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Hinge Distortion in Platinum(II) Dimers with a Pt_2S_2 Ring. An *ab Initio* Molecular Orbital Study

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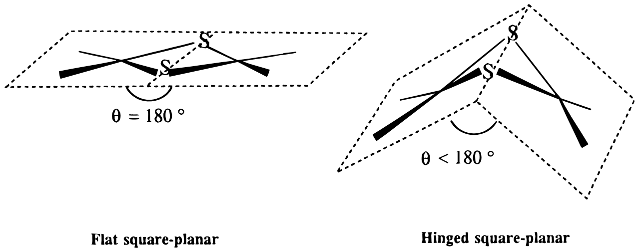
Ab initio calculations have been carried out for Pt(II) dimers with S^{2-} and/or RS^- bridging ligands in order to elucidate the factors governing the structural preference, planar or hinged, of these complexes. Calculations have been performed for systems which model all structurally characterized Pt(II) binuclear complexes. All possible determinants of the hinge angle have been taken into account in the *ab initio* calculations. These show that electronic rather than steric effects govern the geometry of the central Pt_2S_2 ring. Only one minimum of energy has been found for each complex, but the energetic cost of the hinge motion is low. Complexes with two S^{2-}, or with one S^{2-} and one RS^-, bridging ligands are hinged; the decrease of the through-ring antibonding interaction between the in-plane sulfur p orbitals with folding appears to be the determinant for hinging. Complexes with two RS^- bridging ligands can be planar or hinged depending on the relative orientation, *syn* or *anti*, of the R groups, on the nature, L_4 or L_2L_2', of the terminal ligands, and in the latter case on their disposition, *cis* or *trans*. However, the aromatic or aliphatic nature of bridging thiolates does not influence the geometry of the Pt_2S_2 ring significantly. Conclusions drawn from platinum dimers can be extended to the palladium analogs.

Introduction

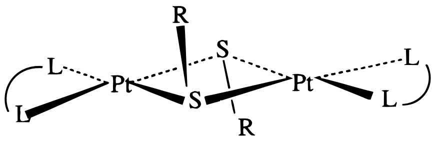
Although binuclear Pt(II) complexes with bridging S^{2-} and RS^- ligands have been known for many years, their preferred geometries are still a matter of debate. In these species each metal atom is bonded to four ligands with a square-planar coordination geometry. However, two possible structural patterns emerge, depending on the geometry of the central Pt_2S_2 ring, which can be hinged or planar. Thus, the *hinge* angle θ, the dihedral angle between the local coordination planes Pt_1SS and Pt_2SS, can be 180° and give rise to a global planar geometry, or less than 180° and thus lead to a hinged structure (Scheme 1).

The aim of this work is to contribute to the study of determinants of geometry, flat or hinged, in platinum(II) dimers with S^{2-} and RS^- bridging ligands. We have already reported the synthesis and structural characterization of a series of dimeric species of formula $[\{M(\mu\text{-SR})L_2\}_2]^{2+}$, where L_2 denotes a chelating ligand and M = Ni, Pd, or Pt.[2−4] Structural data for $[\{Pt(\mu\text{-SC}_5H_9NMe)(dppe)\}_2]^{2+}$ (dppe = $Ph_2PCH_2CH_2PPh_2$)[3] and $[\{Pt(\mu\text{-SR})(en)\}_2]^{n+}$ (en = ethane-1,2-diamine; R = $(CH_2)_3NMe_2$ or C_5H_9NMe, $n = 2$; R = C_5H_9NHMe, $n = 4$),[4] show that in all these cases the two aminothiolate ligands act as thiolate bridges between the metal atoms, giving a precisely planar central M_2S_2 ring. These platinum-containing species **(1)**, together with the significant diversity of other structurally characterized platinum complexes, provide an ideal opportunity for theoretical *ab initio* studies of the hinge distortion in dimeric Pt(II) species containing a Pt_2S_2 ring. Calculations have been carried out in model systems which include all reported Pt(II) binuclear structures with S^{2-} and/or RS^- bridging ligands. These calculations with optimization of the geometry have the great advantage of allowing a satisfactory determination of the molecular geometry and an accurate estimate of the energy difference between the possible molecular structures.

Scheme 1



Flat square-planar **Hinged square-planar**



1

(a):	**L_2= dppe**	**R= C_5H_9NMe**	**θ= 180°**	**(ref. 3)**
(b):	**L_2= en**	**R= $(CH_2)_3NMe_2$**	**θ= 180°**	**(ref. 4)**
(c).	**L_2= en**	**R= C_5H_9NMe**	**θ= 180°**	**(ref. 4)**
(d):	**L_2= en**	**R= C_5H_9NHMe**	**θ= 180°**	**(ref. 4)**

Structural Features of Complexes with a Pt_2S_2 Ring

Complexes characterized by X-ray diffraction containing a Pt_2S_2 ring show considerable structural diversity. Classification can be achieved if the nature of the bridging (S^{2-}, RS^-) and terminal ligands (L, L′) is considered. When both bridging groups reduce to S^{2-} there is a significant distortion from

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(2) Capdevila, M.; González-Duarte, P.; Foces-Foces, C.; Hernández-Cano, F.; Martínez-Ripoll, M. *J. Chem. Soc., Dalton Trans.* **1990**, 143.

(3) Capdevila, M.; Clegg, W.; González-Duarte, P.; Harris, B.; Mira, I.; Sola, J.; Taylor, I. C. *J. Chem. Soc., Dalton Trans.* **1992**, 2817.

(4) Capdevila, M.; Clegg, W.; González-Duarte, P.; Mira, I. *J. Chem. Soc., Dalton Trans.* **1992**, 173.

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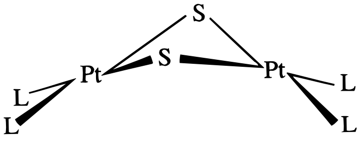
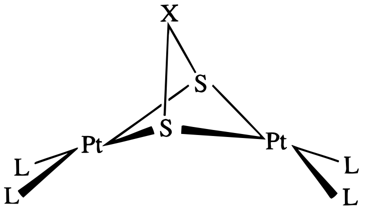
planarity with a value of $\theta = 121°$ for the complex $[Pt_2(\mu\text{-}S)_2(PMe_2Ph)_4]$ (**2**).[5] It has been reported that the closely related complex $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$, although structurally uncharacterized, behaves as a bidentate ligand through the sulfur atoms toward other transition metal ions to form heterometallic complexes. This additional coordination of sulfur can modify the geometry of the Pt_2S_2 ring. Thus, while the structure of $[Pt_2(\mu\text{-}S)(\mu\text{-}SAuPPh_3)(PPh_3)_4]^+$ remains hinged ($\theta = 135°$ as compared to 121° in **2**), complex $[Pt_2(\mu\text{-}SAuCl)_2(PPh_3)_4]$ is planar.[6] Recent reports show that $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ also behaves as a metalloligand toward main-group Lewis acids, and structures of type **3** have been obtained.[7] Geometric parameters of the Pt_2S_2 ring in **3** are slightly different from those in **2**. All complexes of type **3** are hinged with a dihedral angle θ varying between 128.3° and 135.7°.



