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Bonding and Structure in $L_4M_2(\mu\text{-}XR_n)_2$ Diamonds of Tetrahedral d^{10} Ions. Effect of Substituents on the M- -M Interaction

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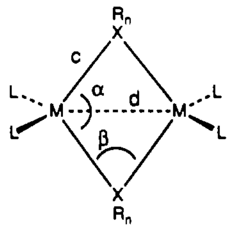
The large range of cross-ring M- -M distances found in the $L_4M_2(\mu\text{-}XR_n)_2$ diamonds of tetrahedrally coordinated d^{10} ions (M = Cu(I), Zn(II), Cd(II), Hg(II); n = 1–3) can be related to the number of electrons involved in the σ-framework bonding. Framework electron counts (FEC) of 4 or 6 give rise to cross-ring bonding, whereas an FEC of 8 results in approximately square, cyclobutane-like structures. The bonding in diamonds with an FEC of 4 or 6 is electron-deficient, with an increasing contribution of d^{10}–d^{10} interactions at short Cu- -Cu distances. The nature of the bridging XR_n ligand and its orientation are crucial in determining the number of framework electrons, hence the existence or not of M- -M or even X- -X bonding. The unsubstituted bridges (n = 0), on the other hand, present a soft potential for ring squeezing and an electron count-independent variability of the M- -M distances. The framework electron count (FEC) is based on orbital topology and can be applied to all diamonds $[(ML_n)_k(XR_m)_{4-k}]$, where M is a d^{10} metal ion, X is a main group element atom, and k = 0–4.

Among the variety of fascinating molecular structures displayed by the coordination compounds of Cu(I) and its isoelectronic d^{10} analogues, Ag(I), Zn(II), Cd(II), and Hg(II), the $L_4M_2(\mu\text{-}XR_n)_2$ diamonds (**1**, n = 0–3) represent a large family with varying degrees of metal–metal distances across the ring. For a given M–X bond distance, the extent of metal–metal interaction across the ring can be calibrated by either the M- -M distance or the XMX bond angle (α in **1**). We have chosen to use the distance criterion for reasons to be found in Appendix 1. Therefore, a through-ring distance is considered as bonding when it exceeds the sum of the convalent radii by not more than 10%. To illustrate the variability of the metal–metal interactions in the title compounds, it is enough to take a look at the representative Cu(I) compounds: The only structure with a trisubstituted bridge known to us is that of CuP_2 with a short bond distance of 2.48 Å.[1] In two structures with XR_2 bridges, one long (3.95 Å) and one short (2.66 Å) Cu- -Cu distances are found.[2,3] When the bridging atom bears one substituent (n = 1; X = S, O), the Cu- -Cu distances adopt values between 2.80 and 3.50 Å (Table IV). Finally, for monoatomic bridging ligands (n = 0; X = Cl, Br, I), the 30 structures detected with the help of the Cambridge Structural Database[4] have distances in the range 2.53 < d < 3.70 Å (Table V).



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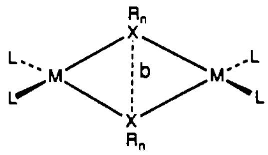

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The close contacts (or weak bonds) between d^{10} metal ions are now well understood in unsupported dimers and chains. In these cases, bonding results from the hybridization of the occupied d_{z^2} and the empty s and p_z orbitals of each metal atom.[5-10] However, as the structure of these diamonds resembles that of diborane, an alternative explanation of the bonding may involve three center-two electron bonds. The first goal of this paper is to determine which is the correct description of the bonding in the title compounds and find out why the M- -M distance is short in some and long in other compounds. Therefore, we have studied the electronic structure of model compounds of the type $L_4Cu_2(\mu\text{-}XH_n)_2$ by performing molecular orbital calculations of the extended Hückel type for n = 3–0 (See Appendix 2 for computational details).

Although this work focuses mainly on Cu(I) compounds, most of our analysis can be applied to other diamonds with M_2X_2 cores, in which identical atoms occupy opposite corners. We also attempt at describing the bonding in such diamonds in terms of electron counts, on the basis of orbital topology and with as wide applicability as possible. For instance, we want the conclusions of the present work to be valid also for diamonds $[ML_n]_4$ having d^{10} metal ions at all four corners, as well as for those having only main group element atoms in those positions, $[XR_n]_4$, e.g., diborane or Al_2Me_6. The electron-counting rules presented here are restricted to four-membered rings but are quite general as for the nature of the groups occupying their corners. Although other electron-counting schemes, such as the effective atomic number (EAN) or the polyhedral skeleton electron pair theory (PSEPT)[11] are quite general as for the number of atoms in a cluster, their application to four-member rings is somewhat restricted. The PSEPT scheme, for instance, considers groups with only one lobe available, such as H or CH_3, as edges of a cluster; hence, a diamond of the type studied here should be described as a two-atom cluster within this scheme. The EAN rule, on the other hand, would lead to different electron counts depending on the number of vertices occupied by a transition metal (or a main group) atom and can hardly account for bonding in diamonds such as diborane.

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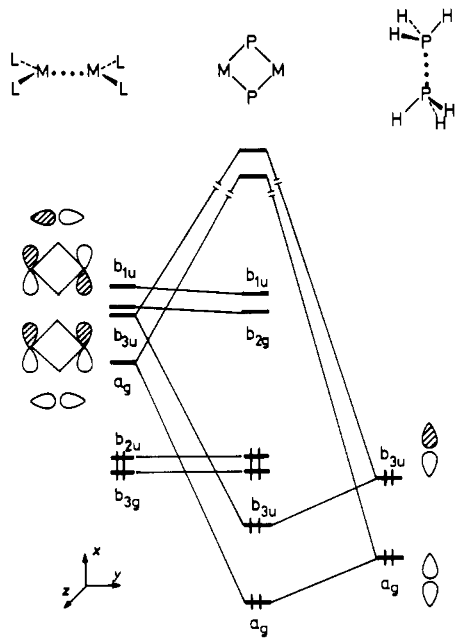

Figure 1. Qualitative interaction diagram for the framework orbitals of $[Cu_2(PH_3)_4(\mu\text{-}PH_3)_2]^{2+}$ without Cu 3d orbitals. The orbital occupation represented in this figure corresponds to a *framework electron count* (FEC) of 4. The b_{3g} and b_{2u} orbitals are the symmetric and antisymmetric combinations of the p_z atomic orbitals of the Cu atoms, of π character relative to the M_2X_2 core.

Finally, Lauher's rules[12] are designed for transition metal clusters and are not easily applied to non-transition metal fragments. It is also well-known that the latter rules do not work well for the late transition elements.

Compounds with XR_3 Bridges

We start our analysis of this class of compounds by looking at the bonding in the model compound $[(PH_3)_4Cu_2(\mu\text{-}PH_3)_2]^{2+}$ and considering only the s and p valence orbitals. The molecular orbitals can be classified according to their symmetry representation in the D_{2h} point group in all cases in order to facilitate comparisons, even if the rigorous symmetry may be smaller (C_{2h} in the present case). The interaction diagram is shown in Figure 1. Each PH_3 ligand can contribute with its lone pair orbital to the framework bonding of the diamond. The symmetric and antisymmetric combinations belong to the a_g and b_{3u} representations, respectively. Each of the $Cu(PH_3)_2^+$ fragments, on the other hand, has two orbitals in the skeletal region: an sp hybrid and a p orbital. Their combinations are represented in Figure 1 (left), together with their symmetry labels. Two of them (a_g and b_{3u}) can combine with the lone pair orbitals of the ligands, while the other two (b_{2g} and b_{1u}) are essentially nonbonding. As the d orbitals of copper are not taken into account, the total number of electrons involved in the skeletal bonding (referred to as the *framework electron count* and abbreviated FEC) is four. It is clear that there are only two bonds to hold the two Cu and two P atoms in a diamond. If the angles in the diamond are varied, keeping the Cu–P distances frozen, the energy minimum is found at a large angle ($\alpha = 111°$, Cu- -Cu = 2.77 Å), as expected for four atoms sharing only four electrons, as in the archetypical diborane molecule. In a Walsh diagram (Figure 2), we can see that the stabilization of the molecule for large values of α is due to the descent of the b_{3u} orbital because of the decrease of its X- -X σ^* character, and is limited by the rise of a_g. The b_{3g} and b_{2u} orbitals, at approximately −13.5 eV (not shown in Figure 1), are of π character relative to the ring and practically insensitive to squeezing except for very large angles.

