

Toroidal Nickel Thiolates: Structure and Bonding

Pere Alemany[†] and Roald Hoffmann*

Contribution from the Department of Chemistry and Materials Science Center, Cornell University, Ithaca, New York 14853-1301

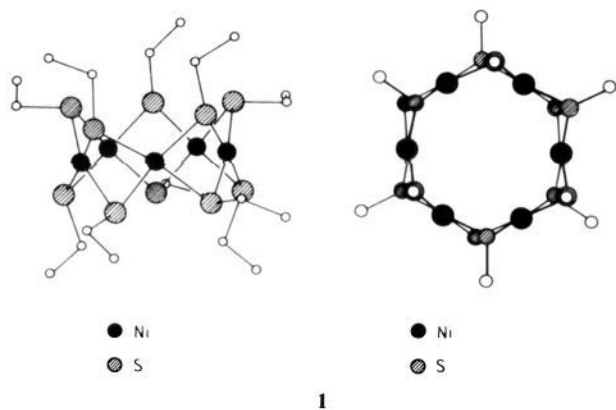
Received February 17, 1993

Abstract: The bonding in toroidal nickel thiolates is studied using extended Hückel calculations. Structural features are found to be dominated by Ni–S bonding. Ni–Ni and S···S interactions do not seem to play important roles in the framework bonding of these compounds, except for the case of three- and four-membered rings, where repulsive metal–metal interactions are responsible for the movement of nickel atoms outward from the toroid. Formation of strongly bound host–guest complexes is unlikely for *tiara*-nickel thiolate compounds. Substitution of sulfur by oxygen, additional ligands on the outer surface of the toroid, and replacement of nickel atoms by transition metals with a lower d-electron count should lead to compounds with good inclusion capabilities.

Thiolate, SR, ligands have been known since the beginnings of coordination chemistry and have played an important role in the development of inorganic chemistry. These ligands have a strong affinity to many metals, to which they bind in terminal, μ_2 -bridging or μ_3 -bridging modes, creating a large variety of structural possibilities.^{1,2} Polynuclear complexes with thiolate or sulfido coordination spheres have been and are intensively studied, mainly due to their importance in biological processes, where these types of compounds play an important function at the active center of many enzymes.³

Tiara Structures

In this paper we address some structural features found in the general class of compounds $[M(SR_2)]_n$ with (M = Ni, Pd). These possess cyclic molecular structures^{4–13} for $n = 4, 5, 6,$ or 8 (see 1). Each metal atom is coordinated by four sulfur atoms in an



1

approximately square planar arrangement. The whole structure

[†] On leave from the Departament de Química Física, Universitat de Barcelona, Barcelona, Catalunya (Spain).

(1) Müller, A.; Diemann, E. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon Press: Oxford, England, 1987; Vol. 2, pp 515–550.

(2) Dance, I. G. *Polyhedron* **1986**, *5*, 1037–1104.

(3) Krebs, B.; Henkel, G. *Z. Naturforsch., Int. Ed. Engl.* **1991**, *30*, 769.

(4) Gaete, W.; Ros, J.; Solans, X.; Font-Altaba, M.; Briansó, J. L. *Inorg. Chem.* **1984**, *23*, 39–43.

(5) Krüger, T.; Krebs, B.; Henkel, G. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 61–62.

(6) Kriege, M.; Henkel, G. *Z. Naturforsch.* **1987**, *42b*, 1121–1128.

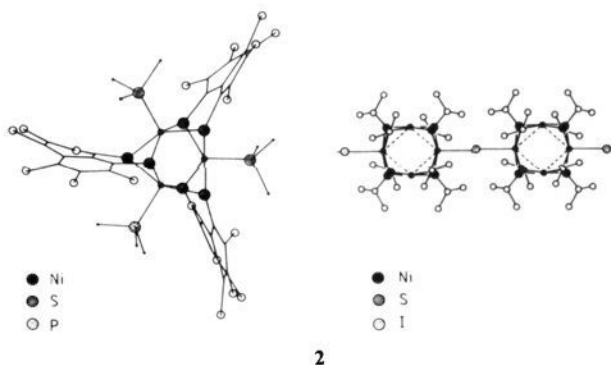
(7) Koo, B.-K.; Block, E.; Kang, H.; Liu, S.; Zubieta, J. *Polyhedron* **1988**, *7*, 1397–1399.

(8) Kunchur, N. R. *Acta Crystallogr.* **1968**, *B24*, 1623–1633.

(9) Woodward, P.; Dahl, L. F.; Abel, E. W.; Crosse, B. C. *J. Am. Chem. Soc.* **1965**, *87*, 5251–5253.

is that of a polygonal toroid with faces formed by MS_4 groups. Alternatively, the structure can be described as a regular polygon of metal atoms sandwiched by two polygons of sulfur atoms. The sulfur atoms then form a prismatic polyhedron. The metal polygon is rotated with respect to the sulfur planes so that the metal atoms lie approximately on the rectangular faces of the sulfur prism. Some authors have also used the descriptive term *tiara* for this type of structure.

Closely related structures (see 2) are obtained by capping some or all of the rectangular faces of the toroid by another substituent.^{14,15} In these compounds the coordination of the metal atoms sitting on the capped faces is changed from the original square planar to square pyramidal. Sharing of these additional substituents can lead to extended structures, as shown in 2. Fusion of six-membered polygonal toroids is the basic structural motif of the metal–chalcogen layers found in $Cs_2Pd_3S_4$.¹⁶



2

In this paper we will use an approximate molecular orbital approach, the extended Hückel method^{17,18} (see Appendix for computational details), to probe diverse questions of bonding and structure in these compounds. In the first section we address the problem of possible metal–metal and sulfur–sulfur bonding

(10) Gould, R. O.; Harding, M. M. *J. Chem. Soc. A* **1970**, 875–881.

(11) Barrera, H.; Bayón, J. C.; Suades, J.; Germain, C.; Declercq, J. P. *Polyhedron* **1984**, *3*, 969–975.

