

sym-P-Trimethyltriphenylcyclotriborophane and Hydrogen Fluoride.—A 10-ml. quantity of anhydrous hydrogen fluoride was added to a 30-ml. stainless steel cylinder cooled to -78° and containing 0.6250 g. (1.532 mmoles) of *sym*-P-trimethyltriphenylcyclotriborophane (isomer m.p. $125-126^{\circ}$). The cylinder was cooled to -196° and the contents degassed by warming to -78° . After standing at ambient temperature for 48 hr. the cylinder was opened *in vacuo* at -196° and 145.6 cc. (6.54 mmoles 71.2%) of hydrogen recovered. An additional 21 hr. at ambient temperature raised the total volume of gas to 153.6 cc. (6.86 mmoles; 74.7%). Finally, it was necessary to heat the tube to 50° for 28.5 hr. to complete the reaction; 208.3 cc. (9.30 mmoles; 101.3%) of noncondensable gas was found which assayed 99.6% hydrogen and 0.4% methane on combustion analysis and corresponded to the replacement of 5.95 moles of hydrogen per mole of triborophane. Work-up of the reaction product provided a brown residue which could not be crystallized. On washing with water the solid appeared to undergo decomposition accompanied by color changes and a strong phosphine odor.

P-Hexaphenylcyclotriborophane and Hydrogen Fluoride.—To 0.300 g. (0.505 mmole) of P-hexaphenylcyclotriborophane in a polyethylene tube at -78° was added 5 ml. of anhydrous hydrogen fluoride. The solid appeared insoluble even as the mixture was allowed to warm to the boiling point. Following evaporation of the hydrogen fluoride the residual white solid was crystallized from benzene-ethanol to recover 0.290 g. (97%) of starting material.

Repetition of the above experiment using 0.2160 g. (0.364 mmole) of P-hexaphenylcyclotriborophane, 3 ml. of anhydrous hydrogen fluoride, and 5 ml. of benzene as a common solvent likewise proved unsuccessful. A 90% recovery of starting material was obtained after one crystallization.

Hydrolysis Experiments.—For these experiments a weighed sample of cyclotriborophane (Table II) was sealed under vacuum in a new Pyrex tube of 5.5-ml. capacity with 1.0 ml. of degassed distilled water. The tube was then heated for 24 hr. at 202° (refluxing acetophenone bath), opened on the vacuum line, and noncondensable gas formed during hydrolysis was collected. The aqueous solution was then analyzed for boric acid and halide ion.

Oxidative Studies.—The apparatus consisted of a 0.5-in. diameter \times 3 in. copper cylinder with a 0.375-in. diameter hemispherical sample well at one end wound with a Nichrome wire heating element and insulated with magnesia. A thermowell extended from the bottom of the block to within $1/32$ in. of the bottom of the sample well. The temperatures were determined with a copper-constantan thermocouple. The apparatus was allowed to warm at a rate of $5-10^{\circ}/\text{min.}$ in the vicinity of the ignition temperature. As the block was heated small samples (*ca.* 5 mg.) were dropped into the carefully cleaned sample well (decomposition and combustion deposits showed a marked but variable lowering of the ignition temperature) until ignition of a fresh sample was observed (Table II).

Acknowledgment.—The authors are indebted to Messrs. Earl M. Evleth, Jr., Stanley E. Gordon, Stanley E. Iversen, and Richard H. Suess, each of whom contributed to the experimental work. Particular thanks are due to Mrs. Nancy J. Nauman for infrared analyses, Messrs. M. Eugene Persons and William M. Birch for combustion analyses, and Mr. Karl H. Sterner for wet analyses.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE 39, MASSACHUSETTS

Metal Atom Clusters in Oxide Systems¹

By F. A. COTTON²

Received March 6, 1964

Compounds of the type $M^{II}_2Mo_3O_8$, described earlier by McCarroll, Katz, and Ward, contain metal atom clusters, Mo_3O_{13} . In this paper, these are treated by an LCAO-MO method similar to that used previously for other metal atom clusters. The pattern of molecular orbital energies which is obtained accounts satisfactorily for the strong metal-to-metal bonding and the absence of unpaired electrons. Moreover, using the orbital energy pattern, a number of predictions can be made of other mixed metal oxides which might be isostructural, and a suggestion is made regarding the nature of molybdenum blue.

