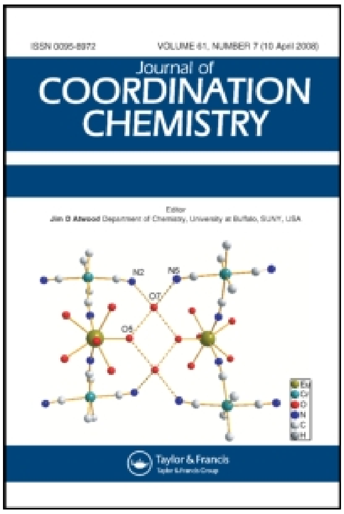

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REVIEW: SOME CONSIDERATIONS ABOUT COORDINATION COMPOUNDS WITH END-ON DINITROGEN

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There have been several reviews on dinitrogen coordination compounds but no special attention has been paid to correlate the electron configuration of the metal ions with the main features of the ligands in order to establish an electron configuration-stability relationship. In this article we consider nearly 200 complexes with terminal dinitrogen to find common characteristics that lead to the synthesis of other stable dinitrogen compounds. This survey shows that for coordination number 6 there is a strong tendency for a d^6 configuration in the metals, with oxidation states between 1- and 2.

On the basis of quantum chemistry, dinitrogen as a ligand can be compared with the isoelectronic species CO, CN^-, NO^+. The MO and orbital energy diagrams indicate that N_2 is not a good donor neither a good acceptor, but with the appropriate symmetry and in the presence of a good π-donor metal it forms an $N_2 \leftarrow M$ π-bond strengthened by an $N_2 \rightarrow M$ σ-back-bonding.

Keywords: Dinitrogen compounds; π acceptor ligands; d^6 transition metal compounds; Low oxidation states

INTRODUCTION

Nitrogen fixation, catalyzed by nitrogenase at normal conditions of pressure and temperature, still constitutes the research interest of several groups since the mechanism of action of the enzyme has not yet been elucidated. Determination of the crystal structure of this enzyme is one of the most

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*Corresponding author. Fax: 57 3165220, e-mail: apovedap@ciencias.ciencias.unal.edu.co recent advances. It is generally accepted that an obligatory step in nitrogen fixation is nitrogen binding to a transition metal ion, either Fe, Mo, or V, but it is still uncertain where and how this binding occurs in the cofactor. Research has also focused on finding synthetic catalysts to fix nitrogen under similar conditions to nitrogenases. Since the synthesis of $[Ru(N_2)(NH_3)_5]^{2+}$ [1], and since the discovery that in $[Mo(N_2)_2(dppe)_2]$ the activated dinitrogen could be converted to NH_3 [2], synthetic chemists have been trying to obtain dinitrogen compounds able to produce NH_3 by simple chemical methods and under normal conditions.

There have been several reviews on dinitrogen coordination compounds as well as on their reactivity and methods of preparation; however, a correlation between the metal ions present and the main features of the ligands bound to the metal has not been attempted, in order to establish a structure-reactivity relationship. Trying to rationalize our efforts on the synthesis of new compounds, we carried out a comparison of nearly 200 complexes with terminal dinitrogen published in the literature to find the common characteristics that lead to more reactive dinitrogen.

Table I lists the compounds [3–89] with terminal dinitrogen classified according to the metal ion present, its oxidation state, coordination number, and electronic configuration. The list does not pretend to be exhaustive but contains enough compounds to draw some conclusions. The compounds presented in the table were taken from previous reviews published by well known researchers, such as Henderson *et al.* [43], Chatt *et al.* [90], Leigh [91], Hidai [92], Shilov [93] and Takahashi [94]. Only Takahashi gives special attention to the electronic structures of the metals. A summary of these data is shown in Table II, in which the periodic correlations are presented.

Transition Metal Ions

One hundred and forty seven ($\cong$75%) out of the 196 compounds listed have metal centers with a d^6 electronic structure; from these, 145 are hexacoordinate and two are heptacoordinate. From the former, 33 compounds have Re(I) as metal ion, 33 have Mo(0), 15 have W(0), 15 have Ru(II), 15 have V(I-), and 13 have Os(II). Also, ten compounds are formed with Fe(II), five with Cr(0), three with Ir(III) and three with Mn(I) (Tab. II). In seventeen hexacoordinated compounds the metal has a d^5 electronic structure.

There are 13 compounds with d^8 metal ions; eight of them tetracoordinate, six with Rh(I), one with Mn(I-), and one with Ir(I), and the other five,

