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Coordination Chemistry Reviews
193–195 (1999) 13–41

COORDINATION CHEMISTRY REVIEWS

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Bonding and stereochemistry of three-coordinated transition metal compounds

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Received 25 November 1998; accepted 13 March 1999

Dedicated to Roald Hoffmann

Contents

Abstract

Transition metal complexes with coordination number three were considered to be characteristic of the late transition elements with d^{10} configurations. The synthesis and characterization of a growing number of compounds with low coordination numbers and electron configurations from d^0 to d^8 calls for a revision of our concepts regarding the bonding and stereochemistry of such compounds. This contribution presents a general survey

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PII: S0010-8545(99)00085-5

of molecular orbital studies on the electronic structure of coordinatively unsaturated three-coordinated complexes and discusses the presently known structures both in discrete molecules and in extended arrays.

Keywords: Three-coordination; Stereochemistry; Transition metal complexes; Molecular orbitals

1. Scope of this Review

The existence of coordination number three for the late elements of the first transition series, notably those of Cu(I) and Ag(I) with the d^{10} electron configuration, is well documented [1–3]. A rationale for the stability of such complexes is given by the 16-electron rule in their planar structure. Among the classical 16-electron trigonal species we can consider Pt(0) compounds of the type $[Pt(olefin)(PR_3)_2]$, in which the carbon–carbon double bond is coplanar with the ML_3 core [4]. It is also worth mentioning what is probably the simplest three-coordinated complex known [5], the $[PdH_3]^{3-}$ anion found in the crystal structure of $NaBaPdH_3$. Also of interest is the existence of the 18-electron three-coordinated carbonylate anions [6] of the cobalt group $[M(CO)_3]^{3-}$. The present contribution will focus rather on the not so well understood ML_3 complexes of early transition metals with d^n configurations ($n < 10$) and on the related solid state compounds with three-coordinated metal atoms. First, the main families of compounds which have been structurally characterized by diffraction techniques will be summarized. Then, the general molecular orbital picture of three-coordinated metal atoms will be discussed, explicitly considering the π-donor or π-acceptor character of the ligands. Finally, some structural features and other properties associated with this geometry will be discussed. Complementary information on the synthesis, structure and reactivity of part of the compounds studied here can be found in recent reviews by Cummins [7] and Gregory [204]. Earlier reviews on three-coordinated complexes [3] and on low-coordinate amido complexes [8] are also noted.

2. Occurrence of three-coordination in non-d^{10} metal compounds

Three-coordinated complexes of non-d^{10} transition metals are generally believed to be rare [9,10]. For instance, in a comprehensive review on coordination numbers and stereochemistry of coordination compounds [10], three-coordinated complexes were not considered. In another review on Rh complexes [11] a section was devoted to three-coordinated complexes, but none of the compounds mentioned had been characterized by X-ray diffraction and most had been detected only in solution. Indeed, a look at the Cambridge Structural Database [12] (CSD, see Appendix for details on the searches) shows that coordination number three is not very common for transition metals (Fig. 1). Although data coming from X-ray crystal structures with at least one C–H or C–C bond cannot be considered comprehensive, the

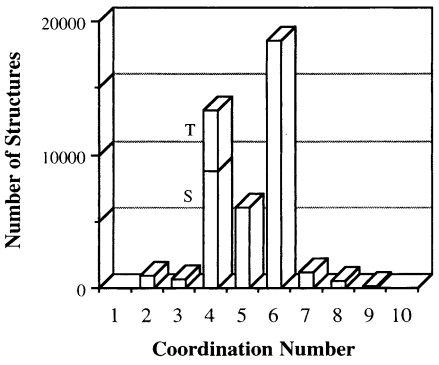


Fig. 1. Distribution of the coordination numbers among the structures of transition metal complexes collected in the Cambridge Structural Database. The four-coordinated complexes with square-planar or tetrahedral geometries are counted separately and labelled S and T, respectively.

distribution shown is probably representative of the relative importance of the different coordination numbers.

The distribution of three-coordinated complexes among the transition metal series, as found in the Cambridge database, regardless of the metal oxidation state, is shown in Fig. 2. It is clear that three-coordinated complexes are most common among the d^{10} ions of Groups 11 and 12. Among the earlier transition metals second and third row complexes are very rare. At least one compound for each of the elements of the first transition series has been structurally characterized, the most common ones being those of manganese and iron. For a more detailed account of the distribution of coordination numbers for each element and oxidation state the recent paper by Moore et al. [13] is highly recommended. It must be noted, however, that structural information on purely inorganic molecules in the gas phase or in the solid state, or on extended inorganic networks is not included in the CSD. In this review, an attempt has been made at collecting structural data for such compounds, in order to provide the reader with a wider perspective of the occurrence and structural features of three-coordinated metal compounds, although

Group									
3	4	5	6	7	8	9	10	11	12
2	3	4	7	20	17	7	6	267	44
1	0	0	1	0	0	2	7	109	10
1	0	0	1	1	1	2	10	41	78

Fig. 2. Distribution of the structures of three-coordinated molecules determined by crystal diffraction among the transition metal series, as found in the Cambridge Structural Database.

one must be aware that the data for purely inorganic structures may not be comprehensive due to difficulties in searching literature by coordination number.

Despite their scarcity, the properties of three-coordinated complexes are of interest. As will be discussed below, these compounds may present interesting magnetic properties that, so far, have not been carefully studied. Another aspect of interest is that three-coordination seems to play an important role in the proposed mechanism for cation migration between trigonal and tetrahedral positions in α-AgI, which is responsible for the good ionic conductivity of this compound [14]. Three-coordinated intermediates are also believed to play a key role in the catalytic processes involving rhodium complexes [3]. An interesting case of three-coordination is found in the MoFe cofactor of nitrogenase, as deduced from crystallographic studies of that protein from two organisms, *Azotobacter vinelandii* [15] and *Clostridium pasteurianum* [16]. In the MoFe cofactor, a Fe_7Mo cluster constitutes the site [17,18] for nitrogen binding and reduction, although its actual coordination mode is not yet known. There, the Fe atoms are coordinated by three sulfur atoms in a trigonal geometry, although short Fe···Fe distances in such cluster (2.4–2.6 Å) suggest the existence of some degree of metal–metal bonding, also supported by theoretical studies [19]. Dinitrogen coordination to Fe has been clearly established in quite a different system that presents an Fe atom trigonally coordinated by three dinitrogen molecules which act as 1,2-bridges to Mo atoms in a tetranuclear complex [20].

The structures of the ML_3 complexes are most frequently planar, as revealed by the sum of the L–M–L bond angles (Σ) close to 360°. Among the planar complexes, most have approximate trigonal symmetry and will be labeled here as D_{3h}. Distortions from this geometry within a planar framework can lead to either T- or Y-type structures, characterized by one or two bond angles significantly larger than 120°, respectively. Throughout this paper, slightly distorted molecules will be classified as trigonal planar (D_{3h}). In some instances a significant degree of pyramidalization is observed, as measured by Σ values well below 360°, and such structures will be classified as C_{3v}.

Among the growing family of structures of ML_3 complexes reported during the last decades there are some examples of three-coordinated complexes with σ-donor ligands, such as $[Rh(PPh_3)_3]^+$, or a few organometallic $[MR_3]$ or $[MR_2(thf)]$ complexes (R = mesityl; M = Mn, Rh, Ir; or R = bis(trimethylsilyl)-methyl, M = Cr, Mn) collected in Table 1. It is noteworthy than even for the rare earths such as La, Sm, and U have three-coordinated organometallic complexes been structurally characterized [21,22].

