The crystal structure was carried out in part to determine the appropriate number of carbon atoms needed to bridge across the tren ligands in order to encapsulate the metal ion. The proposed encapsulation would bridge the closest nitrogens (Table IV): 3 and 7, 6 and 4, and 2 and 8. In the structure of 16-aneN$_4$,[5] nonbonded nitrogens are separated by 2.9 Å and bridged by propyl chains. This appears to be the appropriate length for an encapsulating reaction.

Registry No. [Nd(tren)$_2$(CH$_3$CN)](ClO$_4$)$_3$, 81293-68-7; [Nd-(16-aneN$_4$)][ClO$_4$]$_3$, 81277-15-8; Nd(ClO$_4$)$_3$(CH$_3$CN)$_4$, 81277-16-9.

Supplementary Material Available: Tables of calculated hydrogen atom positions (Table Ib), relationships between planes (Table III), thermal parameters (Table V), ligand bond angles (Table VI), results of a twofold rotation (Table VII), hydrogen bond lengths (Table VIII), structure factors, and general temperature factor expressions (U) (55 pages). Ordering information is given on any current masthead page.

Contribution from the Istituto di Stereochimica di Coordinazione del CNR, Istituto di Chimica Generale e Inorganica dell'Università, 50132 Firenze, Italy

MO Nature of the Collinear M–S–M Bridged Linkages in Dinuclear Thiometal Complexes

Carlo Mealli and Luigi Sacconi*

A few years ago we described two diamagnetic binuclear compounds containing one sulfur atom linearly bridging two metal ions, namely, [(triphos)NiSNi(triphos)](BPh$_4$)$_2$·1.6DMF (A) (triphos = CH$_3$C(CH$_2$PPh$_2$)$_3$) and (np$_3$)CoSCo(np$_3$) (B)[1] (np$_3$ = N(CH$_2$CH$_2$PPh$_2$)$_3$). In both compounds the metals are pseudotetrahedrally coordinated by three phosphorus atoms of a polyphosphine ligand and by one shared sulfur atom. The M–S linkages are unusually short, being 2.034 Å for Ni–S and 2.128 Å for Co–S. In the absence of detailed MO calculations we then adapted to our cases the old qualitative MO procedure introduced by Orgel and Dunitz for Ru$_2$Cl$_{10}$O^{4-}.[2] Thus specific symmetry arguments for A (site symmetry D_{3d}) prompted that the bonding network of the molecule is dominated by e$_u$ bonding, nonbonding, and antibonding molecular orbitals, with the last orbitals being too high in energy for them to be populated. This accounted for the quenching of the paramagnetism on each metal center and predicted the formation of π-type bonds between suitable metal d orbitals and sulfur p orbitals of e$_u$ symmetry (d$_\pi$–p$_\pi$ interactions).

Recently the structure of the compound [(η^5-C$_5$H$_5$)Cr-(CO)$_2$]$_2$S (C) has been reported.[3] This complex too has an almost linear Cr–S–Cr linkage for which the authors proposed the Cr≡S≡Cr formulation. In this manner the closed-shell configuration of the metals that start from an initial 15-electron counting is attained.[4] The same authors also sug-

gested that this argument can be conveniently applied to our compounds as well.

We have now reconsidered the matter by a more quantitative MO treatment based on the extended Hückel method. Our aim is to point out the most important orbital interactions in this type of compound and to probe the role of the sulfur d orbitals, which must enter in an overall triple-bonding VB scheme such as that invoked by Greenhough et al.[3]