TABLE I Coordination compounds with end-on dinitrogen as a ligand

Group	*Compounds*	*No*	*Metal*	*C. N*	*d conf.*	*PR$_3$ coligands*	*Other coligands*	*Ref.*
4	$[Ti(cp)(N_2)MgCl]$	1.	Ti(0)	5	d^4		cp, MgCl	3
	$[\{Ti(cp^*)_2(N_2)\}_2(N_2)]$	2.	Ti(II)	8	d^2		cp*	4
	$[\{Zr(cp^*)_2(N_2)\}_2(N_2)]$	3.	Zr(II)	8	d^2		cp*	3
	$[Zr(cp)(CH_2SiMe_3](N_2)]$	4.	Zr(II)	5	d^2		cp, CH_2SiMe_3	5
5	$[Na(thf)][V(N_2)_2(dppe)_2]$	5.	V(I-)	6	d^6	dppe		6–8
	Trans-$Na[V(N_2)_2(dppe)_2]$	6.	V(I-)	6	d^6	dppe		8
	$Na[V(N_2)(PMe_2Ph)_5]$	7.	V(I-)	6	d^6	PMe_2Ph		8
	Cis-$Na[V(N_2)_2(PMe_2Ph)_4]$	8.	V(I-)	6	d^6	PMe_2Ph		8
	Trans-$Na[V(N_2)_2(PMe_2Ph)_4]$	9.	V(I-)	6	d^6	PMe_2Ph		8
	Cis-$Na[V(N_2)_2(dmpe)_2]$	10.	V(I-)	6	d^6	dmpe		8
	Trans-$Na[V(N_2)_2(dmpe)_2]$	11.	V(I-)	6	d^6	dmpe		8
	Cis-$Li[V(N_2)_2(dmpe)_2]$	12.	V(I-)	6	d^6	dmpe		8
	Trans-$Li[V(N_2)_2(dmpe)_2]$	13.	V(I-)	6	d^6	dmpe		8
	$Na[V(N_2)(dmpe)(bdmpm)]$	14.	V(I-)	6	d^6	dmpe, bdmpm		8
	$Na[V(N_2)(dmpe)(bdepm)]$	15.	V(I-)	6	d^6	dmpe, bdepm		8
	$Na[V(N_2)(dmpe)(bdpep)]$	16.	V(I-)	6	d^6	dmpe, bdpep		8
	$Na[V(N_2)_2(tdmp)]$	17.	V(I-)	6	d^6	tdmp		8
	$Na[V(N_2)_2(tdpp)]$	18.	V(I-)	6	d^6	tdpp		8
	$Na[V(N_2)_2(tdpe)]$	19.	V(I-)	6	d^6	tdpe		8
	$Na[V(N_2)(dmpe)_3]$	20.	V(I-)	7	d^6	dmpe		8
	$[\{Nb(cp)Bu^n\}_2(O_2)(N_2)]$	21.	Nb(I)	4	d^4		Cp , Bu^n, O_2	9
6	$[Cr(\eta^6-C_6H_6)(CO)_2(N_2)]$	22.	Cr(0)	6	d^6		$\eta^6-C_6H_6$, CO	10
	$[Cr(\eta^6-C_6Me_6)(CO)_2(N_2)]$	23.	Cr(0)	6	d^6		$\eta^6-C_6Me_6$, CO	10
	$[Cr(\eta^6-C_6H_3Me_3)(CO)_2(N_2)]$	24.	Cr(0)	6	d^6		$\eta^6-C_6H_3Me_3$, CO	10
	$[Cr(N_2)_2(dmpe)_2]$	25.	Cr(0)	6	d^6	dmpe		11
	Cis-$[Cr(N_2)_2(PMe_3)_4]$	26.	Cr(0)	6	d^6	PMe_3		12
	Trans-$[\{Mo(N_2)_2(dppm)_2]$	27.	Mo(0)	6	d^6	dppm		13
	Trans-$[\{Mo(N_2)_2(dppe)_2]$	28.	Mo(0)	6	d^6	dppe		14–17
	Trans-$[\{Mo(N_2)_2(dppp)_2]$	29.	Mo(0)	6	d^6	dppp		13
	$[Mo(N_2)_2(dtpe)_2]$	30.	Mo(0)	6	d^6	dtpe		16
	$[Mo(N_2)_2(arphos)_2]$	31.	Mo(0)	6	d^6	arphos		17
	$[Mo(N_2)_2(dpae)_2]$	32.	Mo(0)	6	d^6	dpae		17, 18

TABLE I (Continued)