A second family of three-coordinated compounds is that of the amido complexes $[M(NR_2)_3]$, bearing bulky substituents such as $SiMe_3$. These compounds are presented in Table 2, together with the mixed ligand compounds $[M(NR_2)_2L]$ and $[M(NR_2)L_2]$. It is remarkable that all structurally characterized complexes with amido ligands correspond to first row transition metals, with only two exceptions. The fact that a Mo compound has uncovered a wealth of interesting chemical reactions makes the synthesis of new three-coordinated compounds of the heavier transition metals a most interesting goal. Also in this family a few examples of rare

Table 1
Three-coordinated complexes with σ-donor ligands

Compound	Configuration[a]	Shape	Σ (°)	α[b] (°)	M–X (Å)	μ (μ_B)	Ref.	Refcode
Alkyl, aryl and silyl (X = C, Si)								
$[Y\{HC(SiMe_3)_2\}_3]$	d^0	C_{3v}	324		2.357		[23]	Nidcei
$[La\{HC(SiMe_3)_2\}_3]$	d^0	C_{3v}	328				[21]	Gikliv
$[Cr\{CH(SiMe_3)_2\}_3]$	d^3	C_{3v}	353		2.067	–	[24]	Tmsicr
$[Mn\{CH(SiMe_3)_2\}_2(thf)]$	hs-d^5	T	360	160	2.063	5.58	[25]	Sohsud
$[Mn(mes)_3]^-$	hs-d^5	D_{3h}	360	123	2.140	5.9	[26]	Gilhis
$K[Mn\{3\text{-Me-}1,5\text{-}(Me_3Si)_2C_5H_4\}_3]$	hs-d^5	D_{3h}	360		2.18	5.91	[27]	Yajtae
$[FeCl\{Si(SiMe_3)_3\}_2]^-$	hs-d^6	T	360	136	2.489	5.8	[28]	Fekxuo
$[Rh(mes)_3]$	ls-d^6	C_{3v}	314		1.967	0	[29]	Veznix
$[Ir(mes)_3]$	ls-d^6	C_{3v}	322		2.001	0	[30]	Jurlud
$[CoCl\{Si(SiMe_3)_3\}_2]^-$	d^7	D_{3h}	360		2.03	–	[31]	Kozyut
$[Ni(mes)_3]^-$	ls-d^8	T	360		1.89	[c]	[32]	
Phosphine (X = P)								
$[Ni(dppe)\{P(SiMe_3)_2\}]$	d^9	Y	360	140	2.196		[33]	Fowlos
$[Rh(PPh_3)_3]^+$	ls-d^8	T	359	158	2.263	0	[34,35]	Cidhus
$[Ir_2(\mu\text{-}O)(Ph_3P)_2(NO)_2]$	d^8	T	360	170	2.307		[36]	Otpnir

[a] hs, high spin; ls, low spin.
[b] α is the largest bond angle in non-trigonal structures.
[c] Diamagnetic from ^{1}H-NMR spectrum.

Table 2
Three-coordinated complexes with amido ligands

Compound[a]	Configuration	Shape[b]	Σ (°)	M–N (Å)[c]	ϕ (°)	μ_{eff} (μ_B)	Ref.	Refcode
$[M(NR_2)_3]$								
$[Sc\{N(SiMe_3)_2\}_3]$	d^0	C_{3v}	346	2.049	–	–	[46]	Schmsa
$[Sc\{N(SiMe_3)_2\}_3]$[d]	d^0	D_{3h}	360	2.02			[47]	
$[Y\{N(SiMe_3)_2\}_3]$[e]	d^0	C_{3v}	343	2.224			[48]	Yoylaz
$[Ti\{N(SiMe_3)_2\}_3]$	d^1	D_{3h}	360	1.938	50	–	[49]	Tibsom
$[Ti\{N^tBu(C_6H_3\text{-}3,5\text{-}Me_2)\}_3]$	d^1	D_{3h}	360	1.98	75, 26		[50]	Yonjoa
$[V\{N(SiMe_3)_2\}_3]^+$	d^1	D_{3h}	360	1.899	50	2.37	[51]	Popbeb
$[Cr\{N(SiMe_3)_2\}_3]$	d^3	D_{3h}	360	1.889	51	[f]	[52]	Zomjiu
$[Cr(N^iPr_2)_3]$	d^3			1.871	71	3.80	[53]	Crpram
$[Cr(NCy_2)_3]$	d^3	D_{3h}	360	1.858	70	3.81	[53]	Nohkuq
$[Cr\{N(tmpip)_2\}_3]$	d^3	D_{3h}	360	1.916 (12)	58	4.23	[42]	
$[Cr\{NAd(3,5\text{-}Me_2Ph)\}_3]$	d^3	D_{3h}	360	1.868 (14)	68	3.97	[42]	
$[Mo\{N(^tBu)(dmPh)\}_3]$	d^3	D_{3h}	360	1.967	68	3.56	[54–56]	Yupgul10
$[Mn\{N(SiMe_3)_2\}_3]$	d^4	D_{3h}	360	1.890	50	5.38	[57]	Kaxmeb
$[Mn\{N(SiMe_3)_2\}_3]^-$	d^5	D_{3h}	360	2.070	51		[58]	Tegbuc
$[Fe\{N(SiMe_3)_2\}_3]$	d^5	D_{3h}	360	1.918	49	5.9	[59,60]	Hmsiaf10
$[Fe\{N(SiMe_3)_2\}_3]^-$	d^6	D_{3h}	360	1.981	55			
		D_{3h}	360	1.988	51	–	[58]	Tegcaj
$[Co\{N(SiMe_3)_2\}_3]$	d^6	D_{3h}	360	1.870	49	4.73	[57]	Kaxmif
$[Co\{N(SiMe_3)_2\}_3]^-$	d^7	D_{3h}	360	1.976	52		[58]	Tegcen
$[Ni(NPh_2)_3]^-$	d^8	D_{3h}	360	1.887	57	2.6	[61]	Dagkol
$[M(NR_2)_2L]$								
$[V\{N(SiMe_3)_2\}_2\{SeSi(SiMe_3)_3\}]$	d^2	D_{3h}	359	1.926	85	2.65	[62]	Tovvab
$[V\{N(SiMe_3)_2\}_2\{TeSi(SiMe_3)_3\}]$	d^2	D_{3h}	359	1.930	71	2.65	[62]	Tovvef
$[V\{N(SiMe_3)_2\}_2(TeSiPh_3)]$	d^2	D_{3h}	359	1.914	74	2.52	[62]	Tovvij
$[Mn\{N(SiMe_3)_2(diprPh)\}_2(thf)]$	d^5	T	360	1.993 (7)	31 (8)	–	[63]	Jokcuh
$[Mn\{N(SiMe_3)_2\}(\mu\text{-}OR)_2Li]$	d^5	Y	359	2.002	88	–	[64]	Corlie
$[Mn\{N(SiMe_3)_2\}\{\mu\text{-}NMes(SiR_3)\}_2Mn(NH_2Mes)_2\}]$	d^5	D_{3h}	360	2.180	79	2.9	[65]	Jirvah
$[Fe\{N(SiMe_3)_2\}_2(thf)]$	d^6	T	360	1.915	67	–	[66]	Jirxen
$[Co\{N(SiMe_3)_2\}_2(PPh_3)]$	d^7	T	360	1.93, 1.92		4.84	[67]	Cosiam

Table 2 (Continued)

Compound[a]	Configuration	Shape[b]	Σ (°)	M–N (Å)[c]	ϕ (°)	μ_{eff} (μ_B)	Ref.	Refcode
$[Co\{N(Ph)(Bmes_2)\}_2Cl]^-$	d^7	T	360	1.930	90	–	[68]	Fofbil
$[M(NR_2)L_2]$								
$Li[Mn\{N(SiMe_3)_2\}(OC'Bu_3)_2]$	d^5	Y	359	2.001	88	–	[64]	Corlie
$[Mn\{N(SiMe_3)_2\}\{\mu\text{-}NMes(SiR_3)\}_2Mn(NH_2Mes)_2\}]$	d^5	D_{3h}	360	2.180	79	h.s.	[65]	Jirvah
$[Mn\{N(SiMe_3)_2\}\{\mu\text{-}N(SiMe_3)_2\}_2Li(thf)]$	d^5	Y	360	2.023	45	–	[69]	Cuwmow
				2×2.144	73			
$[Co\{N(SiMe_3)_2\}(OC'Bu_3)_2]^-$	d^7	D_{3h}	360	1.985	71	–	[70]	Dozzat
$Li[Co\{N(SiMe_3)_2\}(OC'Bu_3)_2]$	d^7	Y	357	1.907	82	–	[70]	Dozzex
$[Ni\{N(SiMe_3)_2\}(PPh_3)_2]$	d^9	Y	360	1.88	–	1.91	[67]	