(12) Miyamae, H.; Yamamura, T. *Acta Crystallogr.* **1988**, *C44*, 606–609.

(13) Dance, I. G.; Scudder, M. L.; Secomb, R. *Inorg. Chem.* **1985**, *24*, 1201–1208.

(14) Bosman, W. P.; van der Linden, H. G. M. *J. Chem. Soc., Chem. Commun.* **1977**, 714–715.

(15) Krüger, T.; Krebs, B.; Henkel, G. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 54–56.

(16) Huster, J.; Bronger, W. *J. Solid State Chem.* **1974**, *11*, 254.

(17) Hoffmann, R.; Lipscomb, W. N. *J. Chem. Phys.* **1962**, *36*, 2176–2195.

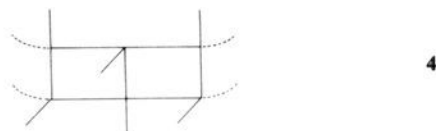
(18) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397–1412.

interactions stabilizing the framework. In a second section we study the possibility, suggested by some authors,^{9,13} of forming inclusion compounds by inserting atoms or small molecules in the central hole of the ring.

As has already been mentioned in the introduction, metal atoms in these complexes are in approximately square planar (or square pyramidal) coordination. All compounds are in fact more or less distorted from the ideal square planar to a rectangular coordination (see 3). Another general trend, especially important for

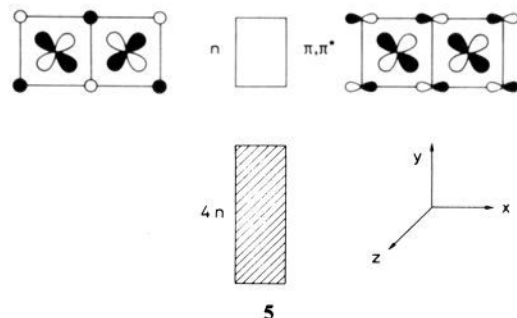


small rings, is the displacement of the metal atoms out of the plane formed by the four sulfur atoms. In all cases known the metal atoms are displaced outward from the torus. Two orientations are found for the ligands R at the sulfurs: some ligands, called "axial", are oriented parallel to the axis passing through the center of the toroid; other ligands, called "equatorial", may be roughly normal to the surface of the toroid. In general the ligands are disposed alternately axial and equatorial (see 4), although perfect alteration is not possible for odd-membered rings. In the latter, two ligands of the same type are found on neighboring sulfur atoms.



Metal-Metal Interactions

With the most important structural features thus described, we move on to the electronic aspects. The first question we will try to answer is that of possible weak metal-metal interactions. Known *tiara*-nickel thiolates possess Ni-Ni distances ranging from 2.64 to 3.05 Å. At the low end of the range, these are relatively short, compared to the distance of 2.49 Å in the metal.¹⁹ Is there any metal-metal interaction in these compounds? Consider first a "monomer" unit of the *tiara* and then the whole ring. The square planar crystal field is strong, and we fully expect a 4 below 1 crystal field splitting in each "monomer". The destabilized orbital is locally *xy*. In the *tiara* (5) the *d* orbitals



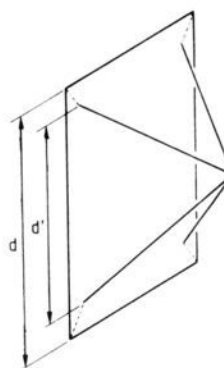
of the *n* metal atoms in the square planar units give upon interaction two blocks of MOs. The lower block, containing 4*n* orbitals, is totally filled for a *d*⁸ electron count. The upper block, formed by the combinations of the strongly destabilized *xy* orbitals, is empty. Each of these blocks contains an equal number of bonding and antibonding orbitals. The result is no net interaction between the metals if the blocks are completely filled or empty, as one expects for the *d*⁸ electron count. Some authors have suggested that the short intermetallic distances are probably due

(19) Pearson, W. B. *Handbook of Lattice Spacings of Metals and Alloys*; Pergamon Press: New York, 1958.

to weak bonding interactions originating from mixing of empty metal *s* and *p* orbitals into the filled *d* combinations.^{4,20} Others have attributed the displacement of metal atoms out from the toroidal frame to avoidance of repulsive metal-metal interactions.²⁰

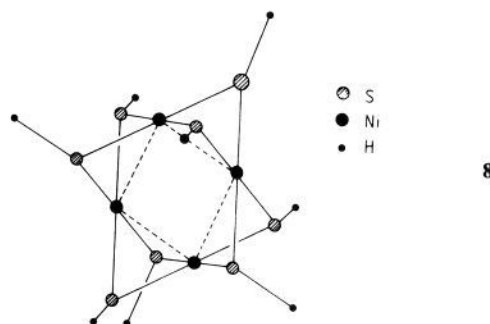
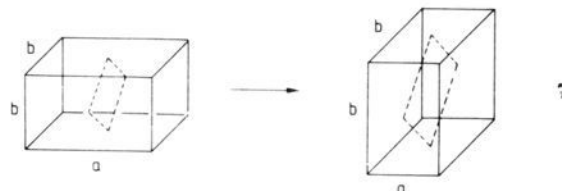
S...S Interactions

A second interesting question raised for these compounds is that of possible stabilizing S...S interactions. The distances between S atoms on different sides of the plane containing the metal atoms are shorter than distances between neighboring sulfur atoms on the same side of the metal plane (see 3). The short S...S distances (2.8–2.9 Å) are quite long, compared to regular S-S bonds (~2.0 Å), but they are certainly shorter than twice the van der Waals radius of sulfur (1.80 Å). Some authors^{4,20} have suggested that metal atoms are displaced out of the sulfur planes in order to provide such short distances. Moving the metal atoms toward the plane of sulfur atoms would separate the sulfurs, as shown in 6, weakening in this way the whole structure.