The level ordering in an hypothetical molecule of D_{3d} symmetry such as [(PH$_3$)$_3$Ni–S–Ni(PH$_3$)$_3$]$^{2+}$ with and without the contribution of sulfur d orbitals is shown in Figure 1, parts e and c, respectively. The construction and the shapes of the MO's of a M$_2$L$_6$ fragment from two ML$_3$ units brought together (Figure 1a,b) have been described in detail by Hoffmann and co-workers.[5] Here we remind the readers that the metal d orbitals of e symmetry in the ML$_3$ units are titled and that there is partial hybridization of d and p metal orbitals in the upper e set. In the M$_2$L$_6$ fragment there are two metal e$_u$ sets that can match the e$_u$ (p$_x$, p$_y$) orbitals of sulfur. The possible interactions are shown in **1**, **2**, and **3** and correspond
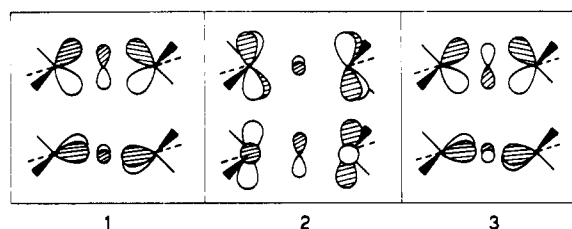
to the 1e$_u$, 2e$_u$, and 3e$_u$ orbitals of Figure 1c. It should be noted that, due to the interaction with the sulfur e$_u$ set, the 1e$_u$ and 2e$_u$ orbitals of the M$_2$L$_6$ fragment intermix in a sense so as to reduce the tilting with respect to the metal–metal vector. As an example **4** shows how the upper component of **2** can
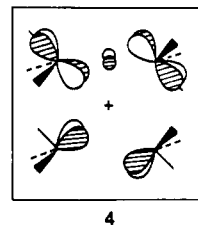
be built up from three combining e$_u$ members. The 2e$_u$ level can be considered metal–sulfur nonbonding and δ metal–metal antibonding. Thus **1**, **2**, and **3** may be closely related to the bonding, nonbonding and antibonding e$_u$ levels first predicted by our MO qualitative description of A. This type of π interaction contributes a value of 0.27 to the Mulliken overlap population of each Ni–S bond. Besides this there are σ-type bonding orbitals that formally allow an overall double-bond VB representation of the Ni=S=Ni linkage. These are the 1a$_{1g}$ and 1a$_{2u}$ orbitals of Figure 1c centered on sulfur s and p$_z$ orbitals, respectively. The bonding partners of the M$_2$L$_6$ fragment are the high-lying 2a$_{1g}$ and 2a$_{2u}$ metal sp hybrids of Figure 1b. The large energy gaps do not totally prevent the possibility of good bonding interactions. In fact the large overlaps obtainable between the highly diffuse s and p orbitals at short Ni–S distances account for a net σ-type contribution of 0.54 to the overlap population of each Ni–S bond. Interestingly the metal d$_{z^2}$ combinations (1a$_{1g}$ and 1a$_{2u}$ of Figure 1b) mix into the Ni–S–Ni bonding network, but their contribution to the Ni–S overlap population is practically vanished,

(1) (a) C. Mealli, S. Midollini, and L. Sacconi, *J. Chem. Soc., Chem. Commun.*, 765 (1975); (b) C. Mealli, S. Midollini, and L. Sacconi, *Inorg. Chem.*, **17**, 632 (1978).

(2) J. D. Dunitz and L. E. Orgel, *J. Chem. Soc.*, 2594 (1953).

(3) T. J. Greenhough, B. W. S. Kolthammer, P. Legzdins, and J. Trotter, *Inorg. Chem.*, **18**, 3543 (1979).

(4) In this electron counting the metal d electrons, calculated by considering the sulfur atom as uncharged, are added to the total number of electrons donated by the terminal ligands.