[a] Abbreviations: Ad, adamantyl; tmpip, 2,2,6,6-Me_4-piperidine.
[b] D_{3h} indicates the approximate symmetry.
[c] When the average of non-equivalent distances is larger than 2 in the last significant figure, the standard deviation is given in parenthesis.
[d] Gas phase electron diffraction data.
[e] Metal atom disordered.
[f] Paramagnetic from the ^{1}H-NMR spectrum: ($\delta_{Me} = +24.9$).

earth three-coordinated complexes $[M\{N(SiMe_3)_2\}_3]$ have been reported in the solid state [37–41] (M = Nd, Eu, Dy, Er, Yb, U) and in the gas phase [40,42] (M = Ce, Pr and Lu). Although the related phosphido complexes $[M(PCy_2)_3]$ have been prepared (M = V and Cr) [43] no structural characterization of such complexes has been reported so far. A Ni compound with one phosphido ligand has been reported (Table 1), but the phosphorus atom in that molecule is far from being planar, in contrast to the nitrogen atom in the structures of the amido ligands. This fact indicates that either the phosphido group should be considered as a pure σ-donor in a d^9-Ni(I) complex, or that the ligand is actually a phosphine with an hydrogen atom undetected in the X ray diffraction experiment. In the latter case this would be a classical d^{10}-Ni(0) complex. Among the families of complexes with ligands of type XR (Table 3) one finds alkoxo, thiolato and imido derivatives. The structures of a thiolato Sm [44] and of an alkoxo Ce complex [45] have also been reported.

Other than these molecules in which the bulky ligands may give sterical protection to the metal center thus favoring the coordinative unsaturation, there is a series of remarkable three-coordinated compounds with monoatomic anions as ligands (Tables 4 and 5). These include the ionic nitrido complexes [81,204] $[MN_3]^{6-}$ in the Ca_6MN_5 (M = Mn, Fe) and A_3MN_3 families [82] (A = alkaline earth; M = V, Cr, Mn, Fe, Co), some trihalides MX_3 (X = F, M = V, Cr; X = Cl, M = Sc, Ti, Fe; X = I, M = Ti) studied by electron diffraction in the gas phase [83–88]. Equally fascinating are the mononuclear Hoppe anions $[MO_3]^{4-}$ (M = Fe, Co), with planar MO_3 units that may appear condensed by sharing vertices in the oxo-bridged binuclear anions $[M_2O_5]^{6-}$ (M = Fe [89–92], Co [93,94]) and in the tetranuclear anion [95,96] $[Co_4O_9]^{10-}$. Local three-coordination can also be found in the extended structures of the transition metal subnitrides M_2N, in which the metal atom appears in a practically planar environment if strongly distorted from trigonal symmetry toward a Y (M = V, Cr, Fe, Co) [97–100] or a T structure (M = Ti, Mo) [101–103]. The same anti-rutile structure is found for several carbides of M_2C stoichiometry (M = V, Co, Y, Nb, Mo, Ta) [100,104–111]. Some metal oxides and sulfides of M_2X_3 stoichiometry may be described as three-coordinated or, alternatively, as distorted octahedral. An example is Mo_2S_3, with three sulfide ions providing a trigonal pyramidal environment for each Mo atom (Mo–S = 2.32–2.37 Å, Σ = 295°) [112,113], while three additional sulfides at longer distances (Mo–S = 2.55–2.64 Å, Σ = 245°) complete a distorted MoS_6 octahedron.

Apparently, the less common three-coordinated complexes of non-d^{10} transition metals are those with π-acid ligands. The only solid state structure obtained by X-ray diffraction is that of the tetranuclear complex $[Fe\{(N_2)Mo(tripod)_3\}_3]$, in which an Fe atom is trigonally coordinated by three dinitrogen molecules which act as 1,2-bridges to the Mo atoms. In this compound, the tripod ligand is $\{N(CH_2CH_2NSiMe_3)_3\}^{3-}$ and Fe has been found to be in its +3 oxidation state [20]. Triscarbonyl complexes of non-d^{10} transition metals, such as $Mo(CO)_3$ and $Fe(CO)_3$, have been characterized by IR spectroscopy in noble gas matrices [132,133].

Three-coordinated metal centers are also present in edge-sharing binuclear M_2L_4 complexes. A variety of such structures bearing amido or phosphido bridges and

Table 3
Three-coordinated complexes with potentially double-faced ligands XR (X = N, O, S)

Compound	Configuration[a]	Shape[b]	Σ (°)	M–X (Å)	M–X–R (°)	μ (μ_B)	Ref.	Refcode
X = N								
$[Ti(NPSPh_2)Cl_2]py$	d^0	T	360	1.721	172	–	[71]	Kethum
$[W(OSi^tBu_3)_2(N^tBu)]$	ls-d^2	D_{3h}	360	1.658	175	0	[72]	Jirpuv
$[Re(NC_6H_3^iPr_2)_3]^-$	ls-d^2	D_{3h}	360	1.599–1.753	169–174	0	[73,74]	Juzted
$[Os(NAr')_3]$	ls-d^2	D_{3h}	360	1.737	178–180	0	[75]	Kehhag
X = O								
$[Sc(OC_6H_2$-2,6-$^tBu_2$-4-$Me)_3]$	d^0	D_{3h}	358	1.869	168		[76]	Cavfio
$[W(Osi^tBu_3)_2(N^tBu)]$	d^2	D_{3h}	360	1.82	170–178	0	[72]	Jirpuv
$[Cr(O^tBu)(\mu$-Cl$)(\mu$-O^{t}Bu$)Li(thf)_2]$	d^4	T	360	1.881	158	–	[77]	Caszeb
$[Fe\{OSi(SiMe_3)_3\}\{\mu$-$OSi(SiMe_3)_3\}_2Na(DME)]$	d^6	Y	359	1.881	155		[59]	
$[CoCl(OC^tBu_3)_2]^-$	d^7	T	360	1.839	138	–	[70]	Dozyum
X = S								
$[Fe\{SPh(^tBu)_3\}_3]^-$	hs-d^6	D_{3h}	360	2.27	115	5.05	[78]	Yompiz
$[Fe\{SPh(^tBu)_3\}_2\{CH(SiMe_3)_2py\}]$	hs-d^6	D_{3h}	360	2.261	101, 113	5.11	[79,80]	Yumwae10
$[Fe\{SPh(^tBu)_3\}\{\mu$-$SPh(^tBu)_3\}_2Li(thf)_2]$	hs-d^6	Y	357	2.259	107	4.80	[78]	Yompev

[a] hs, high spin; ls, low spin.
[b] D_{3h} stands for the approximate symmetry of the MX_3 core.

Table 4
Tricoordinate complexes of transition metals of Groups 3–9 with monoatomic ligands

Compound	Shape[a]	Configuration[b]	Σ (°)	M–X (Å)	Ref.
Oxo					
$Na_4[FeO_3]$	D_{3h}	d^6	359	1.88	[114]
$Na_4[CoO_3]$	T	d^7	360	1.85	[115]
$RbNa_7[CoO_3]_2$	T	d^7	360	1.85	[116]
$A_{10}[Co_4O_9]$ (A = Na, K)	Y, T	d^7	353–360	1.77–1.82[c] 1.85–1.96[d]	[96,117]
Nitrido					
Ca_3VN_3	T	ls-d^2	360	1.823	[118]
Ca_3CrN_3	T	ls-d^3	360	1.82	[119]
Ba_3CrN_3, Sr_3CrN_3	D_{3h}	d^3	360	1.728	[120]
Ca_6MnN_5	D_{3h}	ls-d^4	360	1.757	[121]
Ca_3MnN_3	T	d^4	360	1.795	[122]
Sr_3MnN_3, Ba_3MnN_3	D_{3h}	d^4	360	1.74	[123]
Ca_6FeN_5	D_{3h}	d^5	360	1.769	[124]
$Ba_3[FeN_3]$	D_{3h}	d^5	360	1.730	[125,126]
$Ba_3[CoN_3]$		ls-d^6	[e]	[e]	[127]
Ti_2N	T	$d^{2.5}$	360	2.072	[102]
V_2N	Y	$d^{3.5}$	358	1.98	[97]
Cr_2N	Y	$d^{4.5}$	354	1.93	[98]
Mo_2N	T	$d^{4.5}$	353	2.09	[103]
Fe_2N	Y	$d^{6.5}$	354	1.941	[99]
Co_2N	Y	$d^{7.5}$	356	1.92	[100]
Carbido					
Y_2C	D_{3h}	d^1	360	2.481	[111]
V_2C	Y	d^3	355	2.02	[104,105]
Nb_2C	Y, T, D_{3h}	d^3		2.07–2.27	[106]
Mo_2C	Y	d^4	348, 355	1.99–2.22	[108–110]
Co_2C	Y	d^7	354	1.916	[100]