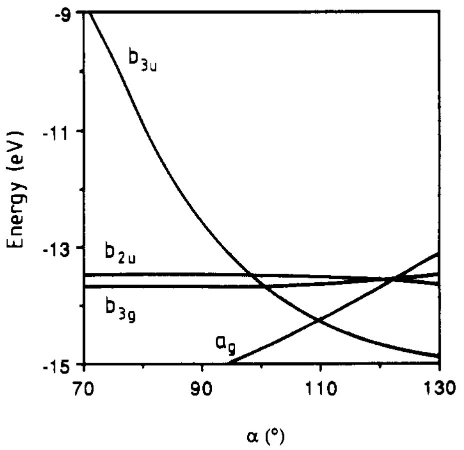

Figure 2. Walsh diagram for the highest occupied orbitals of $[Cu_2(PH_3)_4(\mu\text{-}PH_3)_2]^{2+}$ (FEC = 4) as a function of the ring squeezing, excluding the copper 3d orbitals.

Table I. Number of Lobes and Electrons Contributed to the σ Framework of a M_2X_2 Diamond by Typical XR_n Groups[a]

ligand	lobes	electrons	ligand	lobes	electrons
CH_3	1	1	PR_2	2	3
PR_3	1	2	CR_2, SiR_2	2	2
C_6H_5	1	1	CO, CN^-	2	2
H	1	1	RS^-	2	4
py	1	2	$\eta^2,\mu^2\text{-}C_2R_2$	2	4
pz	1	2	S, Se	2	2
CH=CHR	1	1	Cl^-, Br^-, I^-	2	4
Spy^- (out of plane)	1	2			
$S{=}CR_2$ (out of plane)	1	2	$S{=}CR_2$ (coplanar)	2	4
$R_2C{=}N$; (out of plane)	1	2	$R_2C{=}N^-$ (coplanar)	2	4
$\mu,\eta^1\text{-}C{\equiv}CR$	1	1	$\mu,\eta^2\text{-}C{\equiv}CR$	2	3

[a] The number of electrons corresponds to the neutral groups, except when otherwise specified; py = pyridine; pz = pyrazole.

If we introduce the d orbitals into the picture, the calculated Walsh diagram remains unchanged in its essential trends despite the existence of extensive mixing of the copper d orbitals into the highest occupied molecular orbitals. The Cu- -Cu overlap populations obtained from the calculations with and without d orbitals are 0.034 and 0.031, respectively (for α = 110°), suggesting that the 3d orbitals may not be deeply involved in the bonding. This means that most of the attractive Cu- -Cu interaction (~93%) can be ascribed to the diborane-like delocalized interaction in which only s and p orbitals participate, while d^{10}–d^{10} bonding provides only a small contribution (~7%) to such bonding. However, the description of the bonding appreciably changes with further squeezing of the ring: for angles larger than 120° the four-center delocalized interaction and d^{10}–d^{10} bonding provide similar contributions.

In fact two alternative diborane-like structures can be considered, one with a short Cu- -Cu distance and another one with a short X- -X distance. Why is the first one preferred? This can be understood from the form of the occupied b_{3u} molecular orbital (see Figure 2): a short X- -X distance strongly increases the antibonding interaction between the two σ lone pairs of the X atoms, while a short Cu- -Cu distance decreases such antibonding interaction and simultaneously strengthens its Cu-X bonding nature. The nonexistence of donor orbitals in the bridges with the same symmetry as the Cu- -Cu σ-antibonding combination (b_{1u}) leaves it as an empty orbital. Therefore, the diamond is squeezed in such a way as to avoid the antibonding interaction of the occupied orbital b_{3u} irrespective of the increase in energy of b_{1u}. Simply speaking, the close contact across the diamond is favored for the antipodal groups with two orbitals available for

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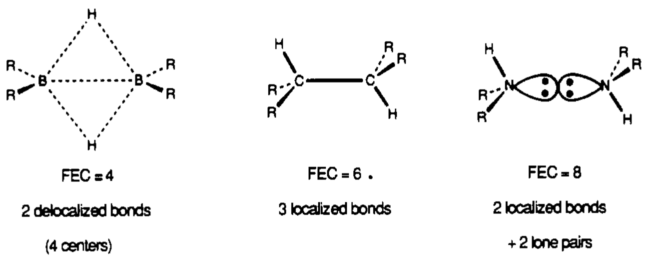
Table II. Framework Electron Count (FEC) and Structural Data for Diamonds of ML_2 Fragments with H, XR_3, and Other Bridges with Only One Framework Orbital[a]

compd	M	X	FEC	α, deg	$2.2r_M$	*d*(M- -M), Å	ref
$[Cu\{MeC(CH_2PPh_2)_3\}(\mu\text{-}H)]_2$	Cu	H	4	90	3.04	2.31	16
$[Cu(HBpz_3)]_2$	Cu	N	4	107	3.04	2.66	17
CuP_2	Cu	P	4	124	3.04	2.48	1, 14
$[Cu(PR_3)_2BH_2(\mu\text{-}H)]_2$	Cu, B	H	4	69, 132	3.04	2.18	18
B_2H_6	B	H	4	96	1.98	1.77	19
Al_2Me_6	Al	C	4	104	2.75	2.61	20
Al_2Ph_6	Al	C	4	103	2.75	2.70	21
$Al_2{}^iPr_6$	Al	C	4	97	2.75	2.62	22
$Al_2Me_4Ph_2$	Al	C	4	101	2.75	2.68	21
$Ga_2Me_4(\mu\text{-}H)_2$	Ga	H	4	80	2.77	2.61	23
$Ga_2H_4(\mu\text{-}H)_2$	Ga	H	4	82	2.77	2.58	26
$Ga(CH_2R)_2(\mu\text{-}CH_2R)_2Li(diox)_2$	Ga, Li	C	4	92, 106	2.92	2.86	27

[a] See Table I. r_M is the covalent radius of M. For boron compounds, see refs 24 and 25.

skeletal bonding. Notice that similar conclusions were reached by Canadell and Eisenstein for the one-dimensional chain $(BeMe)_n$ on the basis of band structure calculations.[13] It is interesting to speculate on the possible existence of the alternative diborane structure for Cu(I) complexes, with X- -X but no Cu- -Cu contact (**2**), and we will undertake this task later on. Besides the pyramidal XR_3 fragments, other groups which can participate with only one orbital to skeletal bonding are displayed in Table I (see below for a discussion on some of these ligands).

If two more electrons are added to our model compound (for an FEC of 6), the b_{2g} orbital becomes occupied. As this orbital does not participate in the σ skeleton of the diamond, the resulting compound could still present a bond across the ring. It must be mentioned, however, that for such a system with 6 framework electrons the diamond may be unstable to ring opening.[14,15] Finally, placing two more electrons in b_{1u} destroys the Cu- -Cu bond across the ring. Notice also that the cyclic structure with two delocalized bonds (a_g and b_{3u}) between the four centers and four nonbonding electrons (b_{2g} and b_{1u}) is less stable than two separate molecules with one localized bond and one lone pair each. The structural preferences for framework electron counts of 4, 6, and 8 are schematically represented in **3**, and correspond simply to the structures of diborane, ethane, and ammonia, respectively, in which a hydrogen atom is substituted for the XR_3 group, since both have only one orbital for skeletal bonding. However, such a simple picture is valid only when the bridging group has only one lobe available for skeletal bonding.