Introduction

Several recent publications³⁻⁵ from this laboratory have discussed some compounds belonging to a general class for which we have suggested the name "metal atom cluster" compounds. The term cluster seems an appropriate one for a finite group of metal atoms which are held together mainly, or at least to a significant extent, by bonds directly between the metal atoms, even though some nonmetal atoms may also be intimately associated with the cluster.⁶ It has been

shown that for several of the best known and most symmetrical of these clusters, fairly simple and straightforward molecular orbital treatments give patterns of orbital energies which well explain their stability and diamagnetism.⁴ In all of the ones treated so far, the nonmetal atoms have been halogens.

In 1957, McCarroll, Katz, and Ward^{7,8} reported the preparation and X-ray structure determination of compounds with the general formula $M^{II}_2Mo_3O_8$, in which there are triangular groups of Mo atoms with Mo-Mo

(1) Supported by the United States Atomic Energy Commission.

(2) Fellow of the Alfred P. Sloan Foundation.

(3) J. A. Bertrand, F. A. Cotton, and W. A. Dollase, *Inorg. Chem.*, **2**, 1166 (1963).

(4) F. A. Cotton and T. E. Haas, *ibid.*, **3**, 10 (1964). In Fig. 3, the lower $T_{2g}(xz,yz)$ orbital should be designated $T_{1g}(xz,yz)$.

(5) F. A. Cotton and J. T. Mague, *ibid.*, **3**, 1094 (1964).

(6) The term "cage" was avoided, since these closely packed groups of metal atoms do not, in general, enclose any other atoms.

(7) W. H. McCarroll, L. Katz, and R. Ward, *J. Am. Chem. Soc.*, **79**, 5410 (1957).

(8) The author is grateful to Professor Ward for directing his attention to this paper, and to Professor Katz for further correspondence concerning it.

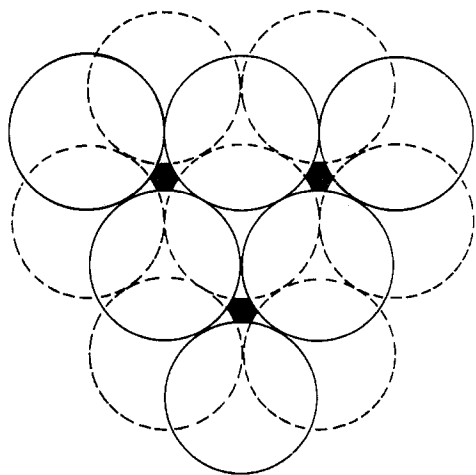


Fig. 1.—A group of three close molybdenum atoms and their thirteen nearest oxygen atoms as they occur in the $M^{II}_2Mo_3O_8$ compounds. The packing of the oxygen atoms has been idealized so that these atoms form a fragment of a perfect close-packed array.

distances of only about 2.5 Å., indicative of strong metal-to-metal bonding. The oxygen atoms form a distorted close-packed array, with the M^{2+} ions occupying both octahedral and tetrahedral interstices. The purpose of the work reported here was to investigate the properties of the group of molybdenum atoms and their immediate neighbors, considering them as a cluster, by the LCAO-MO approach described previously.⁴

Procedure

Figure 1 shows the cluster and its intimately associated oxygen atoms; the arrangement of oxygen atoms has been somewhat idealized so as to be a fragment of an ideally close-packed array. It may be noted that each of these Mo_3O_{13} groups is sufficiently distinct from its closest neighboring ones that treating them singly seems entirely justified. The Mo_3O_{13} group depicted has C_{3v} symmetry. It consists, in its idealized form, of three MoO_6 octahedra fused together with their threefold axes parallel. Therefore, it is convenient to view the bonding of each metal atom to its six neighboring oxygen atoms using a threefold axis (rather than, as usual, a fourfold axis) of the octahedron as the axis of quantization. On this basis, we may regard the d_{xz} , d_{yz} , s , p_x , p_y , and p_z orbitals of each metal atom as being used in forming σ -bonds to the oxygen atoms. The d_{xy} , $d_{x^2-y^2}$, and d_{z^2} orbitals on each metal atom thus remain for metal-to-metal interactions, although they may also be partially utilized in π -bonding to the oxygen atoms.