[a] hs, high spin; ls, low spin.
[b] D_{3h} stands for the approximate symmetry of the MX_3 core.
[c] Terminal ligand.
[d] Bridging ligand.
[e] Only powder diffraction data available.

amido terminal ligands (M = Cr, Mn, Fe, Co, Ni) have been reported in recent years [8,134–137]. There is also an example of an imido compound having a Ti–Ti bond [138]. Finally, the MX_3 building block appears in the edge-sharing binuclear Hoppe anion [139] $[Co_2O_4]^{4-}$, and in the analogous binuclear halides Cr_2Cl_4 and Co_2Br_4 [84]. A larger number of such dimeric compounds can be found in the literature, but no attempt has been made to provide comprehensive coverage in this review, taking into account that some degree of metal–metal bonding has to be taken into account and a more detailed discussion of their electronic structure would be needed.

Finally, let us mention two complexes which can be considered either as three- or four-coordinate $[Co(CO)_2(tmpo)]$ and $[Ni(PMe_3)(PhSN^tBu)_2]$. In the former [140], the 2,2,6,6-tetramethylpiperidin-1-oxyl ligand (tmpo) is coordinated through the

Table 5
Molecular structures of trihalides of transition metals of Groups 3–9 determined by electron diffraction

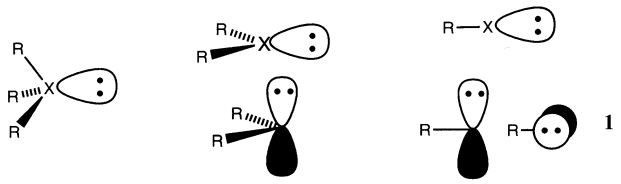
Compound	Shape	Configuration	M–X	Ref.
ScF_3	D_{3h}	d^0	1.847	[84,128]
$ScCl_3$	D_{3h}	d^0	2.291	[129]
ScI_3	D_{3h}	d^0	2.62	[130]
LaF_3	D_{3h}	d^0	2.22	[86]
$LaCl_3$	C_{3v}	d^0	2.56	[84]
$LaBr_3$	D_{3h}	d^0	2.741	[85]
LaI_3	D_{3h}	d^0	2.98	[86]
$TiCl_3$	D_{3h}	d^1	2.205	[84]
			2.178	[83]
TiI_3	D_{3h}	d^1	2.514	[83]
VF_3	D_{3h}	d^2	1.751	[84]
WCl_3	C_{2v} (T)	d^3	2.171, 2.325	[84]
CrF_3	D_{3h}	d^3	1.732	[128]
MnF_3	T	d^4	1.712, 1.735	[126]
FeF_3	D_{3h}	d^5	1.763	[131]
$FeCl_3$	D_{3h}	d^5	2.14	[86]

NO group in an η^2 fashion. If that ligand is considered as a two-electron donor, then the geometry around the Co(I) atom has a planar Y shape with an angle sum of 360°. However, one may alternatively consider tmpo as a bidentate ligand spanning two sites of a square planar coordination sphere, thus being a d^8, 16-electron compound. Similarly, the Ni compound cited [141] has one sulfenamido ligand coordinated in an η^2 mode, the other one in a η^1 mode, and it can either be considered as a three-coordinated T-shaped molecule or square planar with a bidentate ligand.

3. Theoretical studies

3.1. Molecular orbital diagrams

The energy ordering of the metal d orbitals is strongly influenced by the nature of the ligands. Since molecular structure, magnetic and optical properties in



σ-donor **single-faced π-donor** **double-faced π-donor**

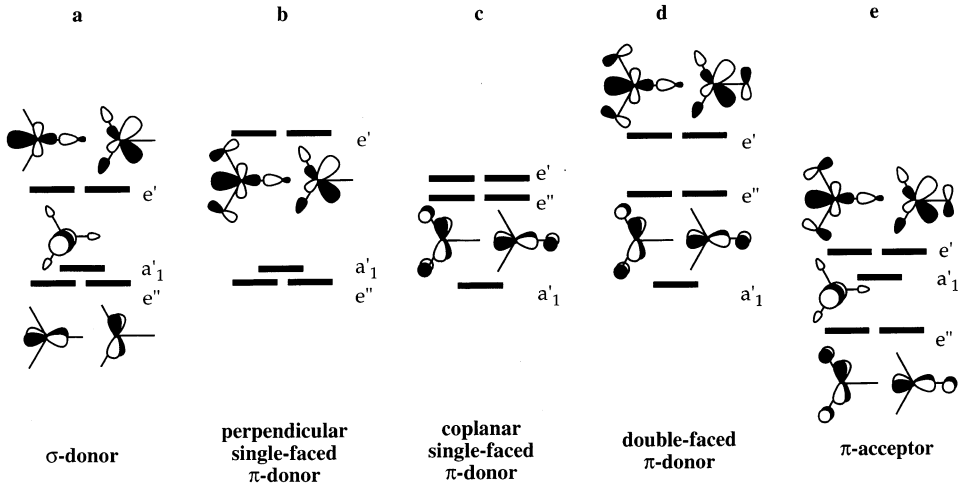
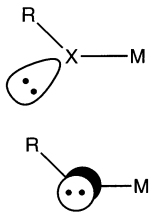


Fig. 3. Qualitative molecular orbital diagrams for the d-block orbitals in planar trigonal ML_3 complexes with ligands of different donor characteristics.

transition metal complexes are mostly determined by the d-block orbitals, a molecular orbital description that takes into account the donor characteristics of the ligands is needed. We may distinguish four types of ligand according to the number of electron pairs they can donate to a metal atom (**1**). First, the pure σ-donor ligands such as phosphines, amines, alkyl, aryl or silyl groups. Second, the single-faced π-donors [142], i.e. those ligands that can in addition donate one pair of π electrons, such as the amido groups NR_2^-. Third, the double-faced π-donors which bear three pairs of electrons, as is the case of the monoatomic ligands: halides, oxides or nitrides, and of the monosubstituted ligands, such as alkoxides, imides, or thiolates. Although the XR ligands such as imides, alkoxides or thiolates can act as σ- and double-faced π donors, this requires the XR and MX bonds to be colinear. If the R–X–M significantly deviates from linearity, one of the lone pairs is directed away from the metal atom (**2**), and only one π lone pair is available for donation, thus becoming a single-faced donor. Finally, one should separately consider π-acceptor ligands, such as CO, even if this constitutes the poorest represented family among non-d^{10} three-coordinated complexes. Let us start by presenting schematic MO diagrams for trigonal complexes with the four types of ligands (Fig. 3), which are consistent with the essential trends found in calculations at different levels of approximation reported by several authors [143–148].



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Consider first the case of a complex with σ-donor ligands only. A qualitative MO diagram for the d-block orbitals of ML_3 complexes, based only on σ interactions, can be found in the early work of Ziegler [145,149], and the description of those orbitals for a pyramidal ML_3 fragment were described by Albright et al. [150]. Such an MO diagram is schematically depicted in Fig. 3 (a). The σ metal–ligand bonding in trigonal planar ML_3 complexes can be essentially described by the interaction of sp^2 hybrids at the metal atom with the corresponding lone-pair orbitals of the ligands. Hence, the d orbitals are formally nonbonding, although some antibonding character is incorporated by the d_{z^2} (a_1'), d_{xy} and $d_{x^2-y^2}$ (e') orbitals. Such antibonding interaction is significantly much stronger for the e' pair because of the concentration of these d functions along the M–L directions. As a result, the a_1' and e'' orbitals are close in energy, whereas the e' pair appears at higher energy. This situation resembles the well known t_{2g}/e_g splitting pattern in octahedral complexes, but the gap is much larger in the latter because of the σ-antibonding nature of the e_g orbitals.

