DALTON

Pyramidality effect on metal–metal single bonds

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A structural database study has been made of the transition-metal compounds $M_2X_8L_n$ with metal–metal single bonds. The existence of a pyramidality effect in d^7–d^7 bonds is supported by qualitative extended-Hückel molecular orbital calculations and experimental data for binuclear rhodium compounds. The results for several families of binuclear complexes of Co^{II}, Ru^{I}, Os^{I} and Pt^{III} show that the metal–metal distance decreases with increasing pyramidality and with increasing torsion angles. The importance of the central metal atom and of the presence of axial ligands is also discussed.

A great research effort has been dedicated in the last decades to the study of metal–metal bonding in M_2X_{2n} complexes. The interaction between the metal atoms in such complexes can be described by the σ, π and δ contributions of the d orbitals in the interacting MX_n (*e.g.* $n = 4$) fragments,[1] the occupation of which determines the bond order and, consequently, the M−M bond length. However, other factors can affect the metal–metal bond length, such as the pyramidality α (the average of all M−M−X angles) and the internal rotation τ (average of the X−M−M−X torsion angles).[2–5] For instance, the wide range of values of α found for the quadruple-bonded Cr−Cr compounds accounts for the large dispersion of Cr−Cr distances, which span the range between 1.8 and 2.6 Å.[6] In these compounds the relationship between the M−M bond strength and the extent of pyramidalization of the metal atoms can be associated with changes in the hybridization of the σ and π orbitals, whereas the δ component is insensitive to pyramidalization.[2,3] An analogous behaviour could also be found for the M···M contacts in weakly interacting dimers and chains of d^8-MX_4 complexes.[7]

In a study devoted to the importance of the σ component for the pyramidality effect,[4] we analysed the metal–metal single bonds in rhodium(II) complexes.[6,8,9] It was found that the Rh−Rh distance *d* decreases with increasing pyramidality (α), although it is useful to obtain a least-squares fitting of *d* as a function of cos α. The resulting fitting parameters are best suited for comparison of the data for different families of compounds. In particular, if we represent that correlation by equation (1), *b* is the intrinsic bond distance corresponding to

$$d = b + 2c{\cdot}\cos\alpha \qquad (1)$$

planar MX_n fragments (*i.e.* $\alpha = 90°$), and *c* gives a measure of the susceptibility to pyramidalization of the metal–metal bond in a family of compounds. For a small range of values of α it is practically equivalent to express *d* as a function of α or as a function of cos α. Hence, we will use in this paper α for graphical display, but cos α for the least-squares fitting of the experimental data.

The square planar $Rh^{II}X_4$ fragment has an unpaired electron in its d_{z^2} orbital, and one can simply describe the Rh−Rh bonding in Rh_2X_8 molecules as resulting from the interaction between the d_{z^2} orbitals of the two RhX_4 fragments. However, the rhodium p_z orbital has the right symmetry to mix with the d_{z^2} orbitals, and an appropriate orbital diagram to describe such interactions is that presented in Fig. 1. The interaction between the d_{z^2} orbitals, labelled 1 in Fig. 1, corresponds to a canonical single bond. Besides, there are the two donor–acceptor interactions, labelled 2 in Fig. 1, between the d_{z^2} orbital of one metal atom and p_z of the other. Since the p_z orbital is strongly hybridized through mixing with the s orbital upon departure of the MX_4 group from planarity, interaction 2 is highly sensitive to the degree of pyramidalization. In contrast, changes in hybridization of the d_{z^2} orbitals are minute, and interaction 1 is practically insensitive to changes in α.[4,7] A similar model, obtained by just adding one electron per MX_4 fragment, has been successfully used to explain the weak M···M interactions in dimers of the d^8-MX_4 complexes.[7,10] Since only the structural data for rhodium(II) compounds were previously analysed to validate the theoretical model,[4] we present here a Cambridge Structural Database study[11] intended to extend the applicability of such a model to other single bonds between d^7 transition-metal ions.

