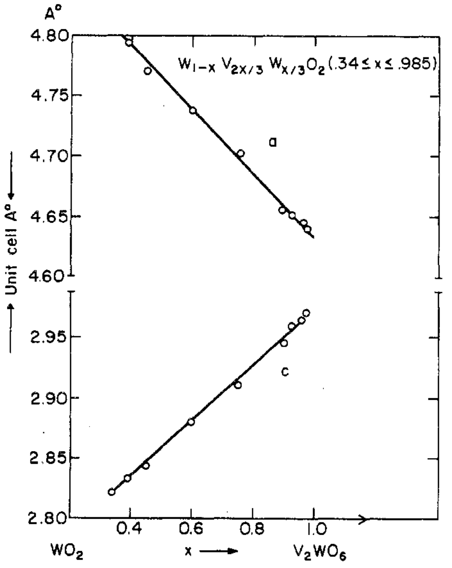

Figure 2. Unit cell parameters, at room temperature, as a function of composition for the rutile crystalline solution $0.34 \leq x \leq 0.985$.

that similar situations have also been reported for $V_{1-x}Mo_xO_2$ and $V_{1-x}W_xO_2$ crystalline solutions. The VO_2–V_2WO_6 system, however, is an exception to this rule. Both *a* and *c* parameters increased with increasing amounts of V_2WO_6 in VO_2.

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Some Anomalous Properties of Oxygen and Nitrogen

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It has been shown that the interaction energies of a fluorine atom with a variety of other species are anomalously low, relative to the trends among the other halogens.[1] Perhaps the best known example is F_2, but the same situation has been found for HF, CH_3F, and the alkali fluorides. In all of these cases the experimental dissociation energy of the fluorine-containing bond is lower than would be anticipated on the basis of the strengths of the analogous bonds in the other hydrogen halides, methyl halides, and alkali halides. The deviation is always approximately 26 kcal/mol of fluorine atoms.[1] In fact, the electron affinity of fluorine, corresponding to the interaction $F(g) + e^- \rightarrow F^-(g)$, is also lower than expected (less than that of chlorine!), and again by the same amount, 26 kcal/mol.

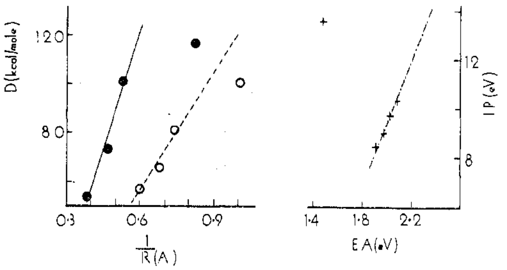

Figure 1. (Left) Relationships between the dissociation energies, *D*, and the reciprocals of the bond lengths, $1/R$, for the molecules X_2 (●) and XH (○) (X = S, Se, and Te). O_2 and OH are seen to deviate. (Right) Relationship between electron affinity and ionization potential for the atoms S–Po; again oxygen deviates.

These anomalous properties of the fluorine atom have been attributed to its very small size, which causes its electronic charge to be very highly concentrated and to consequently exert an exceptionally strong repulsive force upon any external electron that enters its outer shell, whether in forming a negative ion or a covalent bond.[1] This interpretation is not inconsistent with the highly reactive and electronegative nature of the fluorine atom; the point is simply that its electron-attracting and reactive strengths are not quite as great (by about 26 kcal/mol) as the trend among the other halogens implies.

Cotton and Wilkinson have suggested that "a similar effect may account for the low bond energies in H_2O_2 and N_2H_4".[2] They refer to the O–O and N–N bonds. The average energies of O–O and N–N single bonds are only 35 and 38 kcal/mol, respectively, whereas the values for S–S and P–P single bonds are 54 and 50 kcal/mol.[3] More specifically, the dissociation energy of H_2O_2 to two OH radicals is 51.1 kcal/mol, while the corresponding energy for H_2S_2 is 65 kcal/mol.[4] In this paper will be presented evidence supporting Cotton and Wilkinson's suggestion and indicating that there is indeed an anomalous repulsive effect, analogous to that of fluorine, operating in the cases of oxygen and probably also nitrogen. The line of approach will be similar to that used in the fluorine investigation.[1]

Just as for the halogens, the experimentally determined electron affinities of the group 6 elements show a gradual increase in going from polonium (1.9 eV) to sulfur (2.0772 eV), but then a sharp *decrease* for oxygen (1.462 eV).[5] In contrast, the ionization potentials increase monotonically through the same series, including oxygen.[6] For the elements Po–S, there is an excellent linear relationship between electron affinities and ionization potentials, as shown in Figure 1; the correlation coefficient is 0.995. Oxygen deviates very markedly from this relationship. Extrapolation of the line to the ionization potential of oxygen yields a corresponding electron affinity of 2.37 eV, which is 0.91 eV (21 kcal/mol) greater than the observed value. This is the first indication of an anomalous destabilizing effect associated with the interaction of an oxygen atom with an electron.

