$O_2$ 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

**Table I.** Lattice Parameters and Densities for $LiRMo_3O_8$[a, b]

| | This work | | Ref 6 | | Density, g/cm$^3$ | |
|---|---|---|---|---|---|---|
| R | *a*, Å | *c*, Å | *a*, Å | *c*, Å | Obsd | Calcd |
| Sc | 5.724(1) | 4.943(1) | 5.742(9) | 4.950(4) | 5.51(3) | 5.54 |
| Y | 5.781(1) | 5.153(2) | 5.776(8) | 5.155(7) | 5.72(3) | 5.70 |
| In | 5.741(1) | 4.991(1) | 5.749(5) | 4.970(4) | 6.28(4) | 6.27 |
| Sm | 5.802(1) | 5.270(1) | 5.796(7) | 5.274(7) | | 6.19 |
| Gd | 5.798(1) | 5.230(1) | 5.793(8) | 5.225(3) | 6.36(2) | 6.33 |
| Yb | 5.769(1) | 5.111(1) | 5.758(2) | 5.104(3) | 6.70(2) | 6.72 |
| Lu | 5.766(1) | 5.096(1) | | | 6.74(4) | 6.77 |

[a] Least-squares standard deviations given in parentheses for the last decimal place of the lattice constants. [b] Standard deviations given in parentheses for the last decimal place for triplicate measurements of density.

750–850 °C for 65 h. The reactant oxides were weighed out to the nearest milligram, mixed intimately by careful grinding in an agate mortar, and pressed into pellets under 10 000 lb/in.$^2$ before sealing and firing. The oxides used were ROC/RIC $MoO_2$ (99.9% minimum), ROC/RIC $Li_2MoO4$ (99.5% minimum), and Alfa Inorganics rare earth oxides (all 99.9% minimum or better, except for $Lu_2O_3$, which was MCB 99.9% minimum). Molybdenum metal (325 mesh) was obtained from Alfa Inorganics and had a stated purity of 99.9%. The rare earth oxides were ignited at 900 °C for 24 h prior to use, while the $Li_2MoO_4$ and $MoO_2$ were dried at 120 °C. In addition, $MoO_2$ was washed several times with alternate portions of dilute HCl, distilled water, and ammonium hydroxide until the presence of molybdenum blue was no longer observed in the washings.

The products were black in the massive form but dark green when finely ground. Traces of $MoO_2$, observed in the diffraction patterns, could be removed below the level of x-ray detection by treatment with 3 M $HNO_3$, except in the case of samarium compound, which also reacted rapidly with this reagent. It was noted that the extent of this decomposition increased noticeably as the size of the trivalent ion increased. Treatment with warm 3 M HCl was effective in removing any unreacted $R_2O_3$ present.

Densities were determined pycnometrically using $CCl_4$ as a displacement medium. The observed values were all within 1% of the values calculated from the x-ray data. The density of the samarium compound was not determined because of the lack of purity.

Unit cell data was obtained from x-ray powder diffraction photographs taken with a 114.6 mm diameter Philips camera using filtered copper radiation. Lattice parameters were calculated by a least-squares method using several reflections in the 55–90° $\theta$ region, selected so as to avoid possible overlapping reflections. Photographic intensities were estimated using calibrated intensity strips. More accurate intensity data for the forward reflections of the indium compound were obtained from the peak areas of diffractometer traces obtained with a Philips Model 42202 goniometer.

**Lattice Parameter Measurements and Indexing.** All patterns were successfully indexed on the basis of a hexagonal unit cell consistent with the space group *P*3*m*1 (156), as found by DeBenedittis and Katz[4] for the Sc and Y compounds. Additional lines in the Sm compound were attributable to starting materials. The reliability of the indexing is indicated by the fact that $M_{20}$, the de Wolff figure of merit[7] for the first 20 K$\alpha$ lines of all compounds, was in excess of 10. The lowest $M_{20}$ values were found for the Sc and In compounds where numerous line overlaps occur. Further, the critical volumes as defined by Werner[8] were all approximately a factor of 10 in excess of the unit cell volumes.