2

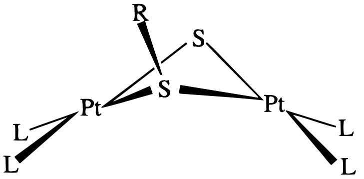
L= PMe₂Ph θ= 121° (ref. 5)



3

L= PPh₃	**X= Tl^+**	**θ= 135.7°**	**(ref. 7 a)**
	$Pb(NO_3)_2$	**θ= 132.2°**	**(ref. 7 b)**
	$Pb(NO_3)^+$	**θ= 133.5°**	**(ref. 7 b)**
	$GaCl_2^+$	**θ= 123.1°**	**(ref. 7 c)**
	$InCl_3$	**θ= 128.3°**	**(ref. 7 c)**

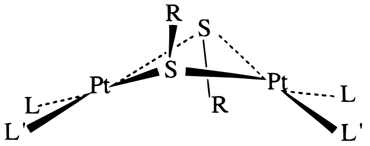
The only reported structure of a binuclear Pt(II) complex containing both S^{2-} and RS^- as bridging ligands, **4**, is also hinged with $\theta = 138°$.[8]



4

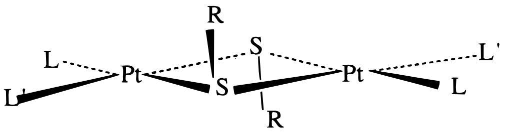
L= PPh₃ R= CH₃ θ= 138° (ref. 8)

If the two bridging ligands are thiolate groups, both structure types, hinged and planar, are found. We will consider only those where thiolate ligands do not chelate metal atoms, otherwise the natural geometry of the complex may be disturbed. In most of these complexes, bridging thiolate groups adopt an *anti* configuration with respect to each other as expected on steric grounds. The structures found for complexes of formula $[Pt_2(\mu\text{-}SR)_2L_2L'_2]$ include hinged[8,9] **(5)** and planar[10] **(6)** geometries. However, to date no relationship has been established between the relative position of terminal ligands and the geometry of the Pt_2S_2 ring, although hinged or planar rings correspond exactly to the *cis*-**5** or *trans*-**6** isomers, respectively.



5

(a):	**L= PPr₃**	**L'= Cl**	**R= CH₂CH₃**	**θ= 130°** **(ref. 9a)**
(b):	**L= PPh₃**	**L'= NO₂**	**R= CH₃**	**θ= 141°** **(ref. 8)**
(c):	**L= PMePh₂**	**L'= SCH₂Ph**	**R= CH₂Ph**	**θ= 138.8°** **(ref. 9b)**



6

L= PPh₃ L'= I R= (CH₂)₂CMe=CH₂ θ= 180° (ref. 10)

The analysis of geometrical data of structurally characterized complexes containing Pt_2S_2 rings indicates that the angle θ is not the only parameter which varies in the hinging distortions. The folding along the S···S axis imposes shorter Pt···Pt distances (for instance, Pt···Pt = 3.206 Å in **5a**[9a] and 3.539 Å in **6**[10]), although they are always too long to consider metal–metal interactions in these species. Other geometric parameters also modified with the folding are the S···S distances, which are significantly shorter in hinged structures (3.040 Å in **5b**,[8] 3.210 Å in **1a**[3]), and also the PtSPt angles, which reduce from 95° in planar structures to approximately 90° in hinged structures. Moreover, if Pt–S bond distances *trans* to phosphine ligands are compared, they tend to shorten in the hinged species.

The factors responsible for the preferred geometries in dimetallic μ-S and μ-SR complexes of platinum remain poorly understood. Several explanations have been offered, although none is conclusive. Bending in related compounds has often been ascribed to crystal–packing forces.[11] However, ^1H and ^{31}P NMR studies indicate that the *cis*-$[Pt_2(SCH_2Ph)_2(\mu\text{-}SCH_2Ph)_2(PMePh_2)_2]$[9b] and *cis*-$[Pt_2(\mu\text{-}SMe)_2Cl_2(PMe_2Ph)_2]$[12] complexes are hinged not only in the solid phase but also in solution. Folding due to steric effects may also be ruled out, since the extent of bending is the greatest in complexes containing μ-S bridges.[5-7] Consequently, electronic effects should account mainly for the hinging distortion in planar dimers. Chatt and Hart[13] proposed that the metal–sulfur interaction in alkanethiolato complexes involved an "inorganic aromatic" Pt_2S_2 ring

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(5) (a) Synthesis of **2**: Chatt, J.; Mingos, D. M. P. *J. Chem. Soc. A* **1970**, 1243. (b) X-ray data of **2** are given in ref 8 as: Mason, R.; Law, B.; Mingos, D. M. P. Unpublished results.

(6) Boss, W.; Bour, J. J.; Schlebos, P. P. J.; Hageman, P.; Bosman, W. P.; Smits, J. M.M.; van Wietmarschen, J. A. C.; Beurskens, P. T. *Inorg. Chim. Acta* **1986**, *119*, 141.

(7) (a) Zhou, M.; Xu, Y.; Koh, L.-L.; Mok, K. F.; Leung, P.-H.; Hor, T. S. A. *Inorg. Chem.* **1993**, *32*, 1875. (b) Zhou, M.; Xu, Y.; Lam, C.-F.; Koh, L.-L.; Mok, K. F.; Leung, P.-H.; Hor, T. S. A. *Inorg. Chem.* **1993**, *32*, 4660. (c) Zhou, M.; Xu, Y.; Lam, C.-F.; Leung, P.-H.; Koh, L.-L.; Mok, K. F.; Hor, T. S. A. *Inorg. Chem.* **1994**, *33*, 1572.

(8) Briant, C. E.; Gardner, C. J.; Hor, T. S. A.; Howells, N. D.; Mingos, D. M. P. *J. Chem. Soc., Dalton Trans.* **1984**, 2645.

(9) (a) Hall, M. C.; Jarvis, J. A. J.; Kilbourn, B. T.; Owston, P. G. *J. Chem. Soc., Dalton Trans.* **1972**, 1544. (b) Bird, P. H.; Siriwardane, U.; Lai, R. D.; Shaver, A. *Can. J. Chem.* **1982**, *60*, 2075.

(10) Abel, E. W.; Evans, D. G.; Koe, J. R.; Hursthouse, M. B.; Mazid, M.; Mahon, M. F.; Molloy, K. C. *J. Chem. Soc., Dalton Trans.* **1990**, 1697.

(11) Parra-Hake, M.; Retting, M. F.; Wing, R. M. *Organometallics* **1983**, *2*, 1013.

(12) Jain, V. K.; Rao, G. S. *Inorg. Chim. Acta* **1987**, *127*, 161.

(13) Chatt, J.; Hart, F. A. *J. Chem. Soc.* **1960**, 2807.

in which p electrons from the sulfur atoms were delocalized. However, the X-ray structure determination of **5a**, showing the Pt_2S_2 ring to be nonplanar ($\theta = 130°$) and the thiolato α-carbons to be out of the PtSPt plane,[9a] rules out this aromatic ring system. Another hypothesis establishes that bridging alkanethiolates lead to hinged geometries while arenethiolates give rise to planar structures.[14] Our structural characterization of a series of complexes **1** with bridging alkanethiolate ligands has shown that they are all exactly planar,[1−4] and thus the nature of the thiol cannot be considered a factor. Recently, Golen et al.,[14] on the basis of an experimental study of the determining effects of sulfur substituents on the geometries of dipalladium μ-SR complexes, suggest that distortion from planarity leads to reinforcement of bonding interactions between sulfur and metal orbitals. This suggestion merits complementary theoretical studies.