Analysis

We will start our analysis by looking at the relative importance of Ni-Ni and S...S interactions in the stability of a model (Ni(SH)₂)₄ compound. The geometry used for this compound (see 7 and 8) consists of a square prism of sulfur atoms that contains



a rhombus of nickel atoms in its interior. All four nickel atoms lie exactly on the rectangular faces of the sulfur prism. We will distort the prism by changing the length of its edges *a* and *b*, while maintaining the Ni-S distance ($d_{\text{Ni-S}} = \frac{1}{2}\sqrt{(a^2 + b^2)}$)

(20) Fackler, J., Jr. *Prog. Inorg. Chem.* 1976, 21, 55-90.

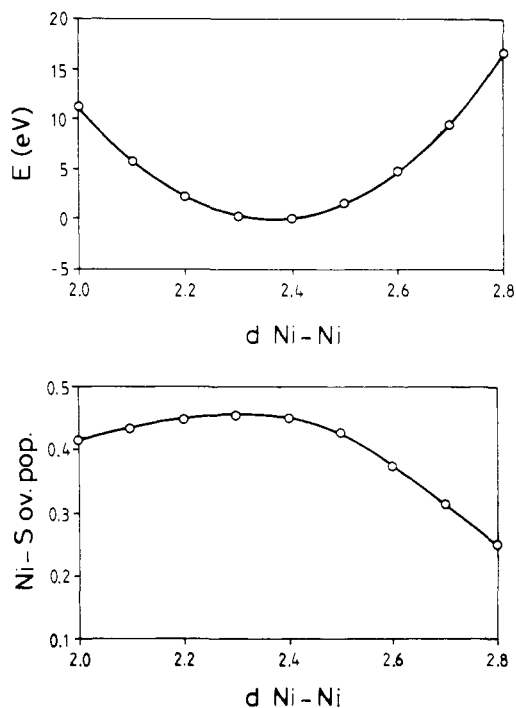
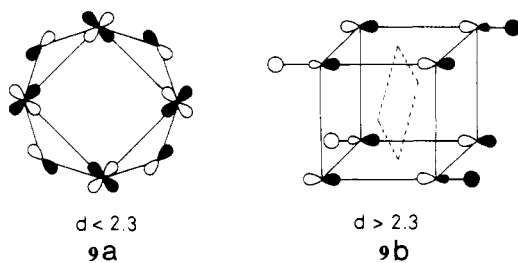


Figure 1. Variation of the total energy (a, top) and the Ni-S overlap population (b, bottom) with the Ni-Ni distance in the $(\text{Ni}(\text{SH})_2)_4$ model compound.

fixed at the average experimental value of 2.21 Å. It is easy to see that bringing the Ni atoms together (reducing the value of b) increases the close S...S contacts a . From this distortion we will try to determine the relative importance of both types of interaction. Figure 1a shows the evolution of the total energy with the Ni-Ni distance. The most stable geometry is found for a Ni-Ni distance of 2.4 Å (corresponding to $a = 2.80$ Å and $b = 3.4$ Å), all values close to the experimental results.

Examining the different interactions in this geometry, one notices that Ni-Ni overlap populations are negative (thus antibonding in character), even at Ni-Ni distances as short as 2.0 Å. On the other hand, the overlap population found for the S...S pairs is negligible, indicating their nonbonding nature. From a Walsh diagram (not shown in the figure) one can see that the energy minimum for $d_{\text{Ni-Ni}} = 2.4$ Å is determined mainly by the variation in energy of the HOMO with the distance. For short Ni-Ni separations the HOMO is a metal-centered orbital with strong Ni-Ni antibonding character (9a) which is highly destabilized on moving the metal atoms together. For long Ni-Ni distances (short S...S contacts) the HOMO is a sulfur-centered orbital with σ antibonding character (9b) and is highly destabilized on separating the nickel atoms (pushing the S atoms together). The slopes of these two orbitals determine the optimal geometry of the compound.



A look at the variation of Ni-S overlap population with Ni-Ni distance (Figure 1b) shows that it is maximal in the optimum geometry. From our analysis we can conclude that it is the Ni-S interactions which are mainly responsible for the geometry of the

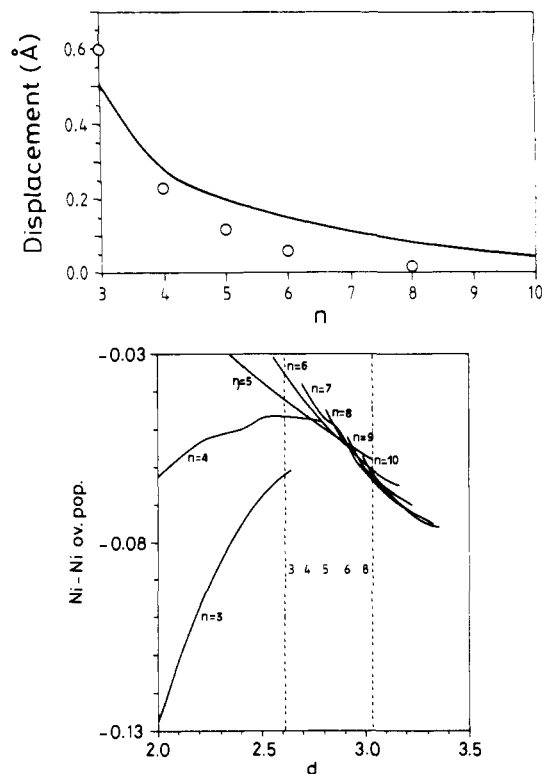


Figure 2. (a, top) Calculated (solid line) and experimental values for the displacement of the nickel atoms from the sulfur planes for rings with $n = 3-10$. (b, bottom) Ni-Ni overlap population vs Ni-Ni distance for toroids with $n = 3-10$. The shortest Ni-Ni distances correspond to nickel atoms displaced into the central hole; the longest distance corresponds to nickel atoms displaced outward from the toroid. Vertical lines indicate the range of Ni-Ni distances found for the known compounds. The numbers between the dashed lines indicate average metal-metal distances for each ring size.

ring. S...S contacts have a negligible role, while Ni-Ni interactions seem to provide, if anything, a destabilizing contribution.