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How do these results match with the experimental data? The only Cu(I) structure of type **1** ($n = 3$) known to us is that of CuP_2, formally a compound of Cu(I) and $P_4{}^{2-}$ in which a Cu_2P_2 diamond exists: the bridging phosphorus atoms have three additional bonds, and the copper atoms also bear two terminal ligands.[1,14] The Cu- -Cu distance in such a diamond with an FEC of 4 is quite short, 2.48 Å, in excellent agreement with our results. Other bridging groups, such as CH_3 or H, contribute one lobe to framework bonding (see Table I). Also the phenyl, pyridine, and pyrazole groups participate with only one lobe each because of the delocalization of the π orbital through the aromatic ring and are therefore analogous to the XR_3 bridges from the orbital point of view. Some examples of isoelectronic molecules (i.e., FEC = 4) are shown in Table II and include diborane, $Al_2(CH_3)_6$, and its analogues. All of them present diamond structures with short M- -M distances.

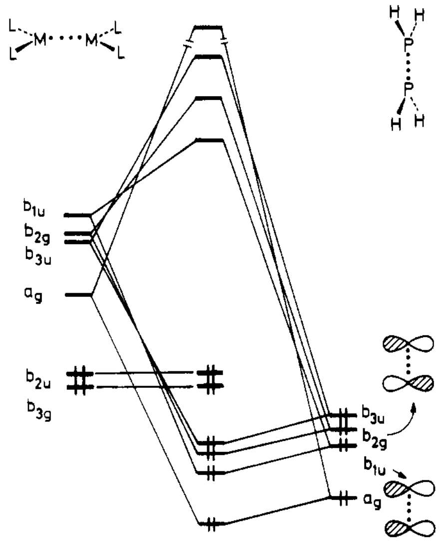

Figure 3. Interaction diagram for the framework orbitals of $[Cu_2(PH_3)_4(\mu\text{-}PH_2)_2]$ without Cu 3d orbitals. The orbital occupation corresponds to an FEC of 8.

Compounds with XR_2 Bridges

When each bridging group has two substituents, as in a thioether or a phosphide, the orbital interaction diagram without the copper

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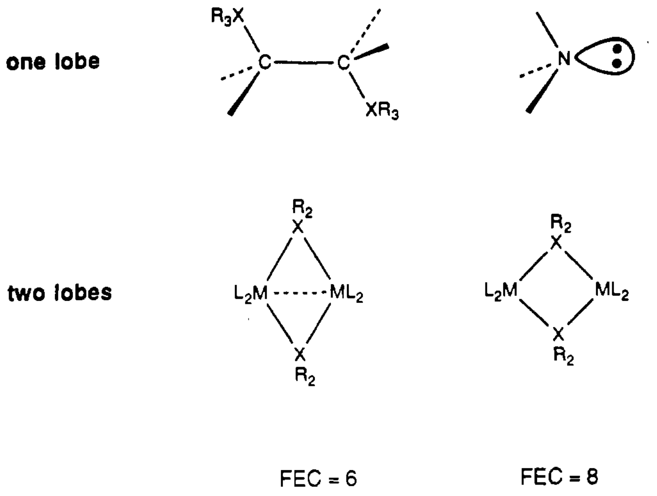
d orbitals can be represented by Figure 3. The main difference with the case of XR_3 bridges resides in the fact that two more orbitals (b_{1u} and b_{2g} in Figure 3) can combine with the formerly nonbonding orbitals of the CuL_2 fragments. These orbitals are not accessible in the XR_3 derivative studied in the previous section, since they are strongly involved in X–R σ-bonding. The energy of b_{1u}, with Cu- -Cu σ-antibonding character, shows a strong dependence on α. This effect can clearly be seen in the Walsh diagram (Figure 4, now including Cu 3d orbitals but similar to the one obtained without them), in which the b_{3u} and b_{1u} orbitals cross at $\alpha \sim 93°$. For d^{10} metal ions and four-electron bridging ligands (e.g., PR_2^- or R_2S), the FEC is 8 and all orbitals in Figure 4 are occupied, resulting in an energy minimum at a small angle ($\alpha = 99°$ for our model compound $[Cu_2(PH_3)_4(\mu\text{-}PH_2)_2]$) and a correspondingly long Cu- -Cu distance (3.19 Å, cf. 2.77 Å for XR_3 bridges). Notice that the orbital and electron counts in this skeleton (4 orbitals and 8 framework electrons) correspond to the canonical situation of four localized bonds, as in cyclobutane (see discussion below). It is interesting to compare this result with that indicated for the XR_3 bridges and schematically shown in **4**. The difference arises from the fact that the four framework bonding orbitals are occupied for XR_2 bridges, as discussed above. The open structure has nearly the same energy as the diamond, and their interconversion has a tiny barrier of ~5 kcal/mol at the extended Hückel level. Hence, the nonexistence of structurally characterized compounds with an open structure may be attributed to the high lability of the terminal XR_2 ligands with partially occupied orbitals.[15]



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For a system with two less electrons (i.e., FEC = 6), either the orbital with Cu- -Cu σ^* character (b_{1u}) or that with X- -X σ^* character (b_{3u}) could be emptied. The potential energy curve presents two troughs corresponding to both cases (Figure 4, bottom). In the former case, the most favorable structure would require a short Cu- -Cu distance, i.e., a large value of α. In the second case, a structure with a short X- -X distance and a small α (**2**) results. This interesting type of structure is uncommon, but a few compounds with carbon–carbon or silicon–silicon bonds across a ring are known.[28-30] Since the minimum at a small α is associated with the presence of a b_{1u} orbital at the X_2R_{2n} fragment, such a structure cannot be found when $n = 3$ (i.e., for XR_3 bridging ligands).

It is interesting to analyze the existence of a through-ring Si–Si bond in the compounds of the type $[L_2Pt(\mu\text{-}Si_2R_2R_2')PtL_2]$.[29] In such complexes, two antipodal vertices are occupied by d^{10} ML_2 fragments, with the terminal ligands L in the plane of the diamond, and the remaining two vertices are occupied by SiR_2 residues. Notice that rotation of the L ligands in **1** to a coplanar position leaves us with only one σ lobe available at each Pt atom (i.e., we cannot lean on the b_{2g} and b_{3u} orbitals for σ framework bonding). Since there are two available lobes at each SiR_2 group, the situation is topologically equivalent to the previously studied case with XR_3 bridges but exchanging the roles of the M and X atoms: now an X- -X bond is indicated (FEC = 4), and no M- -M bond is allowed. Were we able to rotate at will the terminal ligands attached to the d^{10} metal centers, possibly an isomerization between the two alternative squeezed-ring geometries could be observed.

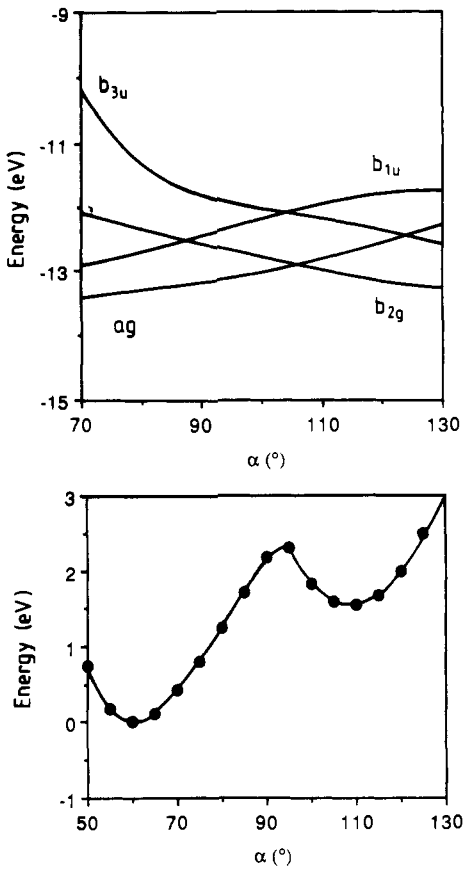

Figure 4. Walsh diagram (top) and one-electron energy curve (bottom) for the ring squeezing of $[Cu_2(PH_3)_4(\mu\text{-}PH_2)_2]$ with Cu 3d orbitals included in the basis set. Only those orbitals occupied for FEC = 8 are shown in the Walsh diagram. The occupied orbitals of π type (b_{3g} and b_{2u}) are omitted for clarity.