(5) (a) A. Dedieu, T. A. Albright, and R. Hoffmann, *J. Am. Chem. Soc.*, **101**, 3141 (1979); (b) T. A. Albright, P. Hofmann, and R. Hoffmann, *ibid.*, **99**, 7546 (1977); (c) M. Elian and R. Hoffmann, *Inorg. Chem.*, **14**, 1058 (1975); (d) R. H. Summerville and R. Hoffmann, *J. Am. Chem. Soc.*, **101**, 3821 (1979).
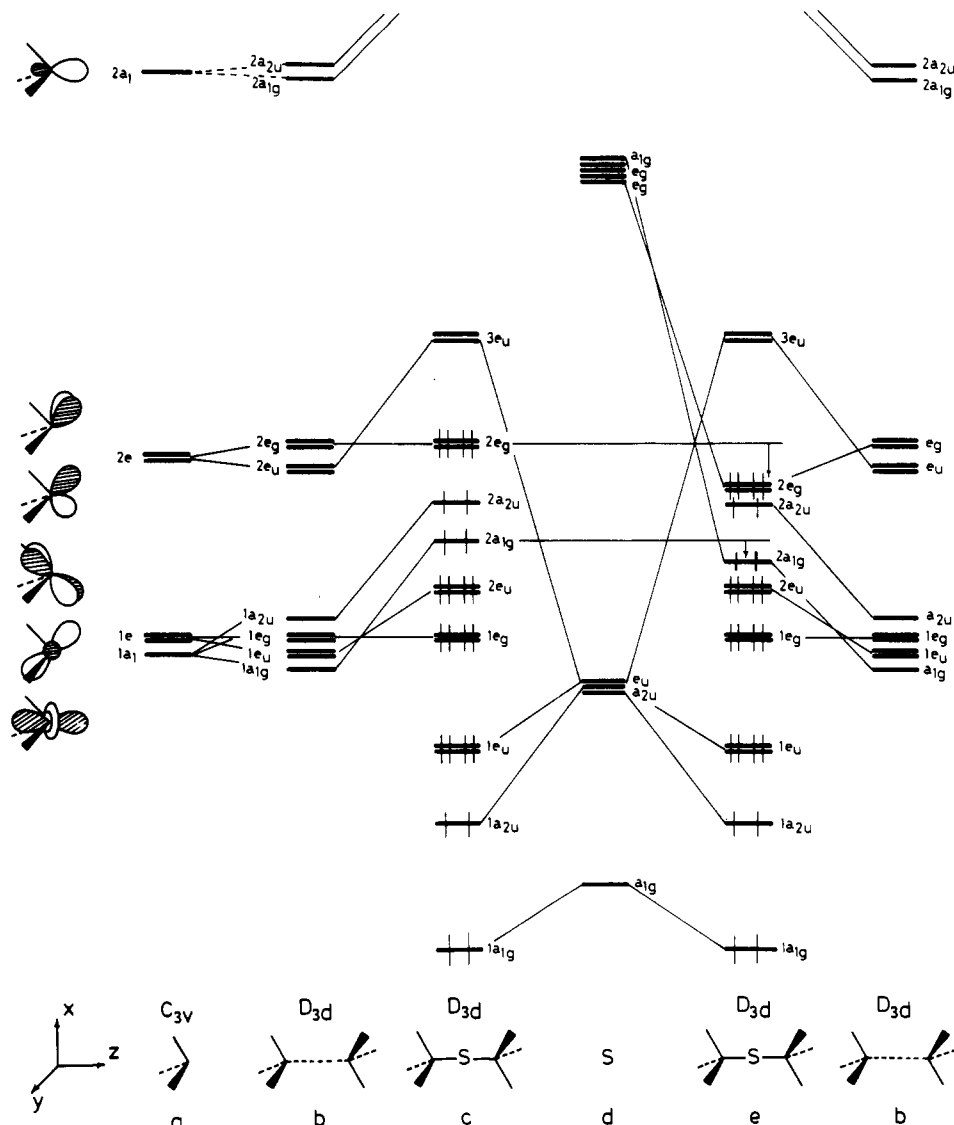
Figure 1. Molecular orbital picture of the D_{3d} [(PH$_3$)$_3$NiSNi(PH$_3$)$_3$]$^{2+}$ cation complex: (a) valence orbitals of a C_{3v} ML$_3$ fragment; (b) orbitals of a M$_2$L$_6$ fragment in a staggered conformation; (c) MO levels for the complex cation without the contribution of the sulfur d orbitals; (d) sulfur s, p, and d valence orbitals; (e) MO levels for the complex cation with the contribution of sulfur d orbitals.

for both the bonding and the antibonding levels in which they enter are occupied.

Figure 1c shows that, when the MO's are filled with the appropriate number of electrons, the HOMO is the nonbonding 2e$_g$ metal level, no contribution from the non-d sulfur valence orbitals being allowed by symmetry. The energy gap between HOMO and LUMO is calculated to be about 35 kcal/mol and seems large enough to rationalize the diamagnetism of the molecule.

On the other hand among the sulfur 3d orbitals one can find an e$_g$ set that matches the metal orbitals of the same symmetry. The interactions, shown in 5, enhances the HOMO–LUMO
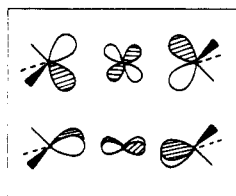
5

energy gap (Figure 1e) and may be regarded as the MO representation of the schematized VB third stick bond between sulfur and nickel atoms. Mixing of the sulfur d$_{z^2}$ orbital in

2a$_{1g}$ adds stabilizing energy to the system. The levels of Figure 1e have been calculated by assigning a standard energy value of -8.0 eV to the sulfur d orbitals. However, the participation in bonding of the sulfur d orbitals in terms of energy parameters is an old problem.[6] We have found that by systematically varying their energy from 0.0 eV (equivalent to no d contribution) to -9.0 eV, the total Ni–S overlap population increases almost linearly from 0.81 to 1.26. The S_{d_π}–Ni$_{d_\pi}$ and S_{p_π}–Ni$_{d_\pi}$ overlap populations are equalized at a relatively high energy (-5.5 eV). To put it in another way, the former type of interaction becomes appreciable without requiring a large participation of the sulfur d orbitals in terms of energy.

