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I. Aluminum dodecaboride, AlB_{12}

(with Dr. J. H. Fang)

This compound has been under investigation for a long time and has so far defied all attempts to solve its structure.

The preparation from $\text{Al} + \text{B}_2\text{O}_3$ by a thermal bomb method is straightforward, single crystals are easily selected and these crystals are found by analysis to have a composition corresponding closely to AlB_{12} . The crystals are shiny black, and belong to space group Ph_{1212} with axes $a = b = 10.17\text{\AA}$, $c = 14.28\text{\AA}$. The unit cell contains 14.5 formula units of the compound instead of a normal number of 16 as expected from the space group symmetry. Weissenberg photographs of seven levels around the b-axis were made and estimated visually, resulting in well over 1000 independent reflections.

Methods used in the various attempts to solve the structure have been trial and error, interpretation of the three-dimensional sharpened Patterson function, superposition of three-dimensional Pattersons, and direct methods of phase determination. The structures of most higher borides reported so far, as well as the known modifications of elemental boron (tetragonal and α -rhombohedral) contain icosahedral or cubo-octahedral configurations of boron atoms. The total diameter of a boron icosahedron found in these studies is $5.08\text{\AA}$. It is indicative that the a-axis of AlB_{12} is almost exactly twice that value, while the c-axis is $\sqrt{2}$ times as large as a. It therefore seemed likely that AlB_{12} should also consist of icosahedral units and a large number of computations were based on that assumption. They were however unsuccessful, as were the computations based on cubo-octahedral units.

Until very recently the structure determination of β -rhombohedral boron was in the same impasse as that of AlB_{12} . For the β -rhombohedral boron, however a successful structure determination was reported two months ago. (1.) The structure, although based on icosahedra, is of a much more complex nature than had been expected. The basic unit is not a simple icosahedron but an 84 atom complex consisting of icosahedra and half-icosahedra linked in a characteristic way. This basic network of B-atoms will be tried out for the AlB_{12} structure. Contact has been established with Prof. R. E. Hughes at the University of Pennsylvania for purpose of calculation of this model.

II. Ammonium 12-tungstocobaltcobaltate, $(\text{NH}_4)_2 [\text{Co}^{+2}\text{Co}^{+3}_{11}\text{W}_{12}\text{O}_{42}]$

(with Dr. J. H. Fang)

Crystals of this heteropolysalt are obtained in the form of very dark green cubes. The preparation is carried out as described in the Ph.D. dissertation of Miss V. E. Simmons. (2).

(1.) Hughes, R. E. et alii, J. Am. Chem. Soc. 85, 361 (1963)

(2.) Simmons, V. E., Ph.D. dissertation, Boston University, 1963

The space group is cubic, $Fm\bar{3}m$, with axes $a = b = c = 22.44 \text{ \AA}$. The unit cell contains 8 molecules of the substance, but since the space group is highly symmetrical and positions of high multiplicity are used for many of the atoms the number of parameters to be determined is relatively small, viz. 16 for the atoms of the anion, or 27 if isotropic thermal parameters are included. It was proved that the anion contains the Keggin configuration $[Co^{+3} W_{12} O_{40}]$ which is a highly compact structure featuring an essentially close-packed arrangement of oxygen atoms with the smaller W-atoms in octahedral interstices and the Co^{+3} ion in a tetrahedral environment at the center of the structure. All the atoms of this configuration have been located, including the oxygens.

For the location of the second group of Co-ions, the Co^{+2} , a number of possibilities arose. These ions are situated somewhere on the outside of the compact Keggin configuration, and the first and most obvious choice was to put this set of 8 atoms into the special 4-fold positions 000 and $\frac{111}{222}$. This would put these ions into the centers of the relatively large interstices between the Keggin units. Calculation of structure factors and subsequent computation of an electron density map showed that, although the Co at 000 may be correctly located, the one at $\frac{111}{222}$ is not, since no peak of appreciable magnitude appeared in the map at that position. Also refinement of that particular model did not drop the R-factor below 0.18. Several other possibilities were tried for the Co^{+2} locations. The best one, which also is most closely in agreement with chemical information known for this substance, is a random distribution of the Co^{+2} atoms over one fourth of the 32-fold position xxx . The R-factor for this arrangement is 0.15. It implies that there are, on the average, 2 Co^{+2} ions in the cavity around 000. These ions are presumably in octahedral environment, and they are closely linked to the Keggin unit. In this manner the units

$[\text{Co}^{+2}\text{O}_8\text{Co}^{+3}\text{W}_{12}\text{O}_{36}]$ appear as discrete units in the structure of the crystal. There is a great deal of evidence that similar or identical units exist in solutions of the compound.

