$]$^+$ | 1.78(1) | 1.29(1) | 166.8(8) | 360 | 6 | 18 | 10 | 54 |
| | 1.777(9) | 1.30(1) | 166.9(9) | 360 | | | | |
| **100** [W{N(NC$_5$H$_6$Me$_4$-2,2,6,6)}$_2$(OSiMe$_3$)Cl$_3$] | 1.841(5) | 1.248(7) | 173.8(4) | 359 | 6 | 16 | 10 | 82 |
| **101** * [Re{N(NC$_5$H$_6$Me$_4$-2,2,6,6)}$_2$(OSiMe$_3$)Cl$_2$] | 1.732(12) | 1.308(17) | 172.8(9) | 358 | 5 | 16 | 10 | 82 |
| | 1.758(12) | 1.282(18) | 174.3(10) | 359 | | | | |
| | 1.759(12) | 1.294(17) | 174.9(10) | 358 | | | | 82 |
| | 1.763(12) | 1.278(17) | 172.2(10) | 357 | | | | |
| **102** [Re{N(NC$_5$H$_6$Me$_4$-2,2,6,6)}$_2$Cl$_3$] | 1.753(8) | 1.287(11) | 177.1(8) | 358 | 5 | 16 | 10 | 82 |
| | 1.741(9) | 1.280(12) | 178.1(8) | 360 | | | | |
| **103** [{Re[{N(NC$_5$H$_6$Me$_4$-2,2,6,6)}$_2$]$_2$($\mu$-O)-(NCMe)$_2$}$_2$]$^{4+}$ | 1.795(8) | 1.265(12) | 179.5(10) | 360 | 6 | 17 | 10 | 82 |
| | 1.779(11) | 1.271(16) | 178.1(7) | 360 | | | | |
| **104** [{ReO[{N(NC$_5$H$_6$Me$_4$-2,2,6,6)}$_2$]$_2$}$_2$] | 1.782(6) | 1.304(9) | 172.8(7) | 353 | 4 | 14 | 10 | 82 |
| | 1.778(6) | 1.297(8) | 169.7(6) | 356 | | | | |
| **105** * [Mo(NNPh$_2$)$_2$Cl$_2$(PPh$_3$)] | 1.76(1) | 1.33(1) | 176.8(8) | 360 | 5 | 16 | 10 | |
| | 1.76(1) | 1.30(1) | 172.9(9) | 360 | | | | |
| | 1.75(1) | 1.33(1) | 172.7(8) | 360 | | | | 83 |
| | 1.75(1) | 1.34(1) | 169.3(8) | 360 | | | | |
| **106** * [Mo(NNMePh)$_2$Cl$_2$(PPh$_3$)$_2$] | 1.78(1) | 1.30(2) | 170.2(11) | 360 | 6 | 18 | 10 | |
| | 1.81(1) | 1.30(2) | 163.9(11) | 360 | | | | |
| | 1.80(1) | 1.31(2) | 159.4(11) | 360 | | | | 83 |
| | 1.83(1) | 1.30(2) | 164.7(12) | 360 | | | | |
| **107** [Re(NNPh$_2$)$_2$(cat)$_2$]$^-$ | 1.77(1) | 1.33(2) | 159.6(8) | 360 | 6 | 18 | 10 | 84 |
| | 1.77(1) | 1.32(2) | 159.7(8) | 360 | | | | |
| **108** [Mo(NNMePh)$_2$(acac)$_2$] | 1.777(6) | 1.299(8) | 172.6(6) | 360 | 6 | 18 | 10 | 85 |
| | 1.784(6) | 1.308(8) | 175.7(6) | 360 | | | | |
| **109** [Mo(NNPh$_2$)$_2$(acac)$_2$] | 1.781(3) | 1.310(5) | 171.3(3) | 360 | 6 | 18 | 10 | 85 |
| **110** [Mo(NNPh$_2$)$_2$Cl$_2$(dme)] | 1.749(2) | 1.324(3) | 173.4(2) | 359 | 6 | 18 | 10 | 69 |
| | 1.771(2) | 1.326(3) | 154.6(2) | 360 | | | | |
| **111** [Mo(NNPh$_2$)$_2$Cl$_2$(PMe$_3$)$_2$] | 1.793(3) | 1.306(4) | 175.2(3) | 360 | 6 | 18 | 10 | 69 |
| **112** [Mo(NNPh$_2$)$_2$Cl$_2$(phen)] | 1.779(3) | 1.309(4) | 171.3(3) | 360 | 6 | 18 | 10 | 68 |
| | 1.773(4) | 1.319(5) | 170.1(2) | 360 | | | | |
| **113** [Mo(NNMePh)$_2${HB(pz)$_3$}Cl] | 1.771(4) | 1.308(5) | 169.4(3) | 360 | 6 | 18 | 10 | 86 |
| **114** [Mo(NNPh$_2$)$_2${HB(pz)$_3$}Cl] | 1.773(3) | 1.319(4) | 167.1(3) | 360 | 6 | 18 | 10 | 87 |
| | 1.780(3) | 1.312(4) | 170.9(3) | 360 | | | | |
| **115** [Mo(C$_5$H$_5$)(NNPh$_2$)$_2$(PPh$_3$)]$^+$ | 1.815(4) | 1.310(6) | 158.7(4) | 360 | 6 | 18 | 10 | 88 |
| | 1.798(4) | 1.316(6) | 168.1(4) | 360 | | | | |
| **116** [Ta{N(NC$_5$H$_6$Me$_4$-2,2,6,6)}$_2$Cl$_4$]$^-$ | 1.865(7) | 1.283(9) | 176.5(5) | 358 | 6 | 16 | 10 | 89 |
| | 1.882(6) | 1.259(8) | 176.4(5) | 357 | | | | |
| **117** [V$_2$O($\mu$-O)(OSiMe$_3$)$_4${N(NC$_5$H$_6$Me$_4$-2,2,6,6)}$_2$] | 1.725(2) | 1.285(3) | 176.4(2) | 357 | 5 | 14 | 10 | 89 |
| | 1.781(3) | 1.245(4) | 174.3(2) | 360 | | | | |
| **118** [Mo(NNPh$_2$)$_2$(acac)(PPh$_3$)$_2$]$^+$ | 1.805(4) | 1.319(5) | 172.3(3) | 360 | 6 | 18 | 10 | 90 |
| | 1.806(4) | 1.322(5) | 173.2(3) | 360 | | | | |

* Two independent molecules. cat = Catecholate; dme = 1,2-dimethoxyethane; pz = pyrazolyl.

usually considered formal dianionic charge of the hydrazide ligand. This fragment presents a set of four orbitals which are associated with the $\pi_{NN}$ system and the two lone pairs on N$_\alpha$. The highest (2b$_2$) is the $\pi^*_{NN}$ orbital which lies at a rather low energy ($-11.2$ eV). The N–N overlap population in this level is $-0.443$. The 1b$_1$ levels lies 1.7 eV below. This FMO can be associated with the $\pi$ in-plane ($\pi_\sigma$) lone pair on N$_\alpha$. It has a 89% localization on this atom and presents some N–N antibonding character, the corresponding overlap population in this level being $-0.118$. About 2.2 eV below lie the two lowest FMOs. The bonding $\pi_{NN}$ orbital is 1b$_2$ in which the N–N overlap population is $+0.278$. Orbital 1a$_1$ is associated with the $\sigma$-lone pair of the N$_\alpha$ ($\sigma_n$). It has a 67% localization on this atom and

presents a weak NN bonding character with an overlap population of $+0.107$. The total N–N overlap population is $+0.599$ for the dianion. It increases to $+1.042$ in the neutral ligand, due to the depopulation of the antibonding 2b$_2$ level.