Pyramidalization at Ni

What is the driving force for the displacement of the Ni atoms from the sulfur planes? For this purpose we performed calculations for the model compounds $[\text{Ni}(\text{SH})_2]_n$ with $n = 3-10$. In these calculations we use a fixed value of 2.21 Å for the Ni-S distances. The arrangement of sulfur atoms on each side of the metal plane is kept constant during the distortion. The only sulfur framework structural parameter that is changed upon moving the nickel atoms is the distance between both sulfur planes (short S...S contacts). The radius of the circumscribed circle of the sulfur polygon is taken from the experimental data. For the 7-, 9-, and 10-membered toroids, for which no experimental structure is known, it is extrapolated.

Figure 2a shows both the calculated optimum displacements, as well as the experimental values found for the different toroids. Calculations and experiments agree reasonably in their trends. The magnitude of the displacement diminishes with increasing ring size. This effect has been attributed by some authors to Ni-Ni repulsive interactions, which should be stronger in small rings where the metal atoms are closer together.⁶

Our calculations indicate a slightly different explanation. The variation of Ni-Ni overlap population with the Ni-Ni distance (Figure 2b) reveals that small rings ($n = 3, 4$) behave in a different way than larger ones. In this figure, the longest Ni-Ni distance corresponds to the maximum displacement of nickel atoms out of the toroid, while the shortest distance corresponds to a displacement of the metal atoms into the central hole of the compound. Ni-Ni overlap populations are negative, indicating

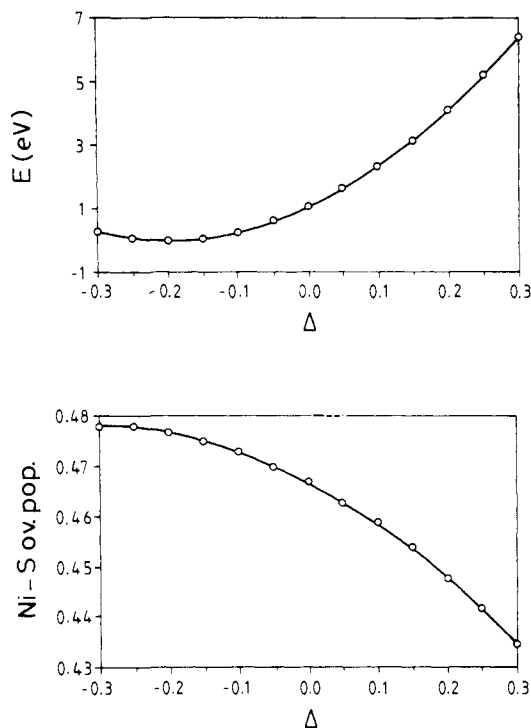


Figure 3. Variation of energy and Ni-S overlap population with the displacement of the nickel atoms from the sulfur planes. Positive values for the displacement indicate movement toward the interior of the toroid.

repulsive antibonding interactions between metal atoms. For small rings (three- and four-membered rings), this antibonding interaction decreases strongly in magnitude on increasing the Ni-Ni distance by moving the nickel atoms out of the toroid. This is no longer the case for the larger rings. For these, the opposite behavior is found: separating the metal atoms results in a stronger repulsive interaction (decrease in the overlap population). Our calculations predict significant antibonding interactions for nickel atoms separated by distances over 3.0 Å. This counter-intuitive behavior is an indirect interaction,²¹ as may be checked by performing a calculation for the isolated metal ring with the same geometry. In that case the metal-metal overlap populations at such long distances are vanishingly small.

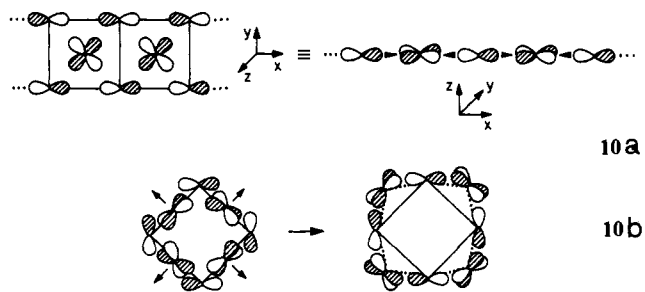
If Ni-Ni repulsive interactions are not responsible for the displacement of metal atoms out of the toroids for the five-membered rings, how can we explain the experimental displacement of 0.1 Å found for these compounds? Why don't we find for larger rings a displacement of the metal atoms to the interior of the toroid, minimizing in this way the Ni-Ni repulsive interactions?

To answer these questions we analyzed in detail the case of the five-membered ring. The optimum position for the nickel atoms (Figure 3) is reached when the Ni-S overlap population reaches its maximum. On moving the nickel atoms toward the center of the toroid, the Ni-S overlap population diminishes rapidly.

It is possible to explain qualitatively why the Ni-S overlap population peaks at a 0.3-Å displacement out of the ring. Take a typical Ni-S bonding orbital **10** (one of several, the one shown is for a four-membered ring) and look at it "from the top", along the toroid axis, as in **10a**. Note that the bonding overlap is not optimal and can be improved if the Ni centers move "out", as in **10b**.

We can deduce thus that the most important factor determining the structure of the nickel-sulfur framework is maximum Ni-S bonding and that Ni-Ni repulsive interactions are only a secondary effect, at least for large rings. We think that short S...S contacts are unimportant in determining the stability of the toroids.

(21) Alemany, P.; Alvarez, S. Unpublished work.