When the three d_{z^2} orbitals are combined into symmetry-correct LCAO-MO's they give one of A_1 symmetry, which should have bonding character, and a degenerate pair, of E symmetry, which should be antibonding. Similarly, the three d_{xy} orbitals give a bonding, A_1 , and antibonding, E, molecular orbitals, while the three $d_{x^2-y^2}$ orbitals combine to furnish an antibonding A_2 orbital and a doubly degenerate E pair which is bonding.

In order to assess more accurately the relative energies of these six LCAO-MO's, Hückel-type calculations were carried out. The expressions for the energies were derived and evaluated according to the procedures previously described.⁴ In the present instance, the interactions between MO's of the same symmetry do not in any case vanish; they were all evaluated using the appropriate quadratic equations.

The results of the computations are embodied in the form of an energy level diagram, Fig. 2. As before, the unit of energy is the valence state ionization potential (VSIP) of the metal atom, and the energy of the d-orbitals prior to interaction with one

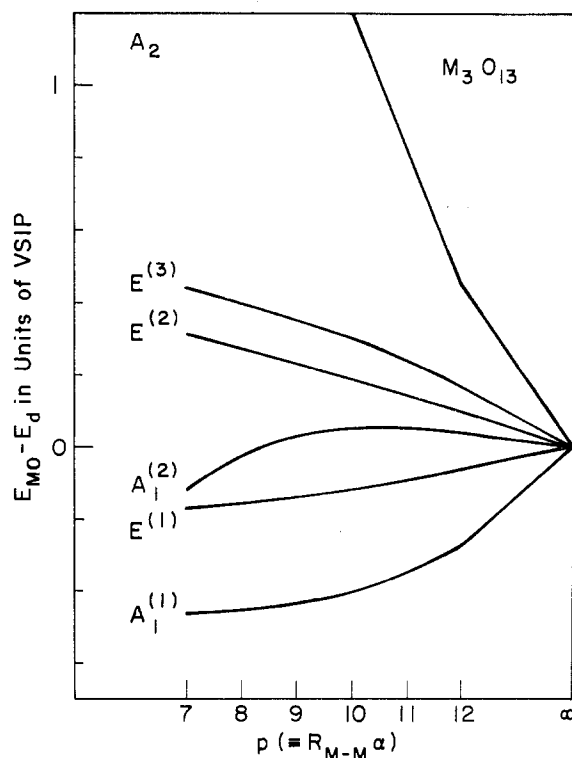


Fig. 2.—A diagram of the MO energies as a function of the product of the orbital exponent for the metal 4d orbitals and the (fixed) metal-metal distance. The zero of energy is the energy of noninteracting 4d t_{2g} electrons in one MoO_6 octahedron.

another serves as the zero of energy. The parameter, p , has been varied over a range which, for reasons given previously,⁴ appears likely to include all reasonable values. Finally, it may be noted that the exceptionally steep rise of the A_2 orbital is an artifact of the calculation, because of the occurrence of $1 + 2S$ in the denominator of the energy expression with rather sizable negative values of S in the range of p used.

Discussion

The structure of $Zn_2Mo_3O_8$ was reported in detail by McCarroll, Katz, and Ward, but in a relatively unrefined state, by present-day standards. An attempt to refine it further using the published intensity data was not entirely successful. The results did suggest that no shifts in positional parameters large enough to be relevant in this investigation were likely to occur, but some temperature factors behaved unrealistically.⁹ However, there does not appear to be any doubt that the published structure is correct in all essentials.

The energy level diagram neatly explains the reported diamagnetism,⁷ since each molybdenum atom, with formal oxidation number IV, contributes two electrons to the orbitals of the cluster. These six electrons just fill the consistently strongly bonding $A_1^{(1)}$ and $E^{(1)}$ MO's.