Group	*Compounds*	*No*	*Metal*	*C. N*	*d conf.*	*PR_3 coligands*	*Other coligands*	*Ref.*
	$[Mo(N_2)_2(diars)_2]$	33.	Mo(0)	6	d^6	diars		17
	$[Mo(N_2)_2\{P(Bu^n)_3\}]_4$	34.	Mo(0)	6	d^6	$P(Bu^n)_3$		17
	Trans-$[Mo(N_2)(p\text{-}NH_2C_6H_4CN)(dppe)_2]$	35.	Mo(0)	6	d^6	dppe	p-$NH_2C_6H_4CN$	19
	trans-$[Mo(N_2)(p\text{-}MeC_6H_4CN)(dppe)_2]$	36.	Mo(0)	6	d^6	dppe	p-MeC_6H_4CN	19
	trans-$[Mo(N_2)(p\text{-}HC_6H_4CN)(dppe)_2]$	37.	Mo(0)	6	d^6	dppe	p-HC_6H_4CN	19
	trans-$[Mo(N_2)(p\text{-}ClC_6H_4CN)(dppe)_2]$	38.	Mo(0)	6	d^6	dppe	p-ClC_6H_4CN	19
	trans-$[Mo(N_2)(p\text{-}COMeC_6H_4CN)(dppe)_2]$	39.	Mo(0)	6	d^6	dppe	p-$COMeC_6H_4CN$	19
	trans-$[Mo(N_2)(CO)(dppe)_2]$	40.	Mo(0)	6	d^6	dppe	CO	20
	$[Mo(N_2)_2(PMePh_2)_4]$	41.	Mo(0)	6	d^6	$PMePh_2$		17, 21–24
	$[Mo(N_2)_2(PMe_2Ph)_4]$	42.	Mo(0)	6	d^6	PMe_2Ph		17, 21–24
	$[Mo(N_2)_2(PEt_2Ph)_4]$	43.	Mo(0)	6	d^6	PEt_2Ph		17, 21–24
	$[Mo(N_2)(PMe_3)_5]$	44.	Mo(0)	6	d^6	PMe_3		25–27
	$[Mo(N_2)_3tdpe]$	45.	Mo(0)	6	d^6	tdpe		28
	$[Mo(N_2)_2(PMe_3)(dppppp)]$	46.	Mo(0)	6	d^6	PMe_3, dppp		28
	$[Mo(N_2)_2(PMePh_2)\{Ph_2P(CH_2)_3SMe\}]$	47.	Mo(0)	6	d^6	$PMePh_2$, $Ph_2P(CH_2)_3$ SMe		28
	trans-$[Mo(N_2)_2(PPr^n{}_2Ph)_4]$	48.	Mo(0)	6	d^6	$PPr^n{}_2Ph$		27
	mer-$[Mo(N_2)_3(PPr^n{}_2Ph)_3]$	49.	Mo(0)	6	d^6	$PPr^n{}_2Ph$		27
	$[Mo(N_2)_2(PhSCH_2CH_2SPh)(PMe_2Ph)_2]$	50.	Mo(0)	6	d^6	PMe_2Ph	$PhSCH_2CH_2SPh$	23
	$[Mo(N_2)_2(PS\text{-}difos)(PMePh_2)_2]$	51.	Mo(0)	6	d^6	PS-difos, $PMePh_2$		29, 30
	trans-$[Mo(N_2)_2(Me_8[16]anoS_4)]$	52.	Mo(0)	6	d^6		$Me_8[16]anoS_4$	31
	$[Mo(N_2)(bdpep)(PMe_2Ph)_2]$	53.	Mo(0)	6	d^6	bdpep, PMe_2Ph		32
	$[Mo(N_2)(bdpep)(Me_2PCH_2PMe_2)_2]$	54.	Mo(0)	6	d^6	bdpep, dmpm		32
	$[Mo(N_2)(bdpep)(dppm)_2]$	55.	Mo(0)	6	d^6	bdpep, dppm		32
	$[Mo(N_2)(bdpep)(L')_2]$	56.	Mo(0)	6	d^6	bdpep	L′	32
	$[Mo(N_2)(bdpep)(diars)_2]$	57.	Mo(0)	6	d^6	bdpep	Diars	32
	$[Mo(N_2)_2(NP_3)]$	58.	Mo(0)	6	d^6	NP_3		33
	$[Mo(N_2)(CO)(NP_3)]$	59.	Mo(0)	6	d^6	NP_3		33
	trans-$[Mo(N_2)_2(dppe)_2]I_3$	60.	Mo(I)	6	d^5	dppe		34

	trans-$[Mo(N_2)_2(dppe)_2]Br$	61.	Mo(I)	6	d^5	dppe		34
	trans-$[Mo(N_2)_2(dppe)_2]Cl$	62.	Mo(I)	6	d^5	dppe		34
	$[MoCl(N_2)(PMe_3)_4]$	63.	Mo(I)	6	d^5	PMe_3	Cl^-	27
	trans-$[MoCl(N_2)(dppe)_2]$	64.	Mo(I)	6	d^5	dppe	Cl^-	35, 36
	trans-$[MoBr(N_2)(dppe)_2]$	65.	Mo(I)	6	d^5	dppe	Br^-	35
	$[Mo(N_2)(cp^*)_2]$	66.	Mo(II)	7	d^4		cp*	37, 38
	$[Mo(N_3N)(N_2)]$	67.	Mo(III)	5	d^3		N_3N	39, 40
	trans-$[W(N_2)_2(dtpe)_2]$	68.	W(0)	6	d^6	dtpe		22
	$[W(N_2)_2(PMe_3)_4]$	69.	W(0)	6	d^6	PMe_3		28
	$[W(N_2)(PMe_3)_5]$	70.	W(0)	6	d^6	PMe_3		41
	$[W(N_2)_2(PMePh_2)_4]$	71.	W(0)	6	d^6	$PMePh_2$		41, 42
	cis-$[W(N_2)_2(PMe_2Ph)_4]$	72.	W(0)	6	d^6	PMe_2Ph		41
	trans-$[W(N_2)_2(PMe_2Ph)_4]$	73.	W(0)	6	d^6	PMe_2Ph		41
	$[W(N_2)_2(PMePh_2)_3\{4\text{-}COOH(py)\}]$	74.	W(0)	6	d^6	$PMePh_2$	4-COOH(py)	28
	trans-$[W(N_2)_2(dppe)_2]$	75.	W(0)	6	d^6	dppe		21
	$[W(N_2)_2(PmePh_2)_3\{4\text{-}Me(py)\}]$	76.	W(0)	6	d^6	$PMePh_2$	4-Me(py)	28
	$[W(N_2)_2(dppe)(PMePh_2)_2]$	77.	W(0)	6	d^6	dppe, $PMePh_2$		28
	$[W(N_2)(dppe)_2(SCN)]^-$	78.	W(0)	6	d^6	dppe	SCN^-	28
	$[W(N_2)(dppe)_2(CN)]^-$	79.	W(0)	6	d^6	dppe	CN^-	28
	$[W_2(N_2)_4(PEt_2Ph)_6(\mu-N_2)]$	80.	W(0)	6	d^6	PEt_2Ph		28
	$[W_2(N_2)_4(PPr^n{}_2Ph)_6(\mu-N_2)]$	81.	W(0)	6	d^6	PEt_2Ph		28
	$[W(\eta^6-C_6H_5PR_2)(N_2)(PEt_2Ph)]$	82.	W(0)	6	d^6	PEt_2Ph	$\eta^6-C_6H_5PR_2$	21, 22
	$[WCl(N_2)(PMe_3)_4]$	83.	W(I)	6	d^5	PMe_3	Cl^-	28
	$W(N_2)_2(PMePh_2)_4]^+$	84.	W(I)	6	d^5	$PMePh_2$		28
7	$[Mn(N_2)(NO)_3]$	85.	Mn(III-)	4	d^{10}			43
	$[Mn(CO)_2(N_2)(NO)]$	86.	Mn(I-)	4	d^8			43
	$[Mn(CO)_3(N_2)(NO)]$	87.	Mn(I-)	5	d^8			43
	$[Mn(cp)(CO)_2(N_2)]$	88.	Mn(I)	6	d^6		cp, CO	44, 45
	$[Mn(CO)(N_2)(dppe)_2]BAr'_4$	89.	Mn(I)	6	d^6	dppe	CO	46
	$[MnH(N_2)(dmpe)_2]$	90.	Mn(I)	6	d^6	dmpe	H^-	47
	$[ReCl(N_2)(PMe_2Ph)_4]$	91.	Re(I)	6	d^6	PMe_2Ph	Cl^-	48 – 52
	$[ReCl(N_2)(PMePh_2)_4]$	92.	Re(I)	6	d^6	$PMePh_2$	Cl^-	49
	$[ReCl(N_2)(Me_2NPF_2)_4]$	93.	Re(I)	6	d^6	Me_2NPF_2	Cl^-	49