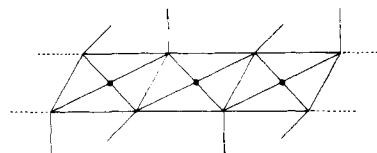


Capping Ligands

The effect of a capping substituent on the displacement of the nickel atoms out of the torus has also been analyzed, although it has been found that it does not affect the general trend. For the case of the three-membered ring, calculations with SH-ligands on the nickel atoms show that the addition of these substituents helps to pull the metal atoms away from the sulfur frame. The optimum displacement increases from 0.6 to 0.7 Å when these ligands are included in the model. This effect seems to be especially important for the three-membered rings; the only known compound of this class has these extra ligands, which help to reduce metal-metal repulsions. Another important effect of the capping substituents is that of localizing an orbital (the z^2 orbital if the four sulfur atoms are located in the xy plane) pointing into the central hole of the compound. This important feature will be discussed below; it influences the possibility of inclusion of atoms or small molecules in the toroids.

Planar Ribbon

Would the nickel atoms lie in the sulfur planes for very large rings? The energetics of the displacement of the atoms out of the plane (Figure 2a) seems to indicate that this is the case. To further analyze this question we have performed tight-binding extended Hückel band structure calculations^{22,23} on the one-dimensional model shown in **11**, which may be considered as an infinite-membered toroid. This ribbon-like structure of square planar metal atoms has been proposed by some authors for some insoluble nickel mercaptides of as yet undetermined structure.²⁴



11

The band structure (Figure 4) shows that the general features described above for the rings apply in this case as well. Two empty π -type bands (bonding and antibonding) are well-separated from the rest of the d block. Negative overlap populations indicate an antibonding interaction between metal atoms separated by 3.30 Å. Indirect interactions result also in this case in an unexpectedly high overlap population (-0.09) at large distances. Figure 5 shows that (as predicted from the calculation on small rings) in this case the preferred position of the nickel atoms is in the sulfur plane. A possible distortion that would decrease the Ni-Ni antibonding interactions would move the nickel out of the sulfur plane but in opposite directions for neighboring nickel atoms (**12**). The structure with this zig-zag atom chain is calculated to be less stable than the regular ribbon. The reason for this is again the loss in Ni-S bonding caused by the distortion.

We've also done some calculations for the ribbon with all the "equatorial" ligands on the same side. The result is slightly

(22) Whangbo, M.-H.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 6093.
 (23) Whangbo, M.-H.; Hoffmann, R.; Woodward, R. B. *Proc. R. Soc. London, A* **1979**, *366*, 23.
 (24) Jensen, K. A. Z. *Anorg. Allg. Chem.* **1944**, *252*, 227.

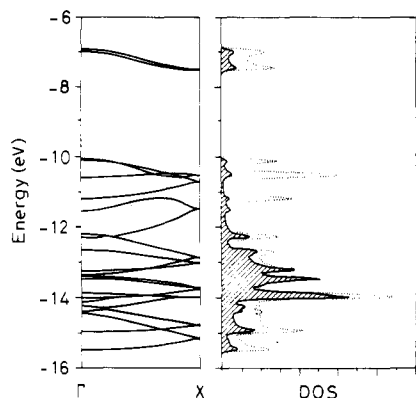


Figure 4. Band structure and density of states plot for the hypothetical $\text{Ni}(\text{SH})_2$ infinite chain.

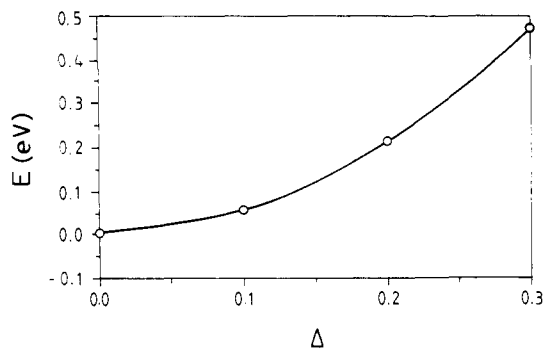
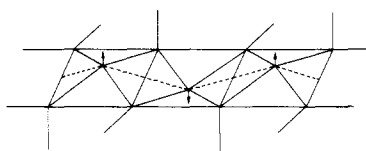


Figure 5. Relative energy for the displacement of nickel atoms from the ideal square planar coordination in the sulfur plane for the $\text{Ni}(\text{SH})_2$ infinite chain.



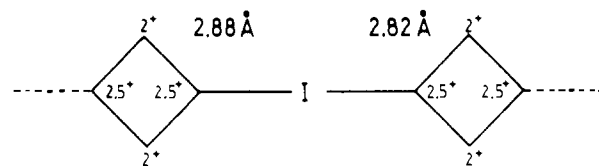
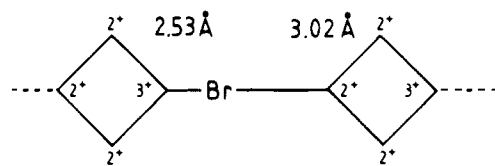
12

different: The minimum energy is obtained when the nickel atoms lie a little bit (0.1 Å) out of the plane, on the opposite side from the ligands. The energy difference between this geometry and the one with the metals in the plane is very small (about 0.03 eV/Ni atom). Moving the atoms further outside (around 0.3 Å) results in a large destabilization (1.5 eV/Ni atom). Moving the metal atoms out of the plane on the side of the ligands results in a strong destabilization. From these results one can extrapolate that in large ribbons the nickel atoms could be slightly displaced toward the interior of the toroid.

Asymmetry in Halogen-Bridged Necklaces

The syntheses of other interesting extended systems related to the family of the *tiara*-nickel thiolates have been recently reported by Krüger, Krebs, and Henkel.¹⁵ The crystal structures of these compounds reveal that they are one-dimensional infinite chains consisting of individual $[\text{Ni}_4(\text{S}(i\text{-C}_3\text{H}_7))_8\text{X}]$ ($\text{X} = \text{I}, \text{Br}$) molecules threaded in necklace fashion along their Ni-X axes (see right side of 2). Two different types of nickel atoms may be distinguished in these compounds: there are square planar nickel atoms and square pyramidal ones, the latter coordinated to the four sulfur atoms of the toroid and the halogen atom shared by two neighboring *tiaras*.