Table I gives a comparison of the lattice parameters obtained in this work with those found by Kerner-Czeskleba and Tourne. Their reported *c* parameter for the Sc and In compounds has been halved for purposes of comparison. In general, the agreement falls within the range of standard errors given, the most notable difference being in the *c* parameter of the indium compound.

**Table II.** X-Ray Data for $LiInMo_3O_8$: *aba* Layering[a]

| *hkl* | $\theta$, deg | $d_{obsd}$, Å | $d_{calcd}$, Å | $I_{obsd}$ | $I_{calcd}$ |
|---|---|---|---|---|---|
| 001<br>100 | 7.996[b] | 5.004 | 4.9910<br>4.9719 | 1 | |
| 001<br>100 | 8.901 | 4.982 | 4.9910<br>4.9719 | 64 | 40 |
| 101 | 11.401[b] | 3.526 | 3.5224 | 1 | |
| 101 | 12.628 | 3.526 | 3.5224 | 100 | 91 |
| 110 | 15.559 | 2.874 | 2.8705 | 0.5 | 0.8 |
| 002<br>111<br>200 | 16.279[b] | 2.483 | 2.4895<br>2.4883<br>2.4859 | 0.8 | |
| 002<br>111<br>200 | 18.063 | 2.486 | 2.4895<br>2.4883<br>2.4859 | 83 | 87 |
| 102<br>201 | 20.279 | 2.224 | 2.303<br>2.225 | 19 | 21 |
| 202<br>211 | 23.302[b] | 1.760 | 1.7612<br>1.7587 | 0.5 | |
| 112<br>210 | 24.200 | 1.881 | 1.8832<br>1.8792 | 3 | 4 |
| 202<br>211 | 25.985 | 1.759 | 1.7612<br>1.7587 | 72 | 75 |
| 003 | | | 1.6637 | <0.5 | 0.6 |
| 300 | 27.723 | 1.657 | 1.6571 | 3 | 3 |
| 103<br>301 | 29.303 | 1.575 | 1.5787<br>1.5728 | 21 | 23 |
| 212 | 30.896 | 1.501 | 1.5012 | 2 | 3 |
| 113<br>222 | 32.434 | 1.437 | 1.4394<br>1.4352 | 16 | 19 |
| 203<br>302<br>221<br>310 | 33.900 | 1.382 | 1.3826<br>1.3806<br>1.3793<br>1.3789 | 8 | 12 |
| 311 | 35.453 | 1.329 | 1.3291 | 3 | 6 |
| 004<br>213<br>222<br>400 | 38.246 | 1.2452 | 1.2477<br>1.2456<br>1.2442<br>1.2430 | 20 | 21 |
| 312<br>401 | 39.721 | 1.2063 | 1.2069<br>1.2061 | 1 | 3 |
| 303 | 41.022 | 1.1745 | 1.1741 | 3 | 4 |
| 114<br>320 | 42.463 | 1.1419 | 1.1443<br>1.1406 | 1 | 2 |
| 204 | | | 1.1152 | | |
| 402<br>321 | 43.815 | 1.1135 | 1.1126<br>1.1120 | 20 | 21 |
| 223<br>410 | 45.233 | 1.0858 | 1.0867<br>1.0849 | 1 | 2 |
| 313<br>410 | 46.601 | 1.0610 | 1.0617<br>1.0602 | 4 | 8 |

[a] $M_{20} = 10.1$, $V_{crit} = 1690$ Å$^3$, $R' = 0.15$, and $\lambda_{K\alpha_1\alpha_2} = 1.54178$ Å. [b] Apparent $\beta$ reflections.