TABLE I (Continued)

Group	*Compounds*	*No*	*Metal*	*C. N*	*d conf.*	*PR_3 coligands*	*Other coligands*	*Ref.*
	$[ReCl(N_2)(PHPh_2)_4]$	94.	Re(I)	6	d^6	$PHPh_2$	Cl^-	49
	$[ReCl(N_2)\{P(CH_2OH)_3)\}_4]$	95.	Re(I)	6	d^6	$P(CH_2OH)_3$	Cl^-	49
	$[ReCl(N_2)(PH_2Ph)_2(PPh_3)_2]$	96.	Re(I)	6	d^6	PH_2Ph, PPh_3	Cl^-	49
	$[ReCl(N_2)\{P(OCH_2)_3CMe\}_2(PPh_3)_2]$	97.	Re(I)	6	d^6	$P(OCH_2)_3$ CMe, PPh_3	Cl^-	49
	$[ReCl(N_2)(PF_3)_2(PPh_3)_2]$	98.	Re(I)	6	d^6	PPh_3	Cl^-, PF_3	49
	$[ReCl(N_2)\{P(OMe)_3\}_2(PMe_2Ph)_2]$	99.	Re(I)	6	d^6	PMe_2Ph, $P(OMe)_3$	Cl^-	49
	$[ReCl(CO)_2(N_2)(PPr^nPh_2)_2]$	100.	Re(I)	6	d^6	PPr^nPh_2	Cl^-, CO	49
	$[ReCl(CO)_2(N_2)(PEtPh_2)_2]$	101.	Re(I)	6	d^6	$PEtPh_2$	Cl^-, CO	49
	$[ReCl(CO)_2(N_2)(PPh_3)_2]$	102.	Re(I)	6	d^6	PPh_3	Cl^-, CO	49
	$[ReCl(N_2)(dppe)_2]$	103.	Re(I)	6	d^6	dppe	Cl^-	49
	$[ReCl(N_2)(dppm)_2]$	104.	Re(I)	6	d^6	dppm	Cl^-	49
	$[ReCl(N_2)(dppp)_2]$	105.	Re(I)	6	d^6	dppp	Cl^-	49
	$[ReCl(N_2)(dppm)_2]$	106.	Re(I)	6	d^6	dppm	Cl^-	49
	$[ReCl(N_2)(dppp)_2]$	107.	Re(I)	6	d^6	dppp	Cl^-	49
	$[Re(cp)(CO)_2(N_2)]$	108.	Re(I)	6	d^6		cp, CO	53, 54
	$[ReCl(N_2)(py)(PMe_2Ph)_3]$	109.	Re(I)	6	d^6	PMe_2Ph	Cl^-, py	55
	$[ReCl(N_2)L(PMe_2Ph)_3]$ L = 3-picoline	110.	Re(I)	6	d^6	PMe_2Ph	Cl^-, 3-picoline,	55
	$[ReCl(N_2)L(PMe_2Ph)_3]$ L = 4-picoline	111.	Re(I)	6	d^6	PMe_2Ph	Cl^-, 4-picoline,	55
	$[ReCl(N_2)L(PMe_2Ph)_3]$ L = piridazine	112.	Re(I)	6	d^6	PMe_2Ph	Cl^-, piridazine	55
	mer-$[Re(N_2)(S_2CNMe_2)(PMe_2Ph)_3]$	113.	Re(I)	6	d^6	PMe_2Ph	S_2CNMe_2,	56
	mer-$[Re(N_2)(S_2CNEt_2)(PMe_2Ph)_3]$	114.	Re(I)	6	d^6	PMe_2Ph	S_2CNEt_2	56
	mer-$[Re(N_2)(S_2COEt)(PMe_2Ph)_3]$	115.	Re(I)	6	d^6	PMe_2Ph	S_2COEt	56
	mer-$[Re(N_2)(S_2PPh_2)(PMe_2Ph)_3]$	116.	Re(I)	6	d^6	PMe_2Ph	S_2PPh_2	56
	$[ReH(N_2)(dppe)_2]$	117.	Re(I)	6	d^6	dppe	H^-	57
	$[ReH_2(N_2)(dppe)_2]BF_4$	118.	Re(I)	6	d^6	dppe	H^-	57
	$[ReCl\{P(OMe)_3\}_3(MeNC)(N_2)]$	119.	Re(I)	6	d^6	$P(OMe)_3$	MeNC, Cl^-	28
	$[Re(N_2)(PMe_3)_4(NHPh)]$	120.	Re(I)	6	d^6	PMe_3	NHPh	28