When the ligands are single-faced π donors, the orbital interactions are different depending on the orientation of the π lone pairs. For amido ligands, a coplanar conformation of the ligands relative to the coordination plane implies that the π lone pairs are perpendicular. In that case, these ligand orbitals interact with the e' orbitals of the metal, converting them into π antibonding MOs (Fig. 3 (c)). If the ligands are perpendicularly oriented, then the π lone pairs are coplanar to the coordination plane, the e' (d_{xy} and $d_{x^2-y^2}$) orbitals incorporate metal–ligand π-antibonding character and become further destabilized (Fig. 3 (b)). Since experimentally the tris(silyl)amido complexes present rotation angles of around 50°, the MO ordering is expected to be in between those presented in Fig. 3 (b) and (c), but closer to the former. Such a qualitative picture is consistent with the ligand field description [151] obtained from magnetic measurements, visible and ESR spectra of $[M\{N(SiMe_3)_2\}_3]$, where M = Ti, V, Cr, Fe, for which the splitting between the a_1' and e'' orbitals varies between -4800 and 1900 cm^{-1}, whereas the e' set is separated from the lower orbitals by 12600–19300 cm^{-1}.

In the presence of double-faced π donors, both the e' and e'' orbitals acquire π antibonding character and the MO diagram that applies [144] is the one depicted in Fig. 3 (d). Qualitative MO diagrams based on EH and Xα calculations for the model imido complexes $[Os(NH)_3]$ and $[Re(NH)_3]^-$ have been reported by Schrock and coworkers [74,143]. Our studies of the CoO_3^{4-} group in the dimeric Hoppe anion $[Co_2O_4]^{4-}$ at the EH level [147] indicate an MO diagram similar to that reported for the nitrido complexes [144]. However, the weaker π interactions of the oxo ions compared to the nitrides result in a lesser destabilization of the e'' and e' orbitals, explaining the different magnetic behavior of the two families of compounds, as discussed below.

The M–L bond energy calculated by Ziegler for the families of CrX_3 and MoX_3 compounds was found [145] to follow the order $OH^- > Cl^- > NH_2^- > CH_3^- > H^-$. Notice that the most stable bonds are formed by double-faced π-donors, followed by single-faced π-donors, while the weakest bonds correspond to the pure

π-donors. Ziegler also found that, for the same ligand, the bond energy was larger for Mo than for Cr, and attributed such difference to the better overlap of the difuser d orbitals of Mo with the ligands.

The energy ordering of the d orbitals in three-coordinate carbonyl complexes was analyzed by Burdett [152] using the angular overlap model and by Elian and Hoffmann [153] by means of extended Hückel calculations. The π-acid nature of the carbonyl ligands imparts π-bonding character to both the e″ and e′ orbitals, resulting in the qualitative MO pattern shown in Fig. 3 (e), reminiscent of the e/t_2 splitting present in thetrahedral complexes.

3.2. Spin states

The molecular orbital diagrams (Fig. 3) are useful to rationalize the magnetic behavior of the different families of compounds. Given the relatively small energy separation between the d orbitals associated to their formal non-bonding, π-antibonding or π-bonding character, high spin configurations are to be expected for the trigonal planar complexes if two-electron repulsions are large enough. Roughly speaking, one can anticipate that the low spin state will be favored by large orbital gaps and for metal ions with a weaker electron repulsion. According to the values of the Racah parameters, obtained from gas phase atomic spectra [154], electron repulsion decreases with increasing oxidation state, and down the periodic table. Hence, it is more likely to find low spin complexes for second and third row metal ions. Also, the choice between low or high spin states depends on the type of ligand and on the electron configuration.

Our studies on $[M(NR_2)_3]$ complexes at the DFT level [146] showed that the high spin configuration is preferred over the low spin one for all d^n electron configurations, and the energy difference between high and low spin states is strongly dependent on the angle of rotation of the amido groups.

For several Cr(III) and Mo(III) ML_3 complexes with ligands of different donor characteristics ($L = H^-$, CH_3^-, NH_2^-, OH^-, or Cl^-), DFT calculations carried out by Ziegler [145] indicated a $^4A_2'$ ground state corresponding to the $(e'')^2(a_1')^1$ configuration. However, CI calculations for trigonal complexes of Cr(III) and Fe(III) with the double-faced π-donor nitrido ligands reported by Yee and Hughbanks, qualitatively consistent with the diagram shown in Fig. 3 (d) [144], predicted a low spin ground state for the nitrido Cr(III) and Fe(III) complexes. For the oxo complexes, the smaller separation between the a_1', e″ and e′ orbitals associated with the more ionic M–O interaction compared to the M–N, results in high spin ground states.

3.3. Structural preference

Several attempts have been made to provide a qualitative framework for the prediction of the structural choice among three-coordinated complexes, although these have not taken into account the differences in orbital energies and composition illustrated in Fig. 3. By assuming σ-donor ligands only, a Walsh diagram for

the distortion from D_{3h} to the C_{2v} Y or T structures (schematically shown in Fig. 4) has been proposed by Albright, Burdett and Whangbo [155]. Earlier attempts at using the angular overlap model [152,156] to establish the preference between the trigonal planar, pyramidal and T structures proved to be inconclusive for several electron configurations. The two approaches, though, consistently predict the low spin d^8 complexes to be distorted toward a T structure (see discussion of experimental structures below). Ortiz, Hay and Martin [157], performed CAS-SCF calculations for related actinide organometallic complexes $[M(CH_3)_3]$ (M = U, Np, Pu) and found that the pyramidal structure is preferred to the planar, by about 3 kcal mol^{-1}. Ab initio calculations [158,159] predicted d^0 complexes $[ScH_3]$, $[TiH_3]^+$, $[TiMe_3]^+$ and $[ZrH_3]^+$ to be pyramidal, with planarization energies for the first three compounds close to 10 kcal mol^{-1}. Ziegler [145] found that in the similar d^3 complexes of Cr and Mo the planar structure is always preferred. Finally, MP2 calculations predict $[RhH_3]$ to be pyramidal, with bond angles of 79° [159].

Walsh diagrams for the different distortions from the D_{3h} structure have not been reported for complexes with single-faced π donors. DFT calculations on $[M(NH_2)_3]$ [146] for different metal ions gave a planar trigonal structure as the most stable one with the exception of the Mn(III) compound. Previous DFT calculations by Ziegler [145] focused on the trisamido complexes of Cr(III) and Mo(III), and also found the planar structure to be more stable than the pyramidal. DFT calculations on $[M(NH_2)_3]$ show [146] that the preferred orientation for the high spin state varies

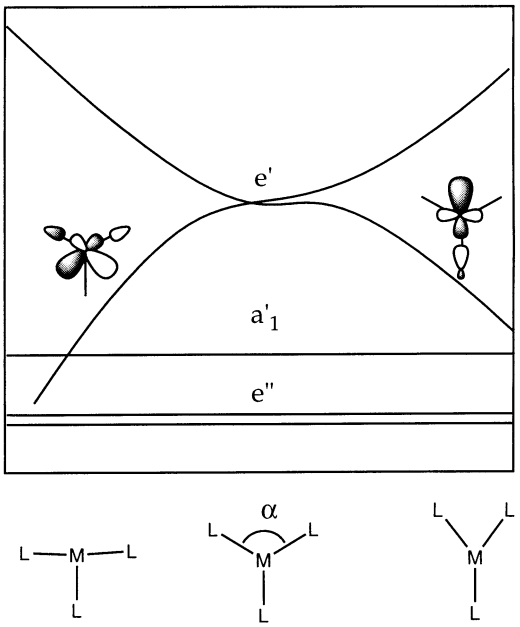
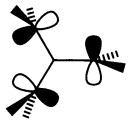


Fig. 4. Walsh diagram for the d-block orbitals of a ML_3 complex with σ-donor ligands upon distortion from the planar trigonal geometry to Y- (right) or T-shaped (left) structures.

with the number of d electrons. The perpendicular orientation ($\phi = 90°$) is prevented by the ligand···ligand antibonding character of the a_2' combination of the ligands' lone pairs (**3**). Substitution of the H atom by SiH_3 groups highly destabilizes the coplanar orientation, setting up a threshold value for the rotation angle of about 30°, with the d^3 and d^8 ions showing a larger degree of rotation. The same trend is found in the experimental data, in which R is most frequently $N(SiMe_3)_2$, for which the experimental threshold rotation angle is approximately 50°.