Several structural aspects of dimeric complexes of the $L_2M(\mu\text{-}X)_2ML_2$ type have been studied theoretically by means of extended Hückel calculations. Hoffmann et al.[15] have analyzed those factors that influence the geometry and electronic structure of dimeric tetrahedral and square-planar transition metal complexes of the M_2L_6 type. The work of Albright et al.[16] considers $[Rh_2(CO)_4(PH_2)_2]$ as a model of a bridging phosphide transition metal dimer. Both studies show that there is an extremely flat potential for hinging and conclude that no single orbital is responsible for controlling the distortion. Recently, Alvarez et al.[17] have developed a qualitative bonding model to interpret bonding and structure in binuclear complexes of d^{10} metals with a tetrahedral coordination[17a] and have extended it to edge-sharing dimers of square-planar complexes, emphasizing the presence of M···M bonding.[17b] To our knowledge no single theoretical *ab initio* study has been devoted to the analysis of the hinge distortion in dimeric species of d^8-ML_4 square-planar fragments.

Results and Discussion

In order to perform theoretical studies, the following complexes of known structure were chosen: $[\{Pt(\mu\text{-}S)(PMe_2Ph)_2\}_2]$ [5,8] **(2)**, $[Pt_2(\mu\text{-}S)(\mu\text{-}SMe)(PPh_3)_4]^+$ [8] **(4)**, $[\{Pt[\mu\text{-}SC_5H_9NMe](dppe)\}_2]^{2+}$ [3] **(1a)**, and *cis*-$[Pt(\mu\text{-}SEt)Cl(PPr_3{}^n)]_2$[9a] **(5a)**, as representative of different coordination environments in dinuclear platinum complexes containing a central Pt_2S_2 ring, in an attempt to illustrate the geometrical regularities. Bridging groups in the first three complexes are, respectively, both sulfide, sulfide and thiolate, or both thiolate groups, the main feature of the fourth complex lying in the different nature of terminal ligands. Then, a theoretical *ab initio* study was carried out in order to find the most stable geometry for the complex. The first step involved modeling the system so that the number of basis functions is markedly reduced. Accordingly, phosphine ligands were replaced by PH_3, and thiolate or aminothiolate by SCH_3 groups. Then, the optimization of the geometry led to the most stable structure, which corresponds to a minimum on the full potential energy surface. In some cases geometrical restrictions were imposed to approximate the model more closely to the experimental complex. Finally, the energy difference between the planar and the hinged structures was calculated in each case. The results thus obtained for each complex are now given under separate headings.

Complexes with Two Sulfide Bridges, Pt(μ-S)$_2$Pt. As a model for complexes with two sulfide bridges we chose $[Pt_2(\mu\text{-}S)_2(PH_3)_4]$ **(7)**. The optimized geometry of this model compound (Figure 1) shows a hinged structure with a rather small dihedral angle, $\theta = 134°$, between the two PtSS planes. This angle and the calculated bond distances and angles corresponding to the Pt_2S_2 ring (Table 1) compare well with the experimental values found for **2**.[5,18,19] The calculated dihedral angle is also close to the experimental values found in the series of complexes **3**.[7]

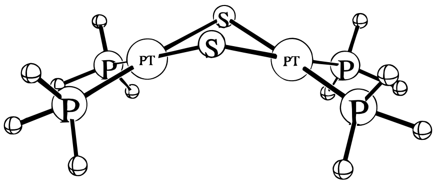


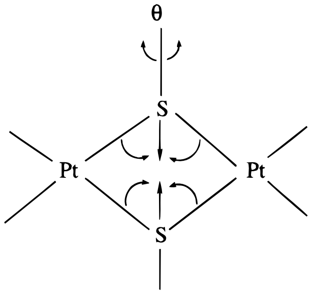
Figure 1. Optimized geometry of $[Pt_2(\mu\text{-}S)_2(PH_3)_4]$ **(7)**.

Table 1. Most Relevant Optimized Geometrical Parameters[a] for $[\{Pt(\mu\text{-}S)(PH_3)_2\}_2]$ **(7)** and X-ray Diffraction Values for $[\{Pt(\mu\text{-}S)(PMe_2Ph)_2\}_2]$ **(2)**

	opt[b]	planar[c]	expt[d] (**2**) (refs 5 and 8)
Pt−S	2.391	2.389	2.340
Pt−P	2.279	2.287	2.265
Pt···Pt	3.271	3.512	3.175
S···S	3.200	3.294	3.060
∠PtSPt	86.3	94.6	85.5
∠SPtS	84.0	85.4	81.6
∠PPtP	100.9	99.9	*e*
θ	134.0	180.0[c]	121

[a] Distances in Å; angles in deg. [b] Fully optimized. [c] θ angle fixed at 180°. [d] Mean values. [e] Not given.

Scheme 2



In order to analyze the effects of distortion, the value of the dihedral angle was fixed at 180° in the model compound and the geometry was optimized (Table 1). The comparison of the hinged and planar structures of $[Pt_2(\mu\text{-}S)_2(PH_3)_4]$ indicates that besides the expected decrease in the PtPt distance, the hinge distortion is accompanied by a significant decrease in the SS distance (0.1 Å), and also by a decrease in the PtSPt angle, which closes by about 8°. As already indicated, all these structural consequences of folding are observed when comparing compounds structurally characterized by X-ray diffraction. The main movements that folding involves are depicted in Scheme 2.

The energy difference between the two geometries calculated for **7** gives the energy cost of the distortion: 6.1 kcal/mol. The optimization of the geometry, starting from the planar structure and removing the constraint, leads to the same hinged structure, confirming that this geometry corresponds to the only minimum in the potential surface of the system. Therefore, it is not

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(14) Padilla, E. M.; Golen, J. A.; Richmann, P. N.; Jensen, C. M. *Polyhedron* **1991**, *10*, 1343.

(15) Summerville, R. H.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 7240.

(16) Kang, S.-K., Albright, T. A.; Wright, T. C.; Jones, R. A. *Organometallics* **1985**, *4*, 666.

(17) (a) Alemany, P.; Alvarez, S. *Inorg. Chem.* **1992**, *31*, 4266. (b) Aullón, G.; Alemany, P; Alvarez, S. *J. Organomet. Chem.* **1994**, *478*, 75.

(18) Very recently, the X-ray structure of $[Pt_2(\mu\text{-}S)_2(dppy)_4]$ (dppy = 2-diphenylphosphinopyridine) has been reported, but in contrast with **2** it shows a flat square-planar geometry.[19]

(19) Yam, V. W. W.; Yeung, P. K. Y., Cheung, K. K. *J. Chem. Soc., Chem. Commun.* **1995**, 267.