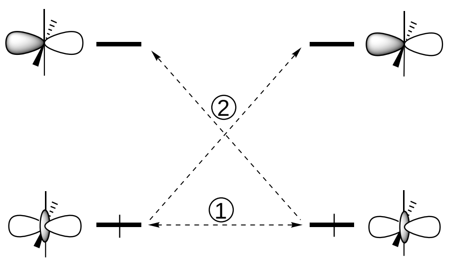
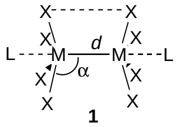


Fig. 1 Schematic diagram for the orbital interaction between two d^7-MX_4 fragments. Interaction of type 1 corresponds to the canonical two centre-two electron bond and is practically insensitive to pyramidality; interactions of type 2 are one-electron donor–acceptor interactions strongly sensitive to pyramidality



1

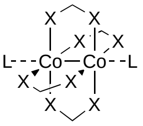
Structural Analysis

A structural database search was carried out for compounds with a metal–metal bonded M_2X_8 core **1** of d^7 ions of Periodic Groups 8 to 11. Those compounds having the same metal atoms and analogous equatorial ligands X were grouped in families and the metal–metal distance, *d*, the pyramidality α and the internal rotation angle τ were computed for each crystallographically independent molecule. We have found

Table 1 Structural data for cobalt(II) complexes with carboxylate or analogous bridging ligands

Compound*	Co–Co/Å	α/°	τ/°	refcode	Ref.
$[Co_2(Ph_2N_3)_4]$	2.264	87.8	17.0	JEDDAU	25
$[Co_2\{PhC(NPh)_2\}_4]$	2.301	88.7	18.4	VOZTEJ	26
$[Co_2(Bu^tCO_2)_4(mpy)_2]$	2.683	83.1	0.0	DOCWOH	27
	2.694	83.1	0.0		
$[Co_2(PhCO_2)_4(quin)_2]$	2.832	81.6	0.0	BZQUCO10	28,29
$[Co_2(PhCO_2)_4(mquin)_2]$	2.863	81.0	0.0	BZMQCO	30

* mpy = 4-Methylpyridine, quin = quinoline, mquin = 4-methylquinoline.



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structurally characterized examples of compounds with the basic framework **1** for $\mathrm{Fe^{I}}$, $\mathrm{Co^{II}}$, $\mathrm{Ru^{I}}$, $\mathrm{Rh^{II}}$, $\mathrm{Os^{I}}$, $\mathrm{Ir^{II}}$ and $\mathrm{Pt^{III}}$. Attempts to synthesize nickel(III) and palladium(III) dimers have been described by several authors, but mixed-valence (II, III) compounds were obtained instead.[12–15] Of these, only for cobalt is there an extensive Werner chemistry,[16] but recently also structural determinations of mononuclear compounds of $\mathrm{Rh^{II}}$,[17–19] $\mathrm{Ir^{II}}$ [20,21] and $\mathrm{Pt^{III}}$ [22–24] have been reported.

Rhodium(II) compounds

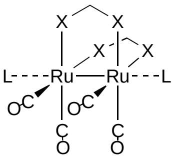
In our previous work[4] we analysed the pyramidality effect for two families of rhodium(II) complexes. The largest family, that of the tetrakis(carboxylato) and analogous complexes (101 crystallographically independent molecules), shows a strong susceptibility of the Rh–Rh bond length to the pyramidality. A similar trend was observed for the much smaller family of compounds with two carboxylato and two orthometallated arylphosphines as bridging ligands (nine data sets).

Cobalt(II) compounds

Let us now examine the corresponding family of tetrakis(bridge) complexes of $\mathrm{Co^{II}}$, in which carboxylato or analogous bidentate ligands act as bridges between two metal atoms, with possibly one or two extra ligands co-ordinated to Co in axial positions (**2**). In Table 1 we show the Co–Co distance and the pyramidality (α, defined in **1**) for these species. The values of α for these compounds vary within the range $81 < \alpha < 88°$, accompanied by a large variation of the metal–metal bond lengths ($2.26 < d < 2.86$ Å). Even if the number of structures in the family of tetrabridged cobalt(II) complexes is small, a good correlation between the Co–Co bond lengths and the pyramidality α is found. A least-squares fitting of the six structural data sets yields equation (2) (regression coefficient $r = 0.989$; α in degrees, other parameters in Å).

$$d(\mathrm{Co{-}Co}) = 2.141 + 4.605 \cos \alpha \qquad (2)$$

The weakening of the Co–Co bond at small values of α is nicely illustrated by the magnetic properties of these compounds. Density functional Xα-SW calculations on $[Co_2(H_2N_3)_4]$, reported by Cotton and Feng,[31] showed that the short Co–Co distance of 2.264 Å in the triazido complex is associated with a $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*4}$ electronic configuration and a strong σ bond between the cobalt atoms. However, the full pairing of all electrons in this compound is in contrast to the magnetic properties of a bis(quinoline) carboxylate complex.[28,29] In this case, the long M–M distance of 2.832 Å is in keeping with the weak antiferromagnetic coupling ($J \approx -19$ cm^{-1}), *i.e.* a low-lying $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*3}\sigma^{*1}$ configuration. Such a difference is consisitent with the expected hybridization of the σ orbitals away from the metal–metal region for small values of α.[4]