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Ab initio calculations were reported by Cundari and coworkers for several model imido complexes [148,160]. For the homoleptic compounds $[M(NH)_3]^{n-}$, the pyramidal structure was found to be preferred when M has the d^0 electron configuration ($M = Tc^{VII}$), whereas for d^1 and d^2 analogues ($M = Tc$, $n = 0$, 1; $M = Mn$, Tc, Re, $n = 1$; $M = Fe$, Ru, Os, $n = 0$), the trigonal planar structure is more stable. Similarly, mixed ligand complexes of the types $[MX_2(NR)]$ (M = Ti, Zr, Hf; X = H, Cl; R = H, Cl) are predicted to be pyramidal. In the homoleptic complexes the M–N–H groups deviate strongly from linearity ($124 \leq M–N–H \leq 137°$), but in the mixed ligand complexes they appear to be practically linear. The disagreement of these structural parameters with those experimentally found (see below) suggest that in some cases the steric bulk of the substituents may be important in determining a symmetric planar structure. Also, $[La(H_2O)_3]$ and $[La(NH_3)_3]$ have been predicted [161] to be pyramidal at the MP2 level, although the energies of planarization, 0.4 and 0.8 kcal mol^{-1}, respectively, are quite small.

For trigonal complexes of Cr(III) and Fe(III) with the double-faced π-donor nitrido ligands [144], the expected Jahn–Teller distortion for the $[CrN_3]^{6-}$ ion was analyzed by means of extended Hückel and ab initio calculations and the Y and T planar shapes were found to be of similar energies, but only slightly stabilized with respect to the symmetric structure. These authors suggested that the N–M–N bond angles observed are probably more influenced by the interaction of the nitrido ligands with the surrounding alkaline earth cations than by the Jahn–Teller effect. Ab initio calculations reported by the same authors for the low spin states of $[MN_3]^{6-}$ predict slight distortions toward T ($\alpha = 119°$) or Y ($\alpha = 122°$) structures for Cr(III) and Fe(III), and symmetric D_{3h} structure for V(III). For both the Cr(III) and Fe(III) anions, it was found that the ab initio optimized M–N distances are longer for the high spin than for the low spin state, in keeping with the π-antibonding nature of the e′ and e″ orbitals. For the d^3 complexes of other double-faced π donors (Cl^- and OH^-), DFT calculations have found that the planar structure is preferred to the pyramidal [145]. The instability of the pyramidal form was attributed to steric repulsions between ligands, but the changes in energy of the σ and π bonding orbitals were not analyzed.

Ab initio calculations on MF_3 molecules (M = Sc, Ti, V, Cr, Mn, Co and Ni) were reported by Yates and Pitzer [162]. There has been some controversy on whether the d^0 MX_3 molecules have planar or pyramidal structures. Although a planar structure now seems well established from both gas electron diffraction [128–130] and theoretical [129,158,163] studies for ScX_3 (X = F, Cl, I) and $[TiX_3]^+$ (X = F, Cl), some debate still exists for the halides of the heavier elements [164,165], e.g. YCl_3 and $LaCl_3$. For most first row transition metal trihalides, Yates and Pitzer found a D_{3h} geometry to be the preferred one in the high spin ground state, with the exception of CrF_3 and MnF_3. The former seems to be more stable in a pyramidal shape [162]. For the latter, Hargittai et al. [166] found the global minimum to correspond to a T-type structure in a quintet state.

4. Magnetic behavior

Unfortunately, no detailed studies have been reported on the magnetic behavior of three-coordinated complexes, and only in some cases has the magnetic moment at room temperature been reported. Since the separation between the different sets of metal-nd orbitals is associated with π interactions, high spin states are not expected to be rare for three-coordinated compounds with d^2 to d^8 configurations. Given the variety of orbital patterns that can be found (Fig. 3), it is likely that spin crossover could be observed in some cases.

According to the MO picture for complexes with σ donor ligands (Fig. 3 (a)), those complexes with d^2 or d^3 electron configurations are expected to present a high spin ground state. For compounds with d^4 to d^7 electron configurations, the choice between a high spin or a low spin ground state will depend on the importance of the electron repulsion terms. In principle, the $e'–a_1'$ gap is not expected to be large, given the formal nonbonding character of these orbitals, and it is not surprising that all complexes of first row metal ions present a high spin ground state, with the exception of $[Ni(mes)_3]^-$, which shows a ^{1}H-NMR spectrum consistent with a diamagnetic ground state, undoubtedly associated with the strong distortion toward a T shape. A similar explanation should apply to the diamagnetism found for the Rh(I) phosphine complex. In a Co(II) complex with σ-donor ligands only, a sharp signal in the RSE spectrum has been interpreted as an indication of a non-degenerate ground state [31], consistent with a high spin $(e'')^4(a_1')^1(e')^2$ configuration (Fig. 3). For second and third row transition metals, electron repulsion is less and low spin ground states can be anticipated, as found for the Rh(III) and Ir(III) mesityl complexes. Nevertheless, one should be cautious about taking these trends as general rules, since the amount of data on the magnetic behavior of such compounds is still scarce.

The trisamido complexes of the first row transition metal ions all appear in high spin states. For example, the visible and ESR spectra of $[Fe\{N(SiMe_3)_2\}_3]$ have been interpreted according to a $^6A_1$ ground state [59]. In contrast to the amido complexes, the d^2 compounds with double-faced π donor imido or alkoxo ligands have a low spin ground state, in agreement with the qualitative orbital diagram of

Fig. 3. The bent thiolato ligands behave as single-faced π donors and give high spin compounds for the d^7 ions. Little is known about the magnetic properties of complexes with other double-faced π donors (i.e. oxo, nitrido, carbido or halo compounds). Only for Ca_3MN_3 (M = V, Cr, Co) and Ca_6MnN_5 has the magnetic behavior been studied and a low spin ground state [118,119,127] was proposed in all cases.

5. Metal–ligand bonding

According to the MO diagrams (Fig. 3), varying degrees of metal–ligand π bonding should be expected depending on the π donor/acceptor characteristics of the ligands and on the electron configuration of the metal ion. The simplest case, in terms of formal metal–ligand bond order, is that with occupied bonding and non bonding molecular orbitals and empty antibonding MOs. Such a situation corresponds to low spin states that are not often encountered in three-coordinated complexes, but it deserves some discussion because it presents the maximum possible degree of metal–ligand π bonding. For complexes of σ donor ligands (Fig. 3 (a)), in which all d orbitals are formally non-bonding, this means a d^{10} electron configuration, a total of 16 valence electrons for the metal atom and a formal bond order of one per each M–X bond.

For single-faced π donors (Fig. 3 (b)), the optimum bonding situation would require the two π-antibonding MOs (e′) to be empty, i.e. a d^6 metal atom. In this case the ligands provide a total of four π electrons to metal–ligand bonding, since the a_2' lone pair MO (**3**) is non bonding. Together with the three σ electron pairs, they account for 16 valence electrons and a formal M–X bond order of 1.66. It is worth stressing that the metal–ligand π bonding is coplanar to the MX_3 skeleton if the ligands are oriented perpendicular to that plane, which is approximately the situation experimentally found in all trisamido complexes.

In the presence of double-faced π donors (Fig. 3 (d)), both the e′ and e″ MOs are π-antibonding, and the adequate electron configuration is d^2, whereupon an average bond order of 2.33 results for each M–X bond. Counting the four π and three σ lone pairs donated by the ligands, a total of 16 valence electrons result. One may think that the π donation to the metal p_z orbital should also be considered, although it was found that for the highly electronegative oxo ligands such interaction is negligible [147]. In that case, the maximum M–X bond order for the low spin d^2 metal ions would be 2.67 and these compounds could be considered as 18-electron species. The latter approach was adopted by Schrock and coworkers [143], who pointed out that from the total of 20 valence electrons in $[Os(NR)_3]$, two are in the non bonding ligand orbital a_2' (**3**). The structurally characterized three-coordinated imido complexes of Re and Os (Table 3) can thus be considered electron precise with formal M–N bond orders between two and three.

