Inorg. Chem. **1980**, *19*, 3865–3866

Correspondence

Counterintuitive Consequences of Filled Ligand π Interactions with Metal d Orbitals[1]

Sir:

A recent paper[2] describes "an interesting dichotomy concerning the ligating properties of NS and NO" in $(\eta^5\text{-}C_5H_5)Cr(CO)_2NO$ and -NS complexes. The authors point out that "on the one hand, IR and electron-impact data suggest that NS is a better remover of electron density from the chromium atom than is NO. On the other hand, NMR and ionization potential measurements imply that it is a better provider of electrons to the metal center. A similar contradiction in experimental observations has been reported for the related complexes $(\eta^5\text{-}C_5H_5)Mn(CO)_2CS$ and $(\eta^5\text{-}C_5H_5)Mn(CO)_3$." From our previous results of valence photoelectron and parameter-free molecular orbital studies of thiocarbonyl complexes, we have shown that the NMR and ionization potential shifts from the carbonyl to the thiocarbonyl complexes are not inconsistent with a decrease of electron density at the metal center.[3] The important feature is a more strongly interacting π-bonding orbital (bonding between carbon and sulfur) of the CS ligand.

Although the description is straightforward in terms of usual orbital interaction considerations, care must be taken not to misinterpret the consequences. This is illustrated by the statement in the thionitrosyl paper that "such an explanation cannot be invoked for the NS ligand ... since currently accepted bonding formulations require an increase in electron density at the metal center (whether by σ or π donation from the ligands) to be manifested in increased M → CO π back-donation." We have recently conducted a photoelectron and theoretical investigation of the nitrosyl and thionitrosyl complexes and have found the description to be the same as the thiocarbonyl case. A preliminary report of our results was in press when reference 2 appeared.[4] It has also been our experience that such orbital interactions are not generally well understood. The consequences can have significance in other applications and need to be emphasized.

The filled π-bonding orbitals of the free ligands are the correct symmetry to interact with the filled metal d orbitals in these complexes. This interaction is illustrated with the familiar schematic diagram in Figure 1. The bonding combination is largely ligand π in character with metal d mixing in. The antibonding combination is largely metal d in character with some delocalization into the ligand π orbital. Because both orbitals are totally occupied, there is no net change in metal d electron density by this interaction. However, the metal d electron density in the bonding combination is less accessible for π back-donation because of the stability of the orbital. The antibonding combination has a more favorable energy for back-donation than the unpertubed metal orbital, but it is partially delocalized onto the ligand and has less available metal electron density. In the cases of NS and CS the removal of accessible metal π back-bonding density is enhanced by the low-lying and effective π*-acceptor orbitals of these ligands.[6] The calculations[4] show that the combined result of these interactions is a *decreased stability* of the molecular orbital which is mostly metal d in character along with a *decrease* in metal d electron density, consistent with the IR, electron-impact, and ionization potential measurements. The NMR shifts of the thiocarbonyl complexes have also been studied and are understood in terms of the importance of the paramagnetic contribution and the influence of the ligand π orbital on the ΔE term.[5]

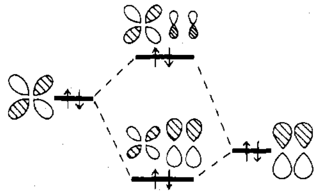

Figure 1. Schematic diagram of orbital energies and characters resulting from a filled ligand π orbital interacting with a filled metal d orbital.

It should be noted that the parameter-free molecular orbital calculations[3,4] agree with the trend in ionization energies without invoking errors in Koopmans' approximation.[7] Different electron relaxation energies associated with ionization of the NS and NO complexes might also contribute to the trend because the relative bonding interactions of NS and NO are expected to be different with the more positively charged metal center in the positive molecular ions.[8] For instance, the interaction of the NS π orbital with the metal will be greater in the positive ion because the orbital energies are more similar. Also, similar to the analysis of Andrews on CS and CO complexes,[8] the σ-donor to π-acceptor ratio of NS may be greater than that of NO in the positive ions. Exact calculation of the electron relaxation energies associated with this charge redistribution in the positive ions is difficult, but qualitative indications from general experimental and theoretical studies are that orbitals that are more delocalized and have lower metal character will have the smaller relaxation energies.[7] This means that ionization from the predominantly metal levels in the NS complex will involve a smaller relaxation energy than ionization of the corresponding levels of the NO complex. Thus consideration of relaxation energies alone would lead to an incorrect trend in the ionization energies.[9]

The important point is that such observable quantities do *not* directly reflect the change in charge on the metal atom, as is often assumed. The observables are associated with *molecular* properties, and the various orbital interactions and

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[1] We wish to acknowledge the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

[2] Greenhough, T. J.; Kolthammer, B. W. S.; Legzdins, P.; Trotter, J. *Inorg. Chem.* **1979**, *18*, 3548. We thank B. W. S. Kolthammer and M. B. Hall for discussions on this topic.