$[Re(cp)(CO)_2(N_2)]$	121.	Re(I)	6	d^6		cp, CO	22
$[Re(cp^*)(CO)_2(N_2)]$	122.	Re(I)	6	d^6		cp*, CO	58
$[Re(cp^*)(CO)L(N_2)]$	123.	Re(I)	6	d^6	phosphine or phosphite	cp*, CO	59
$[ReCl(N_2)(dppe)_2]^+$	124.	Re(II)	6	d^5	dppe	Cl^-	49
$[ReCl(N_2)(dppe)_2]Cl$	125.	Re(II)	6	d^5	dppe	Cl^-	49
$[ReCl(N_2)(dppe)_2]Br$	126.	Re(II)	6	d^5	dppe	Cl^-	49
$[ReCl(N_2)(dppe)_2]I_3$	127.	Re(II)	6	d^5	dppe	Cl^-	49
$[ReCl(N_2)(dppe)_2]BF_4$	128.	Re(II)	6	d^5	dppe	Cl^-	49
$[ReCl(N_2)(dppe)_2]PF_6$	129.	Re(II)	6	d^5	dppe	Cl^-	49
$[ReCl(N_2)(dppe)_2]FeCl_4$	130.	Re(II)	6	d^5	dppe	Cl^-	49
$[Re(N_2)(SC_6H_2Pr^ir_3\text{-}2,4,6)_3(PPh_3)]$	131.	Re(III)	5	d^4	PPh_3	$SC_6H_2Pr^ir_3$-2,4,6	60
$[FeH(N_2)(dppe)_2]BPh_4$	132.	Fe(0)	5	d^8	dppe	H^-	61
$[Fe(N_2)(dppe)_2]$	133.	Fe(0)	5	d^8	dppe		62
$[Fe(N_2)(NP_3)]$	134.	Fe(0)	5	d^8	NP_3		33
$[FeH_2(N_2)(PEtPh_2)_3]$	135.	Fe(II)	6	d^6	$PEtPh_2$	H^-	63–66
$[FeH_2(N_2)(PPh_3)_3]$	136.	Fe(II)	6	d^6	PPh_3,	H^-	63–66
$[FeH_2(N_2)(PBu^nPh_2)_3]$	137.	Fe(II)	6	d^6	PBu^nPh_2	H^-	63–66
$[FeH_2(N_2)(PMePh_2)_3]$	138.	Fe(II)	6	d^6	$PMePh_2$	H^-	63–66
$[FeH(N_2)(tdpe)]BPh_4$	139.	Fe(II)	6	d^6	tdpe	H^-	61
$[FeH(N_2)(NP_3)]BPh_4$	140.	Fe(II)	6	d^6	NP_3	H^-	33, 61
$[FeH(N_2)(depe)]BPh_4$	141.	Fe(II)	6	d^6	dppe	H^-	67
$[FeH(N_2)(dmpe)]BPh_4$	142.	Fe(II)	6	d^6	dmpe	H^-	61
$[Fe(N_2)(edta)_2$	143.	Fe(II)	6	d^6		edta	68
$[FeH(N_2)_2(dppe)_2][w(CO)_3\mu(CO)_3(CO)_6(Co)_3]$	144.	Fe(II)	7	d^6	dppe	H^-, CO	28
$[Ru(NH_3)_5(N_2)]^+$	145.	Ru(I)	6	d^7		NH_3	1
$[Ru(NH_3)_5N_2]^{2+}$	146.	Ru(II)	6	d^6		NH_3	1
$[Ru(NH_3)_4(H_2O)(N_2)]^{2+}$	147.	Ru(II)	6	d^6		NH_3, H_2O	28
$[Ru(NH_3)_4(N_2)_2]^{2+}$	148.	Ru(II)	6	d^6		NH_3	1
$[Ru(H_2O)_5(N_2)]^{2+}$	149.	Ru(II)	6	d^6		H_2O	28
$[RuH_2(N_2)(PPh_3)_3]$	150.	Ru(II)	6	d^6	PPh_3	H^-	69
$[RuH_2(N_2)(p\text{-}tol)_3]$	151.	Ru(II)	6	d^6		p-tol	69
$[RuCl(N_2)(diars)_2]BPh_4$	152.	Ru(II)	6	d^6	diars	Cl^-	28
$[Ru(Cl)_2(H_2O)_2(N_2)(thf)]$	153.	Ru(II)	6	d^6		Cl^-, H_2O, thf	28
$[Ru(N_2)_2(en)_2]^{2+}$	154.	Ru(II)	6	d^6		en	28