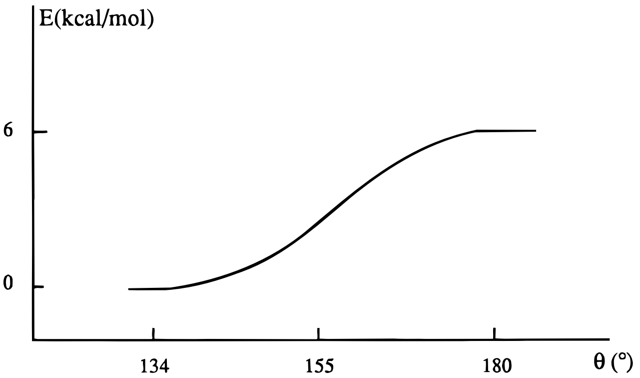


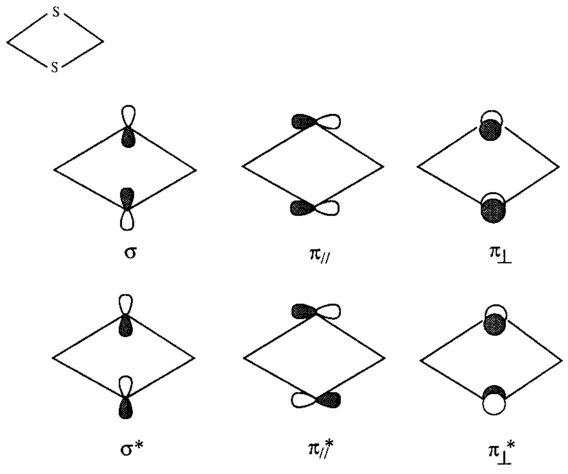
Figure 2. Potential curve for the hinging motion in $[Pt_2(\mu\text{-}S)_2(PH_3)_4]$ **(7)**.

possible to observe an equilibrium between the two structures. Starting from the geometry corresponding to the minimum energy ($\theta = 134°$), we calculated the potential curve for the hinging motion, optimizing the rest of the geometric parameters at different values of θ (Figure 2).

The potential curve for hinging is very flat, as previous extended Hückel calculations indicated.[15,16] The planar structure is exactly the transition state for the process of ring inversion, which connects two equivalent folded structures. The fact that the potential barrier for the process is rather low suggests that compounds of this type may show fluxionality associated with ring inversion. This possibility has been discussed in the complex $[(dppe)Pt(\mu\text{-}SMe)_2PtClMe_3]$ from ^1H and ^{31}P variable temperature studies.[20]

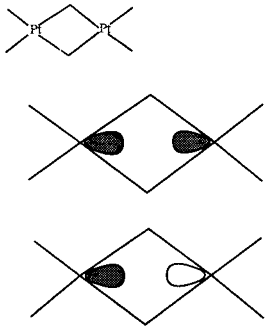
Although structural data on experimental complexes with two bridging sulfide and terminal chelating ligands are not available, the effect of the latter on the folding of the Pt_2S_2 ring was analyzed. A chelating phosphine imposes a rigid PPtP angle, which is about 85° in complexes with sulfur-bridged aminothiolate and terminal dppe ligands.[3] This is significantly narrower than 100°, which is often found in nonchelating terminal phosphine ligands. In order to model dppe in the calculations, we optimized the geometry of **7** while fixing the value of the PPtP angle at 85.1°. In this case we also found that the most stable geometry is hinged. However, the degree of folding was smaller, since the resultant θ is 146° rather than 134° in the unconstrained compound. We also optimized the system with PPtP = 85.1° and an imposed planar Pt_2S_2 ring. Now the energy difference between the planar and hinged structure was 3.0 kcal/mol, which is lower than in the unconstrained one. Accordingly, terminal chelating ligands favor less-folded structures.

Factors Governing the Hinge Distortion in Pt(μ-S)$_2$Pt Complexes. Extended Huckel studies[15] on the hinging motion in several d^8 square-planar bridged dimers, although not conclusive, show that the factors responsible for the distortion do not come from the occupied d block orbitals of the species. These orbitals are bonding and antibonding combinations of a square-planar splitting pattern. The two highest occupied orbitals in a d^8-d^8 dimer are derived from z^2. Below these are the six occupied levels which originate from xz, yz, and $x^2 - y^2$. Their energy ordering follows the normal sequence $\sigma < \pi < \delta < \delta^* < \pi^* < \sigma^*$.[16] However, only a small splitting is expected due to the long Pt−Pt distance. Consequently, we will concentrate on the analysis of the four MOs responsible for the four Pt−S bonds in the dimer. These orbitals can be constructed from the interaction of orbitals of two fragments, $[Pt_2L_4]^{4+}$ and $(S_2)^{4-}$, according to previous analysis.[17] The final orbitals in the $(S_2)^{4-}$ fragment are the bonding and the antibonding combinations of the p_s orbitals, **8**. In agreement with the electron-counting scheme that we have adopted, all these orbitals are full. Two of these orbitals, which evolve in the plane perpendicular to the Pt_2S_2 ring ($\pi_\perp$ and $\pi_\perp^*$), do not participate significantly in interactions with empty orbitals of the metallic fragment. In fact, they are responsible for the complex $[Pt_2(\mu\text{-}S)_2(PR_3)_4]$ behaving as a metalloligand toward Lewis acids.

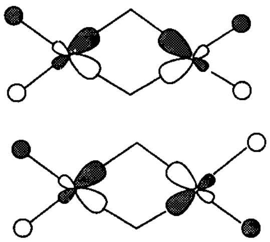


8

Let us consider the ring Pt_2S_2 to be planar. The orbitals σ-(S_2) and $\pi_{\parallel}(S_2)$ interact with the bonding and antibonding combinations of the sp orbitals of the metallic fragment **9a**, while the $\sigma^*(S_2)$ and $\pi_{\parallel}^*(S_2)$ interact with the bonding and antibonding xy orbitals of the same fragment **9b**, which are antibonding metal terminal ligand orbitals.



9a



9b

The four orbitals of the metallic fragment are empty, and only the bonding Pt−S orbitals resulting from the interactions are occupied. The highest coefficients in these MOs are those corresponding to the sulfur atoms. The final result of the interactions between the two fragments is the formation of four bonding Pt−S MOs, together with the stabilization of the four orbitals of the fragment $(S_2)^{4-}$. However, two of these MOs have antibonding S−S character. The antibonding interaction within the π^* cannot be strong owing to the long S−S distance, but the one due to the frontal overlap of the two $p_s(\sigma^*)$ may still be significant.

If the Pt_2S_2 ring folds, the orbitals described are modified. Folding involves the disappearance of the Pt_2S_2 plane as a symmetry plane of the molecule and allows mixing of those orbitals that were symmetric or antisymmetric in respect to this symmetry element. Specifically, bonding and antibonding

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[20] Abel, E. W.; Cooley, N. A.; Kite, K.; Orrell, K. G.; Sik, V.; Hursthouse, M. B.; Dawes, H. M. *Polyhedron* **1987**, *6*, 1261.