Similar general conclusions can be drawn from a MO calculation on the hypothetical molecule [(CO)$_5$Cr–S–Cr(CO)$_5$]$^{2+}$, a reasonable model for C, where three carbonyls have been replaced by a Cp ring[7] and the charge has been adjusted accordingly. Figure 2 shows the interactions between the orbitals of the Cr$_2$(CO)$_{10}$ fragment, already amply described by Hoffmann et al.,[8] and the sulfur valence orbitals

(6) R. Hoffmann, H. Fujimoto, J. R. Swenson, and C. C. Wan, *J. Am. Chem.*, **95**, 7644 (1973).

(7) M. Elian, M. M. L. Chen, D. M. P. Mingos, and R. Hoffmann, *Inorg. Chem.*, **15**, 1148 (1976).

(8) S. Shaik, R. Hoffmann, C. R. Fisel, and R. H. Summerville, *J. Am. Chem. Soc.*, **102**, 4555 (1980).
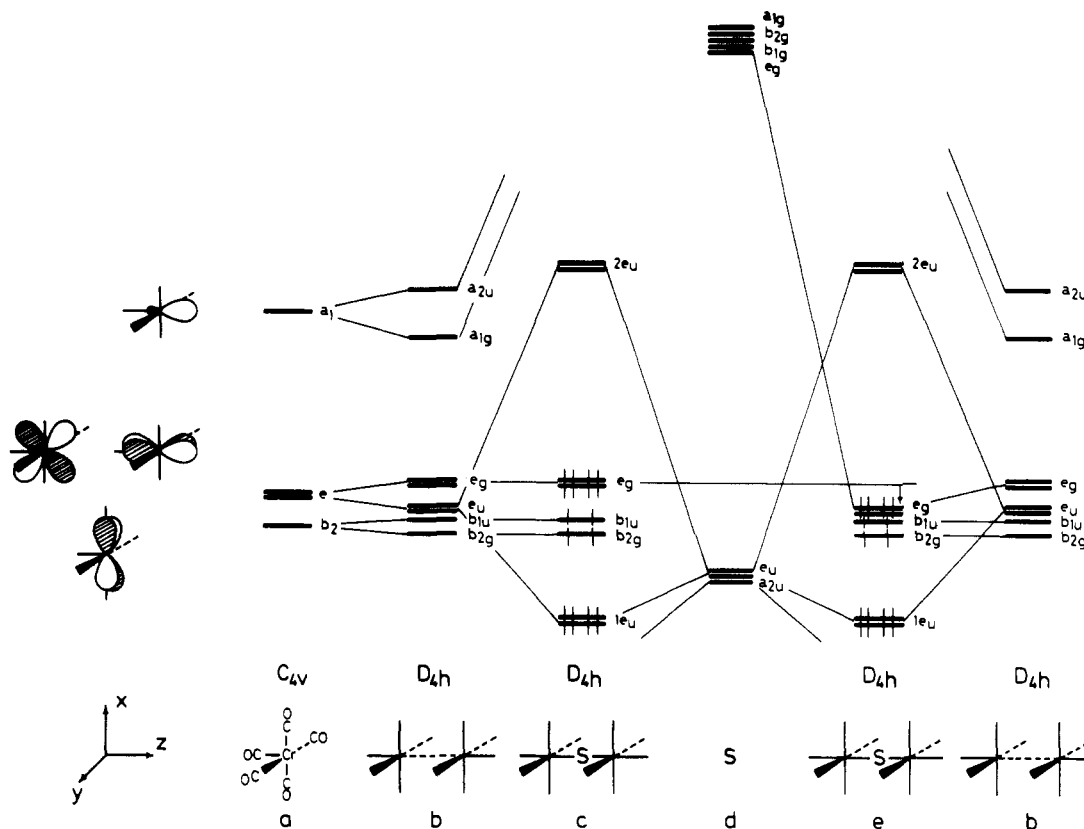
Figure 2. Molecular orbital picture of the D_{4h} [(CO)$_5$CrSCr(CO)$_5$]$^{2+}$ complex cation: (a) important valence orbitals of a C_{4v} ML$_5$ fragment; (b) orbitals of a M$_2$L$_{10}$ fragment in an eclipsed conformation; (c) MO levels for the complex cation without the contribution of sulfur d orbitals; (d) sulfur s, p, and d valence orbitals; (e) MO levels for the complex cation with the contribution of sulfur d orbitals.