TABLE I (Continued)

Group	*Compounds*	*No*	*Metal*	*C. N*	*d conf.*	*PR$_3$ coligands*	*Other coligands*	*Ref.*
	$[Ru(N_2)(en)_2(N_3)]^+$	155.	Ru(II)	6	d^6		en, N_3^-	28
	$[Ru(N_2)(en)_2(H_2O)]^{2+}$	156.	Ru(II)	6	d^6		en, H_2O	28
	$[Ru(PPh_3)_2Cl(\mu-Cl)_3Ru(PPh_3)_2N_2]$	157.	Ru(II)	6	d^6	PPh_3	Cl^-	28
	$[Ru(N_2)_2(tmp)]$	158.	Ru(II)	6	d^6		tmp	70, 71
	$[Ru(N_2)(tmp)(thf)]$	159.	Ru(II)	6	d^6		tmp, thf	70, 71
	$[Ru(N_2)(tmp)(dmf)]$	160.	Ru(II)	6	d^6		tmp, dmf	70, 71
	$[Os(N_2)(thf)(oep)]$	161.	Os(II)	6	d^6		thf, oep	72
	$[OsCl_2(NH_3)_3(N_2)]$	162.	Os(II)	6	d^6		NH_3, Cl^-	28
	$[OsI_2(NH_3)_3(N_2)]$	163.	Os(II)	6	d^6		NH_3, I^-	28
	$[OsI(NH_3)_4(N_2)]^+$	164.	Os(II)	6	d^6		NH_3, I^-	28
	$[Os(NH_3)_5(N_2)]^{2+}$	165.	Os(II)	6	d^6		NH_3	73
	$[Os(NH_3)_4(N_2)_2]Cl_2$	166.	Os(II)	6	d^6		NH_3	74
	$[OsBr_2(NH_3)_3(N_2)]$	167.	Os(II)	6	d^6		NH_3, Br^-	28
	$[OsCl_2(N_2)(PEt_3)_3]$	168.	Os(II)	6	d^6	PEt_3	Cl^-	28
	$[OsCl_2(N_2)(PEt_2Ph)_3]$	169.	Os(II)	6	d^6	PEt_2Ph	Cl^-	28
	$[OsHCl(N_2)(PMe_2Ph)_3]$	170.	Os(II)	6	d^6	PMe_2Ph	H^-, Cl^-	75
	$[OsHCl(N_2)(PEt_2Ph)_3]$	171.	Os(II)	6	d^6	PEt_2Ph	H^-, Cl^-	75
	$[OsHCl(N_2)(PEtPh_2)_3]$	172.	Os(II)	6	d^6	$PEtPh_2$	H^-, Cl^-	75
	$[OsCl(PMe_2Ph)_3(SC_6F_5)(N_2)]$	173.	Os(II)	6	d^6	PMe_2Ph	SC_6F_5, Cl^-	76
	$[OsCl_2(NH_3)_3(N_2)]^+$	174.	Os(III)	6	d^5		NH_3, Cl^-	28
	$[Os(NH_3)_5(N_2)]^{3+}$	175.	Os(III)	6	d^5		NH_3	28
9	$[Co(N_2)(PPh_3)_3]^-$	176.	Co(I-)	4	d^{10}	PPh_3		77
	$Na[Co(N_2)(PEt_2Ph)_3]$	177.	Co(I-)	4	d^{10}	PEt_2Ph		78
	$Na[Co(N_2)(PPh_3)_3]$	178.	Co(I-)	4	d^{10}	PPh_3		78
	$K[Co(N_2)(PMe_3)_3]$	179.	Co(I-)	4	d^{10}	PMe_3		79
	$[CoH(N_2)(PPh_3)_3]$	180.	Co(I)	5	d^8	PPh_3	H^-	80
	$[RhCl(N_2)(PPr^i_3)_2]$	181.	Rh(I)	4	d^8	PPr^i_3	Cl^-	81
	$[RhH(N_2)(PPhBu^t_2)_2]$	182.	Rh(I)	4	d^8	$PPhBu^t_2$	H^-	82
	$[RhCl(N_2)(Pcy_3)_2]$	183.	Rh(I)	4	d^8	Pcy_3	Cl^-	83, 84
	$[RhH(N_2)(Pcy_3)_2]$	184.	Rh(I)	4	d^8	Pcy_3	H^-	28
	$[L_1Rh(N_2)L_2Rh(N_3)_2(Pr^nCONCO)L_1]^*$	185.	Rh(I)	4	d^8	L_2	N_3^-, *Prn*CONCO, L1	85
	$[L_1Rh(N_2)L_3Rh(N_3)_2(Pr^nCONCO)L_1]^*$	186.	Rh(I)	4	d^8	L_3	N_3^-, *Prn*CONCO, L1	85