It has been checked in the calculations that all the other orbitals of the hydrazide ligand always play a secondary role in the interaction with a metal centre. Thus, it is clear that the way these FMOs interact with the metal atom will determine their occupations and therefore the N–N overlap population as well as the hybridization of the N atoms.

**(b) *Ab initio* calculations.** Previous *ab initio* studies on isodiazene NNH$_2$ have shown that the energy difference between
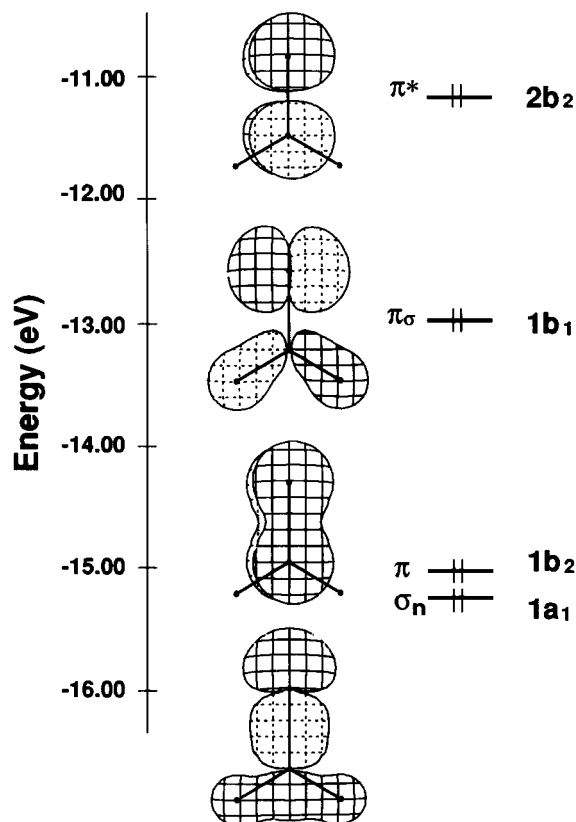
**Fig. 1** The MO diagram and CACAO plots of the frontier orbitals of the planar ($C_{2v}$) hydrazide ligand, assuming the arbitrary charge of $-2$

the singlet state $(1b_1)^2(2b_2)^0$ and the triplet state $(1b_1)^1(2b_2)^1$ is small.[107,108] This reflects the relatively low energy of the $\pi^*_{NN}$ ($2b_2$) orbital. Our MP2 calculations found the singlet state more stable than the triplet state by 13.1 kcal mol$^{-1}$. The triplet state is computed to be the lowest at the HF level, by 0.3 kcal mol$^{-1}$. This difference is related to the overestimation of the triplet stability by HF calculations.[107] The N–N bond length of the singlet ground state (1.23 Å) is typical of a double bond. The corresponding value for the triplet state (1.35 Å) is closer to the one computed for the $[NNH_2]^-$ anion (1.38 Å) which has the $(1b_1)^2(2b_2)^1$ ground-state configuration. Both systems have a formal bond order of 1.5. The difference comes in part from their different occupation of the weakly antibonding $1b_1$ orbital. In the hydrazido $[NNH_2]^{2-}$ dianion the N–N separation is large (1.57 Å), indicative of a significantly elongated single bond, due to the large negative charge. Except for the singlet ground state of the neutral isodiazene molecule which is planar ($C_{2v}$), all the optimized geometries are more or less pyramidalized. The dianion is strongly pyramidalized at $N_\beta$, while $[NNH_2]^-$ and the triplet state of $NNH_2$ exhibit a pyramidalization intermediate between sp$^2$ and sp$^3$ hybridization of $N_\beta$. These results are fully consistent with the structures **a** and **b** of Scheme 1 for the singlet states of $NNH_2$ and $[NNH_2]^{2-}$, respectively.

### *Ab initio* investigation of the $HNNH_2{}^q$ and $[Li(NNH_2)]^q$ ($q = +1, 0$ or $-1$) models

Following a previous approach[108] we have modelled a $\eta^1$-bonded metal atom first by a proton, which is a simple $\sigma$ acceptor, and secondly by Li$^+$ which has both $\sigma$- and $\pi$-accepting properties. The ligands considered were $NNH_2$, $[NNH_2]^-$ and $[NNH_2]^{2-}$. As found by others,[106] $[HNNH_2]^+$ is planar (Table 3), with a N–N double bond (1.24 Å). The small H–N$_\alpha$–N$_\beta$ angle (110°) indicates that the proton interacts more strongly with the ligand $1b_1$ lone pair than with the $1a_1$ one. Protonation of $[NNH_2]^{2-}$ leads to a complex of $C_s$ (non-planar)
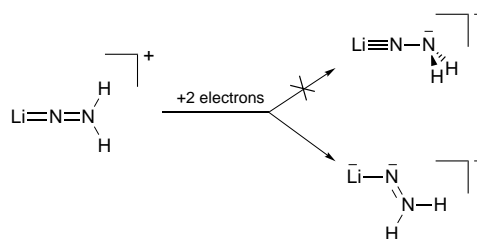


**Scheme 2**

symmetry, with the $HN_\alpha N_\beta$ plane as the symmetry plane. The N–N separation (1.49 Å) is consistent with a single bond. The optimized geometries of $[HNNH_2]^+$ and $[HNNH_2]^-$ are consistent with structures **a$_2$** and **b$_3$** (Scheme 1, M = H), respectively. The geometry of the $HNNH_2$ radical is intermediate between those of the cation and the anion.

Having $\pi$-accepting 2p orbitals, Li$^+$ is a better model for a hydrazido complex of a d$^0$ or d$^2$ transition metal. Unlike $[HNNH_2]^+$, $[Li(NNH_2)]^+$ is planar with a linear Li–N–N arrangement ($C_{2v}$ symmetry, see Table 3). The Li–N bond is short (1.89 Å) indicating a double-bond character, as well as for the N–N separation (1.22 Å). This structure corresponds to the **a$_1$** formula of Scheme 1. Adding one electron results in shortening of the Li–N bond, associated with a lengthening of N–N and a slight bending of the Li–N–N angle as well as a weak pyramidalization of $N_\beta$. The LiNNH$_2$ radical has a $C_s$ non-planar symmetry (Table 3). This trend indicates that the single electron is located in a Li–N$_\alpha$ $\pi$-bonding orbital which has some $\pi^*_{NN}$ ($2b_2$) character. Consequently, $N_\beta$ tends to pyramidalize, in order to lower the $\pi^*_{NN}$ character of the singly occupied HOMO. This result indicates that the $\pi^*_{NN}$ ($2b_2$) FMO of the ligand is involved in the interaction with the metal preferentially to the $\pi_{NN}$ ($1b_2$) FMO. Clearly, one is on the way to building a structure of type **b$_1$** (Scheme 1). Surprisingly, the addition of a second electron to the $\eta^1$-bonded system does not increase the effect of the addition of the first (Table 3). Conversely, it restores the planarity of the molecule ($C_s$), while the N–N bond is shortened again to 1.23 Å, corresponding to a bond order of 2, and the Li–N$_\alpha$ distance becomes rather long. The net charge on Li is largely negative ($-1.35$). The electronic structure of $[Li(NNH_2)]^-$ is best described by formula **a$_2$** of Scheme 1, with a non-bonding electron pair on M = Li. Clearly, the system is more stable with a N–N double bond and with two lone pairs located on Li and $N_\alpha$ rather than with a Li–N triple bond and a N–N single bond. This is exemplified in Scheme 2. In other words, $[Li(NNH_2)]^-$ is better described as a neutral $NNH_2$ ligand co-ordinated to Li$^-$ rather than as a $[NNH_2]^{2-}$ dianion bonded to Li$^+$. The question of the preference of $[Li(NNH_2)]^-$ for a single rather than a double Li–N bond (*i.e.* structure **a$_2$** rather than **a$_1$**) remains unclear. It may be related to the poor $\pi$-accepting ability of Li. It should be noted that a similar structure was found for the isoelectronic $[B(NNH_2)]^+$ model.[108]

These results suggest that co-ordinated $NNR_2$ ligands are reluctant to accept more than one electron in their $\pi^*_{NN}$ orbital, *i.e.* to fully break the NN double bond and significantly pyramidalize $N_\beta$. This finding is in full agreement with the experimental structures reported in Tables 1 and 2. In order to investigate this tendency with transition-metal compounds, EHMO calculations have been carried out on various models of molybdenum complexes.