first without (Figure 2c) and then with (Figure 2e) the 3d set. The bonding e$_u$ interactions between metal orbitals, mainly d$_{xz}$ and d$_{yz}$, and the sulfur p$_x$ and p$_y$ orbitals are shown in **6**.
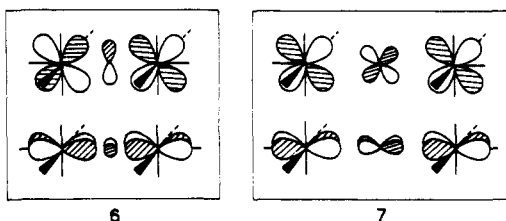
Nonbonding e$_g$ metal orbitals may interact with sulfur d orbitals upon their inclusion as shown in **7**. It is noteworthy that the metal d orbitals in **6** and **7** are not hybridzed as in the case of the M$_2$L$_6$ fragment. This renders their overlap with both the p and the d orbitals of sulfur less effective, but the relative positions of the e$_u$ and e$_g$ sets on the energy scale now enhance the extent of the M$_{d_\pi}$–S$_{p_\pi}$ interactions and lessen that of the M$_{d_\pi}$–S$_{d_\pi}$ interactions. Thus, so that the two types of interactions might be equally strong, a much larger participation of the sulfur d orbitals is required in terms of lower energy parameters.

We are aware of a fourth structure,[9] which contains an almost linear Mo–S–Mo linkage. This is the [(CN)$_6$Mo–S–Mo(CN)$_6$]$^{6-}$ complex anion. Each molybdenum atom is seven-coordinated with pentagonal-bipyramidal geometry. Once again the initial electron count on each metal sums up to 15.[4] We have not performed specific EHMO calculations on this compound, but from qualitative considerations we argue that the bonding network is very similar to that of the previous compounds. The splitting of the metal d orbitals in the C_{5v}

ML$_6$ fragment (a$_1$ + e$_1$ + e$_2$)[10] resembles that of the C_{3v} ML$_3$ fragment. Mo$_{d_\pi}$–S$_{p_\pi}$ bonding is allowed by the e$_1'$ (D_{5h}) combination of d$_{xz}$ and d$_{yz}$ metal orbitals with sulfur p$_x$ and p$_y$ orbitals, as shown in **8**. Upon activation of sulfur d orbitals the metal orbitals of e$_2''$ symmetry also find a bonding partner and the Mo$_{d_\pi}$–S$_{d_\pi}$ interaction type is triggered.
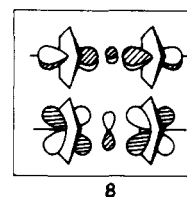
Returning to our compounds A and B, we may ask the question why are the two ML$_3$ fragments of A staggered, while those of B are eclipsed?

As shown by Hoffmann and co-workers[5a] the tilting of the metal d orbitals belonging to the e sets in the pyramidal ML$_3$ fragments creates cylindrical asymmetry. If matched by an equivalent asymmetry of the π orbitals of the potential bridging fragment, this asymmetry may give rise to conformational preferences. These are not expected for our binuclear species bridged by a single sulfur atom. The e$_u$ set on sulfur is cylindrical and, as shown, serves as a relay to undo the tilting of the 1e$_u$, 2e$_u$, and 3e$_u$ orbitals of the molecule. Our MO calculations confirm that the energies of staggered and eclipsed models of [(PH$_3$)$_3$Ni–S–Ni(PH$_3$)$_3$]$^{2+}$ are essentially the same. We note parenthetically that the essence of the M=S=M bonding description is intrinsically different than that in allenes (R$_2$C=C=CR$_2$) and related non-transition-metal analogues,

(9) M. G. B. Drew, P. C. H. Mitchell, and C. F. Pygall, *Angew. Chem., Int. Ed. Engl.*, **15**, 784 (1976).