Positions for the cations and for the water molecules of hydration have not yet been established, but work on this and similar structures is continuing, particularly in view of transitional changes that are believed to exist for these substances at temperatures somewhat above room temperature. (3)

(3) Baker, L.C.W. and McCutcheon, T.P.; JACS, 78, 4503 (1956).

III. Pyridine-boron trichloride, $C_5H_5N.BCl_3$

(with Mr. S.A. Brenner)

Crystals of the complex, obtained from direct combination of the components, grow in transparent plates from ethanol solution. The crystals are monoclinic, space group $P 2_1/n$, with unit cell dimensions $a = 9.043$, $b = 15.315$, $c = 6.161 \text{ \AA}$, $\beta = 102^\circ 50'$. There are four molecules in the unit cell. Intensity data were collected from Weissenberg photographs around the a and c axes. A total of 1340 independent reflections were obtained by visual estimation. Lorentz and polarization corrections were applied, but not absorption corrections.

A three-dimensional sharpened Patterson map showed a large number of well-defined, strong peaks. It would undoubtedly have been possible to interpret a number of these peaks as chlorine-chlorine interactions, thus getting a good starting model for the heaviest atoms in the crystal. As it was, the structure was solved by application of Karle and Hauptmann's statistical relationships and subsequent refinement by full matrix least squares. The R-factor at present is 0.164 for all except 26 observed reflections. Further refinement cycles will be carried out with a proper weighting scheme for the observed structure factors, but it can be expected that this will not cause any major changes in the bond distances and angles found so far, some of which are given below.

<u>atoms</u>	<u>distance</u> ($\text{\AA}$)	<u>atoms</u>	<u>angle</u> ($^\circ$)
B-Cl ₁	1.83	Cl ₁ -B-N	111.5
B-Cl ₂	1.87	Cl ₂ -B-N	107.7
B-Cl ₃	1.82	Cl ₃ -B-N	107.8
B-N	1.58	B-N-C ₁	119.7
N-C ₁	1.32	B-N-C ₅	121.0
C ₁ -C ₂	1.39	C ₁ -N-C ₅	119.3
C ₂ -C ₃	1.41	N-C ₁ -C ₂	124.0
C ₃ -C ₄	1.39	C ₁ -C ₂ -C ₃	118.2
C ₄ -C ₅	1.41	C ₂ -C ₃ -C ₄	118.6
C ₅ -N	1.36	C ₃ -C ₄ -C ₅	119.5
		C ₄ -C ₅ -N	120.5

In general these distances and angles appear normal, but a comparison with the structure of $C_5H_5N.BF_3$ reported by Zvonkova (4) is of great interest, although the latter determination is probably not of very high accuracy. In particular the B-N distance reported by Zvonkova is 1.53 Å (a calculation by us from the given cell dimensions and atomic parameters gives 1.49 Å) for the BF_3 complex, while the distance found here for the BCl_3 complex is 1.58 Å.

It has been found feasible (Geller (5)) to correlate bond strength with bond distance and if this assumption is applied here, it would follow that the complex stability, and therefore the acceptor strength, is less for BCl_3 than for BF_3 . This is in direct contradiction to other experimental findings (6), such as thermodynamic measurements.

It is also noteworthy that in Zvonkova's determination three of the C-C-distances in the pyridine ring are calculated to be 1.31, 1.34 and 1.34 Å, while the fourth one is 1.47 Å. In the present study all C-C distances are found equal within the limits of accuracy.

IV. Trimethylphosphine borane, $(H_3C)_3P.BH_3$

(with R. Thomas)

Several complexes between borane and ammonia or phosphine or their derivatives have already been studied and the investigation of trimethylphosphine borane was undertaken to make comparisons between their structures possible. The analogous compound trimethylamine borane was reported by Geller e.a.(7)

Preparation from the components was carried out in a vacuum line

(4) Zvonkova, Z. V., Kristallografiia SSSR, 1, 73 (1956)

(5) Geller, S., J. Phys. Chem. Solids, 10, 340 (1959)

(6) Greenwood, N. N. and Perkins, P. G., J. Chem. Soc. 1141 (1960)

(7) Geller, S., Hughes, R.E. and Hoard, J.L., Acta Cryst., 1, 380 (1951)

designed for the purpose. Crystalline product of melting point 103°C was obtained. The analysis agreed with that expected for the substance. Single crystals were grown in thin walled capillaries and Weissenberg and precession photographs were taken, which showed the crystals to be tetragonal with cell dimensions $a = 7.64$, $c = 6.46 \text{ \AA}$. With $Z = 2$ the value of the calculated density is $D_x = 0.793 \text{ gr/cc}$. The space group is $P \frac{1}{n}$ mm.