	Trans-$[IrCl(N_2)(PPh_3)_2]$	187.	Ir(I)	4	d^8	PPh_3	Cl^-	86
	$[IrH(N_2)Cl(PPh_3)_2][BF_4]$	188.	Ir(III)	6	d^6	PPh_3	H^-, Cl^-	86
	$[Ir(Me)Cl(CF_3SO_2)(N_2)(PPh_3)_2]$	189.	Ir(III)	6	d^6	PPh_3	Me, Cl^-, CF_3SO_2	87
	$[IrHCl(N_2)(PPh_3)_2\{OS(O_2)(CF_2)_3CF_3\}]$	190.	Ir(III)	6	d^6	PPh_3	H^-, Cl^-,	28
10	$[Ni(CO)_2(N_2)_2]$	191.	Ni(0)	4	d^{10}		CO	28
	$[Ni(CO)_3(N_2)_2]$	192.	Ni(0)	5	d^{10}		CO	28
	$[Ni(N_2)(PEt_3)_3]$	193.	Ni(0)	4	d^{10}	PEt_3		88
	$[Ni(N_2)(PBu^n{}_3)_3]$	194.	Ni(0)	4	d^{10}	PBu^n_3		88
	$[Ni(N_2)(PEt_2Ph)_3]$	195.	Ni(0)	4	d^{10}	PEt_2Ph		88
	$[Ni(N_2)(Pcy_3)_2]$	196.	Ni(0)	3	d^{10}	Pcy_3		89

*Rh(III) does not have coordinated N_2.

Ligand Abbreviations arphos: $Ph_2As(CH_2)_2PPh_2$; BAr'_4: $B[C_6H_3(3{,}5CF_3)_2]_4$; bdepm: $MeP\{(CH_2)_3Pet_2\}_2$; bdmpm: $MeP\{(CH_2)_3PMe_2\}_2$; bdpep: $PhP\{(CH_2)_2PPh_2\}_2$; cp: $\eta^5-C_5H_5$; cp*: $\eta^5-C_5Me_5$; cy: Cyclohexyl; diars: o-phenylenbis(dimethylarsine); dmf: Dimethylformamide; dmpe: 1,2-$(CH_3)_2P(CH_2)_2P(CH_3)_2$; dmpm: 1,2-$(CH_3)_2PCH_2P(CH_3)_2$; dpae: 1,2-bis(diphenilarsino)ethane; dppe: 1,2-$Ph_2P(CH_2)_2PPh_2$; dppm: 1,2-$Ph_2PCH_2PPh_2$; dppp: $Ph_2P(CH_2)_3PPh_2$; dppppp: $PhP\{(CH_2)_3PPh_2\}_2$; dtpe: $(tol)_2PCH_2CH_2P(tol)_2$; edta: Ethylendiamintetraacetate; en: Ethylendiamine; L′: 1,1′-$[Ph_2PC_5H_4]_2Fe$; L_1: Acetylacetonate(1-); L_2: 1,4-$C_6H_4(CH_2PPh_2)_2$; L_3: 1,3-$C_6H_4(PPh_2)_2$; Me_8[16]anoS_4)]; 3,3,7,7,11,11,15,15-octamethyl-1,5,9,13-tetrathiacyclohexadecane; N_3N: Triamidoamine ligands; NP_3: $N(CH_2CH_2PPh_2)_3$; NR_3: $N(CH_2CH_2PPh_2)_3$; oep: Octaethylporphyrinate(2-); $P(Bu^n)_3$: $P\{n\text{-}(CH_2)_4\}_3$; PEt_2Ph: $P(CH_3CH_2)_2C_6H_5$; PMe_2Ph: $P(CH_3)_2C_6H_5$; PMe_3: $P(CH_3)_3$; $PmePh_2$: $PCH_3(C_6H_5)_2$; $PPr^n{}_2Ph$: $P\{n\text{-}(CH_2)_3C_6H_5$; PPh_3: $P(C_6H_5)_3$; p-tol: p-$CH_3C_6H_4$; py: Pyridine; tdmp: $P\{(CH_2)_3PMe_2\}_3$; tdpe: $P\{(CH_2)_2PPh_2\}_3$; tdpp: $P\{(CH_2)_3PPh_2\}_3$; thf: Tetrahydrofurane; tmp: Tetramethylporphyrinate(2-); tol: m-$C_6H_4CH_3$.

TABLE II Coordination compounds with end-on dinitrogen, only d^6 hexacoordinated transition metals

4	5	6	7	8	9	10
$_{22}$Ti	$_{23}$V(I-) 15	$_{24}$Cr(0) 5	$_{25}$Mn(I) 3	$_{26}$Fe(II) 10	$_{27}$Co	$_{28}$Ni
$_{40}$Zr	$_{41}$Nb	$_{42}$Mo(0) 33	$_{43}$Tc	$_{44}$Ru(II) 15	$_{45}$Rh	$_{46}$Pd
$_{72}$Hf	$_{73}$Ta	$_{74}$W(0) 15	$_{75}$Re(I) 33	$_{76}$Os(II) 13	$_{77}$Ir(III) 3	$_{78}$Pt

pentacoordinate, three with Fe(0), one with Mn(I-), and one with Co(I). The other twelve compounds have d^{10} metal ions, of which nine are tetracoordinate, two pentacoordinate, and one tricoordinate. The other d^n electronic structures appear only sporadically.