On the basis of the energy level pattern, Fig. 2, formulas for other compounds possessing the M_3O_{13} arrangement shown in Fig. 1 may be derived. For the most part, attention will be restricted to compounds

(9) Professor Katz has informed the author that he expects to continue his X-ray studies of these compounds with a view to obtaining more fully refined structures.

which could have exactly the same stoichiometry and over-all structure as the $M^{II}_2Mo_3O_8$ compounds, since it is known that such an over-all structure is compatible with general packing and electrostatic requirements. It is, of course, quite possible that there may be other satisfactory general structures in which this particular trinuclear cluster might occur.

As an example of a fairly simple but nontrivial prediction of a possible new compound, $M^{III}_2Mo_3O_8$ might be cited. The M^{3+} ions might be Ga^{3+} , which is similar in size to Zn^{2+} and about equally capable of occupying both octahedral and tetrahedral interstices (as demanded by the over-all structure). The two extra electrons would occupy the nonbonding, or slightly bonding, $A_1^{(2)}$ orbital.

Another idea is suggested by the fact that the $A_1^{(1)}$ orbital is so much more strongly bonding than the $E^{(1)}$ orbitals. If the two M^{2+} cations and the four electrons occupying the $E^{(1)}$ orbitals are removed, one is left with the stoichiometry Mo_3O_8 . Of course, the over-all structure would be unlikely to survive the excision of the M^{2+} ions, but fragments with this stoichiometry, perhaps hydrated, protonated, or combined with MoO_3 , and containing the Mo_3O_{13} cluster with only the $A_1^{(1)}$ molecular orbital occupied, might be stable. This possibility is of interest in connection with the long-standing question of the nature of molybdenum blue. Studies of this problem are legion, but, in general, the experimental results have been of the sort presented relatively recently by Sacconi and Cini,¹⁰ who report the blues to be essentially diamagnetic,¹¹ amorphous substances containing comparable fractions of both Mo(V) and Mo(VI), with the actual ratio variable. Virtually any ratio of Mo(V)/Mo(VI) could be accounted for by assuming the cluster-containing Mo_3O_8 , which has, formally, Mo(V)/Mo(VI) = 2, to be associated with MoO_3 or some other molybdenum oxide containing mainly Mo(VI). It is highly probable that the cluster-containing Mo_3O_8 would be colored, since nearly all metal atom clusters have visible absorption,⁵ but it cannot be said whether their color would be that characteristic of the molybdenum blues.

In order to search more systematically for other compounds which might contain M_3O_{13} clusters, the following procedure can be used. Let the general formula be ABM_3O_8 , where A is a cation of charge Q_t in a tetrahedral hole and B is a cation of charge Q_o in an octahedral hole. Let N be the number of valence electrons in the neutral atom, M, and n the number of electrons in the molecular orbitals of the M_3O_{13} cluster. Electroneutrality of ABM_3O_8 then requires that

$$Q_t + Q_o + 3N - n = 16$$

If we further assume that electron configurations $[A_1^{(1)}]^2$, $[A_1^{(1)}]^2[E^{(1)}]^4$, and $[A_1^{(1)}]^2[E^{(1)}]^4[A_1^{(2)}]^2$ are all

(10) L. Sacconi and R. Cini, *J. Chem. Phys.*, **18**, 1124 (1950); a number of references to previous papers are given here.

(11) The feeble paramagnetism reported by these and some other authors could be of the temperature-independent type, which is possible in the electron configuration being suggested here.

possibilities, n may take the values 2, 6, and 8, respectively. It is then possible to tabulate the magnitudes of $Q_o + Q_t$, which are required to give the proper values of n for various values of N , the periodic group number of the metal atom, M. These are listed in Table I. The values $N = 6$ and charge sum of 4 in bold type are those of the known $M^{II}_2Mo_3O_8$ compounds.