[3] Lichtenberger, D. L.; Fenske, R. F. *Inorg. Chem.* **1976**, *15*, 2015.

[4] Lichtenberger, D. L.; Hubbard, J. L. *Inorg. Chem.* **1980**, *19*, 1388.

[5] Block, T. F. *Diss. Abstr.* **1977**, *37*, 4477.

[6] This may be thought of as a 3 center–4 electron type interaction: Hoffmann, R.; Chen, M. M. L.; Thorn, D. L. *Inorg. Chem.* **1977**, *16*, 503. The present calculations indicate that the NS π-donor and π*-acceptor orbitals are almost equally responsible for the greater delocalization of metal density into the NS ligand than into the NO ligand. The orbital normally thought to be predominantly metal 3d with donation into the ligand π* (mostly nitrogen) is actually an orbital of roughly equivalent metal and sulfur character and with much lower nitrogen character.

[7] Calabro, D. C.; Lichtenberger, D. L. *Inorg. Chem.* **1980**, *19*, 1732 and references therein.

[8] Andrews, M. A. *Inorg. Chem.* **1977**, *16*, 496.

[9] Although the relaxation energies are expected to trend in the opposite direction indicated by the eigenvalues, deviations from Koopmans' approximation are likely to be significant in a total quantitative evaluation of the ionization of such systems.

[10] Alfred P. Sloan Fellow, 1979–1981.

0020-1669/80/1319-3865$01.00/0

ligand competition effects must be considered.

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Received May 30, 1980

Interconversion of Polyoxometallates

Sir:

The interface between the chemistry of solid-state lattices and discrete cluster molecules is becoming less sharply defined as parallels emerge[1] between the principles which determine the structural features of the two classes. The advantages of viewing cluster molecules as fragments of close-packed arrays, rather than as assemblies of atoms joined by directed bonds, is one interesting aspect.[1b,c] One of the "oldest" classes of metal clusters is the polyoxometallates, and interest in their chemistry is sustained by their complex (and incompletely understood) structural and reactivity patterns.[2] Interconversion of these large anions in solution is an intriguing feature of their chemistry,[3] and a mechanism for the isomerization of α- and β-$[Mo_8O_{26}]^{4-}$ via a series of intermediates has been presented[4] recently. The two isomers can be viewed as distorted arrays of cubic close-packed oxygen atoms with molybdenum atoms occupying interstitial sites.

This paper considers an alternative isomerization mechanism based upon concerted translations of close-packed fragments along molecular mirror planes. The process is reminiscent of the crystallographic shear concept which accounts for the structural features of certain molybdenum, and other early transition-metal, oxide phases.[5] This alternative mechanism (i) is consistent with current literature data and our ^{95}Mo NMR studies on the α and β forms and (ii) suggests that similar interconversions are possible in the paramolybdate $[Mo_7O_{24}]^{6-}$ and other systems. Although such processes have not been unequivocally detected for these systems as yet, we start by considering $[Mo_7O_{24}]^{6-}$ as the argument is developed most simply from that molecule.

In principle, paramolybdate could have either of the molecular structures of Figure 1. The observed[6] solid-state structure (designated P; C_{2v} point symmetry) is idealized in Figure 1b with use of the condensed polyhedron convention.[7] Figure 1a illustrates an alternative structure (designated A; D_{3d}) actually observed[8] for $[Cr^{III}Mo_6O_{24}]^{9-}$.

Interconversion of A and P can be achieved by concerted translation of an eight-oxygen, two-molybdenum fragment (O_8, Mo_2; idealized in Figure 2a as a pair of edge-shared, incomplete octahedra) along a mirror plane common to A and P. This translation is conveniently monitored by following[9] the marker oxygen highlighted in Figure 2, which is converted from a triply bridging (in A) to a doubly bridging (in P) ligand. In fact, multiple conversions of P → A followed by A → P *along a different mirror plane* scramble six of the seven mo-

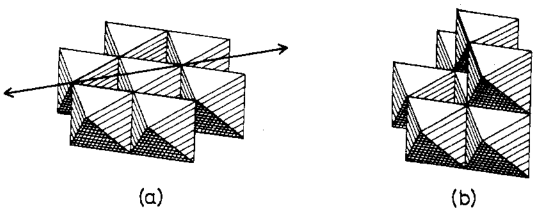

Figure 1. Idealized molecular structures of (a) $[CrMo_6O_{24}]^{9-}$ (structure A) and (b) $[Mo_7O_{24}]^{6-}$ (structure P) represented as condensed MO_6 octahedra. The common mirror plane is highlighted by the arrow.