(10) R. Hoffmann, B. F. Beier, E. L. Muetterties, and A. R. Rossi, *Inorg. Chem.*, **16**, 511 (1977).
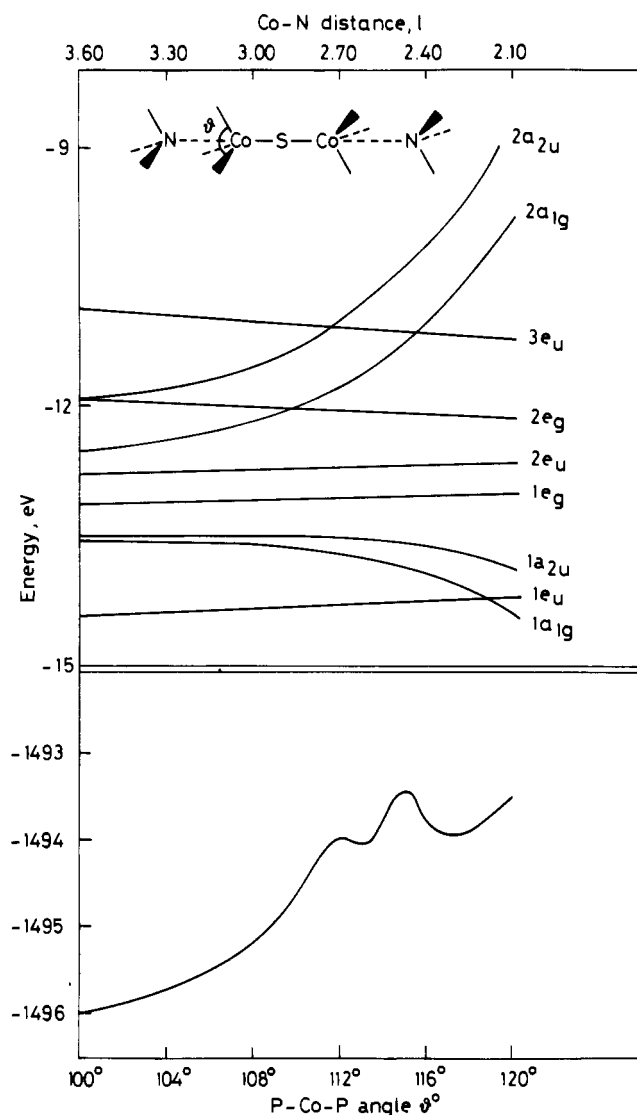
Figure 3. Above: Walsh diagram showing the energies of the frontier orbitals in the $(NH_3)(PH_3)_3CoSCo(PH_3)_3(NH_3)$ D_{3d} model as a function of the Co–N distance or the P–Co–P angle. Below: variation of the total energy as a function of the same coordinates.

where the barriers of rotation about the double bonds are quite high.

Another point of interest is the observed nonbonding distance of 3.485 Å between the cobalt and the apical nitrogen atom of the np_3 ligand in compound B. By rejecting the nitrogen lone pair and adopting a pseudotetrahedral geometry similar to that of the nickel derivative, A, the metal keeps its electron configuration at 15, which is the assumption for the formation of an overall Co≡S≡Co triple linkage. We have carried out some calculations with the aim of determining the origin of the repulsion between the metal and the apical nitrogen atom. In the upper part of Figure 3 a Walsh diagram shows the variation of the frontier orbital energies in the $(NH_3)(PH_3)_3Co-S-Co(PH_3)_3(NH_3)$ D_{3d} model vs. the combined variation of the P–Co–P angle θ and the Co–N distance l. A linear relationship between these structural parameters has been experimentally determined from a number of structures containing the variously elongated np_3 ligand.[1b,11]

At $\theta = 100°$ and $l = 3.60$ Å the energy levels are approximately those of Figure 1c, also including symmetric ($2a_{1g}$) and antisymmetric ($2a_{2u}$) combinations of the nitrogen lone pairs. The simultaneous increasing of θ and decreasing of l induce progressively greater destabilization of the above orbitals, which acquire more metal and sulfur character. Their combinations are shown in **9** and **10**, respectively. For values of
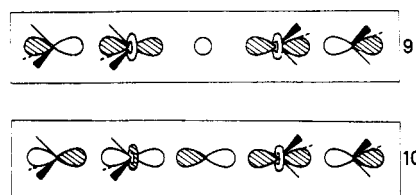
$\theta > 116°$ and M–N distances <2.40 Å the HOMO becomes the $3e_u$ orbital, which is the LUMO of Figure 1c. There is also a net destabilization of the total energy of the system as the amines approach the metals (see lower part of Figure 3). Two minima are observed that correspond to the crossover of electrons from $2a_{1g}$ and $2a_{2u}$ to $3e_u$ orbitals. These minima are about 45 kcal/mol higher than the energy of the ground state with the nitrogen atoms at nonbonding distances. The other important effect due to the electron crossover is relative to the overlap populations of M–N and M–S bonds. **9** and **10** are strongly M–N antibonding and weakly M–S antibonding due to the small involvement of the sulfur orbitals in these MO's. The M–N overlap population jumps in two steps from a negative value to zero and then to a positive value of 0.27. Conversely the small gain of M–S overlap population when $2a_{2u}$ and $2a_{1g}$ are emptied is amply counterbalanced by the filling of $3e_u$, the π-type antibonding orbitals shown in **3**. Consequently, the M–S overlap population drops from 0.74 to 0.54 and then to 0.40. These results are obtained with the exclusion of the sulfur d orbitals, but their activation does not alter the important trends of the Walsh diagram. The diagram also suggests that a structure where two trigonal bipyramids share one apex can be predictably stabilized for d^7 metal ions, which, curiously, again start from a total 15-electron count for each metal atom.