For optimum bonding, complexes with π-acid ligands should all have the d orbitals occupied, since two of them are π-bonding (e″ set, Fig. 3 (e)), and the rest formally non bonding. Thus, a d^{10} configuration is prescribed, with formal M–L bond orders of 1.67 and a total of 16 valence electrons.

A look at the electron configuration of the complexes in the different families of compounds (Tables 1–5), indicates that the electron counting rules are more often violated than not. Perhaps one should not put much emphasis on electron counting rules for complexes with π donor ligands. Such rules work well for complexes with good σ donor and, eventually, π-acceptor properties for two reasons. First, the high energy of the metal centered σ* orbitals makes their occupation destabilizing, since it favors metal oxidation or ligand dissociation processes. Second, partial occupation of the low lying non bonding d orbitals may facilitate the reduction of the metal atom or the association of additional ligands. In the case of the π-loaded complexes, the highest d orbitals are much less destabilized because of their π* nature, thus decreasing the instability or lability associated with the occupation of such orbitals compared to the σ* orbitals (such as the e_g set in octahedral complexes). In addition, the lability associated with low-energy d orbitals is strongly reduced in most of the studied complexes by steric crowding. In the case of the bare nitrido and oxo complexes, it has been suggested that the interaction of these anions with the alkaline or alkaline earth cations contribute to the stabilisation of such electron configurations. Hopefully the synthesis and characterization of a larger number of members of these families will help clarify this point.

Let us recall that the nitrido ligands are more likely to stabilize low spin states than the oxo ones, a difference that is attributed to the stronger π donor character of the former. In this regard it is interesting to recall here the theoretical study of Kapp et al. [167] on the π-donor ability toward CH_2^+ of the elements of Groups 15, 16 and 17. These authors found that the π stabilization energy is largest for the Group 15 atoms and weakest for Group 17. On the other hand, the π stabilization energy increases down the group for elements of Groups 16 and 17, but decreases for those of Group 15.

6. Experimental structures

The general trends of the structural features of three-coordinated complexes are discussed in this section, separately considering the families of compounds with different types of ligands. The theoretical predictions on molecular structure discussed above will only be briefly commented here as confronted to the experimental data. Looking first at complexes with σ donors (Table 1), some regularities appear, even if these should be taken cautiously given the small amount of structural data available. Hence, a d^0 La(III) organometallic complex is pyramidal as predicted by calculations for other d^0 ions. The analogous d^3 derivative of Cr(III) is also pyramidal, in contradiction with the trigonal planar structure predicted for [$CrMe_3$]. Both trigonal planar and T structures have been so far reported for the d^5 Mn(II) complexes. The d^6 ions appear to present pyramidal structures in their low spin states, whereas a high spin Fe(II) compound is planar with a T shape, a difference that can be rationalized with the schematic Walsh diagram of Fig. 4. Finally, the low spin d^8 complexes present T structures, as predicted by theory.

The transition metal trisamido complexes (Table 2) are all planar trigonal, and the M–N distances are shorter than in analogous amino compounds [146]. The amido groups in such compounds are rotated relative to the MN_3 plane, in agreement with the stereoelectronic preference for a non coplanar structure compensated by the strong repulsion between the ligands' lone pairs (**3**) in a perpendicular conformation [146]. The M–N bond distance in trisamido complexes is seen to increase by 0.1 Å when going from a neutral complex to its monanion, i.e. in the series of compounds $[M\{N(SiMe_3)_2\}_3]$ and $[M\{N(SiMe_3)_2\}_3]^-$, where M = Mn, Fe or Co (Table 2). Remarkably, some rare earth trisamido complexes have also been characterized. Whereas the Eu and Yb complexes present a planar Y shape [38], the uranium one is trigonal pyramidal [37]. The latter structure has also been assigned to the Ce, Pr and Lu complexes in the gas phase, based on electron diffraction data [42,47].

The three-coordinated bisamido complexes are all planar but a marked distortion from the trigonal symmetry toward a T shape is often found. Notice that the d^2 complexes are trigonal whereas the d^5–d^7 derivatives appear in a T structure. The rotation angle of the amido groups relative to the coordination plane in the bis- and mono-amido complexes is significantly larger than in the trisamido analogues. This is accompanied by increased N–M–N angles (T-shaped molecules) in the former case. Notice that such an effect can be understood from our proposed orbital control of the rotation angle [146], since at larger N–M–N angles the repulsion between the amido lone pairs associated with the a_2' MO (**3**) is decreased. The three-coordinated complexes with only one amido ligand are all planar, but a distortion from the trigonal symmetry toward a Y structure is frequently observed. The rotation angle ϕ indicates a nearly-perpendicular orientation of the NR_2 groups, as in the case of the bisamido derivatives.

Transition metal complexes with potentially double-faced π donors of type XR (Table 3) are seen to be all practically planar. Remarkably, a couple of rare earth compounds with this type of ligand are also known: a trigonal planar Sm(III) complex [44] with thiolato ligands, and a pyramidal Ce(III) complex. In the three-coordinated imido complexes known so far, the double-faced π-donor character of the NR ligands is consistent with the linearity of the MNR bonds. Examples of the single-faced or double-faced π-donor nature of the imido ligands in penta- and six-coordinated complexes, depending on the linear or bent nature of the MNR group, have been discussed by Wigley [168]. All d^2 imido and alkoxo complexes with practically linear M–X–R groups have been shown to be diamagnetic, as would be expected from the qualitative MO scheme (Fig. 3 (d)). While the alkoxo ligands present varying degrees of bending (M–O–R = 138–180°), the thiolato ligands are strongly bent (M–S–R = 100–115°, Table 3) and should be considered as single-faced π donors. The thiolato complex of Sm(III) mentioned above also presents a strongly bent M–S–R angle (83°) [44]. No apparent correlation exists between the degree of bending of the M–X–R backbone and the geometry of the MX_3 coordination sphere (D_{3h}, Y or T).

In the families of compounds with monoatomic double-faced π donors (Tables 4 and 5), the coordination geometry is in general practically planar ($\Sigma > 350°$) with

the exception of a few halides whose electron diffraction spectra in the gas phase are consistent with strongly pyramidalized structures. In contrast to the trihalides, which present mostly trigonal symmetry (either planar or slightly pyramidalized), the oxoanions, nitrides and carbides are frequently distorted to T or Y shapes in the solid state. At first sight there is no simple correlation between the electron configuration of the transition metal and the structural distortion observed. Comparison of the metal–ligand bond distances of these compounds with those discussed previously is illustrative of the different degree of π bonding depending on the π donor characteristics of the ligands. For example, the Co–O distance in the $[CoO_3]^{4-}$ anion is identical to that in an alkoxo complex, since both the oxo and alkoxo groups are double-faced π donors. The M–N distances (M = V, Cr, Mn or Fe) in the $[MN_3]^{6-}$ ions with double-faced π donor ligands are at least 0.1 Å shorter than those for the corresponding amido complexes with single-faced π donors, which are in turn shorter than in analogous amino complexes. Longer M–N distances are observed in the M_2N compounds, because of the bridging nature of the nitrido ligands.

Trihalides of metals belonging to Groups 3–7 have been characterized in the gas phase mostly as trigonal molecules (Table 5). Although effective bond angles of about 116° are encountered in several cases, these can be interpreted with a planar equilibrium structure and a low frequency out-of-plane vibration [169]. Nevertheless, MnF_3 presents a strongly distorted T structure that can be rationalized as due to a Jahn–Teller effect [166] consistent with a high spin configuration $(e'')^2(a')^1(e')^1$ (Fig. 3 (d)). The only other transition metal trihalide that appears to be strongly distorted toward a T structure in the gas phase is WCl_3. As a note of caution, the reader is referred to a discussion on the reliability of the geometry assignments based on electron diffraction data, presented by Hargittai [169].

As for three-coordinated complexes with π-acceptor ligands, the only X-ray characterized structure is that of $[Fe\{(N_2)Mo(tripod)_3\}_3]$ discussed in the Section 1. Triscarbonyl complexes, $[M(CO)_3]$ have been identified in noble gas matrices [3] for a variety of non-d^{10} metals (M = V, Ta, Cr, Fe, Mn, Re, Co, Rh and Ir) and trigonal planar or pyramidal structures have been proposed based on the IR and Raman spectra.