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In the cobalt(II) complexes one can observe (Table 1) that the longest metal–metal distances correspond to complexes with axial ligands, as reported for the Cr–Cr quadruple bonds in chromium(II) compounds[2,3] and for the Ni···Ni contacts in nickel(II) dimers.[7] The influence of the axial ligands on the $\mathrm{Rh^{II}}$–$\mathrm{Rh^{II}}$ single-bond distances[4] was not as clear as it is in the cobalt(II) analogues. The current interpretation given to this fact is that the presence of axial ligands induces six-co-ordination, which requires a smaller degree of pyramidalization ($\alpha \approx 90°$), indirectly favouring longer metal–metal distances. Another interesting feature of the structural data is that the susceptibility to pyramidalization is much larger for cobalt(II) [$c = 2.302$, equation (1)] than for rhodium(II) compounds with analogous ligands ($c = 1.467$).[4,7] A similar observation was made for other families of compounds with metal–metal bonds of different bond orders, *i.e.* the susceptibility to pyramidalization is much larger for the compounds of first-row transition metals than for their second- and third-row analogues.

It will be shown that, for some families, the torsion angle τ is correlated with the metal–metal distance. For this group of cobalt(II) complexes, however, inclusion of the torsion angle in the least-squares fitting does not improve the correlation [equation (3), $r = 0.989$] and the resulting coefficients are quite

$$d(\mathrm{Co{-}Co}) = 2.254 + 4.849 \cos \alpha - 0.147 \cos 2\tau \qquad (3)$$

similar to those in equation (2). Therefore, for the cobalt(II) compounds it suffices to consider the effect of the pyramidality to account for the variations in the metal–metal bond distances.

Ruthenium(I) compounds

A family of metal–metal bonded ruthenium(I) complexes has been charcterized,[32] mostly in the last decade, with general formula $[Ru_2(bridge)_2(CO)_4L_n]$ **3** (where bridge represents a carboxylato or analogous bridging ligand), for which we have retrieved 25 structural data sets (Table 2). Notice that all these compounds have two ligands in axial positions. At a first glance those complexes having phosphines as axial ligands present longer Ru–Ru distances. For these 25 structural data sets no good correlation [equation (4), regression coefficient $r = 0.686$]

$$d(\mathrm{Ru{-}Ru}) = 2.642 + 1.673 \cos \alpha \qquad (4)$$

is found between the Ru–Ru distances and the pyramidality. A possible explanation for the anomalous behaviour of this family of compounds is that they present a wide range of

Table 2 Structural data for bis(bridge)tetra(carbonyl) complexes of Ru^I and Os^I