An interesting problem that arises is the different position of the halogen atom between two successive toroids in the chain arrangement. For the compound formed with bromine, the molecular $[\text{Ni}_4(\text{S}(i\text{-C}_3\text{H}_7))_8\text{Br}]$ units are clearly distinguished, and the halogen atom is located in an asymmetric position between both nickel atoms (13 top). Krüger et al.¹⁵ assign a 3+ oxidation



13

state to the nickel atom with the short Ni-Br distance and 2+ to the three remaining metal atoms of each thiolate complex. In the iodine compound, the halogen atom is found in a symmetric position midway between both nickel atoms. In this case Krüger et al.¹⁵ propose a formal oxidation state of 2.5+ for both nickel atoms bonded to the iodine atom and 2+ for the remaining nickel atoms in the structure (13 bottom). Here we try to determine if the differing positions of the halogen atom are dictated by electronic factors.

Our calculations indicate (Figure 6a) that in both cases the symmetric position of the halogen atom is favored over the distorted one. If one looks at the average overlap population for both Ni-X bonds in these compounds, the minimum is also found for the symmetric position (Figure 6b), although there is a much larger gain in bonding with asymmetrical distortion for the compound with bromine. We repeated our calculations for $\text{X} = \text{Cl}, \text{F}$ and there are no new features. Our conclusion is that there is no clear electronic origin for the distortion observed for the bromine compound. Crystal packing effects are probably responsible for the structures observed.

Possible Inclusion Structures

The last question we will address is the possibility of inserting atoms or small molecules in the central hole of the toroid, as suggested by some authors.^{9,13} In these compounds the "d_{z²}" and "p_z" type orbitals of the nickel atoms are oriented radially, in principle available for bonding with centrally placed atoms or molecules. In this section we will analyze the interaction of the six-membered *tiara*-nickel thiolate with several atomic and molecular species.

Figure 7 (left) shows schematically the orbital interactions observed for the inclusion compound formed with a main group element cation (In^{3+} in our example). The complex is calculated to be weakly stabilized, mainly due to the interaction of the empty s orbital on the cation with two filled ring orbitals of high symmetry. A reviewer has suggested that a proton might fit well into some of these toroids. Indeed we obtain a very similar stabilization for H^+ as for In^{3+} .

The case of a halide ion (Cl^-) shown in Figure 7 (right) is different. Interaction with the now much lower lying s orbital is not strong enough to push the antibonding combination into the region of empty orbitals. The net result is a destabilization of the inclusion complex, due to the two-orbital-four-electron interaction.²⁵ In the case of the halide anions, p orbitals of the central atom interact with symmetry-matching orbitals of the ring, yielding a second destabilizing factor. These interactions were negligible for the case of In^{3+} , due to the poor energy match.

(25) Albright, T. A.; Burdett, J. K.; Whangbo, M. H. *Orbital Interactions in Chemistry*; John Wiley & Sons: New York, 1985.

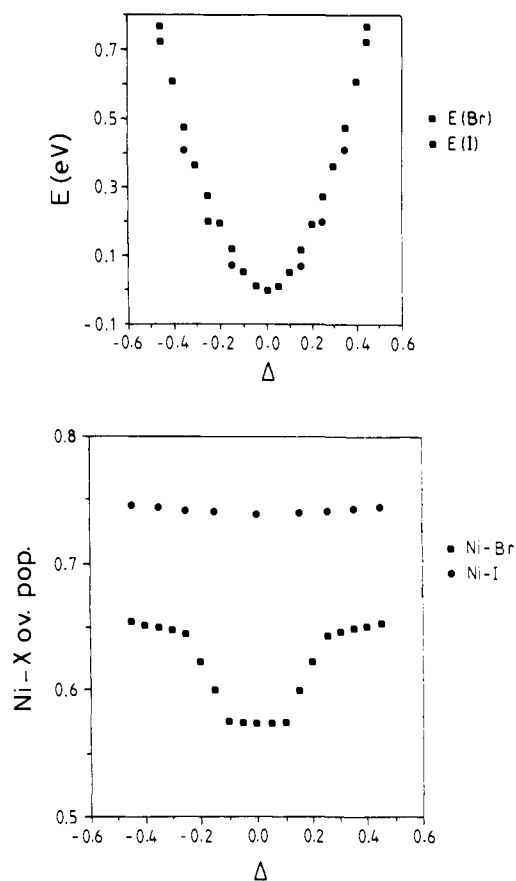


Figure 6. Relative energies (a, top) and averaged Ni-X overlap populations (b, bottom) for the movement of Br or I between two neighboring nickel thiolate units. $\Delta = 0$ corresponds to the symmetric position. The Ni-Ni distance is kept fixed at the experimental values found for both compounds.

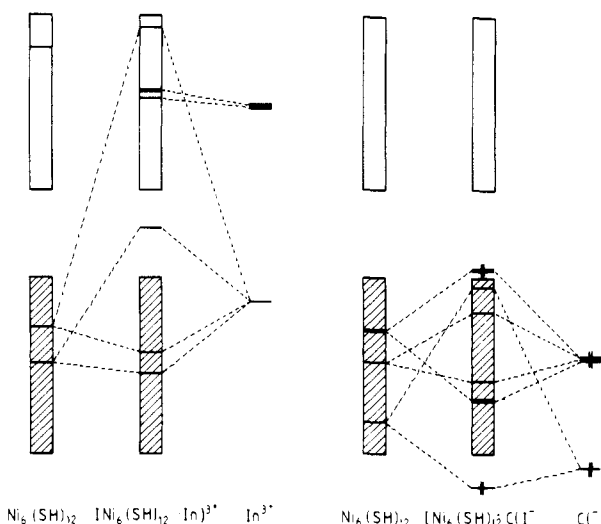


Figure 7. Schematic interaction diagrams for $[\text{Ni}(\text{SH})_2]_6$ and In^{3+} (left) and for $[\text{Ni}(\text{SH})_2]_6$ and Cl^- (right).