TABLE I
CHARGES ON A AND B IN ABM_3O_8 FOR CERTAIN ELECTRON CONFIGURATIONS (OF 2, 6, OR 8 ELECTRONS) WITH M FROM VARIOUS PERIODIC GROUPS

Periodic group no., N , of metal atom	Sum of charges on A and B ($Q_t + Q_o$) for the several electronic populations, n , of the cluster		
	$n = 2$	$n = 6$	$n = 8$
M			
4	6	10	12
5	3	7	9
6	0	4	6
7	.. ^a	1	3
8	0

^a Indicates negative value would be required.

Charge sums as high as 9, 10, and 12 would require A and B ions so highly charged as to be relatively unlikely, while charge sums of 0 and 1 would seem incompatible with the general electrostatic requirements of the over-all structure. Charge sums of 3, 4, 6, and 7 appear to be plausible and could be achieved by the combinations suggested in Table II. Again, the figures in bold type refer to the known compounds, $M^{II}_2Mo_3O_8$.

TABLE II
PLAUSIBLE CHARGES FOR THE A AND B CATIONS IN ABM_3O_8 WITH CATIONS, M, FROM VARIOUS GROUPS, N

N	(Q_t, Q_o) and (Q_o, Q_t)
	$n = 2$
4	(1, 5), (2, 4), (3, 3)
5	(1, 2)
	$n = 6$
5	(1, 6), (2, 5), (3, 4)
6	(1, 3), (2, 2)
	$n = 8$
6	(1, 5), (2, 4), (3, 3)
7	(1, 2)

One of the possibilities in Table II, namely, the one with $N = 6$ and (Q_t, Q_o) of (1, 3) or (3, 1) could certainly have been foreseen more directly and in fact was foreseen independently by others.¹²

An extended discussion of A and B cations, as well as M ions, which might be used to explore the other possibilities will not be given here. A few isolated examples may be given for illustration, however. Compounds with M from group V (say Nb or Ta) and the same electron configuration as the $M^{II}_2Mo_3O_8$ compounds might be the best ones to study first, since they involve the smallest extrapolation from the known. Taking (Q_t, Q_o) as (3, 4) or (4, 3), the A and B ions might

(12) By Professor Katz and his colleagues, who have prepared a compound which they believe to be $LiScMo_3O_8$; see P. C. Donohue and L. Katz, *Nature*, **201**, 180 (1964).

be Sc, Y, or one of the lanthanides, together with Zr, Hf, or Sn. For a compound with M from group VI and $n = 8$, there is, in addition to the possibility $Q_0 =$

$Q_t = 3$, one with (Q_t, Q_0) of (2, 4) or (4, 2). For these, A and B might be Mg or Ca, together with Zr, Hf, or Sn.

CONTRIBUTION FROM RCA LABORATORIES,
PRINCETON, NEW JERSEY

The Preparation, Properties, and Crystal Structures of Some Scandium Sulfides in the Range Sc_2S_3 –ScS

By J. P. DISMUKES AND J. G. WHITE

Received March 6, 1964

Scandium sesquisulfide, Sc_2S_3 , was prepared by the high-temperature reaction of hydrogen sulfide with scandium sesquioxide. Due to the problem of stoichiometry associated with the high melting point, 1775° , stoichiometric crystals of Sc_2S_3 were prepared by chemical transport with I_2 at 950° . A nonstoichiometric material containing an excess of scandium compared with Sc_2S_3 was prepared by heating Sc_2S_3 under vacuum at 1650° . Crystals of ScS were prepared by the reaction of scandium metal with sulfur. The crystal structure of Sc_2S_3 is closely related to that of NaCl, but the unit cell is twelve times as large due to a complex ordering arrangement of the cation voids. Each "octahedron" surrounding sulfur has two vertices empty, and the bond angles are all very close to 90° . The nonstoichiometric material has a much simpler structure which is also closely related to that of NaCl, with $\text{Sc}_{1.37}\text{S}_2$ per rhombohedral unit cell. This structure, in which one cation site is filled and the other is only partially occupied, could exist over the whole range between Sc_2S_3 and ScS, which was found to have the NaCl structure. Stoichiometric Sc_2S_3 is a semiconductor with a band gap of about 2 e.v., but the materials between Sc_2S_3 and ScS are good electrical conductors. Electrical conduction in the latter materials appears to involve a 3d band.