Compound*	M−M/Å	α/°	τ/°	refcode	Ref.
$[Ru_2(Bu^iCO_2)_2(CO)_4(Bu^iCO_2H)_2]$	2.630	89.4	14.4	CUFMOF10	33, 34
$[Ru_2(PhCO_2)_2(CO)_4(PhCO_2H)_2]$	2.635	89.9	10.0	CUFMIZ10	34
$[\{Ru_2(PhCO_2)_2(CO)_4\}_n]$	2.639	89.9	4.0	FAFPUX	35
$[Ru_2(4\text{-}FC_6H_4CO_2)_2(CO)_5(H_2O)]$	2.649	88.5	17.3	DAWYEF10	34
$[\{Ru_2(tart)(CO)_4(MeCN)_2\}_3]$	2.650	88.5	20.4	SEVFEE	36
	2.654	88.7	19.2		
	2.657	88.2	20.4		
$[\{Ru_2(C_3H_5CO_2)_2(CO)_4(NMe_3)\}_2]$	2.655	89.3	15.2	WASJIJ	37
$[Ru_2\{(4\text{-}MeC_6H_4)_2N_3\}_2(CO)_4(MeC_6H_4NH_2)_2]$	2.664	87.6	23.7	JIBYOI	38
$[Ru_2(hp)_2(CO)_4(Hhp)_2]$	2.671	88.3	23.0	VORLET	39
$[Ru_2\{(4\text{-}MeC_6H_4)_2N_3\}_2(CO)_6]$	2.675	86.4	28.5	GEVYAH	40
$[\{Ru_2(MeCO_2)_2(CO)_4(PBu_3)\}_2]$	2.682	89.5	6.4	ACBRUB10	41
$[Ru_2(MeCO_2)_2(CO)_4\{(MeS)_2CH_2\}]$	2.682	89.4	4.4	GECLEF10	42
$[Ru_2(PhCONH)_2(CO)_4(MeCN)_2]$	2.688	88.9	9.4	SEHSIH	43
$[Ru_2(MeCO_2)_2(CO)_6]$	2.688	88.4	10.0	FAFREJ	35
	2.690	88.2	10.7		
$[Ru_2(PhCO_2)_2(CO)_6]$	2.704	88.8	0.0	FAFRAF	35
$[Ru_2\{MeC(NPh)_2\}_2(CO)_6]$	2.713	86.9	22.5	WEWYOM	44
$[Ru_2(CF_3CO_2)_2(CO)_4(PPh_3)_2]$	2.728	87.7	17.6	WATFIG	45
$[Ru_2(PrCO_2)_2(CO)_4(PBu^t{}_3)_2]$	2.728	86.0	23.9	BURPRU	46
$[\{Ru_2[C_3H_6(CO_2)_2](CO)_4(PBu_3)_2\}_2]$	2.734	88.7	4.5	ACBRUA10	41
$[Ru_2(MeCO_2)_2(CO)_4(PBu^t{}_2H)_2]$	2.735	88.5	2.1	SEDKOB	47
$[Ru_2(MeCO_2)_2(CO)_4(PPh_3)_2]$	2.736	88.3	2.1	WATFAY	45
$[Ru_2(PhCO_2)_2(CO)_4(PPh_3)_2]$	2.741	88.7	0.2	WATFEC	45
$[Ru_2(hp)_2(CO)_4(PPh_3)_2]$	2.885	84.5	21.0	SAZRIU	48
$[Os_2(MeCO_2)_2(CO)_5Cl]^-$	2.713	88.8	12.3	FOVHAZ	49
$[Os_2(MeCO_2)_2(CO)_6]$	2.729	88.5	4.4	ACHCOS	50
	2.732	88.4	5.8		
$[Os_2(MeCO_2)_2(CO)_4(dppm)_2]$	2.740	89.0	0.6	SEDFOW	51

* tart = Tartrate, dppm = $Ph_2PCH_2PPh_2$.

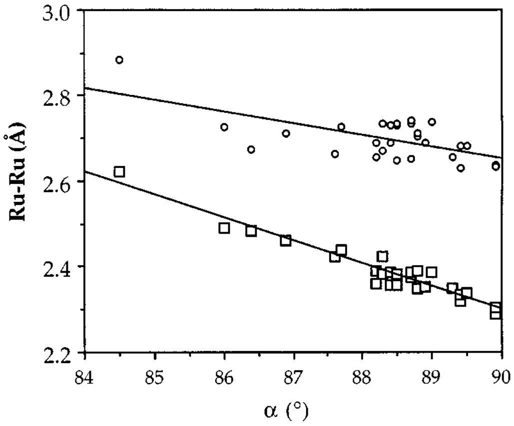


Fig. 2 Experimental (circles) and corrected Ru−Ru distances [$d_c = d_{exp} - e{\cdot}\cos 2\tau$, squares, see equations (6) and (7)] as a function of the pyramidality α for compounds of Ru^I (data from Table 2)

torsion angles ($0 \leqslant \tau < 30°$). If we restrict our least-squares fitting to those compounds having similar torsion angles (*i.e.* $\tau < 8°$), equation (5) is obtained with a much better correlation

$$d(\text{Ru−Ru}) = 2.641 + 3.652 \cos \alpha \qquad (5)$$

coefficient ($r = 0.953$ for eight data sets) but practically the same value for the intrinsic bond distance.

To account for the dependence of d on both α and τ we have carried out a multilinear regression analysis, fitting the Ru−Ru distances by expression (6). In this equation we use cos 2τ since

$$d = k + 2c{\cdot}\cos \alpha + e{\cdot}\cos 2\tau \qquad (6)$$

τ is expected to vary between 0 and 45°.[3] The result, represented by equation (7), shows a fair correlation ($r = 0.945$). It can be

$$d(\text{Ru−Ru}) = 2.296 + 3.148 \cos \alpha + 0.353 \cos 2\tau \qquad (7)$$

seen that the coefficient of the internal rotation term is important, inducing changes in the metal–metal distances as large as ≈0.2 Å for the largest torsion angle (≈30°) experimentally found (Table 2). Fig. 2 provides a visual representation of that correlation by plotting the corrected Ru−Ru distance ($d_c = d_{exp} - e{\cdot}\cos 2\tau$) as a function of the pyramidality.