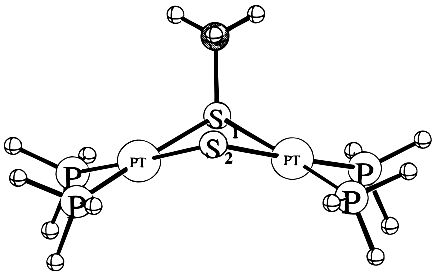


Figure 3. Optimized geometry of $[Pt_2(\mu\text{-}S)(\mu\text{-}SCH_3)(PH_3)_4]^+$ **(11)**.

combinations of *xy* orbitals can be mixed with the corresponding combinations of the *xz* orbitals **(10)**.

10

The result of folding is a better overlap of σ^* and π^* orbitals with the appropriate combinations of *xy* from the metallic fragment. This leads to a greater stability of these antibonding S−S combinations, especially that of σ^*, with a greater electron transfer to the empty metal orbitals and the concomitant reduction of the antibonding S−S interactions. In agreement with that, the S−S distance shortens with folding. The occupied metal *xz* combinations are destabilized upon folding, but the fact that **7** shows a hinged structure indicates that the stabilization effects induced by folding should overcome the accompanying destabilization. The hinge distortion is related to the through-ring antibonding interaction between the sulfur p orbitals. The driving force for folding is the decrease in this antibonding interaction, and the energy gain associated may compensate the destabilization linked to distortion (narrower Pt−S−Pt angles).

The destabilization of the *xy* orbitals of the metallic fragment decreases their interaction with the orbitals of the $(S_2)^{4-}$ fragment and, consequently, the tendency to fold. This is exactly the effect of chelating terminal ligands. The dppe ligand imposes a much narrower P−Pt−P angle and thus raises the energy of the *xy* orbitals.

Complexes with Sulfide and Thiolate Bridges, Pt(*μ*-S)(*μ*-SR)Pt. We chose the complex $[Pt_2(\mu\text{-}S)(\mu\text{-}SMe)(PPH_3)_4]^+$ **(11)** as a model for complexes with sulfide and thiolate bridges, **4**. The optimization of the unconstrained geometry led to a folded structure with a hinging angle of 136.9° (Figure 3). The main parameters of the optimized structure and those of the experimental complex $[Pt_2(\mu\text{-}S)(\mu\text{-}SMe)(PPh_3)_4]^+$ **(4)**[8] are given in Table 2.

Table 2. Most Relevant Optimized Geometrical Parameters[a] for $[Pt_2(\mu\text{-}S)(\mu\text{-}SCH_3)(PH_3)_4]^+$ **(11)** and X-ray Diffraction Values for $[Pt_2(\mu\text{-}S)(\mu\text{-}SCH_3)(PPh_3)_4]^+$ **(4)**

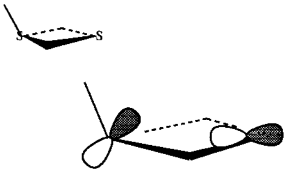
	opt	expt[b] (**4**) (ref 8)
$Pt-S_1$	2.438	2.363
$Pt-S_2$	2.373	2.320
$Pt-P_1$	2.322	2.292
$Pt-P_2$	2.273	2.268
S_1-C	1.838	1.810
$Pt\cdots Pt$	3.359	3.306
$S_1\cdots S_2$	3.178	3.060
$\angle PtS_1Pt$	87.1	88.9
$\angle PtS_2Pt$	90.1	90.9
$\angle S_1PtS_2$	82.7	81.6
$\angle P_1PtP_2$	96.4	100.6
$\angle CS_1Pt$	102.2	102.0
θ	136.9	138.0

[a] Distances in Å, angles in deg. [b] Mean values.

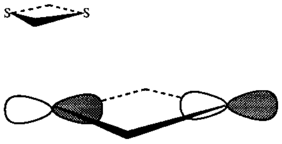
All the features of the experimental complex **4** are well reproduced in the calculated geometry. This agreement is particularly good for the hinging angle, $\theta_{exp} = 138°$ and $\theta_{calc} = 136.9°$. The optimized Pt−SR distance, 2.438 Å, is somewhat longer than that of Pt−S, 2.373 Å. The sulfur atom of the thiolate group shows a significant distorted pyramidal geometry with a $C-S_1-Pt$ angle of 102.2° and $Pt-S_1-Pt$ angle of 87.1°. Optimization of **11** imposing planarity in the Pt_2S_2 ring leads to a structure which has an energy 6.8 kcal/mol above the minimum. Those geometric parameters that have changed most are the PtPt and SS distances, which have increased up to 3.562 and 3.227 Å, respectively, and the PtS_1Pt and PtS_2Pt angles, which have opened up to 93.7 and 97.7°, respectively (see Scheme 2).

Optimization of the geometry of **11** fixing the P−Pt−P angles at 85.1°, simulating the bite angle of the dppe ligand, also leads to a hinged structure, although deviation from planarity is now less marked. The hinging angle is 140.9°, compared with 136.9° calculated when the system has no constraints on the angles of terminal ligands.

The results obtained for **11** with sulfur and thiolate bridging ligands are close to those found for **7**, with two sulfide bridging ligands. In both cases complexes tend to adopt a hinged structure, with a slightly lower folding in the case of **11**. This fact can be explained following the analysis already developed, which emphasized the antibonding S−S interactions as the main cause for the distortion. This interaction is smaller in complexes (*μ*-S)(*μ*-SR) **12a** than in complexes $(\mu\text{-}S)_2$ **12b** owing to the fact that the participating p orbital of sulfur in SR points out of the plane.



12a



12b

Complexes with Two Thiolate Bridges, LL′Pt (*μ*-SR)₂PtLL′. *Complexes with L = L′ = PR₃.* The structurally characterized platinum complex **1a** with bridging thiolate and terminal phosphine ligands is planar, $\theta = 180°$.[3] This complex has dppe as chelating terminal ligands and sulfur-bonded aminothiolate bridging ligands with an *anti* conformation. Theoretical studies have been carried out with $[Pt_2(\mu\text{-}SR)_2(PH_3)_4]^{2+}$ **(13)** as a model complex, and we have analyzed separately how the presence of chelating or nonchelating terminal ligands, the aliphatic or aromatic nature of the bridging aminothiolate groups, and their *anti* or *syn* conformation influence the structure.

The geometry of the complex $[Pt_2(\mu\text{-}SMe)_2(PH_3)_4]^{2+}$ has been optimized considering an *anti* configuration of the bridging ligands (*anti*-**13**). As shown in Figure 4a this geometry is planar, $\theta = 180°$, with PtPt and SS distances of 3.613 and 3.262 Å, respectively. The energetic cost for the hinge motion is small. A 20° folding, $\theta = 160°$, corresponds to an energy of only 1.8 kcal/mol above the minimum.

