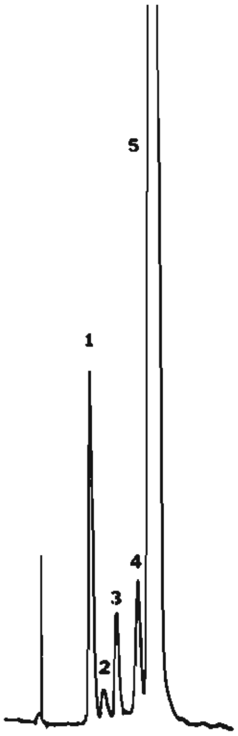

Figure 1. HPLC profiles of products formed from *cis*-stilbene following treatment with Mn(III)–bleomycin + C_6H_5IO. Peaks 1–5 correspond to unreacted *cis*-stilbene, *trans*-stilbene oxide, *cis*-stilbene oxide, benzaldehyde, and deoxybenzoin, respectively. The retention times of 1–5 were 2.4, 2.8, 3.5, 4.5, and 5.0 min, respectively. The response factors of individual products (UV detection 254 nm) differed substantially.

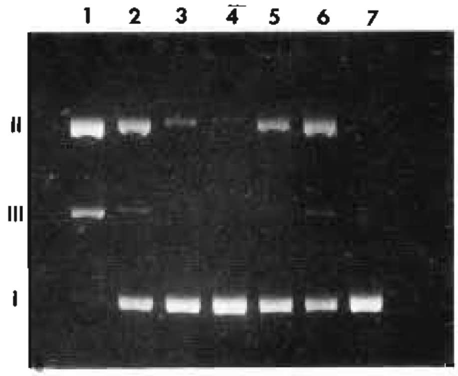

Figure 2. SV40 DNA strand scission by Mn(II)–bleomycin + O_2. Individual reaction mixtures contained, in addition to 50 mM sodium cacodylate buffer, pH 7.0, and 500 ng of SV40 form I DNA, the following: (lane 1) 25 μM bleomycin B_2 and 125 μM $\mathrm{Mn^{II}SO_4}$; (lane 2) 10 μM bleomycin B_2 and 50 μM $\mathrm{Mn^{II}SO_4}$; (lane 3) 1 μM bleomycin B_2 and 5 μM $\mathrm{Mn^{II}SO_4}$; (lane 4) only DNA and buffer; (lane 5) 25 μM bleomycin B_2; (lane 6) 1 μM bleomycin B_2 and 5 μM $\mathrm{Fe^{II}(NH_4)_2(SO_4)_2}$; (lane 7) 125 μM $\mathrm{Mn^{II}SO_4}$. Reactions were initiated by the addition of bleomycin; the reaction mixtures were incubated at 25 °C for 30 min prior to analysis on a 1.4% agarose gel.

diated by Mn(II)–bleomycin + O_2 and by Mn(III)–bleomycin + C_6H_5IO produced no detectable malondialdehyde.[17]

The finding that Mn-bleomycin can mediate oxygen transfer to olefinic substrates and oxidative DNA strand scission in analogy with Fe–bleomycin and Cu–bleomycin is particularly important in that the corresponding metalloporphyrins have been studied in some detail[11,12,14] as analogues of cytochrome P-450. That three different metallobleomycins produced products from several olefinic substrates very similar to those observed with metalloporphyrins that are analogues of cytochrome P-450 strengthens the correlation between the two and suggests strongly that bleomycin can function as a monooxygenase.

As is evident from Figure 2 MnBLM was about 10-fold less active than FeBLM under the experimental conditions employed. This parallels the situation observed for the (TPP)-$\mathrm{Fe^{V}O}$ complex, which has an oxidation potential approximately 0.3 V greater than that of the corresponding manganese–porphyrin complex.[18] On this basis, it would be expected that MnBLM might be a more selective reagent than FeBLM; the possibility that MnBLM might react only with a subset of those DNA sites modified by FeBLM seems worthy of investigation and might provide important insights into the design of more selective bleomycin congeners.

Acknowledgment. This work was supported by Research Grant CA-29235, awarded by the National Cancer Institute, Department of Health and Human Services.

---

(17) In addition to contributing to the characterization of Mn(II)–bleomycin, this experiment demonstrated that the activity of this metallobleomycin could not be due to contaminating Fe, as the latter is known to produce malondialdehyde (base propenal) concomitant with DNA cleavage. That the observed activity in DNA strand scission cannot be due to contaminating Cu may be appreciated from the fact that Cu(I)–bleomycin + O_2 does not cleave DNA in the absence of agents such as dithiothreitol.