An interaction diagram (not shown in the figure), calculated for a transition metal ion (Ni^{2+}) in the hole, gives results very similar to those obtained for main group elements. The low lying d orbitals of the central atom interact with appropriate symmetry filled orbitals of the ring, giving bonding and antibonding combinations that are not very much separated in energy due to the poor overlap. For high d electron counts, two-orbital-four-electron interactions predominate and only very weak binding due to the interaction of empty d levels and filled thiolate orbitals is found. s and p

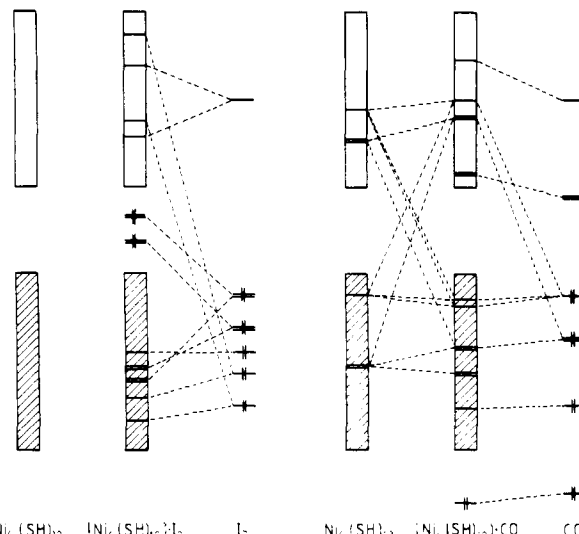


Figure 8. Schematic interaction diagrams for $[\text{Ni}(\text{SH})_2]_6$ and I_2 (left) and for $[\text{Ni}(\text{SH})_2]_6$ and CO (right).

levels of the metal do not interact strongly with the orbitals of the ring due to their poor energy match.

We have looked at the possible insertion of small linear molecules into the central hole of the *tiara* structure. Figure 8 shows schematically the interaction diagrams for the insertion of I_2 and CO into the six-membered ring toroid. Both molecules are aligned on the central axis of the toroid. The case of I_2 is similar to that of a single halogen ion. Two-orbital-four-electron repulsive interactions are dominant; there is no binding. For the case of CO , weak binding is obtained as a result of empty *tiara* orbitals mixing into the CO -thiolate bonding combinations. As a consequence the Ni-S framework bonding is generally weakened.

Calculations with more complex molecules (CO_2 and acetylene) also give repulsive binding energies due to two-orbital-four-electron interactions.

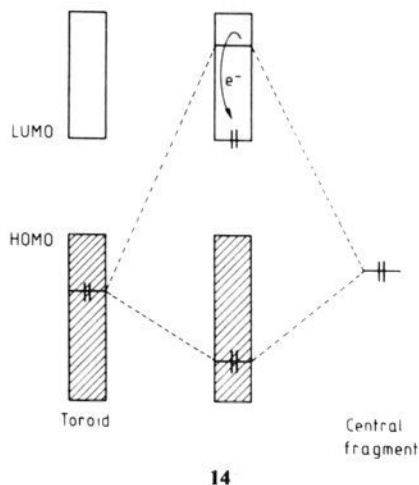
Summarizing the results found in our calculations, we think one should not expect strong bonding interactions in these host-guest species. Only weak interaction (van der Waals and hydrogen bonding) could provide some stabilization of these compounds.

Can one suggest modifications of the *tiara* compounds that would lead to stronger interaction between the central species and the surrounding environment? Two possible ways of achieving this can be suggested. If one could modify the ring in such a way that the interaction with the central fragment would be strong enough to push the host-guest antibonding orbital above the antibonding orbitals of the *tiara* compound, the two electrons in this highly destabilized orbital could be transferred to a lower lying orbital of the toroid. This situation, shown in 14, is typical of the interaction of molecules with surfaces, where the empty levels of a partially filled band can act as acceptors for electrons that would otherwise lie in highly destabilized adsorbate-surface antibonding levels.²⁶

To achieve this situation in a molecular case is more difficult. It is not easy to find an appropriate orbital to which the destabilized electrons can be transferred. Another problem in the molecular case derives from the typically strongly antibonding character of the empty orbitals. Transfer of electrons to these levels would cause a severe weakening of one of the interacting species.

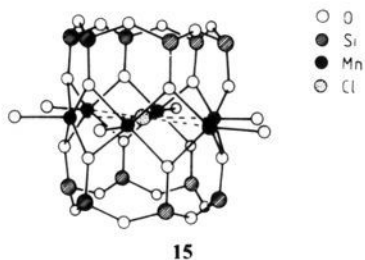
There may be two ways to strengthen inclusion bonding for the *tiara* complexes discussed above: one of them is to lower the energy of the antibonding orbitals of the *tiara*; the other is to increase the overlap between orbitals of the central fragment and those of the ring, in this way pushing the antibonding combination

(26) Hoffmann, R. *Solids and Surfaces: A Chemist's View of Bonding in Extended Structures*; VCH Publishers: New York, 1988.



over the empty ring orbitals. The first possibility is achieved by replacing the sulfur atoms of the *tiara* compound by more electronegative oxygen atoms. Our calculations (with the geometry of the toroid fixed) then give attractive energies for interaction with a chloride anion. A second possibility is the "focusing" of the d_{z^2} and p_z type orbitals of the ring toward the central hole, provided by adding additional ligands on the external surface of the toroid, giving square pyramidal coordinated nickel atoms.