This survey shows that for coordination number six, there is a strong trend for a d^6 configuration with the metals in low oxidation states, mainly (I-), (0), (I), and (II).

Most compounds studied in this work fulfill the Effective Atomic Number (EAN) rule, which indicates that hexacoordinate compounds are mainly formed by d^6 metal ions, whereas tetrahedral compounds are formed by d^{10} metal ions. There are also square planar complexes with d^8 metal ions, which show EAN of 16.

A large number of compounds with a specific metal ion does not necessarily indicate an easy route of synthesis but the interest of research groups in emulating the structure or function of nitrogenases.

Coligands

Forty-seven of the 145 hexacoordinated compounds with d^6 structure have some type of phosphine as the only coligand, 58 have in addition some other ligand; four have NH_3 as the only coligand, one has only azide and one has only water. The remaining ligands have other than phosphines. Among the various coligands, the following order of appearance may be established: phosphine derivatives (72%) $\gg Cl^- > H^- >$ CO > aromatic derivatives > η^5-ligands > NH_3 > η^6-ligands > H_2O > other coligands.

Among the phosphines, 1,2-bis(diphenylphosphino)ethane (dppe) and 1,2-bis(dimethylphosphino)ethane (dmpe) are the most abundant. Both are good σ-donors and fair π-acceptors. The ligands Cl^-, H^-, and NH_3, are σ-donors but not π-acceptors. Taking into account the metal ions present, we suggest that the best ancillary ligands for forming dinitrogen complexes are good σ-donors and also π-acceptors.

The Dinitrogen Molecule

Dinitrogen as a ligand may be compared with isoelectronic species such as CO, CN^-, or NO^+. Recent papers or texts correlate them from the point of view of qualitative molecular orbitals [95, 96].

There are many organometallic compounds reported in the literature with CO as unique ligand most of which fulfill the EAN rule. The majority of them have metal ions in low oxidation states, (0), (I), (I-). CN^- is also a common ligand, either as unique ligand or combined with others. On the other hand, NO^+ is normally encountered combined with other ligands, generally CO. In contrast, there are usually only one or two N_2 ligands in dinitrogen complexes; the other coligands have already been mentioned. The published MO diagrams for these species indicate a $(\pi_{x,y})^4$ $(\sigma_z)^2$ configuration which means that the ligands are σ-donors and π^*-acceptors.

To compare the difference of N_2 from other isoelectronic ligands we use a quantum mechanical calculation for this series (see preceding paper) [97].

In octahedral compounds, the low spin d^6 electron configuration on the metal is a good π-donor to the N_2 π^* molecular orbitals, and the e_g-type empty metal orbitals are necessary to allow $L \rightarrow M$ σ-backbonding. When the coaxial e_g orbitals are partially filled ($d^4 - d^7$ high spin, d^7 low spin or $d^8 - d^{10}$) the σ-backbonding $L \rightarrow M$ is more difficult, and the possibility of forming octahedral end-on dinitrogen complexes with these electron configurations is low. On the other hand, a d^5 low spin structure is a good π-donor and also σ-acceptor, therefore a good structure to bind dinitrogen end-on as Table I shows (17 d^5 compounds). Dinitrogen complexes with d^8 metal ions in square planar geometry, in which there is a b_1 ($d_{x^2-y^2}$) empty orbital could also be stable. These ideas can be better understood with the excellent d^{1-10} diagrams that result from the combination of the d orbital functions published by Takahashi [94].

It is also necessary to take into account the symmetry and spatial orientation of the orbital function graphics since there is some evidence from IR that the σ $M \leftarrow L$ bond goes from the $2\sigma_u$, σ^* ligand orbital (by symmetry) and not from the $3\sigma_g$, σ^b orbital, more energetically favored. The CN^- vibration that appears at $2080\,cm^{-1}$ for the free ion, is shifted by coordination above $2100\,cm^{-1}$, since the bond is strengthened by σ^* donation [98].

These facts also explain why a reductant is employed when this type of complex is used as catalyst; we propose that for octahedral complexes reduction should attain a d^6 electron configuration on the metal. Schrauzer [99, 100], states: "In aqueous methanolic solution, a molybdenum complex derived from either $Na_2[Mo_2O_4(cys)_2]$, cys = $[SCH_2CH(NH_2)CO_2]_2^-$ or $K_2[MoO(CN)_4(H_2O)]$ will, in the presence of an excess of sodium borohydride, effect the reduction of dinitrogen gas to ammonia." In these compounds, we have Mo(V) and Mo(IV), and in our opinion the metal should be taken to Mo(0), a d^6 configuration, so that it can bind N_2 and reduce it to NH_3 while the metal is oxidized. As to the coligands, the reactivity of dinitrogen is improved with good σ-donors and not too good π-acceptors in order to avoid competition for the metal d^6 electron density.

As a result it could be expected that, if the above mentioned aspects are taken into account, more octahedral complexes with terminal dinitrogen should be formed with those d^6 ions where not many dinitrogen complexes are known, such as Cr(0), Mn(I), Fe(II), Ir(III), Rh(III), Co(III), Nb(I-), or Ta(I-). In the case of ions with high positive oxidation states, the coligands should be such that they substantially increase the electron density on the metal. These considerations do not apply to dinuclear dinitrogen complexes, which will be studied later.

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