When the metal–metal bond distance is given by equation (6) the intrinsic bond distance can be defined as that corresponding to a standard bond angle of 90° and an eclipsed conformation ($\tau = 0°$), *i.e.* $b = k + e$. For the case of quadruple metal–metal bonds, the effect of the torsion angle could be explained by the gradual annihilation of the δ bond on going from $\tau = 0$ to 45°. Since shorter bonds must be expected for the eclipsed conformation ($\tau = 0°$) in which a δ bond exists, negative values result for the susceptibility to internal rotation measured by the parameter e.[3] In contrast, for triple bonds, the four-electron repulsion between d_{xy} orbitals favours the staggered conformations, hence positive e values are obtained. The results for compounds with single metal–metal bonds should be explained in the same way as for triple bonds. Notice, however, that the presence of bridging ligands restricts the range of attainable rotation angles τ (*i.e.* <30°). Indeed the e parameter is also positive in equation (7), only it is an order of magnitude larger than for complexes with triple bonds ($e = 0.038$ and 0.018 Å for triple-bonded complexes of Re and Os, respectively). Although there are not enough data to draw clear-cut conclusions, the present results suggest that the susceptibility of M−M single bonds to internal rotation is greater than that of M−M triple bonds, and that the effect of internal rotation is more important for second- than for first-row transition metals.

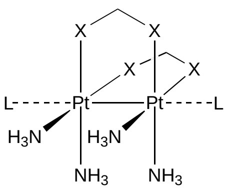
Osmium(I) complexes

A few osmium(I) compounds with structure **3** have been found in our literature search, and relevant structural data are presented in Table 2. Although the amount of available data is not

Table 3 Structural data for tetra(phosphato)- and bis(bridge)tetra(ammine)-diplatinum(III) complexes

Compound	Pt–Pt/Å	α/°	τ/°	refcode	Ref.
HH-$[Pt_2(hp)_2(NH_3)_4(H_2O)(NO_3)]^{3+}$	2.540	91.4	23.1	BAVBAB10	67, 68
HT-$[Pt_2(hp)_2(NH_3)_4(NO_3)_2]^{2+}$	2.547	91.2	26.4	BEXWUW10	68, 69
HT-$[Pt_2(mura)_2(NH_3)_4(H_2O)(NO_3)]^{3+}$	2.556	91.4	29.4	DUXBED	70
HT-$[Pt_2(mura)_2(NH_3)_4(H_2O)(NO_3)]^{3+}$	2.560	91.2	28.7	DUXBIH	70
HT-$[Pt_2(hp)_2(NH_3)_4Cl_2]^{2+}$	2.568	90.9	27.5	CEGBIZ	71
HH-$[Pt_2(mura)_2(NH_3)_4Cl_2]^{2+}$	2.572	90.9	23.5	DOKJIW	62
HT-$[Pt_2(mura)_2(NH_3)_4(H_2O)(NO_2)]^{3+}$	2.574	91.0	29.0	CASDAB	72, 73
HT-$[Pt_2(hp)_2(NH_3)_4(NO_2)_2]^{2+}$	2.576	91.0	27.1	BEXXAD10	69,71
HT-$[Pt_2(hp)_2(NH_3)_4Br_2]^{2+}$	2.582	90.8	28.1	CEGBOF	71
HT-$[Pt_2(mcyt)_2(NH_3)_4(NO_2)_2]^{2+}$	2.584	90.6	25.2	MCTPTB	74
HH-$[Pt_2(mura)_2(NH_3)_4(NO_2)]^{3+\,a}$	2.606	91.9	3.2	DIRGEQ	73
HH-$[Pt_2(mura)_3(NH_3)_4]^{3+\,b}$	2.684	92.4	6.4	DIPTOL	75
HH-$[Pt_2(Bu^tCONH)_2(NH_3)_4(CH_2COMe)(NO_3)]^{2+\,b}$	2.689				76
$[Pt_2(HPO_4)_3(H_2PO_4)(py)_2]^-$	2.494	89.7	13.3	CAJFAU	77
$[Pt_2(HPO_4)_4(dmpy)_2]^{2-\,c}$	2.494	90.4	0.0	CAYKOC	78
$[Pt_2(HPO_4)_4(tht)_2]^{2-\,d}$	2.525	90.1	0.0	DOXHAZ	79
$[Pt_2(PO_4)_4(gua)_2]^{10-\,e}$	2.534	90.3	0.0	FADKUQ	80
$[Pt_2(HPO_4)_2(H_2PO_4)_2Cl_2]^{2-}$	2.529	89.9	0.0	FINHIT	81
$[Pt_2(HPO_4)_4(H_2O)_2]^{2-}$	2.485	90.7	0.0		81, 82
	2.487	90.9	0.0		