Notice that the three occupied framework orbitals (a_g, b_{3u}, and b_{2g}) are M–X bonding; hence, the cyclic structures with a bond across the diamond are more stable than the open one, in contrast to our above results for the case with XR_3 bridges (**3**). This conclusion is in good agreement with the finding that all diamond structures with an FEC of 6 have bridging ligands with two framework lobes (see Tables II–V). Finally, removal of two more electrons yields an FEC of 4, adequate to account for a delocalized bonding in the diamond with one short distance across and clearly more stable in our calculations than the ethane-like structure (~20 kcal/mol). For compounds with XR_2 bridges and an FEC of 4 or 6, the ring structure is calculated to be more stable than the open one.

Only one structure of complexes of d^{10}-ML_2 groups with XR_2 bridges was found in the literature (Table III), that of [Cu-

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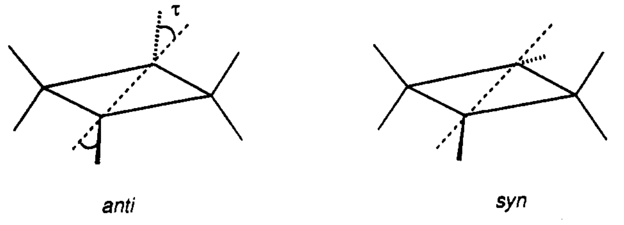
Table III. Framework Electron Count (FEC) and Structural Data for Diamonds of d^{10} and Main Group ML$_2$ Fragments with XR$_2$ Bridges[a]

compd	M	X	FEC	α, deg	2.2r_M	d(M- -M), Å	ref
$[Cu(PMe_3)_2\{Sb(mesityl)_2\}]_2$	Cu	Sb	8	85	3.04	3.95	2
(BR′)(BR″)(BH$_3$)(NR)	B	B, N	6	110	1.98	1.78	31
C_4H_8	C	C	8		1.65		32
$Al_2(\mu\text{-}Me)(\mu\text{-}NPh_2)$	Al	C, N	6	98	2.75	2.72	33
$Al_2{}^iBu_4(\mu\text{-}CH{=}CH{}^tBu)_2$	Al	C	4	101	2.75	2.68	34
$Al_2(NR_2)_4(\mu\text{-}NH_2)_2$	Al	N	8	84	2.75	2.87	35
$Al_2Me_4(NMe_2)_2$	Al	N	8	88	2.75	2.81	36
$Ga_2{}^nBu_4(P{}^tBu_2)_2$	Ga	P	8	87	2.77	3.59	37
$Ga_2Me_4(P{}^tBu_2)_2$	Ga	P	8	86	2.77	3.60	37
$Ga_2Me_4(As{}^tBu_2)_2$	Ga	As	8	84	2.77	3.78	37
$Ga_2{}^nBu_4(As{}^tBu_2)_2$	Ga	As	8	85	2.77	3.76	37
$(InCl{}^iPr)_2(NH{}^tBu)_2$	In	N	8	83	3.17	3.26	38

[a] r_M is the covalent radius of M. More data on compounds with M = Al, Ga and X = P, As with FEC = 8 and long M- -M distances can be found in ref 39.

(PMe$_3$)$_2$SbR$_2$]$_2$, with an FEC of 8. It fits nicely with the cyclobutane description, as shown by its bonding parameters.[2]

It is obvious that the resulting electron-counting rules coincide with those for main group elements, such as B, Al, and C. A few examples of such diamonds are gathered in Table III. In all those cases in which the FEC is 8, the experimental structures correspond to *regular* four-membered rings without bonds across. It is interesting to remark that the existence or not of a short Al- -Al distance in the compounds of Tables II and III is dictated by the number of electrons (FEC) and not by the number of substituents at the bridging atoms. Cyclobutane, a four-membered ring with an FEC of 8, has no cross-ring interaction. The fact that cyclobutane is not planar but puckered does not affect the present analysis. In fact both experimental data and SCF calculations[40] suggest that the bent structure is barely 1 kcal/mol more stable than the planar one.



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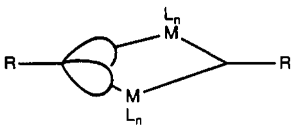

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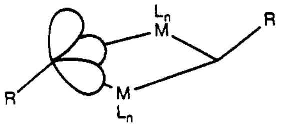

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Compounds with XR Bridges

If the only substituent on the bridging atom is oriented coplanar to the diamond, the molecular orbitals are quite similar to those of the previous case (XR$_2$ bridges), except for the existence of one lone pair located in a π orbital perpendicular to the plane of the Cu$_2$X$_2$ framework. Hence, each XR group contributes with two orbitals to the framework bonding (**6**). Both orbitals form combinations of symmetries b$_{2u}$ and b$_{1g}$. In general, the X atom is more electronegative than Cu and, for electron-counting purposes, it is reasonable to assume that the π orbital is occupied, i.e., three valence electrons of the X atom do not participate in skeletal bonding (one involved in X–R bonding and a π lone pair). As a model compound, we now choose $[Cu_2(PH_3)_4(\mu\text{-}PH)_2]^{2-}$. Our calculations show that the energies of the b$_{2u}$ and b$_{3g}$ orbitals change little with α, and changes in total energy correspond mostly to the a$_g$, b$_{3u}$, and b$_{1u}$ orbitals, in much the same way as in the compound with an XH$_2$ bridge. Therefore, for an FEC of 8, the calculated energy minimum appears at a somewhat smaller angle (α = 93°, Cu- -Cu distance = 3.37 Å) than that for the XH$_2$ bridges (α = 99°). These results are in excellent agreement with the experimental values (Table IV) for thiolato-bridged complexes. The alkoxo-bridged compounds present much smaller bond angles (78°) but still long Cu- -Cu distances. Clearly, the smaller angles of the alkoxo