The present MO analysis also offers an explanation of the observed difference between Ni–S and Co–S distances in compounds A and B (2.034 vs. 2.128 Å). In retrospect[1b] we suggest that the effects of the different pyramidalizations[5c,7] of the ML_3 units in A and B are more substantial than the effects due to different metal nuclear charges (metal radii) or repulsive steric forces between rings of the ligands. The larger the P–M–P angles (100.7° in B vs. 92.4° in A) the less hybridized with metal s and p orbitals are the higher 2e and $2a_1$ levels. In fact we calculated diminished values of the spatial overlap of these orbitals with the appropriate sulfur orbitals and of the total M–S overlap population as well.

As a concluding remark, the proposed M≡S≡M linkage cannot be completely ruled out even in the light of our EHMO results since the sulfur d orbitals have a precise role in reinforcing the metal–sulfur bonding. However, an overreliance on VB terminlogy for highly delocalized systems such as these may be dangerous and lead to contradictory conclusions. We observe, for example, that a number of metal binuclear complexes containing linear M–O–M linkages either are diamagnetic or show antiferromagnetic behavior; moreover, the M–O distances are short enough to suggest bond orders greater than 1. We refer, for example, to complexes such as $(Cl_{10}W_2)O^{4-}$,[12] $[(NH_3)_{10}Cr_2]O^{4+}$,[13] and $(Cl_{10}Ru_2)O^{4-}$.[2] By counting the initial electron configuration of each metal atom

(11) (a) L. Sacconi, M. Di Vaira, and A. Bianchi, *J. Am. Chem. Soc.*, **92**, 4466 (1970); (b) P. Dapporto, S. Midollini, and L. Sacconi, *Angew. Chem., Int. Ed. Engl.* **18**, 469 (1979); (c) M. Di Vaira, C. A. Ghilardi, and L. Sacconi, *Inorg. Chem.*, **15**, 1555 (1976); (d) F. Cecconi, P. Dapporto, S. Midolini, and L. Sacconi, *ibid.*, **17**, 3292 (1978); (e) P. Stoppioni, P. Dapporto, and L. Sacconi, *ibid.*, **17**, 718 (1978); (f) P. Dapporto and L. Sacconi, *Inorg. Chim. Acta*, **39**, 61 (1980).

(12) T. Glowiak, M. Sabat, and B. Jezowska-Trzebiatowska, *Acta Crystallogr., Sect. B*, **B31**, 1783 (1975).

(13) M. Yevitz and J. A. Stanko, *J. Am. Chem. Soc.*, **93**, 1512 (1971).

as indicated above,[4] we are in the presence of d^{13}, d^{14}, and d^{15} species, respectively, but metal–oxygen triple bonding cannot be obviously proposed, for the closed-shell configuration of the metals is far from being obtained and involvement of oxygen d orbitals in bonding seems quite unrealistic. The magnetic and structural features in compounds of this type with the metals in octahedral environments have been often rationalized through qualitative MO pictures similar to that of Figure 2b.[14] Notice that the HOMO e_g level is nonbonding and that the removal of two or four electrons from it (corresponding to d^{14} or d^{13} initial electron counts) does not alter the overall M–O–M bonding network.

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Appendix

All calculations were performed with use of the extended Hückel methods.[15] The programs, kindly supplied by Professor Roald Hoffmann, were implemented and run on an SEL 32/70 computer. The parameters used for Co, Ni, and Cr were taken from ref 5b. P–H, N–H, and C–O distances were idealized at 1.40, 1.09, and 1.15 Å, respectively. The M–S, M–P, and M–C bond lengths were taken from the experimental values of related structures.
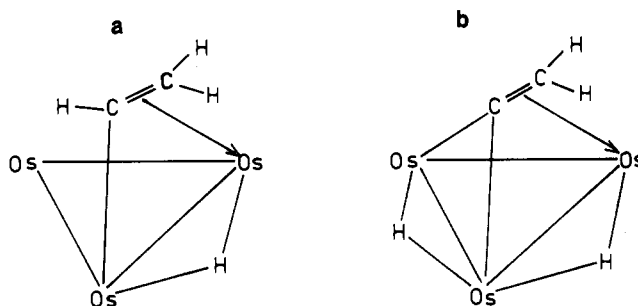
(14) T. R. Weaver, T. J. Meyer, S. A. Adeyemi, G. M. Brown, R. P. Eckberg, W. E. Hatfield, E. C. Johnson, R. W. Murray, and D. Unterreker, *J. Am. Chem. Soc.*, **97**, 3046 (1975).
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Infrared and Raman Spectra of HOs₃(CH=CH₂)(CO)₁₀, H₂Os₃(C=CH₂)(CO)₉, and H₂Os₃(CO)₁₀: Wavenumbers Associated with Olefinic and Hydride Ligands and the Metal Skeleton