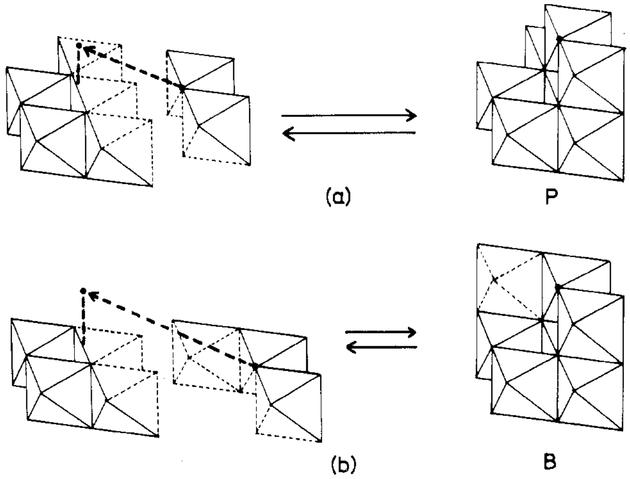

Figure 2. Schematic representation of the proposed (a) A ⇌ P interconversion and (b) A ⇌ B interconversion illustrating the (a) eight-oxygen, two-molybdenum (O_8, Mo_2) and (b) ten-oxygen, three-molybdenum (O_{10}, Mo_3) translations. The fragments, represented as incomplete (dashed lines) octahedra, are separated here for clarity *only* but are in contact throughout the translation. Marker oxygens are indicated by ●.

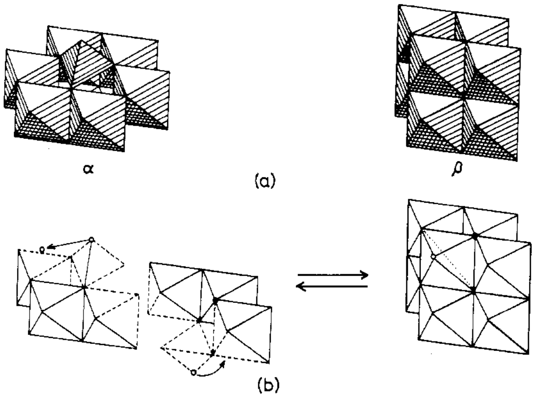

Figure 3. (a) Idealized molecular structures of α- and β-$[Mo_8O_{26}]^{4-}$. (b) Proposed interconversion $\alpha \rightleftharpoons \beta$ via concerted translation of a (O_{12}, Mo_3) fragment and the accompanying conversion of the tetrahedral Mo sites in α to octahedral sites in β. The fragments are separated for clarity *only*. Open circles represent the capping oxygens of α. The final positions of the four oxygens which define a capping "tetrahedron" in α are indicated by dotted lines in β.

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(1) (a) Burdett, J. K. *Nature (London)* **1979**, *279*, 121–125; *J. Am. Chem. Soc.* **1980**, *102*, 450–460. (b) Johnson, B. F. G.; Benfield, R. E. *J. Chem. Soc., Dalton Trans.* **1978**, 1554–1568. (c) Gillespie, R. J. *Chem. Soc. Rev.* **1979**, *8*, 315–352. (d) Muetterties, E. L.; Rhodin, T. N.; Band, E.; Brucker, C. F.; Pretzer, W. R. *Chem. Rev.*, **1979**, *79*, 91–137.

(2) (a) Tsigdinos, G. A. *Top. Curr. Chem.* **1978**, *76*, 1–64. (b) Tytko, K.-H.; Glemser, O. *Adv. Inorg. Chem. Radiochem.* **1976**, *19*, 239–315.

(3) Tytko, K.-H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1976**, *31*, 737–748 and references therein.

(4) Klemperer, W. G.; Shum, W. *J. Am. Chem. Soc.* **1976**, *98*, 8291–8293.

(5) Wells, A. F. "Structural Inorganic Chemistry", 4th ed.; Oxford University Press: London, 1975; pp 184–6.

(6) Evans, H. T., Jr.; Gatehouse, B. M.; Leverett, P. *J. Chem. Soc., Dalton Trans.* **1975**, 505–514.

(7) The idealized condensed polyhedron model is used here for illustrative convenience in two dimensions. However, we emphasize that many of the points are best appreciated by consideration of spatial and, particularly, cubic close-packed hard-sphere models.

(8) Perloff, A. *Inorg. Chem.* **1970**, *9*, 2228–2239.

(9) If a right-handed coordinate system is defined in Figures 1a and 2a with the origin at the marker oxygen, the z axis parallel to the C_3 symmetry axis, the y axis defined by the translational mirror plane, and octahedral edges defining unit length, the marker oxygen is translated to $(0, 3^{1/2}/2, {}^{1}/_{2})$.

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