### Six-co-ordinated monohydrazido compounds

In most of the monohydrazido compounds listed in Table 1 the metal centre is six-co-ordinated. Thus, we start the analysis of the metal–hydrazido bonding by looking at the electronic structure of the $C_{2v}$ model $[MoH_5(NNH_2)]^{3-}$ **I** shown in Scheme 3. Its EHMO diagram is sketched in Fig. 2, based on the interaction of the $[NNH_2]^{2-}$ ligand (right) with the $[MoH_5]^-$ unit

**Table 3** Energy and geometrical data of the MP$_2$/6-31+G** optimized geometries of NNH$_2^q$ ($q = 0$, $-1$ or $-2$) and XNNH$_2^q$ (X = H or Li; $q = +1$, 0 or $-1$)

| Compound | Energy/ hartree | Distance (Å) | | Angle (°) | | | X–N$_\alpha$ (Å) | X–N$_\alpha$–N$_\beta$ (°) |
|---|---|---|---|---|---|---|---|---|
| | | N–N | N$_\beta$–H | N$_\beta$–N$_\alpha$–H | H–N$_\alpha$–H | $\Sigma\alpha_i{}^a$ | | |
| NNH$_2$ (S)[b] | 110.2978 | 1.226 | 1.035 | 123.6 | 112.7 | 360 | | |
| (T) | 110.2769 | 1.350 | 1.016 | 112.8 | 111.8 | 337 | | |
| [NNH$_2$]$^-$ | 110.2574 | 1.383 | 1.025 | 116.9 | 108.8 | 342 | | |
| [NNH$_2$]$^{2-}$ | 109.9849 | 1.571 | 1.016 | 105.4 | 103.1 | 314 | | |
| [HNNH$_2$]$^+$ | 110.6474 | 1.240 | 1.027/1.030[c] | 116.8/124.9[c] | 118.3 | 360 | 1.031 | 110.0 |
| HNNH$_2$ | 110.9129 | 1.350 | 1.007/1.012[c] | 113.5/120.7[c] | 115.1 | 349 | 1.021 | 105.5 |
| [HNNH$_2$]$^-$ | 110.8959 | 1.496 | 1.019 | 106.8 | 104.4 | 318 | 1.025 | 101.2 |
| [Li(NNH$_2$)]$^+$ | 117.6056 | 1.221 | 1.032 | 122.5 | 115.1 | 360 | 1.890 | 180.0 |
| Li(NNH$_2$) | 117.7810 | 1.316 | 1.014 | 119.9 | 114.6 | 354 | 1.705 | 176.4 |
| [Li(NNH$_2$)]$^{-d}$ | 117.7501 | 1.231 | 1.032/1.040[c] | 122.0/123.6[c] | 114.3 | 360 | 2.071 | 112.0 |

$^a$ Sum of bond angles at N$_\beta$. $^b$ S = Singlet, T = triplet. $^c$ The first value corresponds to the dihydrogen atom *trans* to X. $^d$ $\eta^1$-Bonded, secondary minimum.
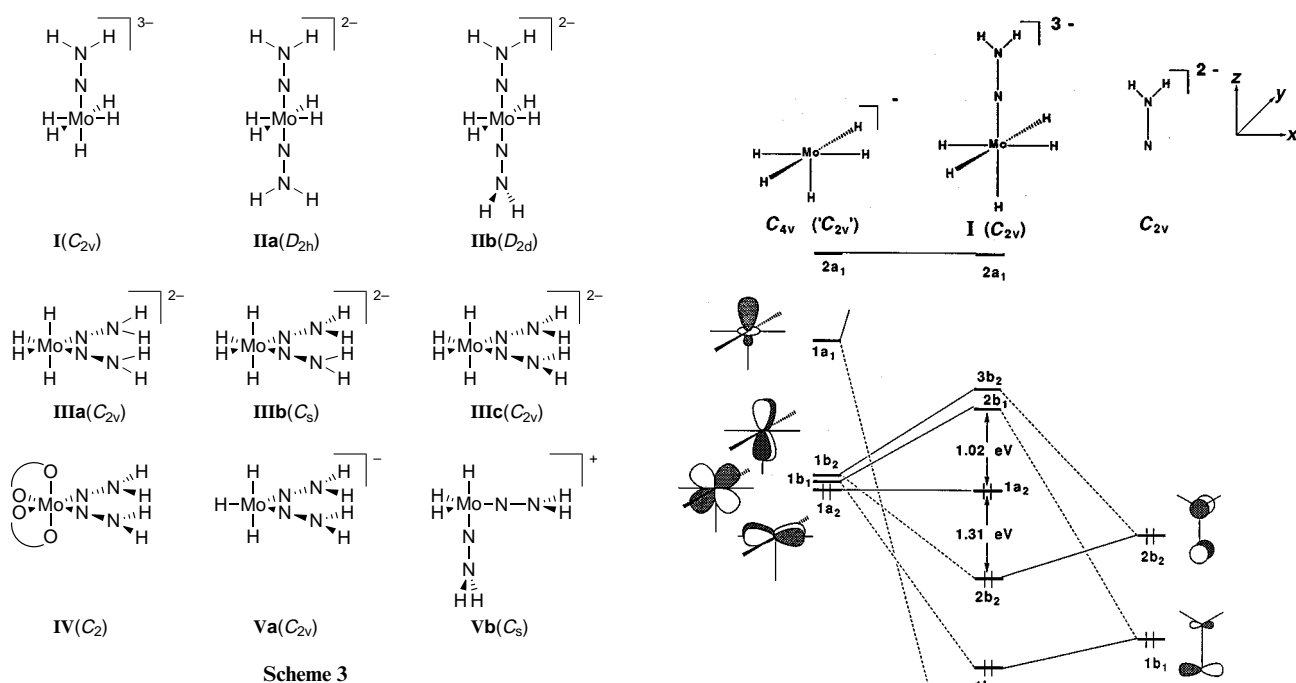
**Scheme 3**