In order to evaluate the effect of R linked to the sulfur atom, the geometry of complex $[Pt_2(\mu\text{-}SR)_2(PH_3)_4]^{2+}$ with R = $CH{=}CH_2$ in *anti* conformation **(14)** has been optimized. We assumed that a vinyl group could be taken as the simplest model for an arenethiolate. Complex **14** is also planar, and there are only minor changes in the geometry compared with *anti*-**13** (PtPt = 3.625 Å; SS = 3.280 Å) (Figure 4b). The S−C distance

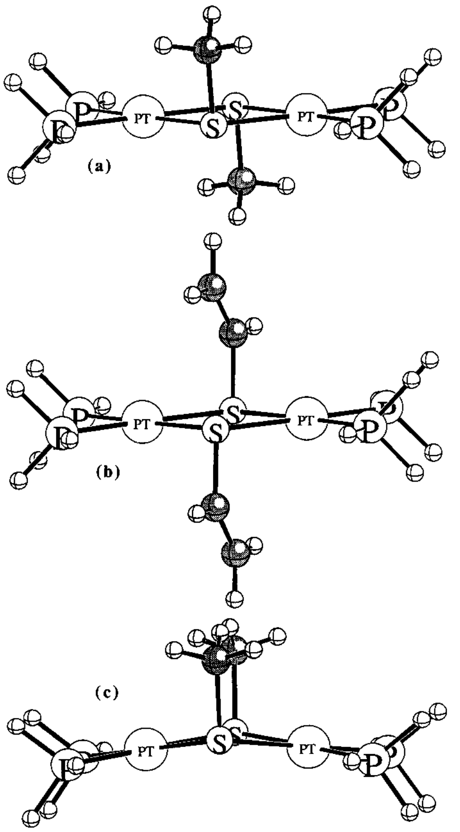


Figure 4. Optimized geometry of the complexes (a) *anti*-$[Pt_2(\mu\text{-}SCH_3)_2(PH_3)_4]^{2+}$ (*anti*-**13**), (b) *anti*-$[Pt_2(\mu\text{-}SCHCH_2)_2(PH_3)_4]^{2+}$ (**14**), and (c) *syn*-$[Pt_2(\mu\text{-}SCH_3)_2(PH_3)_4]^{2+}$ (*syn*-**13**).

Table 3. Most Relevant Optimized Geometrical Parameters[a] for *anti*-$[\{Pt(\mu\text{-}SCH_3)(PH_3)\}_2]^{2+}$ (*anti*-**13**) and X-ray Diffraction Values for $[\{Pt(\mu\text{-}SC_5H_9NMe)(dppe)\}_2]^{2+}$ **(1a)**

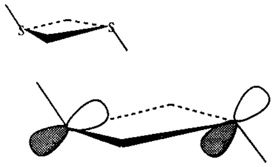
	opt	expt[c] (**1a**) (ref 3)
Pt−S	2.427	2.393
Pt−P	2.323	2.263
S−C	1.843	1.873
Pt···Pt	3.588	3.550
S···S	3.268	3.210
∠PtSPt	95.4	95.7
∠SPtS	84.7	84.3
∠PPtP	85.1[b]	84.7
∠CSPt	102.7	102.6
θ	180.0	180.0

[a] Distances in Å; angles in deg. [b] Fixed. [c] Mean values.

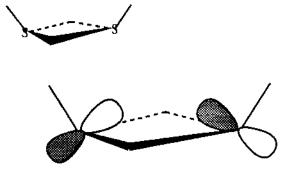
decreases slightly from 1.844 to 1.799 Å, thus reflecting the π system delocalization.

Both previous calculations show that $(\mu\text{-}SR)_2$ complexes containing terminal nonchelating phosphines should be planar. In order to compare theoretical and experimental results in complexes **1**, we reoptimized the system *anti*-**13** while constraining both P−Pt−P angles to 85.1°. We have already shown that terminal chelating ligands decrease the tendency to fold in complexes with $(\mu\text{-}S)_2$ and $(\mu\text{-}SR)(\mu\text{-}S)$ bridges. With this constraint, the optimized geometry remained planar, as expected. Optimized geometric parameters together with the experimental X-ray values for **1a** are given in Table 3. The calculated geometry for *anti*-**13** agrees well with experimental values found for **1a**.[3]

The preference of *anti*-**13** for a planar structure can also be explained by taking into account the antibonding SS interaction. If bridging thiolate ligands in **13** adopt an *anti* configuration, then the strongest antibonding SS interaction is significantly decreased because the participating p_s orbitals point up and down from the Pt_2S_2 plane, **15a**, and thus do not have a frontal overlap. In agreement with this argument it can be deduced that when R groups adopt a *syn* conformation there must be a change in order to decrease the stronger antibonding **15b**.



15a



15b

The geometry of **13** was then optimized with a *syn* orientation of the methyl groups (*syn*-**13**). The energy of **13** optimized with either *anti* or *syn* configuration is practically the same, the latter being only 0.7 kcal/mol more stable, which shows that although most of the experimental $(\mu\text{-}SR)_2$ complexes have an *anti* configuration, it should be possible to obtain them with a *syn* configuration unless steric repulsions involving the R substituents prevent it. The recently reported complex $[Pt_2(\mu\text{-}L\text{-}accys\text{-}S)_2(bpy)_2]$ (accys = $SCH_2CH(COO)NHC(O)CH_3$)[21] **(16)** shows that the accys ligands are in a *syn* configuration. The *syn* and *anti* isomers are interconverted by inversion at the sulfur atom. This process is fast in solution, as NMR studies for complex $[Pt_2(\mu\text{-}L\text{-}accysH_2\text{-}S)_2(NH_3)_4]^{2+}$ have shown.[22]

The optimized geometry of *syn*-**13** is slightly hinged with $\theta = 163.2°$ (Figure 4c). The Pt_2S_2 ring has folded away from the R groups. This value agrees well with $\theta_{exp} = 166.2°$ of **16**. The rest of the optimized geometric parameters are similar to those of the *anti* isomer. The *syn* planar structure is only 1.3 kcal/mol above the minimum corresponding to the hinged geometry. If the P−Pt−P angle is fixed at 85.1°, the system keeps the hinged geometry with $\theta = 164.3°$.

Although the puckering of the $M_2(CO)_2$ rhomboid in *cis*-$Cp_2Fe_2(CO)_4$ has been interpreted in terms of reinforcement of the metal−bridging ligands interactions with folding,[23] this argument seems not to be at work here. If Pt−S distances in the hinged ($\theta = 166°$) *syn*-$[Pt_2(\mu\text{-}L\text{-}accys\text{-}S)_2(bpy)_2]$[21] are compared with those found in the planar complexes $[Pt_2(\mu\text{-}SR)_2(en)_2]^{n+}$ (R = $(CH_2)_3NMe_2$ or C_5H_9NMe, $n = 2$; R = C_5H_9NHMe, $n = 4$),[4] no significant differences are found. The same happens in the case of sulfur-bridged $Pt(\mu\text{-}S)_2Pt$ complexes, as the Pt−S bond distance is 2.340(8)Å in $[Pt_2(\mu\text{-}S)_2(PMe_2Ph)_4]$ ($\theta = 121°$)[5,8] and 2.333(1) Å in $[Pt_2(\mu\text{-}S)_2(dppy)_4]$ ($\theta = 180°$).[19] Thus, the fact that important variations in the dihedral angles are not accompanied by relevant changes in the Pt−S distances allows us to conclude that in our systems the Pt−S interactions cannot be responsible for the geometry adopted by the Pt_2S_2 ring.

Complexes with L ≠ L′ (Where L = PR₃). Among the dimers of formula $LL'Pt(\mu\text{-}SR)_2PtLL'$ characterized structurally, some are known to have hinged (**5a**−**c**[8,9]) and other planar (**6**[10]) central Pt_2S_2 rings. In all cases the R groups of bridging thiolates adopt an *anti* configuration. The theoretical study has been carried out with the model complex $[Pt_2(\mu\text{-}SCH_3)_2Cl_2(PH_3)_2]$ **(17)**. Both *cis* and *trans* isomers have been considered with an *anti* configuration of the thiolate ligands.