7. Coordinative unsaturation

According to the above discussion on the extent of π bonding in three-coordinated complexes, it is clear that most of these compounds can be considered as coordinatively unsaturated. Besides, the presence of unpaired electrons must determine their redox behavior. In this section, some relevant data that can be associated with these two features will be presented.

The three-coordinated complexes show a clear tendency to increase their coordination number, thus explaining the small frequency of coordination number three among the structural data. Perhaps a combination of strong metal–ligand π bonding and steric hindrance are needed to make some complexes inert enough

toward the coordination of additional ligands. Among the compounds with σ donor ligands, some evidence of such a tendency can be found. The open T structure of the $[Ni(mes)_3]^-$ anion has been shown to be associated with agostic interactions with methyl groups of one of the mesityl ligands, thus completing a pseudotetragonal coordination sphere [32]. In a similar way, one phenyl group in $[Rh(PPh_3)_3]^+$ presents a close approach to the Rh atom (Rh–C = 2.50 and 2.61 Å) in the open position of the T-shaped cation [34,35]. At the orbital level, the T-shaped molecules should be expected to be better acceptors through an a_1 orbital (the leftmost e′ orbital in Fig. 3) as found in the Walsh diagram proposed by Hughbanks [144]. It is noteworthy that complexes with σ donor ligands present short M···H distances that can be associated with agostic interactions when the structure is strongly pyramidalized (2.2–2.8 for M = Rh, Ir, Y or La). In contrast, M···H distances longer than 2.9 Å are found for the weakly pyramidalized Cr compound or for other planar organometallic complexes (Table 1).

Among the complexes with π donor ligands, less evidence for weak association of extra ligand is found. A clear case is that of the diphenylthiphosphinimido titanium compound (Table 3), which can in fact be described as a distorted octahedron, with the three short bonds indicated, complemented with three bonds at longer distance (2.2–2.4 Å) to pyridine molecules [71]. The two other complexes reported in Table 3 to have a T structure also show some extra interactions, if different in nature. The chromiun alkoxide complex presents a short contact (2.83 Å) between the Cr atom and a carbon atom of a ^{t}Bu group at the open side of the T. In contrast, the alkoxo cobalt compound shows a relatively short Co···H contact (2.22 Å) but above the coordination plane, practically in an axial position.

An indication of the coordinative unsaturation of tris(amido) complexes comes from the presence of tris(amido)metal fragments in four-coordinated complexes. In this family we can include $[V(NPh_2)_4]^-$ [170,171], $[V(NPhSiMe_3)_3(thf)]$ [172], and $[V(NPh_2)_3(thf)]$ [173], which can be considered as resulting from ligand association to the putative $[V(NR_2)_3]$ complexes, or those with general formula $[Ti(NR_2)_3X]$, where X = F, Cl, Br, Me or η^1-Cp [174–182]. Also, tetrakis(amido) complexes $[Ti(NR_2)_4]$ have been characterized (M = Zr, Hf, V, Nb, Ta and Mo; R = Me, Et, Ph) with electron configurations from d^0 to d^2. The absence of the bis(trimethylsilyl)amido ligand in this family [171,183–189] is in keeping with the usual attribution of steric hindrance as a stabilizing factor in the isolated trisamido complexes. In some cases, the four-coordinated complexes have been obtained by reacting a three-coordinated precursor with an additional ligand. Such is the case for the reaction between a tris(alkoxo) Ta(III) complex with olefins [190], or even with benzene or pyridine, which coordinate in an η^2 fashion [191]. Also, $[W(O^tBu)_2(N^tBu_2)]$ has been shown to coordinate ethylene or 2-butyne [72]. However, one must be aware that coordinative unsaturation and reactivity are not synonimous, and even if the tris(amido) [192] or organometallic Cr(III) complexes react with NO to yield diamagnetic four-coordinated species, the latter does not react with pyridine or CO [7]. A molecular orbital analysis of the interaction of a three-coordinated complex with a ligand has been reported by Wolczanski and coworkers [193].

Very often when a four-coordinated species results from reaction of a substrate with a three-coordinated one, the coordination of an additional ligand goes together with a redox process that takes the metal electron configuration to d^0 or d^1, eventually resulting in the cleavage of the incoming ligand. A nice example is provided by the variety of reactions of a Mo trisamido complex developed by Cummins and coworkers [194]. Ti(III) alkoxides react with iodine or CX_4 to give the Ti(IV) four-coordinated complexes of the type $[TiX(OR)_3]$ [195]. Similarly, V(III) complexes react with elemental sulfur or selenium to give the corresponding V(V) sulfido- and selenido-species. Reaction of $[Ta(OR)_3]$ with CO results in the acetylide-bridged binuclear complex $[(RO)_3Ta{=}C{=}C{=}Ta(OR)_3]$ in which the metal atoms have the formal oxidation state Ta(V). Splitting of CO is effected by a tris(alkoxo) Ta(III) complex, resulting in a four-coordinated carbido species [196]. Similarly, tris(amido) Mo(III) complexes form nitrido [56] or phosphido [54] four-coordinated Mo(V) species upon reaction with dinitrogen or P_4. The tendency of early transition metals to achieve the d^0 configuration in three-coordinated complexes is well illustrated by the reactions of the trisimido Re(V) complex with electrophiles such as H^+ or Hg^{2+} to afford $[HRe(NAr_2)_3]$ and $[(\mu\text{-}Hg)Re_2(NAr_2)_6]$, respectively [73,74].

The proposed isolobal analogy [7] between d^3 trisamido complexes and the N or P atoms is useful to rationalize the reactivity of such compounds. Hence, $[Cr(NR_2)_3]$ reacts with O_2 producing four-coordinated $Cr(NR_2)_2O_2$ species [197]. Similarly, nitrogen abstraction from $[NMo(O^tBu)_3]$ by a trisamido molybdenum complex results in dimerization of the $Mo(O^tBu)_3$ fragment, forming $[Mo_2(O^tBu)_6]$ with a triple Mo–Mo bond [198]. Notice that the $Mo(NR_2)_3$ groups also appear as dimers in the triply bonded $[Mo_2(NMe_2)_6]$ complexes [199].

The most interesting evidence of the tendency of non-d^{10} ML_3 groups to increase their coordination number corresponds to double-faced π donors. In contrast to the handful of structurally characterized three-coordinated complexes in those families (Table 3), more than 100 structures of four-coordinated complexes of transition metals belonging to Groups 4–9 present such groups as $M(OR)_3$, $M(SR)_3$, $M(NR)_3$, even when R is a sterically crowded group, such as 2,4,6-$^tBu_3Ph$, as indicated by a structural database search [12] in which compounds with multiple metal–metal bonds of stoichiometry M_2L_6 have been disregarded.

Trihalides of metals belonging to Groups 4–7 have been also characterized in the gas phase as trigonal molecules (Table 5), but present solid state structures based in MX_6 octahedra [200], including the one-dimensional ZrI_3 structure with face-sharing octahedra, the two-dimensional edge-sharing BiI_3 or YCl_3 structures, and the three-dimensional ReO_3-type structure with vertex-sharing octahedra. At low temperature, $FeCl_3$ consists entirely of dimers, and $ReBr_3$ appears in the gas phase with the same trimeric structure it presents in the solid state [169]. A dimeric structure is also found in the three-coordinated Yb(II) alkoxo-bridged complexes with either alkoxo [201] or amido [202] terminal ligands. Also, ScF_3 that exists in the gas phase as trigonal planar molecules, appears in the solid state with octahedral coordination in a ReO_3 structure [203].

Acknowledgements

The author is grateful for financial support provided by DGES through project PB95-0848-C02-01, and by CIRIT grant number 1997SGR-072.

Appendix A

Structural searches were carried out on the Cambridge (CSD) [12] and Karlsruhe (ICSD) databases, versions 5.16 and 98/1, respectively. For the searches of three-coordinated complexes in the CSD, molecules with groups π-bonded to a transition metal atoms were excluded, and only transition metal atoms of Groups 3–9 were retrieved.

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