(left). The fragment charges have to be considered as arbitrary. Some ligand FMO occupations and overlap populations are reported in Table 4. The FMOs of an ML$_5$ moiety such as [MoH$_5$]$^-$ are well known.[109,110] They are composed of a σ-type hybrid (1a$_1$) lying above a set of three d-type levels (isoenergetic in the case of MoH$_5$) which split into 1a$_2$ + 1b$_1$ + 1b$_2$ in the $C_{2v}$ symmetry of **I**. The two a$_1$ FMOs of both fragments interact in such a way that the occupation after interaction of the 1a$_1$ (σ$_n$) orbital of [NNH$_2$]$^{2-}$ is 1.77. Similarly, the two-orbital interaction of b$_1$ symmetry leads to an occupation of the 1b$_1$ (π$_\sigma$) hydrazido FMO of 1.61. The b$_2$ three-orbital system leads to the occupations of 1.95 and 1.35 for the 1b$_2$ (π$_{NN}$) and 2b$_2$ (π*$_{NN}$) FMOs of [NNH$_2$]$^{2-}$, respectively. Obviously, because of a rather poor overlap and a large energy difference between the metallic 1b$_2$ and the hydrazido 1b$_2$ FMOs, their interaction is very weak. Therefore, neglecting the participation of the hydrazido 1b$_2$ (π$_{NN}$) orbital, the b$_2$ interaction can be also simplified into a two-orbital system. The total electron donation from the [NNH$_2$]$^{2-}$ to the [MoH$_5$]$^-$ metal unit is 1.48, resulting in a net charge of $-0.52$ for the hydrazide ligand. The N–N overlap population in **I** is 0.761, a value significantly larger than that of the free dianion, mainly because of the partial depopulation upon interaction of the antibonding 2b$_2$ and 1b$_1$ ligand FMOs.

It is obvious that the planar hydrazide ligand cannot exhibit

**Fig. 2** Interaction MO diagram of the model [MoH$_5$(NNH$_2$)]$^{3-}$ **I**. The fragment charges are arbitrary

perfect axial bonding abilities. One can evaluate its deviation away from the axial properties by comparing the b$_1$ and b$_2$ (*i.e.* π-type) interactions which should be degenerate for an ideally axial ligand. This is not the case because the hydrazido 1b$_1$ and 2b$_2$ FMOs are not degenerate in free hydrazide. However they are not so different in energy and in shape (Fig. 1). Their occupations after interaction with the metal (see above) differ by 13%. The overlap population between the 1b$_1$ FMOs of both fragments is $+0.200$. The overlap population between the hydrazido 2b$_2$ FMO and the metallic 1b$_2$ orbital is similar ($+0.193$).

The computed HOMO–LUMO gap of [MoH$_5$(NNH$_2$)]$^{3-}$ **I** is significant (1.02 eV). It suggests that complexes of this type might be stable. Considering formally the ligand as a dianion [NNR$_2$]$^{2-}$, six hydrazido valence electrons (HVEs), correspond-

**Table 4** Population of the hydrazido FMOs, hydrazido net charges, Mo–N and N–N overlap populations and relative energies in the calculated models

| | [MoH$_5$(NNH$_2$)]$^{3-}$ | trans-[MoH$_4$(NNH$_2$)$_2$]$^{2-}$ | | cis-[MoH$_4$(NNH$_2$)$_2$]$^{2-}$ | | | cis-[Mo(acac)$_2$(NNR$_2$)] | | cis-[MoH$_3$(NNH$_2$)$_2$]$^-$ | |
| | I ($C_{2v}$) | IIa ($D_{2h}$) | IIb ($D_{2d}$) | IIIa ($C_{2v}$) | IIIb ($C_s$) | IIIc ($C_{2v}$) | IV ($C_2$) | 109 ($C_2$) | Va ($C_{2v}$) | Vb ($C_s$) |
|---|---|---|---|---|---|---|---|---|---|---|
| $\pi^*_{NN}$ (2b$_2$) | 1.35 | 1.67 | 1.60 | 1.70 | 1.49 | 1.35 | 1.48 | 1.55 | 1.36 | 1.64 |
| $\pi_\sigma$ (1b$_1$) | 1.61 | 1.75 | 1.79 | 1.61 | 1.72 | 1.77 | 1.76 | 1.79 | 1.71 | 1.63 |
| $\pi_{NN}$ (1b$_2$) | 1.95 | 1.96 | 1.96 | 1.96 | 1.96 | 1.95 | 1.96 | 1.98 | 1.95 | 1.97 |
| $\sigma_n$ (1a$_1$) | 1.77 | 1.77 | 1.76 | 1.77 | 1.77 | 1.77 | 1.77 | $a$ | 1.76 | 1.76 |
| Ligand net charge | −0.52 | −0.97 | −0.95 | −0.71 | −0.76 | −0.68 | −0.80 | −0.77 | −0.61 | −0.85 |
| Mo–N Overlap population | 0.993 | 0.871 | 0.870 | 0.904 | 0.911 | 0.920 | 0.940 | 0.953 | 1.004 | 0.941 |
| N–N Overlap population | 0.761 | 0.682 | 0.696 | 0.680 | 0.726 | 0.757 | 0.725 | 0.748 | 0.752 | 0.689 |
| Relative energies of the [MoH$_4$(NNH$_2$)$_2$]$^{2-}$ isomers (eV) | — | 0.79 | 0.73 | 0.62 | 0.27 | 0.00 | — | — | — | — |
| Relative energies of the [MoH$_3$(NNH$_2$)$_2$]$^-$ isomers (eV) | — | — | — | — | — | — | — | — | 0.00 | 0.85 |

$^a$ In the case of **V** it was not possible to identify a single dihydrazido orbital associated with the $\sigma_n$ lone pair (see text).

ing to three electron pairs of a$_1$, b$_1$ and b$_2$ symmetry, are given to the formally d$^2$ [MoH$_5$]$^-$ fragment. This leads to a count of 18 metal valence electrons (MVEs). A very large number of the compounds listed in Table 1 correspond to this 18 MVE/6 HVE situation, associated with a large M–N–N angle. Yet, one should note that in all the *cis* oxohydrazido compounds in Table 1 the oxide is considered as a four-electron ligand because these compounds are isolobal to the *cis* bis(hydrazido) derivatives which are discussed below.

Considering [NNR$_2$]$^{2-}$ as a six HVE ligand, one may be tempted to describe complex **I** with a canonical formula of the type **b$_1$** (Scheme 1) in which a planar co-ordination is assumed for N$_\beta$. However, one should be aware that the π-type interactions (principally the b$_2$ one) are rather weak. Therefore, a canonical form of type **a$_1$** should be also considered of equivalent weight.

If two electrons are removed from complex **I**, a significant HOMO–LUMO gap (1.31 eV) is still present in the oxidized form, suggesting also the possibility of existence of 16 MVE/6 HVE L$_5$M(NNR$_2$) complexes, as well as that of the intermediate 17 MVE/6 HVE situation. In these cases the strength and nature of the metal–hydrazido bond are identical to those of 18 MVE species since they differ only by the occupation of the a$_2$ non-bonding level which has no participation in the NNR$_2$ ligand. There are a few examples of 17 MVE/6 HVE (**13**, **17**, **57**, **58**, **62** and **83**) six-co-ordinated species (Table 1).

Adding two supplementary electrons to complex **I** leads to the occupation of the 2b$_1$ antibonding level. The resulting instability is released when the Mo–N–N angle is bent in the *xz* plane. This distortion stabilizes the HOMO by reducing its Mo–N antibonding character. The optimization of this angle in [MoH$_5$(NNH$_2$)]$^{5-}$ leads to a value close to 140°. For this energy minimum there is a non-bonding lone pair on N$_\alpha$, which is a combination of the $\pi_\sigma$ and $\sigma_n$. Consequently, in the bent co-ordination mode, the [NNR$_2$]$^{2-}$ ligand is a four-electron donor. There are six six-co-ordinated 18 MVE/4 HVE compounds (**21**, **27**, **54**, **64**, **76** and **88**) for which the M–N–N angle lies between 130 and 140°. On the other hand, the M–N–N bending (155.5°) of the presumably 18 MVE/6 HVE compound **19** is more difficult to understand. This may be due to π-bonding competition with the oxygen atoms of the two quinolin-8-olate ligands.