**Confirmation of the Structure.** The x-ray powder diffraction pattern for the forward reflections of $LiInMo_3O_8$ is given in Table II. Several very weak reflections, which have been attributed to $\beta$ radiation, have been included since one of them might be taken as evidence for a doubled *c* axis length. The calculated intensities were obtained with a modified version of POWPAT[9] using the atomic position parameters found by DeBenedittis and Katz[4] for $LiScMo_3O_8$ and $LiYMo_3O_8$. Atomic scattering factors were calculated using Moore's approximation.[10] No temperature factors were used in the calculations. Scale factors were taken so that the sum of the observed intensities were equal to the sum of the calculated values. The resultant intensity discrepancy factor $R' = \sum|I_{obsd} - I_{calcd}|/\sum I_{obsd}$ of 0.15 would seem to confirm the essential correctness of the structure. Further attempts at refinement did not seem warranted considering both the overall quality of the data and the prevalence of overlapping reflections. Similar calculations for the remaining compounds listed in Table I indicate that they too are isomorphous with $LiInMo_3O_8$.

Table III compares the observed intensities with those calculated for the first 20 lines of $LiInMo_3O_8$ assuming that the *c* axis should be doubled and that the layering sequence is identical with that found for $Zn_2Mo_3O_8$. The atomic parameters used were those of Ansell and Katz[2] found for $Zn_2Mo_3O_8$ with Li placed in the tetrahedral sites and In occupying octahedral positions. Clearly, this structure is not possible even if one allows for reasonable variation of the atomic parameters since several reflections which should be quite strong were not observed.

## Discussion of Results

The results of these experiments yield no evidence for the *abac* type layering in any of the compounds of the type $LiRMo_3O_8$. It should also be noted that, while the interplanar spacing data of Kerner-Czescleba and Tourne for the Sc and

Table III. X-Ray Data for $LiInMo_3O_8$: *abac* Layering

| hkl | $d_{calcd}$ | $I_{calcd}$ | $I_{obsd}$ |
|---|---|---|---|
| 002 | 4.991 | 34 | 64 |
| 100 | 4.972 | | |
| 101 | 4.450 | 49 | |
| 102 | 3.522 | 45 | 100 |
| 110 | 2.871 | 0.1 | 0.5 |
| 103 | 2.765 | 17 | 0.8 |
| 004 | 2.496 | 54 | 84 |
| 112 | 2.488 | | |
| 200 | 2.486 | | |
| 201 | 2.412 | 34 | |
| 104 | 2.230 | 10 | 19 |
| 202 | 2.225 | | |
| 203 | 1.992 | 36 | |
| 114 | 1.883 | 3 | 3 |
| 210 | 1.879 | | |
| 105 | 1.853 | 15 | |
| 211 | 1.847 | | |
| 204 | 1.761 | 13 | 72 |
| 212 | 1.759 | | |
| 006 | 1.664 | 1 | 3 |
| 300 | 1.657 | | |
| 213 | 1.636 | 21 | |
| 301 | 1.635 | | |
| 106 | 1.578 | 15 | 21 |
| 302 | 1.573 | | |
| 205 | 1.557 | 28 | |
| 214 | 1.501 | 3 | 2 |
| 303 | 1.483 | 3 | |
| 116 | 1.439 | 20 | 16 |
| 220 | 1.435 | | |
| 206 | 1.383 | 3 | 8 |
| 304 | 1.381 | | |
| 222 | 1.379 | | |
| 310 | 1.379 | | |

In compounds is consistent with the unit cell size of $Zn_2Mo_3O_8$, their observed intensities are not compatible with an *abac* layering; e.g., the 101 reflection for $LiInMo_3O_8$ on the basis of this layering should be very strong for x rays and of moderate intensity for neutrons, but Kerner-Czescleba and Tourne did not observe it. This would seem to preclude even the possibility of their phases being a mixture of polymorphs with the *aba* type dominant.