In fact the combination of both factors has been accomplished experimentally. X-ray structures of spherometallosiloxanes²⁷⁻²⁹ (15) show that indeed it is possible to encapsulate chloride ions



in the central hole of these compounds. A calculation of the binding energy of a chloride anion to a model spherometallosiloxane (obtained from the six-membered *tiara*-nickel thiolate by substitution of S by O and addition of six OH⁻ ligands on the nickel atoms) shows that our assumptions are right—a stable inclusion compound results. Antibonding host-guest orbitals are pushed up in energy over some of the empty host antibonding orbitals. Transfer of electrons to these toroid orbitals results in a weakening of bonds in the host; this is seen in the Ni-O overlap populations that decrease when Cl⁻ is introduced in the central hole. This host bond weakening is probably the reason why it has not been possible to introduce chloride anions in the hole of the copper analog of the metallosiloxane.²⁸ The bonding in this compound, with six more electrons than its nickel analog, is much more affected by additional electrons in the antibonding block; the complex is not capable of accepting the electrons provided by the halogen ion.

From these results one may conclude that *tiara* compounds of transition metals with lower d-electron counts, coordinated by oxygen atoms, and with additional ligands capping the metals on

(27) Bürgy, H.; Calzaferri, G.; Herren, D.; Zhdanov, A. *Chimia* **1991**, *45*, 3-8.

(28) Igonin, V. A.; Shchegolikina, O. I.; Lindeman, S. V.; Levitsky, M. M.; Struchkov, Y. T.; Zhdanov, A. A. *J. Organomet. Chem.* **1992**, *423*, 351-360.

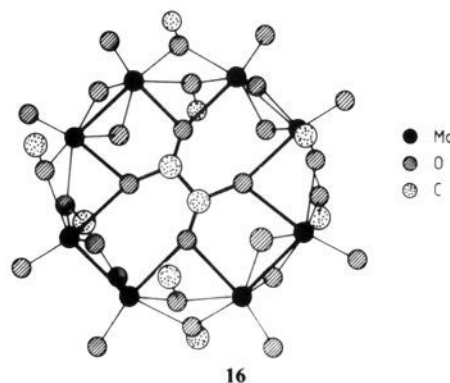
(29) Schegolikina, O. I.; Zhdanov, A. A.; Igonin, V. A.; Ovchinnikov, V. E.; Shklover, V. E.; Struchkov, Y. T. *Metalloorgan. Khim.* **1991**, *4*, 74-84.

Table I. Extended Hückel Parameters

atom	orbital	H_{ii} (eV)	ξ_i
S ³²	3s	-20.00	1.817
	3p	-13.3	1.817
C ¹⁸	2s	-21.40	1.625
	2p	-11.40	1.625
Cl ³³	3s	-26.30	2.183
	3p	-14.20	1.733
Br ³⁴	4s	-22.07	2.588
	4p	-13.10	2.131
I ³⁵	5s	-18.00	2.679
	5p	-12.70	2.322
In ³⁶	5s	-12.60	1.903
	5p	-6.19	1.677
O ¹⁸	2s	-32.30	2.275
	2p	-14.80	2.275
H ¹⁸	1s	-13.60	1.300
	4s	-9.17	1.825
Ni ³⁷	4p	-5.15	1.125
	3d ^a	-13.49	5.750

^a $\xi_2 = 2.000$; $c_1 = 0.5683$; $c_2 = 0.6292$.

the outer surface of the toroid would be the best candidates for host compounds. Some examples of this class of compounds are known: the spherometallosiloxane compounds with manganese or cobalt²⁸ are capable of including chloride anions as guests. Also cyclic octanuclear polyalkoxyvanadates (IV)³⁰ and analogous compounds of molybdenum³¹ incorporate an oxalate anion in the central cavity of the toroid (16).



Conclusions

The structural features of *tiara*-nickel thiolates are dominated by Ni-S bonding. No important Ni-Ni interactions are found, except for the three- and four-membered rings where repulsive metal-metal interactions push the atoms outside of the toroid. In higher membered rings through-bond interactions give rise to Ni-Ni antibonding interactions even at distances as long as 3.3 Å. The short S...S contacts do not seem to play an important role in the stabilization of the ring, as had been suggested earlier.

The simple *tiara*-nickel thiolates should be poor candidates for the formation of host-guest compounds by inclusion of atoms or small molecules in the central cavity of the toroid. Replacement of sulfur by oxygen and addition of capping ligands on the outer surface of the torus helps in stabilizing host-guest complexes. These are more likely to be found for toroids of early transition metals than with compounds of nickel or copper.

(30) Chen, Q.; Liu, S.; Zubieta, J. *Inorg. Chem.* **1989**, *28*, 4433-4434.
 (31) Chen, Q.; Liu, S.; Zubieta, J. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1724-1725.

(32) Jiang, Y.; Alvarez, S.; Hoffmann, R. *Inorg. Chem.* **1985**, *24*, 749-757.

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

(34) Alvarez, S.; Mota, F.; Novoa, J. *J. Am. Chem. Soc.* **1987**, *109*, 6586.

(35) Canadell, E.; Eisenstein, O. *Inorg. Chem.* **1983**, *22*, 2398.

(36) Canadell, E.; Eisenstein, O.; Rubio, J. *Organometallics* **1984**, *3*, 759.

(37) Lauher, J. W.; Elian, M.; Summerville, R. H.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 3219.

Acknowledgment. The stay of P.A. at Cornell University has been made possible through a postdoctoral grant of the Ministerio de Educación y Ciencia of Spain. P.A. is grateful to S. Alvarez for his helpful comments during the development of this paper. Both authors thank two reviewers for their careful reading of the paper and good suggestions. Our work at Cornell was supported by the National Science Foundation, through the Materials Research Center, Research Grant DMR-9121654.

Appendix

All calculations presented in this paper have been performed using the extended Hückel method.^{17,18} The atomic parameters used in the calculations are listed in Table I. Calculations on extended compounds are based on the tight-binding approximation.^{22,23} Density of states and total energy calculations for extended systems have been obtained using a set of 49 k-points in the one-dimensional Brillouin zone.