Although scarcely observed (Table 1), another possible ligand distortion for a six-co-ordinated monohydrazido complex is the sp$^3$ pyramidalization at N$_\beta$. Such a situation hardly

modifies the strength of the Mo–N bond in **I**. Upon sp$^3$ pyramidalization, the Mo–N overlap population varies from +0.993 to +0.999. On the other hand, the N–N overlap population decreases from +0.761 to +0.738. This leads to an overall destabilization of the complex by 0.43 eV.

We now turn to the oxidation states of the metal and the hydrazide ligand. Oxidation states correspond to the charges that the atom or ligand would have if there was no covalency (or orbital interaction) at all. The rounding of its computed FMO occupations to the nearest integer is a good approach for determining the oxidation state of the NNR$_2$ ligand. These FMO populations are listed in Table 4. The occupation in complex **I** of 1a$_1$, 1b$_1$ and 1b$_2$ is closer to 2, while that of 2b$_2$ is closer to 1. This leads to the formal $(\sigma)^2(\pi_{NN})^2(\pi_\sigma)^2(\pi^*_{NN})^1$ FMO configuration and therefore to the oxidation states [NNH$_2$]$^-$ and Mo$^{III}$. In this situation the metal–ligand interaction results in two N–Mo dative bonds (involving the 1a$_1$ and 1b$_1$ ligand FMOs) and one covalent (involving 2b$_2$) interaction. The formal differentiation of the interactions involving 1b$_1$ and 1b$_2$ is somewhat artificial. Nevertheless, the summation of the occupations of these two FMOs (2.96) is also consistent with the [NNH$_2$]$^-$ oxidation state. The N–N overlap population in the complex, which indicates a bond order close to 1.5, is consistent with this electron partitioning, as well as the computed hydrazido net charge (−0.52) which corresponds well to a [NNH$_2$]$^-$ ligand having lost part of its charge through electron donation to the metal.

### Other monohydrazido compounds

Five-co-ordination is also observed for monohydrazido complexes (Table 1). In most cases the metal co-ordination environment is close to an ideal trigonal bypyramid. When the NNR$_2$ ligand occupies an axial position it interacts with a $C_{3v}$ ML$_4$ fragment which presents a set of five FMOs (1σ + 2π + 2δ).[109,110] Assuming a formal charge of 2− on the hydrazide ligand, it will provide the metal with six electrons if the metal σ- and π-type FMOs are vacant. This leads to possible closed-shell MVE counts of 14 or 18, depending on whether the non-bonding metal δ-type orbitals are occupied or not. Our EHMO calculations on the 14 MVE/6 HVE trigonal-bipyramidal [MoH$_4$(NNH$_2$)] model lead to a large HOMO–LUMO gap of 2.07 eV when the hydrazide ligand occupies an axial position. This conformation was found to be the most

stable for this electron count. Adding four electrons in the metal δ-type levels reduces this gap to 0.62 eV. Actually, the 18 MVE/6 HVE trigonal-bipyramidal $[MoH_4(NNH_2)]^{2-}$ model is more stable when the $NNH_2$ ligand is in an axial position, with the hydrogen atoms lying in the axial plane. The five-co-ordinated compounds listed in Table 1 have an oxide or nitride ligand, while the hydrazido group occupies an axial position. This allows one of the $2p_\pi$ lone pairs of the $O^{2-}$ or $N^{3-}$ ligand to interact with one of the metal δ-type unoccupied orbitals, leaving the other one non-bonding. This leads to the observed 16 MVE/6 HVE count. The other $2p_\pi$ $O^{2-}$ or $N^{3-}$ lone pair competes with the $\pi_\sigma$ lone pair of $[NNR_2]^{2-}$ in the interaction with one of the metal π-type FMOs. This may be the reason why compounds **16**, **32**, **34**, **59** and **63** present a somewhat bent M−N−N angle. However, this bending is not reproduced in the calculations.

Calculations on various tetrahedral $[MH_3(NNH_2)]$ models lead to the prediction of two possible closed-shell configurations in which the M−N−N arrangement is linear: 12 MVE/6 HVE or 18 MVE/6 HVE, depending on the occupation or unoccupation of the three non-bonding d-type metal levels. The unique tetrahedrally co-ordinated compound of Table 1, **87**,[72] belongs to the latter type. The EHMO calculations indicate also that bending occurs when two electrons are formally added to the 18 MVE/6 HVE system, leading to a 18 MVE/4 HVE complex.

Similar reasoning can be applied to other co-ordination numbers. In the case of seven-co-ordination for example 18 MVE/6 HVE appears to be the unique closed-shell count if the M−N−N arrangement is linear. Indeed, this type of compound has no non-bonding d orbital left. Compounds **8**, **28**, **33**, **50**, **51**, **84** and **85** belong to this category. In the case of eight-co-ordination, since there are no more than nine valence orbitals on the metal, the EAN rule requires that the hydrazide ligand uses only two FMOs for bonding, *i.e.* M−N−N bending. This is exemplified by compound **22** (18 MVE/4 HVE). Only complexes **5** and **89** appear to have an MVE count larger than 18. In these compounds which are seven- and eight-co-ordinated, respectively, the hydrazide ligand is linearly bonded, which seems to correspond to the 19 and 20 MVE counts, respectively. The EHMO calculations on the $C_{2v}$ model $[Mo(C_5H_5)_2(NNR_2)]$ are in accord with the linear co-ordination being the most stable. A significant HOMO–LUMO gap is computed for this conformation (1.38 eV). The reason lies in the delocalized nature of the bonding and has been similarly explained in the case of related electron-rich imido[95] and oxo[100d,f] complexes. One of the vacant molybdenum(IV) $d_\pi$ orbitals acts as an accepting level with respect to two (not only one) occupied ligand levels: one of the $\pi$-$C_5H_5$ combinations and the $\pi_\sigma$ FMO of $[NNH_2]^{2-}$. Owing to the similar bonding abilities of the $C_5H_5$ and hydrazido FMOs, they mix with the $d_\pi$ orbital in such a way that one of the three combinations is almost perfectly non-bonding, with very little metal participation. As a consequence, none of the occupied levels of $[Mo(C_5H_5)_2(NNR_2)]$ has significant metal–ligand antibonding character and this pseudo-20 MVE species is stable with respect to any significant distortion.§ The reluctance of the $C_5H_5$ ligand to distort away from the $\eta^5$ co-ordination may also play some role. It turns out that the slight tendency for $\eta^5$ to $\eta^3$ deco-ordination observed in **5** and **89** is reproduced by the computed overlap populations. Being independent of the occupation number of the HOMO, this slight distortion should be present for the pseudo-18, -19 and -20 MVE $(C_5H_5)_2$ species.

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§ A simple model for this delocalized bonding would be the linear $H_3^-$ ion which can be described as two hydride ligands competing for bonding to a one-orbital central proton.

## Six-co-ordinated bis(hydrazido) compounds

We now turn our EHMO analysis to the molybdenum bis-(hydrazido) species which are also well documented (Table 2). The first model considered is $[MoH_4(NNH_2)_2]^{2-}$ which is iso-electronic to most of the six-co-ordinated complexes listed in Table 2. Five *a priori* isomers are possible which are depicted in Scheme 3. The important hydrazido FMO populations, some overlap populations and the relative energies of these isomers are reported in Table 4. As one can see, for the electron count considered, the *cis* conformations are more stable than the *trans* ones.