(18) Macdonald, T. L.; Guengerich, F. P.; Eberson, L., personal communication.

(19) To whom correspondence should be addressed at the Department of Chemistry.

Departments of Chemistry and Biology
University of Virginia
Charlottesville, Virginia 22901

Guy M. Ehrenfeld
Natesan Murugesan
Sidney M. Hecht*[19]

Received December 20, 1983

Relation between the Electronic Structure and the Condensation of Metal Clusters in M_5X_4 Compounds

Sir:

Many transition-metal compounds have an octahedral cluster of transition-metal atoms as their basic unit. The clusters may be isolated, as in Mo_6S_8, or condensed at their corners, edges, or faces, depending on the metal to nonmetal ratio or/and the valence electron concentration (VEC) per metal atom.[1] In the family of M_5X_4 (M = Nb, Ta, V, Ti, Mo; X = S, Se, Te, As, Sb) compounds they condense at opposite corners to form infinite chains, with VEC in the range 2.4–3.6 for all known materials.[1] Why compounds only in this range of VEC crystallize in this structure is not clear, though Nohl et al.[2] have correlated the stability of these compounds with the occurrence of a band gap at the Fermi energy E_F by analogy with the Peierls instability argument. In this communication we discussed the matter further from the heat ΔH of condensation of clusters computed for two systems: (i) a model regular octahedral chain of metal atoms and (ii) a chain with the geometry of Nb_5Te_4, where the octahedra are somewhat squashed as in a bcc substructure.[1] We relate ΔH

---

(1) Simon, A. *Angew. Chem., Int. Ed. Eng.* **1981**, *20*, 1; *Angew. Chem.* **1981**, *93*, 23.

(2) Nohl, H.; Klose, W.; Andersen, O. K. In "Superconductivity of Ternary Compounds"; Fischer, ö., Maple, M. B., Eds.; Springer-Verlag: Berlin, 1982.

0020-1669/84/1323-1498$01.50/0

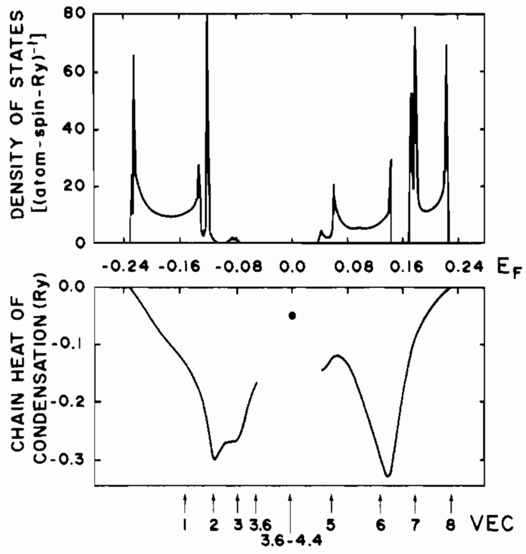

Figure 1. Chain heat of condensation for a regular octahedral chain (lower) and local density of states on a joining atom (upper) as a function of E_F. The bottom scale shows the valence electron concentration per atom (VEC).

to features of the band structure of the chain and discuss some other aspects of the metal–metal bonding due to the d electrons of the clusters.

The stability of the chain and corresponding heat ΔH of condensation of clusters can be formulated in several slightly different ways. First, we can view the chain as the result of adding five-atom units to an existing piece of chain. Since the isolated clusters contain six atoms each, there are extra atoms released by the condensation, which we form into an extra length of chain. Thus we define the "cluster" heat of condensation as

$$\Delta H_{\text{clust}} = U_{\text{inf}} - \tfrac{5}{6}U_{\text{clust}} \qquad (1)$$

where U_{clust} is the energy of a free cluster and U_{inf} is the energy per unit of an infinite chain. Second, we can study the stability of an infinite chain against breaking up into two semiinfinite chains to define the "chain" heat of condensation, ΔH_{chain}, with the extra atom needed to complete the broken end being taken as an "average" atom from the infinite chain. The ΔH_{chain} can be related to ΔH_{clust} by considering the chemical potential $\mu(L)$ for introducing breaks into an assembly of chains of length L units. Then ΔH_{chain} is $\mu(\infty)$ whereas ΔH_{clust} is $\mu(L)$ averaged between $L = \infty$ and $L = 2$. Clearly we expect ΔH_{chain} to reflect most strongly the electronic structure of the infinite chain with its band gaps.