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Table IV. Structural Data for Diamonds of d^{10}-ML_2 Fragments with XR Bridges (Distances in Å; Angles in deg)

compd	M	X	FEC	τ (5)	α	$2.2r_M$	M- -M	C–S	ref
			Bridging Atom with sp^2 or sp^3 Hybridization (Cases 6–8)						
$[Zn_2(SPh)_6]^{2-}$	Zn	S	8	60	91	2.88	3.42	1.775	41
$[Zn_2(SEt)_6]^{2-}$	Zn	S	8	71	98	2.88	3.18	1.829	42
$[Cd_2(SPh)_6]^{2-}$	Cd	S	8	65	93	3.34	3.69	1.775	41
$[Cd_2(SEt)_6]^{2-}$	Cd	S	8		96	3.34	3.48	1.823	41
$[Hg_2(SMe)_6]^{2-}$	Hg	S	8	74	94	3.32	3.94	1.834	43
$[Ag_2\{S_2P(OEt)_2\}_2(PPh_3)_2]$	Ag	S	8	88	100	3.37	3.44		44
$[Cu_2(p\text{-}MeC_6H_4NC)_4(\mu\text{-}OPh)_2]$	Cu	O	8	8	78	3.04	3.22		45
$[Cu_2(p\text{-tic})_4(\mu\text{-}OPh)_2]$	Cu	O	8	8	78	3.04	3.22		46
C_4H_6[a]	C	C	6		103	1.65	1.86		47
Si_4H_6[a]	Si	Si	6		118	2.57	2.37		47
$Al_2Me_4(\mu\text{-}OSiR_3)_2$	Al	O	8		84	2.75	2.76		48
$Al_2(NCR_2)_4(\mu\text{-}NCR_2)_2$	Al	N[b]	8		84	2.75	2.85		49
$Al_2Ph_4(\mu,\eta^2\text{-}C{\equiv}CPh)_2$	Al	C	8	0	88	2.75	2.99		50
$Al_2Me_4(\mu,\eta^2\text{-}C{\equiv}CMe)_2$	Al	C	8		88	2.75	3.03		51
$Ga_2\{Ph(NMe_2)\}_2(\mu\text{-}PSiPh_3)_2$	Ga	P	8		86	2.77	3.50		52
$[In_2Cl_4(\mu\text{-}NPPh_3)_2]$	In	N	8			3.17	3.23		53
			Bridging Atom with sp^2 Hybridization (Case 9)						
$[Cu_2(mimtH)_6](BF_4)_2$	Cu	S	4	72	103	3.04	3.01	1.71	54
$Cu_2(pyH\text{-thiolate})_5Cl_2$	Cu	S	4	70	105	3.04	2.95	1.74	55
$Cu_2(pyH\text{-thiolate})_6Cl_2$	Cu	S	4	69	106	3.04	2.91	1.72	56
$Cu_2(pyH\text{-thiolate})_5Br_2$	Cu	S	4	68	106	3.04	2.91	1.68	55
$[Cu_2(tu)_6]^{2+}$	Cu	S	4	65	107	3.04	2.84	1.72	57
$[Cu_2(Me_2tu)_6]^{2+}$	Cu	S	4	74	108	3.04	2.83	1.73	57
$[Cu_2(tu)_6]^{2+}$	Cu	S	4	71	108	3.04	2.83	1.73	58
$[Cu_2(mac)(SCN)_2]$	Cu	S	4	68	108	3.04	2.80	1.70	59
$[Cu_2Cl_2(HPhNCS_2Me)_4]$	Cu	S	4	70	102	3.04	3.08	1.70	60
$[Cu_2I_2(HMeNCS_2Me)_4]$	Cu	S	4	73	100	3.04	3.27[c]	1.69	60
$[Cu_2Cl_2(tmdtz)_2[$	Cu	S	4	71	98	3.04	3.19[c]	1.71	61
$[Cu_2(puH\text{-}6\text{-thiolate})_2Cl_4]$	Cu	S	4	77	93	3.04	3.46[c]	1.69	62
$[Ag_2(tu)_6]^{2+}$	Ag	S	4	81	112	3.37	2.84	1.73	63

[a] Theoretical values. [b] The R_2CN^- ligand is coplanar to the diamond, hence contributing two lobes and four electrons to framework bonding (see Table I). [c] The long Cu- -Cu distance in these complexes is probably the result of steric hindrance (see text). Abbreviations: mac = tetradentate N_4 macrocyclic ligand; mimtH = 1-methylimidazoline-2-thione; puH = purinium; tic = tolyl isocyanide; tmdtz = trimethyldithiocarbazate; tu = thiourea.

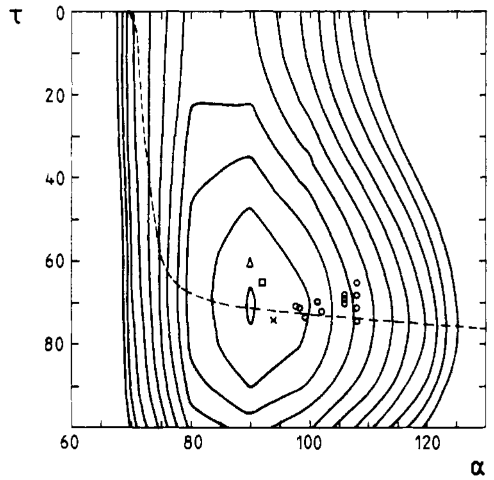


Figure 5. Contour diagram for the one-electron energy of $[Cu_2(PH_3)_4(\mu\text{-}SH)_2]$ as a function of the squeezing angle, α (1), and the orientation of the SH groups, τ (5). Superimposed are the points representing the geometries of several thiolato-bridged compounds of Cu(I) (open circles), Zn(II) (triangles), Cd(II) (squares), and Hg(II) (crosses). For references, see Table IV. Contours are separated by 0.2 eV.

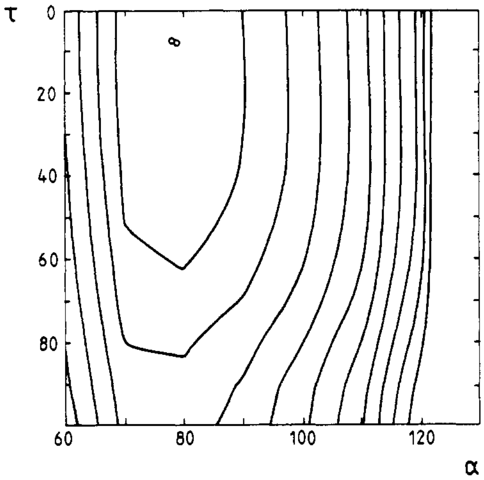
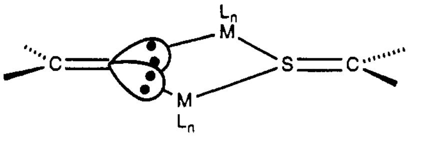


Figure 6. Contour diagram for the one-electron energy of $[Cu_2(PH_3)_4(\mu\text{-}OH)_2]$ as a function of the squeezing angle, α, and the orientation of the OH groups, τ. All specifications are as in Figure 5.

compounds are a geometrical requisite for a long Cu- -Cu distance, since the Cu–O bond distances are much shorter than the Cu–S ones (see Appendix 1).

In fact, the substituent of the bridging ligand is rarely coplanar to the diamond. Its deviation from the coplanar situation can be represented by the angle τ as in **5**, either in the anti or the syn configuration. Let us now consider the effect of that angle on the Cu- -Cu interaction. In order to analyze this problem, the potential energy of the model compound $[Cu_2(PH_3)_4(\mu\text{-}SH)_2]$ was calculated as a function of both angles, α and τ. The corresponding potential energy surface is presented in Figure 5. There, the minimum energy is found for $\alpha \approx 90°$ and $\tau \approx 70°$. The dashed line in Figure 5 represents the optimized value of τ for a given value of α, clearly indicating that τ adapts to α: τ should be close to 0° for α small but approximately 70° for α large. It is easy to understand that having the substituent in the plane of the diamond requires the bridging atom to use sp^2 hybrids (**6**), whereas its bending away from that plane implies the use of sp^3 hybrids (**7**). Clearly, the tetrahedral angle between the two lobes fits better with a larger value of β (i.e., a smaller α). The experimental values for different thiolato-bridged compounds, also represented in Figure 5, are in good qualitative agreement with the calculations: all the points appear practically on the valley of energy. The calculated potential energy surface for the hydroxo-bridged model compound $[Cu_2(PH_3)_4(\mu\text{-}OH)_2]$, presented in Figure 6, shows a flatter energy minimum, displaced to $\alpha \approx 80°$ (i.e., $\beta \approx 100°$), and consequently the optimum value of τ is ~ 0°, consistent with the implication of oxygen sp^2 hybrids in the skeletal bonding and in excellent agreement with the experimental data in Table IV.