Introduction

Trivalent scandium differs from other trivalent ions of the first transition series in that it has a closed outer electron shell with the argon configuration. For this reason the chemistry of trivalent scandium compounds is of particular interest with regard to crystal structure and semiconducting properties.¹ This paper discusses the preparation of scandium sesquisulfide, Sc_2S_3 , a nonstoichiometric sulfide, $\text{Sc}_{1.37}\text{S}_2$, and scandium monosulfide, ScS, some of their chemical and physical properties, and the determination of their crystal structures.

Klemm² first prepared Sc_2S_3 by the reaction of H_2S with ScCl_3 at elevated temperature, but was unable to determine its crystal structure from X-ray diffraction powder photographs. Men'kov, *et al.*,³ also prepared Sc_2S_3 in polycrystalline form and concluded that the material had a β - In_2S_3 structure. In a recent review, however, Hahn⁴ stated, with reference to a private communication from Klemm, that Sc_2S_3 crystallizes in a defect NaCl-type structure with random voids in the metal sublattice and that ScS crystallizes in the NaCl structure. Hahn, therefore, postulated that a range of homogeneity or disordered solid solution exists between them. No details of the preparation of ScS, nor a value for its lattice parameter, have been published.

Cation-deficient structures, with the voids either

ordered or disordered, derived from the zinc blende structure have been known for many years. Indium telluride⁵ is a striking example. However, we have been unable to find in the literature reference to any cation-deficient sodium chloride type structure other than scandium sesquisulfide, and this in itself makes the study of the crystal structure and properties of this compound of fundamental importance.

Experimental

Preparation of Sc_2S_3 .—Scandium sesquisulfide, Sc_2S_3 , was prepared by induction heating at 470 kc. of scandium sesquioxide, Sc_2O_3 , with H_2S in a high-purity graphite crucible at elevated temperature, using a modification (Fig. 1) of the apparatus developed by Eastman⁶ and co-workers for preparing Ce_2S_3 . Pure Sc_2S_3 was obtained when the hydrogen sulfide was passed through a 10-g. charge of finely divided Sc_2O_3 (Michigan Chemical Co.) for 2–3 hr. at 1550° or higher, with the H_2S flow rate adjusted to 15 l. hr.⁻¹. The X-ray diffraction powder photographs of material prepared at 1450° or lower can be explained as a combination of the patterns of Sc_2S_3 and $\text{Sc}_2\text{O}_3\text{S}$. Complete reaction was not obtained at this temperature even when the product was ground to a powder and allowed to react again (Table I).

Emission spectrographic analysis showed that Sc_2O_3 used as a starting material contained the following impurities (p.p.m.): Mn, 100; Fe, 300; Cu, 300; Pb, 300; Al, 100; Si, 100; P, 30; Cr, 30; and Ca, 20. During the synthesis of Sc_2S_3 , Pb, Si, P, Cr, and Ca were reduced to below 1 p.p.m. However, the product was contaminated with about 0.2 wt. % of carbon and about 0.2 wt. % of oxygen. Scandium was determined by complexometric titration with EDTA,^{7,8} and sulfur was determined using

(1) E. Mooser, *Science*, **132**, 1285 (1960).
(2) W. Klemm, K. Meisel, and H. U. von Vogel, *Z. anorg. allgem. Chem.*, **190**, 123 (1930).
(3) A. A. Men'kov, L. N. Komisarova, Yu. P. Simanov, and V. I. Spitsyn, *Chem. Abstr.*, **66**, 9543a (1962).
(4) H. Hahn, Special Publication No. 12, The Chemical Society, London, 1958, pp. 263–283.

(5) J. C. Woolley, B. R. Pamplin, and P. J. Holmes, *J. Less-Common Metals*, **1**, 362 (1959).
(6) E. D. Eastman, L. Brewer, L. A. Bromley, P. W. Gilles, and N. L. Lofgren, *J. Am. Chem. Soc.*, **72**, 2248 (1950).
(7) K. L. Cheng and T. R. Williams, *Chemist Analyst*, **44**, 96 (1955).
(8) K. L. Cheng, *Anal. Chem.*, **33**, 761 (1961).