J. R. Andrews, S. F. A. Kettle, D. B. Powell,* and N. Sheppard

We have recently been investigating the vibrational spectroscopy of metal cluster systems, particularly of osmium carbonyl derivatives. It has been suggested that some clusters may be catalytically important and that they may provide model compounds for the study of chemisorbed species on metal surfaces.[1-3] For this reason a detailed understanding of the vibrational spectra of such compounds should aid the interpretation of the spectra of chemisorbed species. Examples of the use of the infrared spectra of metal cluster compounds in interpreting the vibrational spectra obtained from metal

(1) Robinson, A. L. *Science (Washington, D.C.)* **1976** *194*, 1150.
(2) (a) Muetterties, E. L. *Bull. Soc. Chim. Belg.* **1975**, *84*, 959. (b) Muetterties, E. L.; Thosin, T. N.; Band, Elliot; Brucker, C. F.; Pretzer, W. R. *Chem. Rev.* **1979**, *79*, 91.
(3) Privet, M.; Bassett, J. M.; Labowski, E.; Mattieu, M. V. *J. Am. Chem. Soc.* **1975**, *97*, 3655.
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Figure 1. Structures of (a) $HOs_3(CH{=}CH_2)(CO)_{10}$ and (b) $H_2Os_3(C{=}CH_2)(CO)_9$.

surface species are contained in a number of recent publications (see, for example, ref 4).

In this paper we report the vibrational spectra and assignments of two metal cluster compounds, incorporating unusual olefinic groups, of formulas $HOs_3(CH{=}CH_2)(CO)_{10}$ and $H_2Os_3(C{=}CH_2)(CO)_9$,[5,6] with the structures shown in Figure 1a,b. The spectra and the interpretation described here confirm previous suggestions, based on X-ray crystallographic data,[6] that in these compounds the olefinic groups are both σ and π bonded. In metal surface studies of chemisorbed olefins, both σ and π bonding have been suggested, although not usually in conjunction A third compound, $H_2Os_3(CO)_{10}$,[7] has also been studied in the present work to assist in the interpretation of the bands from hydride ligands in the spectra of the first two compounds.

For the vinyl and vinylidene compounds, only solution infrared spectra in the carbonyl stretching region have been reported previously.[5,6] Our more complete investigation of the vibrational spectra of these compounds in the solid state has shown that the intensity of the peaks associated with the organic groups are almost 1 order of magnitude smaller than those from the carbonyl groups and that those associated with the bridging hydrogen atoms are even weaker. Fortunately, the motions of the olefinic, bridging hydrogen, and carbonyl groups are clearly largely uncoupled and the associated spectral features are therefore discussed separately.

Results

Bands Associated with Vibrations of CO Ligands. The study of metal carbonyls is well documented in the literature, and so bands due to carbonyl vibrations will not be discussed here except to point out that the bands occur in the usual regions,[8] i.e., $\nu(CO)$ near 2000, $\nu(M{-}C)$ and $\delta(MCO)$ at 600–400, and $\delta(OC{-}M{-}CO)$ below 100 cm⁻¹.

The vibrations of the other ligands described here do not normally occur in these regions.

The results are considered in three sections: olefinic bands, metal–hydrogen bands, and skeletal modes involving the metal atoms.

Olefinic Bands. When the spectra of $HOs_3(CH{=}CH_2)(CO)_{10}$ and $H_2Os(C{=}CH_2)(CO)_9$ are compared with that of the parent carbonyl cluster, $Os_3(CO)_{12}$, at high concentrations (5–15% by weight) in pressed potassion bromide disks, the most striking difference is the appearance in the olefin complexes of bands between 1700 and 600 cm⁻¹, which are of fairly low intensity compared to the $\delta(MCO)$ bands and of very low

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