There is a special group of bridging SR ligands which include thiourea, S═C(NH$_2$)$_2$, pyridinethiolato (Spy$^-$), and *N*-methylimidazoline-2-thione (Smim). In each of these ligands, the sulfur atom has an sp^2 hybridization, as indicated by C–S bond distances shorter (~1.72 Å) than found for benzene- and alkanethiolates (1.77–1.83 Å, Table IV). The sulfur atom can then participate in the framework bonding in two different ways: either with the two sp^2 orbitals and four electrons when it is coplanar to the diamond ($\tau \approx 0°$, **8**) or with only one orbital and two electrons when the C–S bond is out of the plane of the diamond (**9**). In all the examples included in the lower part of Table IV, the S–C bond is out of the plane of the diamond, and the bridging ligands should consequently be counted as two-electron donors. The short Cu- -Cu bond distances are in good agreement with the FEC being 4, but the distances increase with the bulkiness of the R group, in an attempt to avoid the repulsions between R and the terminal ligands, becoming nonbonding for the bulkier substituents. Indeed, in Cu$_2$(puH-6-thiolate)$_2$Cl$_4$ (Table IV) there are several hydrogen atoms of the R group at distances close to a Cl atom (2.0–2.6 Å); therefore, a shorter Cu- -Cu distance would result in too short nonbonded H- -Cl distances.



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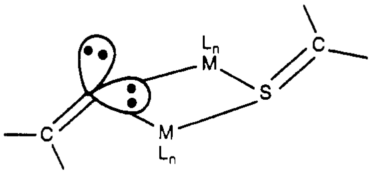

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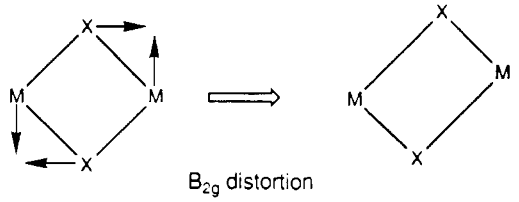

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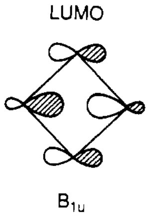
Another group of ligands which may act in different ways is that of the alkynyls, C≡CR. When the alkynyl group is perpendicular to the M- -M vector (μ,η^1-coordination mode), it provides one lobe and one electron to the framework, but when it is bent (μ,η^2-coordination mode), a π orbital of the alkynyl participates also in the framework bonding, therefore providing two lobes and three electrons. Although we are not aware of the existence of such compounds for the d^{10} metal ions studied in this paper, the two coordination modes for alkynyl groups are known in Be and Al compounds,[24,50,51,64] and their M- -M distances are consistent with the proposed counting of lobes and electrons.

Distortions of the M$_2$X$_2$ Diamonds

In compounds with XR bridges and the anti structure, the M$_2$X$_2$ skeleton presents a sharp distortion (**10**), lowering the symmetry from D_{2h} to C_{2v}. Is a second-order Jahn–Teller (SOJT) effect[65] in action? An SOJT distortion is one which allows mixing of one empty and one occupied orbital (typically the HOMO and the LUMO). The HOMO and LUMO of a model compound [Cu$_2$Br$_4$(SH)$_2$]$^{4-}$ are shown in **11** and **12**, respectively, together with their symmetry labels in the D_{2h} point group. The direct product of such representations is B$_{2g}$, coincident with the representation of the distortion (**13**). Hence, the qualitative argument, based on symmetry concepts, points to a HOMO–LUMO mixing driven distortion. However, the calculated energy gap between such orbitals is 6.6 eV, too large for an SOJT effect. It is well-known[66] that inclusion of 3d orbitals in the basis set of the sulfur atoms has little effect on the occupied orbitals but significantly decrease the energy of the empty orbitals, resulting in smaller HOMO–LUMO gaps and correctly predicting SOJT distortions. In the present case, inclusion of the sulfur 3d orbitals diminishes the Cu–S antibonding character of the LUMO (**14**), and the calculated HOMO–LUMO gap becomes 1.0 eV, resulting in the stabilization of the distorted structure for a displacement coordinate (r in **13**) ~ 0.9 Å, too large compared to the experimental values but correctly reproducing the existence of a B$_{2g}$ distortion. What is important is that the main features of the framework bonding and the electron-counting rules remain valid in all cases.



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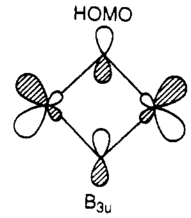

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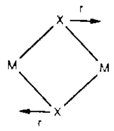

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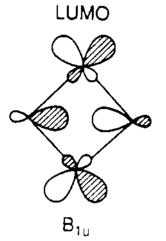

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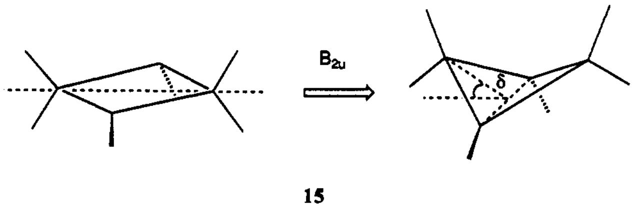
A different kind of distortion appears in the compounds with syn structure: the M$_2$X$_2$ diamond loses the planarity, thus adopting a butterfly shape (**15**). If a SOJT effect were responsible for this distortion, achieved through a B$_{2u}$ mode **15** (still using the point group of the M$_2$X$_2$ core, D_{2h}), the LUMO of B$_{1u}$ symmetry should mix with an occupied orbital belongint to the B$_{3g}$ irreducible



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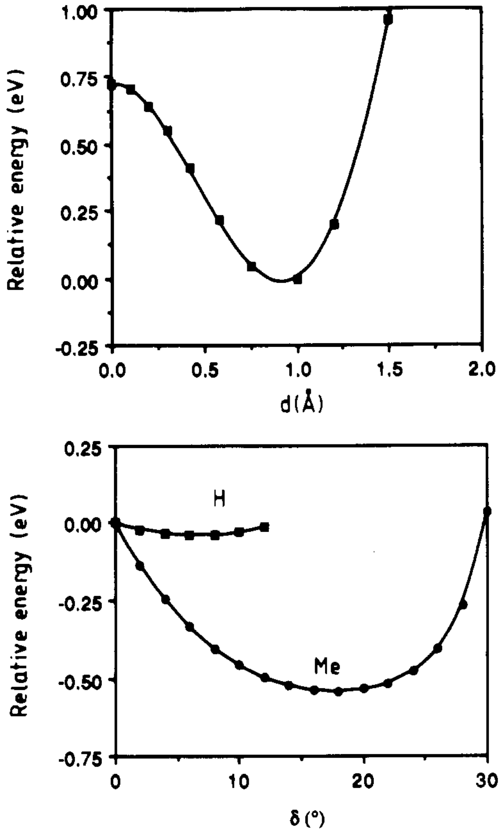

Figure 7. Relative one-electron energy as a function of the B_{2g} distortion (**10**) for $[Cu_2Br_4(\mu\text{-}SH)_2]^{4-}$ (top) and as a function of the ring-folding distortion B_{2u} (**15**) for $[Cu_2Br_4(\mu\text{-}SH)_2]^{4-}$ and $[Cu_2Br_4(\mu\text{-}SCH_3)_2]^{4-}$ (bottom).

representation. But the b_{3g} orbital is too low in energy to be effective in a SOJT mixing. The calculated energy for $[Cu_2(PH_3)_4(\mu\text{-}SH)_2]$ as a function of the angle δ, shown in Figure 7, indicates very little stabilization through the B_{2u} distortion. However, if we use a bulkier thiolate, SCH_3, as bridging ligand, important stabilization results (Figure 7), clearly indicating that the driving force for such a distortion is the minimization of steric repulsions between the terminal ligands and the substituents of the bridging ligands. Obviously, this effect is not present in the anti isomer because the butterfly structure would always approach one of the bridging ligands to the terminal ones. Changing the ligands and/or the metal atoms would therefore produce a variety of situations ranging from the planar diamonds to the bent (butterfly) structures.