(*a*) **The *trans* conformations.** The MO diagrams of the two *trans* isomers of $[MoH_4(NNH_2)_2]^{2-}$, **IIa** ($D_{2h}$) and **IIb** ($D_{2d}$), are shown in Fig. 3, based on the interaction of the $[MoH_4]^{2+}$ and the $(NNH_2)_2^{4-}$ fragments. The fragment charges have to be considered as arbitrary. The frontier orbitals of the square-planar $[MoH_4]^{2+}$, shown in the middle of Fig. 3, are well known:[110] they consist in a high-lying $z$ orbital situated above a set of four d-type levels ($z^2$, $xz$, $yz$ and $xy$). They are all vacant in the formally $d^0$ fragment.

Complexes **IIa** and **IIb** differ only by the respective orientation of their planar $NNH_2$ ligands, *i.e.* parallel or orthogonal. Therefore the axial interactions involving the in- and out-of-phase combinations of the occupied σ-type $1a_1$ hydrazido FMOs (not shown in Fig. 3) with the formally vacant $z$ and $z^2$ metallic orbitals are essentially the same in both isomers. This is not the case for the interactions involving the other (π-type) hydrazido FMOs. As in the case of $[MoH_5(NNH_2)]^{3-}$, the $[NNH_2]^{2-}$ $\pi_{NN}$ FMOs interact very weakly with the corresponding metallic orbitals, because of a bad energy match and of a poor overlap. The $\pi_{NN}$ population after interaction is close to two in both isomers (1.96). Consequently the difference between the electronic structures of **IIa** and **IIb** arises principally from the interactions involving the $\pi_\sigma$ ($1b_1$) and $\pi^*_{NN}$ ($2b_2$) hydrazido orbitals.

As one can see on the left side of Fig. 3, in the case of complex **IIa**, only one $\pi_\sigma$ combination ($b_{2g}$) and one $\pi^*_{NN}$ combination ($b_{3g}$) have the right symmetry which allows them to match the metallic π-type FMOs. The remaining hydrazido combinations, namely $b_{3u}$ and $b_{2u}$, are even somewhat destabilized by some low-lying ligand-type levels not shown in Fig. 3. The occupation after interaction of the $b_{3g}$ and $b_{2g}$ FMOs of the $(NNH_2)_2^{4-}$ fragment are 1.35 and 1.51, respectively. These values are close to that of the hydrazido $\pi^*_{NN}$ and $\pi_\sigma$ FMOs in **I**. Conversely, the occupation of the other π-type $b_{2u}$ and $b_{3u}$ combinations, which do not interact significantly, are very close to two (1.99). This means that the two $[NNH_2]^{2-}$ ligands in **IIa** provide the formally $d^0$ metal with two π-electron pairs, as does the single hydrazide ligand in the $[MoH_5(NNH_2)]^{n-}$ ($n = 1$ or 3) anions. This result corroborates the general predictions on metal π-donor ligand bonding made by Lin and Hall[99] on the basis of symmetry arguments.

Adding the two hydrazido σ-type lone pair combinations of $a_g$ and $b_{1u}$ symmetry leaves the metal with a 16 MVE/8 HVE configuration, with a vacant non-bonding d-type level of $b_{1g}$ symmetry. The occupations after interaction in complex **IIa** of all the FMOs of one single hydrazide ligand are closer to two (Table 4). This suggests the $[NNH_2]^{2-}$ oxidation state for the hydrazide ligand, in reasonable agreement with the ligand net charge and the N−N overlap population (Table 4).

In the case of complex **IIb** both the $\pi_\sigma$ and the $\pi^*_{NN}$ combinations of the $(NNH_2)_2^{4-}$ fragment are of e symmetry and can interact with the metallic 1e ($xz + yz$) set. The resulting bonding combinations afford some destabilization by some lower ligand-type levels. Thus, four π-type bonding interactions are present in **IIb**, while there are only two in **IIa**. However, they are much weaker in **IIa** because of a smaller overlap. This situation
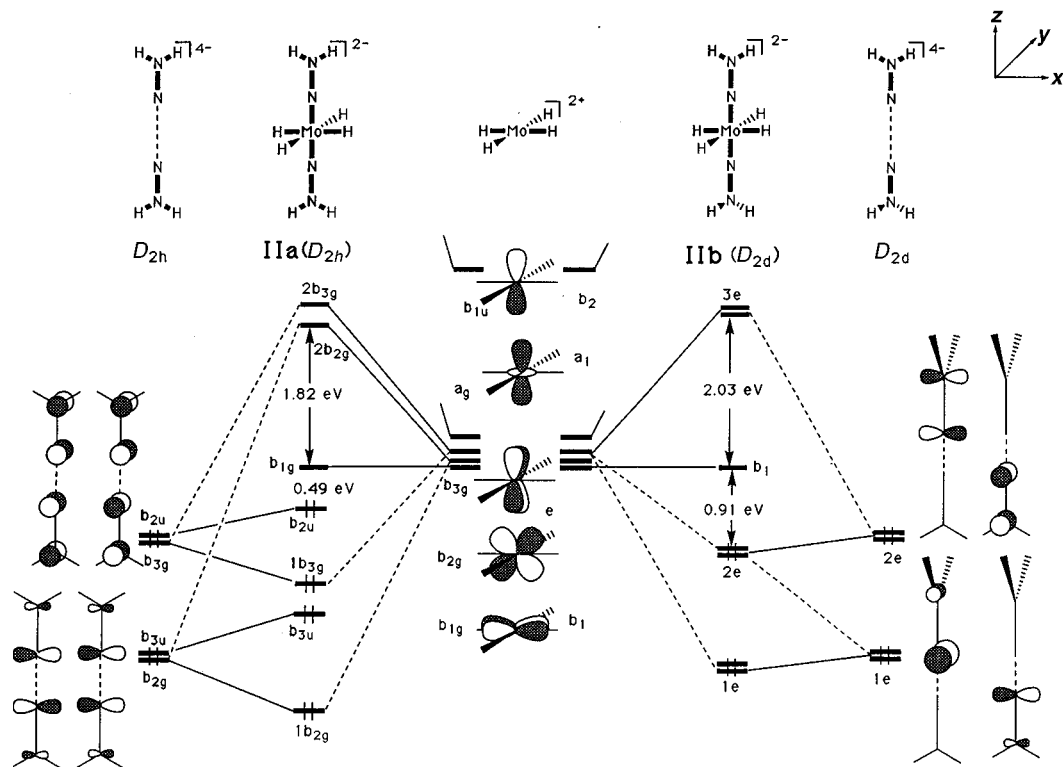
Fig. 3 Interaction MO diagram of the *trans*-[MoH$_4$(NNH$_2$)$_2$]$^{2-}$ models. Left side: IIa ($D_{2h}$). Right side: IIb ($D_{2h}$). The fragment charges are arbitrary

is related to the conformational problem of the *trans*-ML$_4$(CR$_2$)$_2$ complexes.[110] This leads us to consider also IIb as a 16 MVE/8HVE complex. Accordingly, IIb is computed to be slightly more stable than IIa, by only 0.06 eV. This small energy difference illustrates the not-far-to-axial properties of the hydrazide ligand in the *trans* conformations. The occupations of the hydrazido FMOs as well as the ligand net charge and the N–N overlap population in IIb (Table 4) are also close to the corresponding values found in IIa, suggesting also the [NNH$_2$]$^{2-}$ oxidation state.