Not included in the regression analysis: [a] only this compound is eclipsed. [b] One mura ligand is metallated in axial position, and thus the complex is possibly mixed valent. [c] dmpy = 3,4-Dimethylpyridine. [d] tht = Tetrahydrothiophene. [e] gua = Guaninate(2−).



4

amenable to a statistical analysis, a trend can be appreciated: the values of α vary little, and the Os–Os distance decreases with increasing internal rotation angle τ.

Platinum(III) complexes

The last families of compounds analysed in this work are those of the platinum(III) complexes.[52–54] The bis(bridged) molecules of type **4** are characteristic of this metal ion (12 structural data sets). Since the bridging ligands are asymmetric, they can be co-ordinated in either a head-to-head (*HH*) or a head-to-tail (*HT*) fashion. The monodentate ligands that complete the co-ordination spheres of the metal atoms are typically the methyl group[55–58] or different amines.[59] For the case of methyl complexes, $[Pt_2(bridge)_2Me_4L_n]$, 12 structures can be found. However, the ranges of distances and pyramidalities experimentally found are very small (variation of 0.03 Å in Pt–Pt distances) and no statistical analysis could be carried out for these compounds.

For the family of $[Pt_2(bridge)_2(amine)_4L_n]$ complexes the most common amine is ammonia. Several complexes having ethane-1,2-diamine[60,61] or other ligands (substituted amines, chloride)[62,63] have been synthesized, but these are not included in our analysis because they present quite different ligand–ligand repulsions. The pyrrolidone anion complexes[64–66] have been disregarded because they deviate from the general trend, probably because they form six-, rather than five-membered aromatic rings. A similar deviation was previously found for similar ligands in the $Pt^{II}\cdots Pt^{II}$ contacts.[7] The structural data for the rest of the ammonia derivatives with the bidentate bridging ligands pyridin-2-olate (hp^-), 1-methyluracilato ($mura^-$) or 1-methylcytosinato ($mcyt^-$) are shown in Table 3. Most of those complexes (10 data sets) have two axial ligands and similar torsion angles, between 23 and 29°. The least-squares fitting of the structural data for those compounds having similar torsion angles ($23.1 < \tau < 29.0°$) is given by equation (8) (regression

$$d(\mathrm{Pt{-}Pt}) = 2.622 + 3.070 \cos \alpha \qquad (8)$$

coefficient $r = 0.917$). The effect of the torsion angle in this case could not be evaluated due to the small variations found for τ.

Another group of platinum(III) complexes with a statistically significant number of members is formed with four bidentate bridging ligands,[52,53,83–85] including the phosphato complexes (Table 3). These complexes present four μ-PO_4-*O,O′* fragments as bridging bidentate ligands with different extents of protonation at the unco-ordinated oxygen atoms (*i.e.* PO_4^{3-}, HPO_4^{2-} or $H_2PO_4^-$). In this case, the correlation given by equation (9) is

$$d(\mathrm{Pt{-}Pt}) = 2.524 + 2.871 \cos \alpha \qquad (9)$$

obtained (regression coefficient $r = 0.954$ for five data sets). Two compounds have been excluded from our regression analysis because their parameters strongly deviate from the general trend [equation (9)]. One of them, $[Pt_2(HPO_4)_3(H_2PO_4)(py)_2]^-$ (py = pyridine) with a torsion angle $\tau \approx 13°$,[77] is the only one that does not present a perfectly eclipsed conformation within this family. The second compound excluded has a fully deprotonated phosphate bridge, with no apparent reason for its anomalous behaviour. There is also a handful of platinum(III) compounds with $H_2P_2O_5^{2-}$-*P,P′* (10 data sets)[83,84] and sulfate (five data sets)[81,86–91] but no clear correlation between bond distance and pyramidality is found for them. Only two platinum(III) complexes with bridging carboxylate ligands have been characterized[92,93] and no statistical analysis could therefore be carried out for this family of compounds. For these compounds, electronic structure calculations using the Xα-SW method are in agreement with the existence of single metal–metal bonds involving the d_{z^2} orbitals,[94] isoelectronic with analogous rhodium(II) dimers.[95]