Compounds with Monoatomic Bridges

The potential energy curves obtained for the model compound $[Cu_2(PH_3)_4(\mu\text{-}Br)_2]$, shown in Figure 8 (top), and the analogous μ-I derivative, not shown in Figure 8, are surprisingly flat. The corresponding curve for the model compound with XR_2 bridges and an FEC of 8, $[Cu_2(PH_3)_4(\mu\text{-}PH_2)_2]$, is also shown in Figure 8 for comparison. All the halo-bridged complexes presented in Table V have an FEC of 8, and one should expect no M- -M cross-ring bonding. This prediction is in agreement with the structural data for most of the compounds in Table V, but there are a few cases with M- -M distances approximately equal or even clearly smaller than $2.2r_M$. The most remarkable case is that of $[Cu_2I_2(quin)_4]$, whose Cu- -Cu distances vary between 2.866 and 3.364 Å depending only on the nature of the solvent molecules included in the solid.[67] The flat potential well found for monoatomic bridged diamonds accounts for the violation of the electron-counting rule, but we would like to unravel the reasons

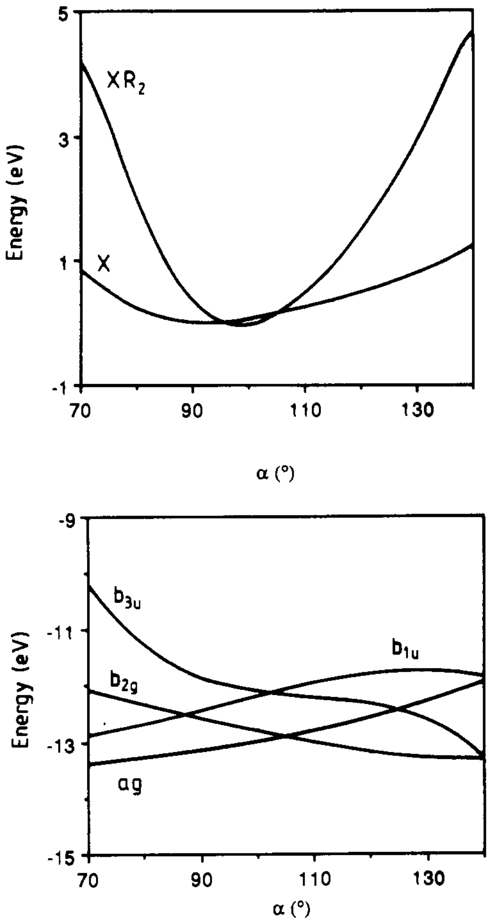

Figure 8. Top: One-electron energy curve as a function of the squeezing angle α for two model compounds with a FEC of 8, $[Cu_2(PH_3)_4(\mu\text{-}Br)_2]$ and $[Cu_2(PH_3)_4(\mu\text{-}PH_2)_2]$. Bottom: Walsh diagram for $[Cu_2(PH_3)_4(\mu\text{-}Br)_2]$ (with Cu 3d orbitals included in the calculation). The occupied orbitals of π type (b_{3g} and b_{2u}) are omitted for clarity.

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Table V. Structural Data for Diamonds of d^{10}-ML_2 Fragments with Monoatomic X Bridges and an FEC of 8[a]

compd	M	X	α, deg	d(M- -M), Å	ref
$Cu_2Cl_2L_4$	Cu	Cl	96	3.21	68
$Cu_2Cl_2\{P(Cy)_3\}_4$	Cu	Cl	97	3.066	69
$Cu_2Cl_2(pbctaH)_2$	Cu	Cl	98	3.697	70
$Cu_2Cl_2(2\text{-}Mepy)_4$	Cu	Cl	100	3.149	71
$Cu_2Cl_2(2\text{-}Mepy)_4$	Cu	Cl	100	3.145	71
$Cu_2Cl_2(quin)_4$	Cu	Cl	101	3.121	71
$Cu_2Cl_2(2,4\text{-}Me_2py)_4$	Cu	Cl	105	2.995	71
$Cu_2Cl_2(dad)_2$	Cu	Cl	99	3.011	72
$[Hg_2Cl_6]^{2-}$	Hg	Cl	88	3.766	73
β-$HgCl_2(PBu_3)$	Hg	Cl	89	3.893	74
$[Hg_2Cl_6]^{2-}$	Hg	Cl	90	3.741	75
$Cu_2Br_2(2\text{-}Mepy)_4$	Cu	Br	100	3.351	71
$Cu_2Br_2(2,9\text{-}Me_2phen)_2$	Cu	Br	103	3.097	71
$Cu_2Br_2(quin)_4$	Cu	Br	104	3.140	71
$Cu_2Br_2(2,4\text{-}Me_2py)_4$	Cu	Br	107	3.091	71
$[Co(dtc)_3]_2(CuBr)_2$	Cu	Br	109	2.697	76
$[Hg_2Br_6]^{2-}$	Hg	Br	90	3.82	77
$[Cd_2Br_6]^{2-}$	Cd	Br	93	3.666	78
$Cu_2I_2(PPh_3SO_2)_2$	Cu	I	97	3.576	79
$Cu_2I_2(quin)_4$	Cu	I	102	3.364	80
$Cu_2I_2(quin)_4$	Cu	I	108	3.137	17
$Cu_2I_2(2,4\text{-}Me_2py)_4$	Cu	I	109	3.140	71
$Cu_2I_2(2,9\text{-}Me_2phen)_2$	Cu	I	110	3.024	71
$Cu_2I_2(2\text{-}Mepy)_4$	Cu	I	110	3.083	81
$Cu_2I_2(quin)_4$	Cu	I	115	2.866	82
$Cu_2I_2(3\text{-}Mepy)_4$	Cu	I	116	2.782	83
$Cu_2I_2(nas)_2$	Cu	I	116	2.73	84
$Cu_2I_2(py)_4$	Cu	I	118	2.699	85
$Cu_2I_2(2,6\text{-}Me_2py)$	Cu	I	119	2.586	86
$[Cu_2I_6]^{4-}$	Cu	I	119	2.612	87
$Cu_2I_2(3,5\text{-}Me_2py)_4$	Cu	I	119	2.683	82
$Cu_2I_2(^iPr\text{-}qdt)_4$	Cu	I	121	2.544	88
$Cu_2I_2(^nBu\text{-}qdt)_4$	Cu	I	121	2.53	88
$Cu_2I_2(Me_4\text{-}pip)_2$	Cu	I	121	2.535	82
$Cu_2I_2(dpa)_2$	Cu	I	121	2.606	89
$[Hg_2I_6]^{2-}$	Hg	I	94	3.95	90

[a] The approximate limit for a bonding Cu- -Cu distance is $2.2r_M$ = 3.04 Å. dtc = pyrrolidinecarbodithioato; quin = quinoline; L = tris(isopropyl phosphito); Cy = cyclohexyl; pip = piperidine; dad = diazadiene; nas = ((dimethylamino)phenyl)dimethylarsine; dpa = bis(2-pyridyl)amine; qdt = quinaldate.

for the flatness of the potential energy curve. The Walsh diagram (Figure 8, bottom) reveals that the b_{3u}, a_g, and b_{1u} orbitals are much less sensitive to changes in α than in the case with XR bridges (Figure 4). Since we are now interested in understanding the existence of short M- -M distances (i.e., large values of α), we focus on the behavior of the a_g orbital, which is responsible for the rise in energy at large α (see discussion for the XR_3 bridges). The energy dependence of a_g depends on three factors: hybridization, electronegativity, and atomic size of the bridging atom. Let us analyze these factors in turn. When no substituents are attached to X, the bridging ligand participates in the a_g with almost pure p rather than with an sp hybrid orbital; hence, it has a lower density in the X- -X region and becomes less sensitive to the X- -X distance. On the other hand, the more diffuse nature of the valence orbitals of Br, and particularly I, compared to those of P and S, makes the X- -X overlap poorer, again diminishing the energy dependence of a_g. Finally, for more electronegative bridging atoms, their participation in the a_g molecular orbital is larger and the energy dependence of a_g is higher. In summary, the factors which favor short M- -M distances for compounds with an FEC of 8 are (a) monoatomic bridging ligands and (b) less electronegative and (c) bulkier bridging atoms. This explanation is in good agreement with the structural data in Table V, where distances significantly shorter than $2.2r_M$ are found only for Br and, especially, I compounds.