Further evidence is found when the dissociation energies of the X_2 and XH molecules (X = S, Se, Te) are plotted against the reciprocals of their bond lengths (see Figure 1).[7] Again following the pattern of the halogens, very good linear relationships are obtained (correlation coefficient = 0.988 for the X_2 molecules, 0.978 for the XH molecules), from which both O_2 and OH deviate. Extrapolation to the $1/R$ values of the latter shows that both of their dissociation energies are too low, by 77 kcal/mol for O_2 and 25 kcal/mol for OH. When the

O_2 deviation is divided by 4, to account for the fact that there are two oxygen atoms and each is interacting with the two electrons contributed to the bond by the other, there results a value of 19 kcal/mol of oxygen atoms per mol of electrons.

Thus, three different sets of experimental data lead to the same conclusion, that the interaction of an oxygen atom with an external electron includes an anomalous destabilizing contribution of approximately 21 kcal/mol. It is important to note that one of the properties with which this is associated is the electron affinity. This confirms that the effect operates even when there is no second atom present. It seems quite reasonable to attribute this extra destabilization, as in the case of fluorine, to the unusually strong repulsion between the oxygen electrons and the external electron, caused by the exceptionally small size of the oxygen atom[8] and the consequent highly concentrated nature of its electronic charge.

There are fewer reliable experimental data, of the type needed in this study, for nitrogen and the group 5 elements than for group 6. However, indications of a destabilizing contribution to the interaction of a nitrogen atom with an external electron can be found. For instance, a plot of electron affinity vs. ionization potential for the elements P, As, Sb, and Bi yields a line with a correlation coefficient of 0.956, and by extrapolation predicts a nitrogen electron affinity that is 6–8 kcal/mol *greater* than the best estimated values.[5,9] It should be noted that the anomalous destabilization energy decreases from fluorine to oxygen to nitrogen. This is in accord with the present interpretation of it, since the electronic charge distributions of the atoms become less concentrated and more diffuse, in the same order. For example, the polarizabilities of the atoms increase in going from fluorine to nitrogen.[10]

This destabilizing effect that has now been found for the fluorine, oxygen, and possibly nitrogen atoms is closely related to Huheey's concept of "charge capacity".[11] This treats the electronegativity of an atom as depending not only upon its inherent electron-attracting power, in some particular valence state, but also upon its capability of absorbing the additional electronic charge. This latter factor, the charge capacity, is of course affected by the strength of the repulsive interaction between the external electron and the electrons already associated with the atom. It is to be expected, therefore, that the atoms showing the anomalous destabilization discussed in this paper should have relatively low charge capacities. This is indeed found to be the case.[11] These considerations have played key roles in clarifying a number of puzzling situations.[12,13]

Registry No. O_2, 7782-44-7; N_2, 7727-37-9.

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Structural Relationships in $ARMo_3O_8$ Metal Atom Cluster Oxides

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Compounds of the type $ARMo_3O_8$ are of interest because they represent one of the few examples of metal atom clusters in oxide systems. Evidence for the presence of the cluster was first established[1,2] by single-crystal x-ray diffraction studies of $Zn_2Mo_3O_8$. These showed that the structure consisted of a distorted hexagonal close-packed array of oxygen atoms of the *abac* type in which tetravalent molybdenum occupies octahedral holes in alternate layers to form trigonal clusters of Mo in which three MoO_6 octahedra each share two edges, resulting in an Mo–Mo bond distance of 2.51 Å. The cluster-containing layers are held together by the A and R cations which occupy tetrahedral and octahedral holes, respectively. The first compounds of this type to be reported were those in which A and R were the same small divalent ion (A, R = Mg, Mn, Fe, Co, Ni, Zn, Cd). Subsequently, Donohue and Katz[3] reported the preparation of $LiScMo_3O_8$ and $LiYMo_3O_8$ in polycrystalline form. The structure of these compounds as determined from x-ray powder diffraction data[4] shows the trigonal Mo cluster interaction with Li occupying tetrahedral holes and Sc or Y in octahedral positions. The primary difference between these two compounds and the $Zn_2Mo_3O_8$ analogues is that the former have a simple oxygen packing of the *aba* type. Additional evidence for the presence of a strong cluster interaction in both types of compounds is given by magnetic measurements which indicate that molybdenum does not make any paramagnetic contribution to the observed moments.[1,4,5,6]

Recently, Kerner-Czescleba and Tourne[6] reported the preparation of a series of compounds of the type $LiRMo_3O_8$, where R is a trivalent ion whose stable binary oxide has the C rare earth structure (R = Sc, Y, In, Sm, Gd, Tb, Dy, Ho, Er, Yb). The unit cell data for these compounds is consistent with the *aba* packing sequence, except in the case of $LiScMo_3O_8$ and $LiInMo_3O_8$, where several very weak lines in the neutron powder diffraction patterns were consistent with a doubled *c* axis, which led to the conclusion that these two compounds were isomorphous with $Zn_2Mo_3O_8$. However, no analysis of the x-ray or neutron diffraction intensity data was presented to confirm this. At the time of their report a similar study was being conducted in this laboratory, the results of which are entirely consistent with the *aba* stacking for all compounds, including those of scandium and indium. The evidence for these conclusions is presented below along with unit cell data for the compounds prepared.

Experimental Section

The $LiBMo_3O_8$ oxides were prepared by heating a mixture of the appropriate molar ratios of MoO_2, Mo, Li_2MoO_4, and R_2O_3 (R = Sc, Y, In, Sm, Gd, Yb, Lu) in evacuated sealed silica capsules at