Finally, it should be noted that both complexes IIa and IIb have a rather small HOMO–LUMO gap (Fig. 3), suggesting instability. Adding two extra electrons to their non-bonding d-type level would result in a much larger HOMO–LUMO gap (Fig. 3), indicating the possibility of existence of stable 18 MVE/8 HVE *trans*-MoL$_4$(NNR$_2$)$_2$ species. The only example for a six-co-ordinated metal bearing two *trans* hydrazide ligands is found in the trinuclear complex 93 (Table 2), where one of the metal atoms lies in a co-ordination sphere close to that of IIa, while the two other Mo atoms are tetrahedrally surrounded by sulfur. Considering the hydrazide ligands as dianonic, one is left with a d$^0$ configuration, in IIa. We have performed EHMO calculations on the idealized $D_{2d}$ model [S$_2$Mo(μ-S)$_2$Mo-(NNMe$_2$)$_2$(μ-S)$_2$MoS$_2$]$^{2-}$ for which the metrical parameters associated with the Mo(NNMe$_2$)$_2$ framework are the same as in IIa. The isoelectronic structure associated with the six-co-ordinated metal centre is similar to that of the 16 MVE/8 HVE model IIa. However, the HOMO–LUMO gap is larger (1.11 eV), due to a significant destabilization of the b$_{1g}$ LUMO by a sulfur lone-pair combination. It is noteworthy that 93 presents a somewhat bent Mo–N–N angle (166°) and a particularly short N–N separation (1.16 Å), in accordance with the **a$_2$** co-ordination mode of Scheme 1. The bending is not reproduced in the calculations. We suggest that, as for some of the 18 MVE monohydrazido complexes, this bending results from a competition between the hydrazido π* and π$_\sigma$ FMOs and the π-type heteroatom (in this case sulfur) lone pairs. We suggest 93 be described as a 18 MVE complex since, in addition to the twelve σ-type electrons, the formally molybdenum(VI) centre receives

three π-type ligand pairs. One, of b$_{1g}$ symmetry, is of pure sulfur origin. The other two, of b$_{2g}$ and b$_{3g}$ symmetry, are of combined sulfur (mainly) and hydrazido (to a lesser extent) origin. Finally, mention should be made of a recently characterized *trans* dioxo 18 MVE/8 HVE rhenium complex isoelectronic to 93.[111]

(*b*) **The *cis* conformations.** The three *cis* isomers of [MoH$_4$(NNH$_2$)$_2$]$^{2-}$, namely IIIa ($C_{2v}$), IIIb ($C_s$) and IIIc ($C_{2v}$), differ simply by the respective orientation of their NNH$_2$ ligands (Scheme 3). Surprisingly, the most stable conformation, IIIc, in which the two hydrazide ligands are coplanar, is the most sterically crowded. Its EHMO diagram is shown in Fig. 4, based on the interaction of the [MoH$_4$]$^{2+}$ and the (NNH$_2$)$_2$$^{4-}$ fragments. As for the preceding fragment partitionings, the fragment charges have to be considered as arbitrary. The frontier orbitals of the $C_{2v}$ [MoH$_4$]$^{2+}$ unit, shown at the left side of Fig. 4, are well established.[109,110] They consist in a set of two hybrids (2a$_1$ and 1b$_1$) lying above a set of three d-type levels of (1b$_2$, 1a$_2$ and 1a$_1$). They are all vacant in the formally d$^0$ fragment. The two combinations of the hydrazido σ$_n$ FMOs (1a$_1$ and 1b$_1$) interact strongly with the metallic 2a$_1$ and 1b$_1$ hybrids. As for all the computed models, the combinations of the π$_{NN}$ FMOs barely participate in the bonding, as exemplified by their occupation close to two (1.95). Among the two π$_\sigma$ FMOs combinations, one (2b$_1$) does not interact because of a very poor overlap with the metallic 1b$_1$ orbital. On the other hand, the 2a$_1$ π$_\sigma$ combination overlaps significantly with the metallic d-type 1a$_1$ level. Finally, both π*$_{NN}$ combinations (2b$_2$ and 2a$_2$) interact significantly with the 1b$_2$ and 1a$_2$ metallic levels which are close in energy. Therefore, the [(NNH$_2$)$^{2-}$]$_2$ fragment uses five electron pairs for the bonding. Unlike the isoelectronic analogues II, this corresponds to a 18 MVE/10 HVE configuration which fits with the general qualitative predictions of Lin and Hall[99] on metal–ligand multiple bonding. Consistently, the computed HOMO–LUMO gap is particularly large (2.63 eV), suggesting a good stability for this type of conformation. The occupations after interaction of the hydrazido FMOs (Table 4) in IIIc are closer to the formal $(\sigma)^2(\pi_{NN})^2(\pi_\sigma)^2(\pi^*_{NN})^1$ configuration which
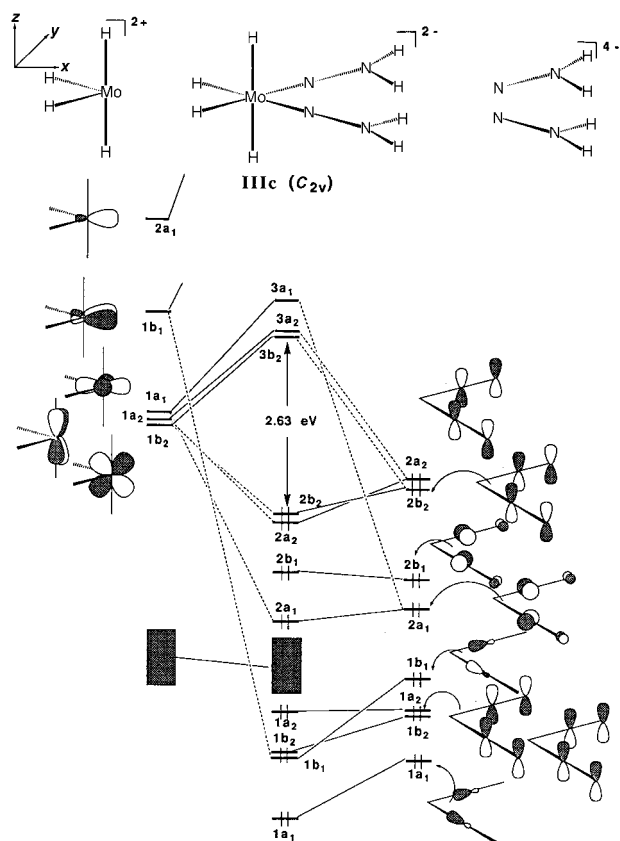
**Fig. 4** Interaction MO diagram of the model *cis*-[MoH₄(NNH₂)₂]²⁻ **IIIc**. The fragment charges are arbitrary

corresponds to the [NNH₂]⁻ oxidation state, as in the case of model **I**. It is noteworthy that in the two models the N–N overlap populations are rather close.

Going from complex **IIIc** to **IIIa** corresponds to a 90° rotation of both NNH₂ ligands, resulting in exchange of the $\pi_\sigma$ and $\pi^*_{NN}$ roles in their interaction with the metal fragment. This corresponds to the exchange of the energies of 2a₂ and 2b₂ with those of the 2b₁ and 2a₁ levels of [(NNH₂)²⁻]₂ (right side of Fig. 4). Since the energy of the d-type orbitals of the metal fragment is higher than that of the hydrazide ligand, this exchange favours the bonding interactions involving 2b₁, but disfavours those involving 2a₂ and 2b₂. The net result is a destabilization, as exemplified by the energy difference between **IIIc** and **IIIa** (0.62 eV). Of course, the energy of **IIIb**, the geometry of which is intermediate between those of **IIIc** and **IIIa**, is also intermediate between that of the other conformers. Thus, the deviation from the axial properties of the hydrazide ligands is higher in the *cis* than in the *trans* conformers.