The optimized geometry of *cis*-**17**, which models the experimental complex **5a**, is hinged, with $\theta = 132°$ (Figure 5a), in excellent agreement with the experimental angle found for **5a**,

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(21) Mitchell, K. A.; Streveler, K. C.; Jensen, C. M. *Inorg. Chem.* **1993**, *32*, 2608.
(22) Appleton, T. G.; Connor, J. W.; Hall, J. R.; Prenzler, P. D. *Inorg. Chem.* **1989**, *28*, 2030.
(23) Jemmis, E. D.; Pinhas, A. R.; Hoffmann, R. *J. Am. Chem. Soc.* **1980**, *102*, 2576.

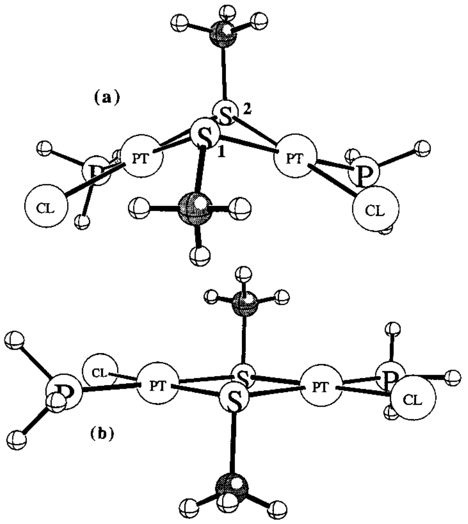


Figure 5. Optimized geometry of the complexes (a) *cis*-[$Pt_2(\mu$-$SCH_3)_2Cl_2(PH_3)_2$] (*cis*-**17**) and (b) *trans*-[$Pt_2(\mu$-$SCH_3)_2Cl_2(PH_3)_2$] (*trans*-**17**).

Table 4. Most Relevant Optimized Geometrical Parameters[a] for *cis*-[{$Pt(\mu$-$SCH_3)Cl(PH_3)\}_2$] (*cis*-**17**) and X-ray Diffraction Values for [{$Pt(\mu$-$SCH_2CH_3)Cl(PPr_3)\}_2$] **(5a)**

	opt	expt[b] (**5a**) (ref 8)
Pt−S_1	2.424	2.371
Pt−S_2	2.424	2.274
Pt−P	2.264	2.262
Pt−Cl	2.451	2.339
C_1−S_1	1.826	1.890
C_2−S_2	1.851	1.860
Pt···Pt	3.363	3.206
S_1···S_2	3.156	2.990
∠PtS_1Pt	87.8	85.1
∠PtS_2Pt	87.8	89.7
∠C_1S_1Pt	107.8	110.9
∠C_2S_2Pt	103.4	106.4
∠ClPtP	87.2	89.0
θ	132.0	130.0

[a] Distances in Å, angles in deg. [b] Mean values.

$\theta = 130°$.[9a] Other geometric parameters of the optimized structure are not in such good agreement with the experimental values as in the other complexes studied. This reflects the difficulty of reproducing in the calculations the delicate *trans* influences, which appear in a square-planar complex with dissymmetric ligands. The main parameters of the optimized structure and those of the experimental complex **5a** are given in Table 4.

Optimization of *cis*-**17** imposing planarity on the Pt_2S_2 ring leads to a structure whose energy is 6.9 kcal/mol above the minimum. The energy difference between the hinged and planar structures is of the same order as those calculated for other complexes. Analogous to previous cases, the geometric parameters that have changed most when imposing a planar Pt_2S_2 ring are PtPt and SS distances, which have increased, and the Pt−S−Pt angles that have opened up.

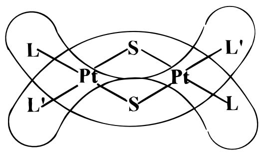
The lack of planarity in the Pt_2S_2 ring in **5a** has been attributed to intramolecular crowding between the alkyl groups on the phosphorus and sulfur atoms.[9a] However, the fact that we have found the same hinging angle for the model complex *cis*-**17**, with PH_3 and SCH_3 as ligands, as for **5a** leads us to disregard the previous hypothesis.

To determine whether the nature of the R group of the thiolate ligand has a significant influence on the geometry of the complex we have optimized the geometry of **17** where the methyl groups have been substituted by vinyl groups (R = $CH{=}CH_2$). The optimized geometry of complex *cis*-[$Pt_2(\mu$-$SCH{=}CH_2)_2Cl_2(PH_3)_2$] (*cis*-**18**) is similar to that of *cis*-**17**. The most remarkable feature is that the hinging angle is modified little. The structure remains strongly hinged, with $\theta = 133.1°$, and PtPt and SS distances are 3.374 and 3.174 Å, respectively. This result is analogous to those found in complexes with terminal phosphine ligands, *anti*-**13** and **14**, where the replacement of CH_3 by $CH{=}CH_2$ does not modify the planar geometry of the Pt_2S_2 ring. Consequently, it seems clear that the nature of substituents in thiolate groups does not have a decisive influence on the geometry of the ring.

In order to take into account the influence of the relative disposition of terminal ligands, *cis* or *trans*, bonded to the two platinum atoms, the structure of **17** with two *trans* chlorine atoms (*trans*-**17**) has been optimized. The result obtained is different from the one found with *cis*-**17**; the geometry of complex *trans*-**17** is practically planar, with $\theta = 178.3°$ (Figure 5b), which agrees with the experimental structure of the complex *trans*-[$Pt_2(\mu$-$S(CH_2)_2C(CH_3){=}CH_2)_2(PPh_3)_2I_2$] with a planar Pt_2S_2 ring.[10] Thus, the results from the theoretical study of complexes *anti*-[$Pt_2(\mu$-$SR)_2L_2L'_2$] clearly indicate that the geometry of the Pt_2S_2 ring is determined by the *cis* or *trans* disposition of the terminal ligands.

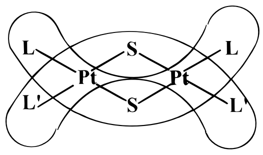
We also checked that *anti*-[$Pt_2(\mu$-$SR)_2L_4$] complexes are planar not only when L = PR_3 but also if L = Cl. Accordingly, the geometry of the model complex *anti*-[$Pt_2(\mu$-$SCH_3)_2Cl_4]^{2-}$ **(19)** has been optimized, and the θ angle found is 178.4°.