To focus on the metal–metal bonding, we have considered a chain of metal atoms (only) with *four* d orbitals per atom: one of the orbitals d_{xy}, d_{yz}, and d_{zx} and the s, p orbitals are effectively removed by hybridization with the nonmetal atoms.[2,3] In computing the total energy, we retained only the sum of the one-electron terms in a simple LCAO model[3] because almost all the structural information resides there, whereas the remaining electrostatic terms give a short-range repulsion with only smooth dependence on VEC.[4]

Figure 1 (lower) shows ΔH_{chain} for the regular chain vs. Fermi energy E_F. It shows marked features, which correlate with the *local* density of states on the "joining" atom common to adjacent octahedral units, shown in the upper half of the figure. The condensation is strongest at $E_F = -0.11$ Ry exactly at the top of the strong bonding band and at 0.14 Ry at the band gap in the antibonding band.[5] Also the total density of states[3] shows a large band gap at VEC = 3.6, and we note in Figure 1 that the range of stability extends up to 3.6 electrons/atom with the heat of fusion beyond this dropping to a small value per atom. *Our results therefore support the general idea of* Nohl *et al.*[2] *of linking stability with filling of the electron states up to a band gap.* The more complicated behavior of ΔH_{chain} around $E_F = -0.08$ Ry arises from other bands that hardly show on Figure 1 but have high density of states on the four central atoms of the octahedral unit. Such bands also largely control the VEC, whose variation with E_F is shown by the bottom scale of Figure 1.

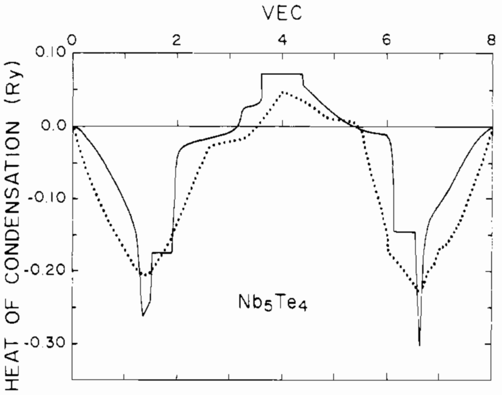

Figure 2. Chain heat of condensation (solid line) and cluster heat of condensation (broken line) for an octahedral chain with the geometry of Nb_5Te_4.

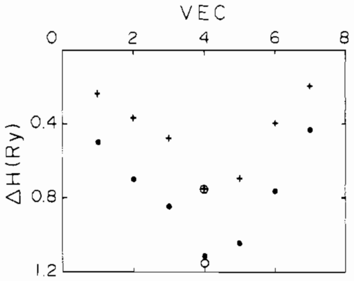

Figure 3. Energy to sever an atom from an octahedron (+) and to cut the joining atom out of a double octahedron (●). Open circles show the corresponding values for a semiinfinite and infinite chain.

Of course the stability of the compound is determined by the "cluster" rather than the "chain" heat of condensation. Figure 2 shows both for the distorted Nb_5Te_4 type of chain, now plotted against VEC. We note that the two curves are quite similar, although the chain heat of condensation has sharper features as expected. We interpret the similarity as implying that the metal–metal bonding between clusters is fairly well localized, i.e. is only moderately affected by whether there is a further unit attached at the opposite end of the cluster: compare also with $\mu(2)$ in ref 3. Thus we may say that *the features of the chain heat, related to the band structure, extended also to the cluster heat of condensation, thus further supporting the link between band gaps and structural stability.* Note also (Figure 2) that the modest distortion of the geometry from the regular to the Nb_5Te_4 chain alters the shape of the curve considerably, although condensation is still favorable up to VEC ≈ 3.2.

We round out the picture with some related remarks about the metal–metal bonding. Figure 3 shows the computed energy ΔH_1 required to cut one atom off an isolated octahedron (four bonds) and ΔH_2 to cut the central joining atom out of an $L = 2$ double octahedron (eight bonds). They are similar to the

---

(3) Kumar, V.; Heine, V. *J. Phys. F* **1984**, *14*, 365.

(4) Heine, V. *Solid State Phys.* **1980**, *35*.