Discussion

For a variety of binuclear compounds $M_2X_8L_n$ ($n = 0$–2) with a single metal–metal bond the M–M bond length can be approximately represented as a function of the pyramidality α (*i.e.* the average of the M–M–X bond angles) through equation (1), where *b* is the intrinsic metal–metal distance and *c* the susceptibility to pyramidalization of the M–M bond. Most of the exceptions can be accounted for by taking into account the internal rotation angle τ as in equation (6), where the parameter

Table 4 Intrinsic metal–metal bond distances (*b*), susceptibility to pyramidalization (*c*) and mean values for the X · · · X and M−X distances in several families of compounds with M−M bonding interactions; *N* is the number of independent data sets in each family. Standard deviations are given in parentheses

Metal	Ligands*	Bond order	*b*	*c*	*r*	*N*	X · · · X	M−X	*N*
$\mathrm{Co^{II}}$	4 Bridges	1	2.141	2.302	0.989	6	2.23(4)	1.99(5)	6
$\mathrm{Rh^{II}}$	4 Bridges	1	2.299	1.467	0.840	101	2.26(2)	2.04(1)	101
$\mathrm{Rh^{II}}$	2 Bridges, 2 metallated phosphines	1	2.463	1.625	0.933	9	2.49(1)	2.14(1)	9
$\mathrm{Ru^{I}}$†	2 Bridges, 4 CO	1	2.649	1.574	0.945	25	2.61(2)	1.98(1)	25
$\mathrm{Pt^{III}}$	2 Bridges, 4 $\mathrm{NH_3}$	1	2.622	1.535	0.917	10	2.81(3)	2.03(2)	10
$\mathrm{Pt^{III}}$	4 Phosphate	1	2.524	1.435	0.954	5	2.53(2)	2.01(1)	7
$\mathrm{Cr^{II}}$	4 Bridges	4	2.241	1.870	0.996	52	2.24(3)	2.02(2)	43
$\mathrm{Mo^{II}}$	4 Bridges	4	2.158	0.887	0.845	62	2.24(2)	2.12(1)	64
$\mathrm{Mo^{II}}$	2 Bridges, 2 phosphines, 2 $\mathrm{X^-}$	4	2.131	0.189	0.945	7	2.83(17)	2.24(5)	9
$\mathrm{Mo^{II}}$	2 Diphosphines, 4 $\mathrm{X^-}$	4	2.085	−0.290	0.892	16			
$\mathrm{W^{II}}$	4 Bridges	4	2.222	0.936	0.878	21	2.27(3)	2.10(2)	21
$\mathrm{Re^{III}}$	4 Bridges	4	2.232	0.754	0.851	5	2.23(2)	2.02(1)	5
$\mathrm{Re^{III}}$	3 Bridges, 2 $\mathrm{X^-}$	4	2.336	1.649	0.985	3	2.52(4)	2.10(1)	3
$\mathrm{Re^{III}}$	2 Bridges, 4 $\mathrm{X^-}$	4	2.361	1.158	0.853	15	2.82(11)	2.18(6)	20
$\mathrm{Re^{II}}$	Diphosphines	3	2.394	0.507	0.850	14			
$\mathrm{Os^{III}}$	Several	3	2.297	0.254	0.924	19			
$\mathrm{Ni^{II}}$	4 Bridges	0	2.291	0.859	0.995	8	2.24(4)	1.99(5)	8
$\mathrm{Pd^{II}}$	4 Bridges	0	2.444	0.486	0.924	10	2.33(3)	2.03(2)	12

* Equatorial ligands: bridge = carboxylate or analogous ligands, $\mathrm{X^-}$ = halides, pseudo-halides or other monodentate ligands. † $b = e + k$ [from equation (6)].

e represents the susceptibility to internal rotation of the M−M bond. In summary, within a family of related complexes, the M−M bond distance is shorter for a larger extent of pyramidalization (*i.e.* larger α), and for rotation angles closer to 45° (*i.e.* the staggered conformation).