When the four hydride ligands in complex **III** are replaced by two more realistic π-donor acac ligands, one obtains the isoelectronic *cis*-[Mo(NNH₂)₂(acac)₂] model. The results are essentially equivalent to those obtained for conformers **III**, with the most stable conformation, **IV**, identical to **IIIc** (Scheme 3). The corresponding HOMO–LUMO gap is 1.98 eV. The crucial numerical data computed for **IV** are given in Table 4. They are close to those obtained for **IIIc**, except that the $\pi^*_{NN}$ orbital is slightly more populated.

We have also carried out calculations on the real compound [Mo(NNPh₂)₂(acac)₂] **109**, using the experimental molecular structure without any idealization. This geometry is of $C_2$ symmetry and has a conformation close to that of **IIIc** or **IV**. In the NNPh₂ ligand there is more delocalization, rendering more difficult the identification of the ligand FMOs. Nevertheless, except for the $\sigma_n$ character which is distributed over too many levels, it was possible to identify the $\pi_{NN}$, $\pi_\sigma$ and $\pi^*_{NN}$ orbitals. Their occupation in **109** is similar to the corresponding values

computed for **IIIc** and **IV** (Table 4). As for **IV**, the best oxidation state seems to lie between [NNH₂]⁻ and [NNH₂]²⁻. The HOMO–LUMO gap is large (1.87 eV). In agreement with our results indicating that this is the most stable geometry for an 18 MVE/10 HVE species, most of the bis(hydrazido) complexes isoelectronic to **III** (Table 2) exhibit a *cis* conformation which is close to that of model **IIIc**, unless steric crowding favours structures of the type **IIIa** or **IIIb**.

With two formally occupied π-type FMOs, the hydrazide-(2−) ligand is isolobal to O²⁻.[109,110] It follows that the location of these two ligands in *cis* position leads to a 10 MVE system. Consistently, the electron counting of the oxo complexes of Table 1 has been carried out assuming that O²⁻ and NNR₂²⁻ are four- and six-electron donors, respectively.

There are also *cis* bis(hydrazido) complexes having one or two electrons less. The 16 MVE/10 HVE compounds **100** and **116** adopt a conformation close to that of **IIIa**.[82,89] In this conformation the level corresponding to the non-bonding 2b₁ orbital of **IIIc** (Fig. 4) is situated at a much higher energy, because of its $\pi^*_{NN}$ nature. In the 16 MVE configuration of [MoH₄(NNH₂)₂] this level is the LUMO, lying 1.28 eV above the HOMO. Therefore, conformation **IIIa** is the favoured closed-shell geometry for 16 MVE/10 HVE species, being more stable than **IIIc** by 1.24 eV. The computed $\pi^*_{NN}$ occupation (0.711) is lower than in the 18 MVE models, in agreement with the shorter N–N separations observed in **100** and **116**.

**Other co-ordination modes for bis(hydrazido) compounds**

Trigonal-bipyramidal five-co-ordination was also investigated through the various isomers of the [MoH₃(NNH₂)₂]⁻ model **V**. The results obtained for the *trans* and *cis* (equatorial) conformations parallel those of the six-co-ordinated model **III**. The reason originates from the isolobal analogy between the corresponding [MoH₄]²⁺ and [MoH₃]³⁺ fragments. In the *trans* arrangement the hydrazide ligands as a whole act as an eight-electron donor, leading to the 14 MVE/8 HVE configuration. In the *cis* (equatorial) conformations the hydrazide ligands provide the metal with two supplementary electrons,[99] which corresponds to the 16 MVE/10 HVE configuration. The most stable conformation of [MoH₃(NNH₂)₂]⁻ was found to be **Va** (Scheme 3) in which both hydrazide ligands are coplanar. In agreement with our results, the 16 MVE/10HVE compounds **91**, **92**, **96**, **101**, **102** and **105** (Table 2) have a molecular structure close to that of **Va**. The *cis* (axial-equatorial) conformations, such as **Vb** (Scheme 3), are not favoured in the case of [MoH₃-(NNH₂)₂]⁻. However, with two electrons less conformation **Vb** becomes the most stable. It corresponds to a 14 MVE/10 HVE closed-shell situation in which the LUMO is of $\pi^*_{NN}$ origin. The empty $\pi^*_{NN}$ levels suggest a shorter N–N separation, as compared to that of the 16 MVE species. Indeed, this is the case for 14 MVE/10 HVE compound **117** in which the 14 MVE metal atom adopts a conformation close to that of **Vb**.

Calculations on the [MoH₂(NNH₂)₂] model found again that the favoured conformation for tetrahedral co-ordination has the hydrazide ligands coplanar and corresponds to the 14 MVE/10 HVE configuration. The computed HOMO–LUMO gap is 1.80 eV. With two supplementary electrons a significant HOMO–LUMO gap is still present (1.09 eV) suggesting that tetrahedral co-ordination should still be stable for the 16 MVE/10 HVE configuration.

**Conclusion**

The hydrazide ligand has three FMOs available for bonding to a metal atom: two of them, $\pi_\sigma$ and $\sigma_n$, are associated with lone pairs on N$_\alpha$, the third being the $\pi^*_{NN}$ orbital. Calculations indicate that the $\pi_{NN}$ orbital is never significantly involved in the interaction with the metal, leaving almost untouched its bonding electron pair. This is one of the reasons why the NN bond

retains some multiple-bond character associated with an almost invariable sp$^2$ hybridization of $N_\beta$. Although the interaction with the metal leads to a partial occupation of the $\pi^*_{NN}$ FMO which tends to decrease the N−N bond order, calculations indicate that the ligand is reluctant to accept a full occupation of this FMO. Moreover, this effect is partly balanced by depopulation of the somewhat N−N antibonding $\pi_\sigma$ FMO. The overall N−N bond-order weakening it is not strong enough to force $N_\beta$ to pyramidalize. The EHMO calculations on various molybdenum complexes indicate that the N−N overlap populations are 25 to 35% lower than in the free neutral $N=NH_2$ molecule. *Ab initio* results on simpler models suggest that these latter values might be overestimated. Although usually considered as hydrazide(2−), the $NNR_2$ oxidation state in most of the studied compounds is close to or slightly larger than 1−, corresponding to the following FMO formal occupation: $(\sigma)^2(\pi_{NN})^2(\pi_\sigma)^2$-$(\pi^*_{NN})^1$. In monohydrazido complexes, if formally considered as a dianion, the hydrazide ligand is a six-electron donor if coordinated in a linear mode. Since the $M−N_\alpha$ π bonding is rather weak, both canonical formulae $a_1$ and $b_1$ (Scheme 1) have to be considered with significant weight, the $b_1$ weight being nevertheless not large enough to cause significant pyramidalization at $N_\beta$. If significant bending of the M−N−N angle occurs, the formally hydrazide(2−) ligand acts as a four-electron donor. However, some bending can also be present when there is competition for π bonding with stronger π-donor ligands. Bis(hydrazido) complexes usually adopt the *cis* conformation rather than the *trans* in order to maximize the $M−NNR_2$ bonding. In this situation the two formally hydrazide(2−) ligands, taken as a whole, act as a 10-electron ligand system. The electron count of all the compounds reviewed in this paper is never larger than 18, with the exceptions of **5** and **89** which are best described as pseudo (rather true) electron-rich complexes.

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