(5) Our calculations may not be very reliable in the antibonding part, where and according to ref 2 the antibonding combinations of the d_{xy}, d_{yz}, and d_{zx} orbitals with the nonmetal orbitals mix with the rest of the d band, whereas we have assumed them to lie above it.

corresponding quantities for cutting the end atom off a semiinfinite chain and a joining atom out of an infinite chain, shown in Figure 3 only for VEC = 4 because the values for other VECs are distorted by (or have to be adjusted for) differences in E_F. The similarity is in accordance with the localization of the bond energy already noted. However, Figure 3 shows clearly that ΔH_2 is *not* in general double the ΔH_1 value: the ΔH is seen to be nearly proportional to coordination number (CN) for low VEC but vary roughly as $(CN)^{1/2}$ for a half-filled band, in accordance with the principles[6] of metallic bonding.

Finally we comment on the relation to experiment. Given that one has the chain structure, our calculations do show that *the existence of band gaps causes the structure to become rapidly less stable at the observed VEC.* However, no compounds with the chain structure are known for VEC around 2 (Figure 1) or VEC ≈ 1.4–2 (Figure 2), where the structure would appear to be most stable. Presumably other structures have an even lower energy: if it is favorable to condense clusters into a chain, it is presumably even better to condense them into layers or three-dimensional arrays. We believe the latter argument is valid for low VEC, but not near a half-filled band (which would be consistent with the experimental facts stated) from the following analogy. Two hydrogen molecules with bonding states completely full have little interaction when approaching each other sideways, whereas two H_2^+ ions would experience strong bonding effects (ignoring the Coulomb repulsion) in a simple LCAO model, in accordance with the principles of metallic (very unsaturated) bonding.[6] More research is planned into the relative stability of different one-, two-, and three-diminsional condensation structures.

Acknowledgment. We have benefited greatly from discussions with Professors A. Simon and O. K. Andersen and from financial support by the Science and Engineering Research Council, U.K.

Registry No. Nb_5Te_4, 12035-11-9.

---

(6) Reference 4, pp 81–84.

Institut für Theoretische Physik
Freie Universität Berlin
D-1000 Berlin 33, Germany

Vijay Kumar

Cavendish Laboratory
Cambridge University
Cambridge CB3 OHE, U.K.

Volker Heine*

Received October 28, 1983

---

^{103}Rh NMR Spectrum of $[(Rh_2(mhp)_4)_2]$: First Measurement of $^1J(^{103}Rh,^{103}Rh)$ for a Rh_2^{4+} Core

Sir:

The synthesis and study of complexes containing the Rh_2^{4+} core has attracted considerable and sustained attention,[1-14] especially with respect to the nature of the metal–metal bonding. A general consensus has now been established[8-13] that, for $Rh^{II}_2L_4$ (where L is a bridging ligand, especially a carboxylate or oxypyridine) and related complexes, a $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*4}$, Rh–Rh (net) single bonding interaction occurs over the metal–metal separation of 2.359[13]–2.486 Å.[7] We considered that it would be of interest to record the ^{103}Rh NMR spectra of such complexes, especially for systems in which the two rhodium atoms are inequivalent, whence a direct measure of the $^1J(^{103}Rh,^{103}Rh)$ coupling constant should be obtained.

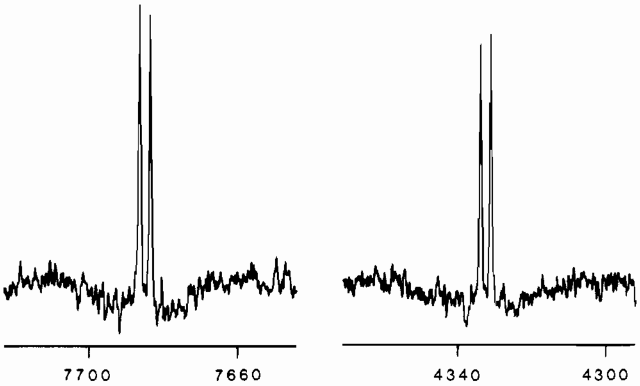

Figure 1. ^{103}Rh NMR spectrum of $[(Rh_2(mhp)_4)_2]$ in CD_2Cl_2/CH_2Cl_2 at ca. 300 K.