In most of the complexes studied in this paper the metal–metal bond is supported by bidentate bridging ligands. In these cases one can assume that the X · · · X bite (*i.e.* the distance between the donor atoms of the same bridging ligand) is roughly constant because of the rigidity of the ligand. If one assumes also that the $\mathrm{M_2X_2}$ chelate rings are approximately planar (*i.e.* $\tau \approx 0°$), a geometrical relationship is to be expected between *d* and α, as in equation (10). If the correlation found

$$d(\mathrm{M{-}M}) = (\mathrm{X \cdots X}) + 2(\mathrm{M{-}X}) \cos\alpha \qquad (10)$$

for the experimental data were only the result of such geometrical constraint, the following relationships should hold: $b \approx \mathrm{X \cdots X}$ and $c \approx \mathrm{M{-}X}$. In Table 4 we have collected the parameters *b* and *c* for the families of compounds with single metal–metal bonds studied in this paper, together with data for other families that present metal–metal interactions of different bond orders and similar ligands. Also given are the mean X · · · X and M−X distances for such complexes. For the different families studied in this paper the value of *b* is close to the average experimental bite (X · · · X distance), with differences of at most 0.2 Å. The intrinsic bond distance spans the range from 2.14 to 2.65 Å, similar to the range of bites ($2.23 \leqslant \mathrm{X \cdots X} \leqslant 2.81$ Å). Significant differences between *b* and X · · · X are found for those families with the largest bites. It must be stressed, however, that it is just in these families of compounds that the torsion angles tend to be larger. As an example, in the family of bridged platinum(III) complexes with ammonia ligands, which shows the largest deviation between *b* and X · · · X, the least-squares fitting was performed for only those structures having $\tau \approx 27°$, and the results are given in Table 4.

Even in comparison of the parameters *b* and X · · · X suggests that in the compounds under study the pyramidality effect is mostly a result of the geometrical constraint imposed by the ligands, the analysis of the susceptibility to pyramidalization rules this out, since the least-squares parameters *c* are in all cases quite different to the average M−X distances. This parameter is highly sensitive to the nature of the equatorial ligands, and varies strongly from one family to another.

To put the present results in a wider context, we compare them with those obtained previously for related complexes with multiple M−M bonds or with only weak M · · · M contacts. The following observations can be made.

(*a*) Those compounds having bridging ligands present shorter intrinsic M−M distances *b*. Those distances are significantly shorter than the sum of their atomic radii (2.51, 2.69, 2.65 and 2.75 Å for Co, Rh, Ru and Pt, respectively).

(*b*) The susceptibility to pyramidalization (*c*) is always more pronounced for the first than for the second- or third-row transition metals. In general, *c* values larger than 1.8 are obtained for the first-row metals, regardless of their metal–metal bond order. In contrast, values smaller than 1.6 are obtained for complexes of second- or third-row transition metals.

(*c*) The presence of axial ligands induces smaller values of α and shorter metal–metal distances. This effect is apparently more pronounced for binuclear complexes of the first-row transition metals Cr, Co and Ni, regardless of the metal–metal bond order.

(*d*) The discrepancies between the M−X and *c* values for each family of compounds (Table 4) indicate that the correlation between pyramidality and metal–metal distance cannot be ascribed only to the geometrical constraint imposed by bridging ligands. It is seen that the deviation from the purely geometrical effect is larger for the second- and third-row transition metals.

(*e*) The single M−M bond lengths are more sensitive to pyramidalization than are multiple bonds or metal–metal contacts. This can be clearly seen by comparing the data for complexes with carboxylato or analogous ligands (Table 4): the susceptibility to pyramidalization (*c*) is similar for $\mathrm{Cr^{II}}$–$\mathrm{Cr^{II}}$ quadruple bonds and $\mathrm{Ni^{II} \cdots Ni^{II}}$ contacts, but much smaller than for the $\mathrm{Co^{II}}$–$\mathrm{Co^{II}}$ single bonds. Similar trends are observed for 4d metals: complexes of $\mathrm{Mo^{II}}$ and $\mathrm{Pd^{II}}$ present similar susceptibilities, whereas the rhodium(II) dimers are far less susceptible.

(*f*) The susceptibility to internal rotation of single M−M bonds is greater than that of the M−M triple bonds. In both types of complexes the staggered conformation favours shorter M−M bonds. The opposite behaviour appears for the M−M quadruple bonds, due to the existence of a δ bond.

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