Although the nearest-neighbor arrangements in the $Zn_2Mo_3O_8$ and $LiRMo_3O_8$ structures are very similar, the second nearest-neighbor arrangements are significantly different. In $Zn_2Mo_3O_8$, both tetrahedral and octahedral zinc atoms have nine second nearest-neighbor molybdenums. For tetrahedral zinc, three Mo's are 3.54 Å distant while six more Mo's are at 3.48 Å. In the case of octahedral zinc these distances are 3.21 and 3.27 Å, respectively. Using $LiInMo_3O_8$ as an example for the $LiRMo_3O_8$ type, each Li is surrounded by a trigonal prism of molybdenums, three of which are 2.97 Å distant with the remaining three at 3.26 Å. On the other hand, In is surrounded by 12 second nearest-neighbor Mo's at the corners of an irregular hexagon, resulting in two sets of In–Mo distances of 3.71 and 3.91 Å respectively. The net effect then is to make the Zn–Mo distances more nearly equal in $Zn_2Mo_3O_8$, while in the $LiRMo_3O_8$ types the Li–Mo distances decrease and the R–Mo distances increase along with the change in coordination number. The differences in coordination number are qualitatively consistent with what might be expected on the basis of the electrostatic repulsions and provides a possible explanation for the observed structural differences. However, it should be noted that the best data currently available do not allow one to locate Li and O with the degree of certainty required for the calculation of electrostatic potentials in these systems.

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**Registry No.** $LiScMo_3O_8$, 12201-19-3; $LiYMo_3O_8$, 12201-20-6; $LiInMo_3O_8$, 64475-44-1; $LiSmMo_3O_8$, 60606-28-2; $LiGdMo_3O_8$, 60606-18-0; $LiYbMo_3O_8$, 60606-30-6; $LiLuMo_3O_8$, 64475-43-0.

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## Deuteration of Triborane(7) Adducts with Anhydrous Deuterium Chloride

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Deuterated boron hydride compounds are useful for structural and mechanistic studies in boron hydride chemistry. A number of hydrogen–deuterium exchange reactions that can be used for preparation of deuterated boron hydride compounds have been reported in the literature. Some of the reactions yield compounds which are deuterated at specific positions of the borane molecules, as represented by the reaction of pentaborane(9) with DCl in the presence of $AlCl_3$ to give 1-deuteriopentaborane(9)[1] and by the reaction of decaborane(14) with $D_2O$ to give $\mu$-tetradeuteriodecaborane(14).[2] Some involve the exchange of all the hydrogen atoms that are bonded to boron atoms. These include the isotopic exchanges between tetraborane(10) and deuterated diborane(6)[3] and between $B_{12}H_{12}^{2-}$ and $D_2O$.[4] A rapid exchange of the hydrogen atoms attached to the boron atom in trimethylamine–borane(3) with the deuterium atoms in acidified heavy water was used successfully to prepare the B-deuterated borane adduct which is useful as a research chemical.[5]

We now report a hydrogen–deuterium exchange reaction between triborane(7) adducts and deuterium chloride which involves all the hydrogen atoms in the $B_3H_7$ moiety and proceeds rapidly even at low temperatures.

### Results and Discussion

Treatment of a dichloromethane solution of trimethylamine–triborane(7) or tetrahydrofuran–triborane(7) with anhydrous deuterium chloride (90% enrichment) at −80 °C for about 5 min resulted in the exchange of the borane hydrogens with deuterium in the deuterium chloride sample. Evidence for the exchange is provided by loss of the fine structure of the $^{11}B$ NMR signal of the triborane(7) adduct and by the increased intensity of the HCl absorption band accompanied by the decreased intensity of the DCl absorption band in the infrared spectrum of the deuterium chloride sample recovered after the treatment.

The equilibrated distribution of the two isotopes in the mixture is reached rapidly. Thus, eight successive treatments of a dichloromethane solution of trimethylamine–triborane(7) with deuterium chloride (90% D), in a 1:4.2 molar ratio at each treatment, gave a sample of the triborane(7) adduct with