Concluding Remarks

The main features of the bonding in the $[(ML_2)_2(XR_n)_2]$ diamonds of d^{10} metal ions discussed above are as follows: (a) The two M atoms of the antipodal d^{10}-ML_2 fragments contribute two empty orbitals (sp^3 hybrids) each to the framework bonding. (b) The two antipodal *bridging* atoms X may contribute with one or two orbitals each to the skeletal σ bonding. In a first approximation, lone pairs of π type with respect to the plane of the diamond should have less importance for framework bonding and can be disregarded for the framework electron count. (c) The framework electron count (FEC) can be obtained by adding the number of electrons in the two sp^3 lobes of each ML_2 fragment (e.g., none for Cu(I)) plus those in the one or two pertinent lobes of the bridging ligands. Some representative examples of bridging ligands, together with their contribution to the FEC, are presented in Table I. (d) When each of two antipodal atoms X (or M) contribute with only one orbital to the skeletal bonding, the situation with small (large) α and a short X- -X (M- -M) distance is highly unstable. (e) Diamonds with an FEC of 4 or 6 are more stable in the diborane than in the cyclobutane structure. Diamonds with an FEC of 8 must present a *regular* (cyclobutane) structure, and no short distances across the ring are expected. (f) For all of the analyzed structures with substituted bridging ligands (XR_n, n = 1–3), a borderline between interacting (FEC = 4 or 6) and noninteracting (FEC = 8) M_2 pairs can be found. Such a borderline is always close to $2.2r_M$, r_M being the covalent radius of M. (g) For the less electronegative, bulkier monoatomic bridges, a soft potential makes the short M- -M distances possible even with an FEC of 8. (h) In the diborane structure, the antipodal atoms with a short distance must have two lobes available for skeletal bonding. If both sets of antipodal atoms have two lobes, two isomers are in principle possible having M- -M and X- -X short distances, respectively.

These conclusions are based on the orbital topology of the fragments forming the diamond and on the framework electron count. The application of the same ideas to a wide variety of diamonds in which other transition metal—or main group element—fragments replace either or both of the two sets of antipodal groups is straightforward. Some cases which agree with the framework electron-counting rules developed in this paper were already studied in detail by other authors and include compounds of boron and aluminum,[24,91] as well as clusters of transition metals of the groups 7–10 (i.e., diamonds with transition metals at all four corners).[92]

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Appendix 1: Distance Criterion for Through-Ring Interactions

In the simplest case atoms M and X have identical covalent radii and the least-interaction geometry is a square (i.e., $\alpha \approx 90°$ as in cyclobutane). The ring can be *squeezed* in two different ways: by approaching the *antipodal* M atoms, hence increasing α, or approaching the X atoms, decreasing α. If there is a bonding interaction between the M atoms, one might expect them to be at a distance $d \approx 2r_M$ (i.e., $\alpha \approx 120°$), where r_M is the covalent radius of atom M, although somewhat longer distances could be expected for both electronic and steric reasons. Similarly, a bonding interaction between the X atoms required them to be at a short distance $b \approx 2r_X$ (i.e., $\alpha \approx 60°$). We could then accept that values of α in the range $80 < \alpha < 100°$ indicate the absence

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Table VI. Atomic Parameters for Extended Hückel Calculations[a]

atom	orbital	H_{ii}	$\zeta_{1\mu}$ (c_1)	$\zeta_{2\mu}$ (c_2)	ref
Cu	4s	−11.4	2.20		97
	4p	−6.06	2.20		
	3d	−14.0	5.95 (0.5933)	2.30 (0.5744)	
S	3s	−20.0	2.122		
	3p	−11.0	1.827		98
	[3d	−8.0	1.500]		99
P	3s	−18.6	1.75		100
	3p	−14.0	1.30		
Br	4s	−22.07	2.588		101
	4p	−13.10	2.131		
O	2s	−32.3	2.275		95
	2p	−14.8	2.275		
H	1s	−13.6	1.300		95

[a] $H_{\mu\mu}$'s are the orbital ionization potentials, $\zeta_{i\mu}$'s the exponents of the Slater orbitals, and c_i's the coefficients in the double-ζ expansion of the d orbitals. 3d orbitals for sulfur atoms were used only for the study of the second-order Jahn–Teller distortions.

of cross-ring bonding.[93] However, if the M and X atoms have different covalent radii, the least-interaction geometry is not a square but a rhombus. Assuming covalent M- -M bonding, the angle α for the squeezed diamond is given by eq 1. At the other

$$\alpha = 2 \arccos (r_M/c) \qquad (1)$$

$$\alpha = 2 \arcsin (r_X/c) \qquad (2)$$

extreme, X- -X bonding corresponds to the geometry given by eq 2. Hence, for a Cu_2P_2 diamond (r_M = 1.38 Å, r_X = 1.10 Å, and $c \approx r_M + r_X$), a geometry with α = 112° would keep the two copper atoms at bonding distance and α = 53° would correspond to a P- -P *bond*. The corresponding values for a Cu_2O_2 diamond (r_X = 0.73) are 98 and 40°, respectively, whereas for a Cu_2H_2 core one finds 76 and 24°. It can be therefore concluded that the actual values of α defining the existence or not of a cross-ring interaction are different for every combination of atoms M and X. On the other hand, M- -M distances of up to 10% longer than $2r_M$ are short enough for us to be able to postulate the existence of cross-ring bonding, and therefore, we use this as an empirical criterion to detect the existence of such interactions. Since different values of covalent radii can be found for some elements in the literature, when comparing with experimental data, we adopt *reasonable* values (given as $2.2r_M$ in the tables below) within the range given by the different authors.[94]

Appendix 2: Computational Details

All the molecular orbital calculations were of the extended Hückel type[95] using the modified Wolfsberg–Helmholz formula[96] and atomic parameters shown in Table VI. The geometries adopted for the model compounds were as follows: PH_3 groups were used as terminal ligands, with Cu–P = 2.30 and P–H = 1.35 Å and with tetrahedral bond angles. The bridging polyatomic groups used were PH_3, PH_2^-, and PH^{2-}, with Cu–P = 2.45 and P–H = 1.35 Å, and were oriented preserving a C_{2h} symmetry for the $Cu_2(PH_n)$ core. The effect of the orientation in monosubstituted bridges was studied on $[Cu_2(PH_3)_4(\mu\text{-}SH)_2]$ and $[Cu_2(PH_3)_4(\mu\text{-}OH)_2]$, with Cu–S = 2.35, Cu–O = 2.05, S–H = 1.35, and O–H = 1.35 Å. Distortions of the diamond were studied on $[Cu_2Br_4(\mu\text{-}SH)_2]^{4-}$ and $[Cu_2Br_4(\mu\text{-}SCH_3)_2]^{4-}$, with Cu–Br = 2.40, Cu–S = 2.35, S–C = 1.72, S–H = 1.35, and C–H = 1.10 Å. For the study of the ring opening, the PH_3 terminal groups were replaced by bromide ions.

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