We chose for our initial ^{103}Rh NMR studies $[Rh_2(mhp)_4]$[13] and $[(Rh_2(mhp)_4)_2]$.[14] $[Rh_2(mhp)_4]$[13] is a member of the family of $[M_2(mhp)_4]$ molecules, known at present for M = Cr, Mo, W,[15] Rh,[13] Ru,[16] and Pd.[17] In each case, the molecules possess approximate D_{2d} symmetry, with each metal atom being coordinated to two nitrogen and two oxygen atoms. In contrast, $[(Rh_2(mhp)_4)_2]$ involves[14] an asymmetric arrangement of the four mhp ligands spanning the dimetal centers; one oxygen and three nitrogen atoms are coordinated to one rhodium(II) and one nitrogen and three oxygen atoms to the other. This arrangement of the ligands has the consequence that three methyl groups are located at one end of the molecule and one at the other: thus additional coordination is possible at the latter, open end of the molecule. In $[(Rh_2(mhp)_4)_2]$(c) this occurs via two $[Rh_2(mhp)_4]$ moieites each binding an oxygen atom of the other to form a central Rh–O–Rh–O ring and ^{1}H NMR studies are consistent with this structure being retained in solution.

The 12.65-MHz ^{103}Rh NMR spectra of saturated solutions of $[Rh_2(mhp)_4]$ and $[(Rh_2(mhp)_4)_2]$ in CD_2Cl_2/CH_2Cl_2 solution at ~300 K have been recorded on a Bruker WH-400 spectrometer, and the data are consistent with the molecular structures. Thus, the spectrum of the former compound consists of a single resonance at $\delta = 5745$ (reference used $\Xi(^{103}Rh) = 3.16$ MHz).[18] The ^{103}Rh NMR spectrum of the

---

(1) Cotton, F. A. *Chem. Soc. Rev.* **1975**, *4*, 27 and references therein.
(2) Koh, Y.-B.; Christoph, G. G. *Inorg. Chem.* **1978**, *17*, 2590 and references therein.
(3) Christoph, G. G.; Koh, Y.-B. *J. Am. Chem. Soc.* **1979**, *101*, 1422.
(4) Koh, Y.-B.; Christoph, G. G. *Inorg. Chem.* **1979**, *18*, 1122.
(5) Drago, R. S.; Tanner, S. P.; Richman, R. M.; Long, J. R. *J. Am. Chem. Soc.* **1979**, *101*, 2897.
(6) Cotton, F. A.; Felthouse, T. R. *Inorg. Chem.* **1980**, *19*, 320, 2347.
(7) Cotton, F. A.; Felthouse, T. R.; Klein, S. *Inorg. Chem.* **1981**, *20*, 3037.
(8) Norman, J. G., Jr.; Kolari, H. *J. Am. Chem. Soc.* **1978**, *100*, 791.
(9) Norman, J. G., Jr.; Renzoni, G. E.; Case, D. A. *J. Am. Chem. Soc.* **1979**, *101*, 5256.
(10) Bursten, B. E.; Cotton, F. A. *Inorg. Chem.* **1981**, *20*, 3042.
(11) Nakatsuji, H.; Ushio, J.; Kanda, K.; Onishi, Y.; Kawamura, T.; Yonezawa, T. *Chem. Phys. Lett.* **1981**, *79*, 299. Nakatsuji, H.; Onishi, Y.; Ushio, J. Yonezawa, T. *Inorg. Chem.* **1983**, *22*, 1623.
(12) Kawamura, T.; Fukanachi, K.; Sowa, T.; Hayashida, S.; Yonezawa, T. *J. Am. Chem. Soc.* **1981**, *103*, 364.
(13) Berry, M.; Garner, C. D.; Hillier, I. H.; MacDowall, A. A.; Clegg, W. *J. Chem. Soc., Chem. Commun.* **1980**, 494.
(14) Berry, M.; Garner, C. D.; Hillier, I. H.; Clegg, W. *Inorg. Chim. Acta* **1980**, *45*, L209.
(15) Cotton, F. A.; Fanwick, P. E.; Niswander, R. H.; Sekutowski, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 4725.
(16) Berry, M.; Garner, C. D.; Hillier, I. H.; MacDowall, A. A.; Clegg, W. *Inorg. Chim. Acta* **1980**, *53*, L61.
(17) Clegg, W.; Garner, C. D.; Al-Samman, M. H. *Inorg. Chem.* **1982**, *21*, 1897.
(18) See: Kidd, R. G.; Goodfellow, R. J. In "NMR and the Periodic Table"; Harris, R. K., Mann, B. E., Eds.; Academic Press: London, 1978; Chapter 8, p 245.