The previous results indicate that *anti* complexes are planar either if the four terminal ligands are equal or if the different terminal $L_2L'_2$ ligands have a *trans* disposition, **20a**. However, if the latter adopt a *cis* arrangement, **20b**, the Pt_2S_2 ring is hinged. The different geometrical preferences of *cis*- and *trans*-[$Pt_2(\mu$-$SR)_2L_2L'_2$] dimers can be related to the structural *trans* influence[24] of terminal ligands. Accordingly, as depicted in **20a**, both bridging sulfur atoms undergo the same *trans* influence in the case of *trans*-[$Pt_2(\mu$-$SR)_2L_2L'_2$], and also in that of [$Pt_2(\mu$-$SR)_2L_4$], and thus the central Pt_2S_2 ring is planar in both families of complexes. This is not the case for the *cis* isomer **20b**, where the different *trans* influence of L_2 and L'_2 terminal ligands on each sulfur atom may give rise to two different Pt−S bond strengths, causing an important strain in the Pt_2S_2 ring, which could be compensated by the loss of planarity. This rationalization agrees well with the finding that *cis*-[$Pt_2(\mu$-$SR)_2(PR_3)_2L'_2$] complexes of known structure, L′ = Cl **(5a)**, NO_2 **(5b)**, and SCH_2Ph **(5c)**, are hinged and have two different Pt−S bond distances. Unfortunately, our theoretical calculations do not lead us to two different Pt−S distances in *cis*- and *trans*-[$Pt_2(\mu$-$SCH_3)_2Cl_2(PH_3)_2$] complexes, which have been taken as models for *cis*-**17** and *trans*-**17**, respectively, so the hypothesis may be invalid. However, the different values calculated for the θ angle in the complexes *cis*-**17** ($\theta = 132°$) and *trans*-**17** ($\theta = 178°$) clearly show that the relative disposition of the terminal ligands, L′, determines the geometry, planar or hinged, of the Pt_2S_2 ring in complexes of formula [$Pt_2(\mu$-$SR)_2L_2L'_2$].



trans

20a



cis

20b

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(24) Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335.

Conclusions

In this work an *ab initio* theoretical study of the determinants of the structure, planar or hinged, of Pt(II) dimers with S^{2-} and RS^{-} bridging ligands has been carried out. Due to computational limitations, the calculations have been carried out for model systems, with PH_3 as phosphine and CH_3 or $CH{=}CH_2$ as the R groups bound to sulfur. Despite these substitutions, the hinging angles in the optimized geometries of all complexes are very close to the experimental values, showing that the theoretical calculations are valid for determining this geometrical parameter and also that the electronic rather than the steric effects determine the structure of these complexes.

In these calculations all the determinants that could influence the geometry of the complexes have been examined. On the one hand, the nature of the bridging ligands has been considered, and thus the cases of having two sulfur, sulfur and thiolate, or two thiolate ligands have been analyzed. In this latter case the effect of the nature of the R groups of the thiolate ligands and their *anti* or *syn* orientation has been considered. Concerning the terminal ligands, several alternatives have been taken into account: four unidentate equal ligands, two chelating equal ligands, or two different types of unidentate ligands adopting either *cis* or *trans* geometries.

For the model systems studied the energy difference between the hinged and planar structures has been calculated. In all cases these energy differences are small, showing that important variations of the hinging angle have a small energetic cost. This fact could explain that hinged complexes may show fluxionality in solution, associated with ring inversion. Owing to the level of calculation employed in our theoretical study, the calculated energetics for the hinge motion must only be taken as an approximate estimation. Unfortunately, the size of the computed systems prevents a more accurate calculation nowadays.

The decrease in the through-ring antibonding interaction between the in-plane sulfur p orbitals with folding appears to be the dominant factor that causes all the complexes with two bridging sulfur ligands to be hinged. The presence of chelating terminal ligands destabilizes the orbitals of the metallic fragment that can interact with sulfur p orbitals and thus decreases the tendency to folding. In complexes with one sulfur and one thiolate as bridging ligands the cause of hinging is the same through-ring antibonding interaction.

In complexes with two thiolate bridging ligands there is greater complexity as the through-ring antibonding interaction between sulfur p orbitals is weaker. Consequently, more factors have to be taken into account. We have shown that the nature of the R group in the bridging thiolate ligands does not influence the geometry of the Pt_2S_2 ring significantly. In contrast, the relative orientation, *syn* or *anti*, of these R groups is important. When the R groups have an *anti* configuration, the through-ring antibonding interaction is very weak, and thus the complexes with the thiolate groups in an *anti* configuration and with four equal terminal ligands are planar. The stronger through-ring antibonding interaction gives rise to folding of the Pt_2S_2 ring in complexes with the same terminal ligands but with the R groups *syn*. However, this hinging is smaller than that observed when the two bridging groups are sulfur ligands. In complexes where the two terminal ligands of each metallic center are different and the bridging ligands have an *anti* configuration, it is the *cis* or *trans* disposition of the terminal ligands that determines the geometry of the ring, which should be planar for the *trans* isomer and hinged for the *cis* one. Due to the fact that the configuration is *anti*, the antibonding interaction of the sulfur p orbitals cannot account for the folding. Although our calculations are not conclusive, this folding can be attributed to the different *trans* influence of the terminal ligands. In *cis* complexes the Pt−S bonds to one sulfur are different from those to the other sulfur atom, and those in which the S atom is *trans* to the ligand with minor *trans* influence are stronger. The difference in Pt−S bond strength may lead to a significant increase in strain in the Pt_2S_2 ring, which could be relieved by the loss of planarity. Finally, it is also noticeable that in all systems folding around the S···S axis is accompanied by other structural changes; not only is there a decrease of PtPt distance, but the SS distance and PtSPt angles also change markedly. On the contrary, Pt−S bond distances do not change significantly with folding.

Although all calculations here reported have been carried out on Pt(II) dimers with a Pt_2S_2 ring, we believe our conclusions could be extended to the homologous Pd(II) complexes, since structural parameters of the Pd(II) dimers with thiolate bridging ligands found in the literature can also be rationalized with the previous arguments.

Details of the *ab Initio* Calculations

Ab initio self-consistent field (SCF) calculations were carried out with the GAUSSIAN 92 system of programs.[25] The basis set used was valence-double-ξ quality for the platinum atoms,[26a] valence-double-ξ + polarization functions for the sulfur atoms,[26b] valence-double-ξ for the chlorine atoms[26c] and for the carbon and hydrogen atoms[26d] of the thiolato ligands, and minimal for the H[26e] and P[26c] atoms of the PH_3 groups. An effective core potential (ECP) operator was used for the core electrons of platinum,[26a] phosphorus,[26c] and chlorine[26c] atoms.

The internal structure of the phosphines was kept frozen (P−H = 1.42 Å; H−P−H = 93.2°). All the other geometrical parameters were optimized by the Schlegel method,[27] using analytically computed gradients. In order to evaluate energy differences between isomeric species, correlation energy was introduced at the SCF-optimized geometries using the Möller−Plesset perturbation theory up to second order (MP2).[28] All the energy differences given in this paper correspond to the MP2 calculations.

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(25) Frish, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M.W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andrés, J. L.; Raghavachari, K.; Binkley, J. S.; González, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. *GAUSSIAN 92*; Gaussian Inc.: Pittsburgh, PA, 1992.

(26) (a) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270. (b) Prieto, W. J.; Franci, M. M.; Hehre, W. J.; Defrees, D. J.; Pople, J. A.; Binkley, J. S. *J. Am. Chem. Soc.* **1982**, *104*, 5039. (c) Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, *82*, 284. (d) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939. (e) Hehre, W. J.; Stewart, R. E.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657.

(27) Schlegel, H. B. *J. Comput. Chem.* **1982**, *3*, 214.

(28) Möller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.