Eighty-two observed and 21 unobserved reflections exist within the measurable range of the Ewald sphere. Aside from these strong streaks were observed connecting reflections of constant $h + k$. These streaks, together with the space group information, leave little doubt that the structure must be disordered at room temperature. Experiments were done to establish the existence of a different crystal form at lower temperatures, first by cooling the crystals on the X-ray camera. A marked change in X-ray pattern was observed at -22°C, but unfortunately single crystals could not be taken through the transition without damage. Attempts to grow crystals at low temperature directly, either from solution or by sublimation, were not successful so far.

For the room temperature modification the arrangement found from Patterson maps and structure factor calculations consists of $(\text{H}_3\text{C})_3\text{P.BH}_3$ molecules, oriented with their P-B axis along the crystallographic C-axis. The molecules either undergo free or hindered rotation along that axis, or they are statistically distributed over at least four equivalent rotational orientations around the P-B axis. No distinction between these possibilities can be made on the basis of X-ray data. For a P-B distance of $1.94 \text{ \AA}$ and a P-C distance of $1.91 \text{ \AA}$ the lowest value of R for the statistical model was 0.25. This relatively high value for the disagreement index shows that refinements in the model still have to be made. At present the disorder conditions are not yet fully under-

stood.

V. Pararosanilin perchlorate, $(\text{H}_2\text{NC}_6\text{H}_4)_3\text{C}.\text{ClO}_4$

(with L.L. Koh)

The compound grows in very dark green crystals of monoclinic symmetry, space group $\text{P2}_1/\text{C}$. The cell dimensions are $a = 8.47$, $b = 21.19$, $c = 10.37$, $\beta = 103.9^\circ$. There are four formula units in the unit cell, giving $D_x = 1.426$ gr/cc as compared to $D_m = 1.408$ gr/cc measured by flotation technique.

Intensity data were collected by equiinclination Weissenberg method from crystals around the a and c axes. Intensities were estimated visually and corrected in the usual way. The structure was solved by superposition of three dimensional, sharpened Patterson functions. The superposition gave initial positions for almost all of the atoms in the structure. Refinement was carried out by full matrix least squares, using Busing-Levy's program for the IBM 7090. The final R -factor for all 1500 observed reflections is 0.105.

This is the second structure of a triarylcarbonium salt that has been studied by X-ray diffraction, the first one being that of triphenylcarbonium (or trityl) perchlorate (8). The present structure consists of $(\text{H}_2\text{NC}_6\text{H}_4)_3\text{C}^+$ cations and ClO_4^- anions. The cation has a propeller shape, as does the cation in trityl perchlorate. The configuration of the central C atom is planar and the three benzene rings are twisted out of that plane over angles of 29° , 34° and 34° , respectively. The benzene rings themselves are planar with quinoid structure. Average distances in the cation are: central C atom to C_1 , the nearest ring carbon = $1.45\text{\AA}$, $\text{C}_1-\text{C}_2 = 1.43\text{\AA}$, $\text{C}_2-\text{C}_3 = 1.37\text{\AA}$, $\text{C}_3-\text{C}_4 = 1.42\text{\AA}$ and $\text{C}_4-\text{N} = 1.41\text{\AA}$. The average Cl-O distance is $1.43\text{\AA}$.

(8) A.H. Gomes de Mesquita, Ph.D. dissertation, Univ. of Amsterdam, 1962

The major differences to be noted between this structure and that of the trityl perchlorate are:

- (a) In the pararosanilin derivative the angles by which the rings are rotated out of the central carbon plane are not equal for the three rings (cf. above). In the trityl perchlorate these angles are the same, as dictated by the symmetry which in that case is cubic $F\bar{4}_132$, with the propeller-shaped cations arranged perpendicular to the body diagonal ($\equiv$ 3-fold axis) of the cube.
- (b) In contrast to the present case the quinoid configuration of the benzene rings is not pronounced (and possibly absent) in the triphenylcarbonium ion. This may, however, be a consequence of the somewhat lower accuracy of the trityl perchlorate structure determination.
- (c) As can already be concluded from the difference in space group, the packing of ions is totally different in the two cases now determined. Whereas in the trityl perchlorate ClO_4^- ions are located on the 3-fold axes between the planes of trityl ions, such is not the case in the pararosanilin perchlorate. In the latter case all ClO_4^- ions lie close to amino groups on the outside of the cations, probably forming hydrogen bonds $\text{O} \cdots \text{H}-\text{N}$ with those groups.
- (d) Most importantly, the propeller shaped cations can of course occur in mirror image configurations (d and l forms). While in the trityl perchlorate crystals all cations have the same configuration (either d or l cations throughout the crystal), in the pararosanilin perchlorate structure half the cations are d; the other half l. This is again seen directly from the space group in each case: $F\bar{4}_132$ contains only rotational operations, whereas $P2_1/c$ contains mirror operations which will convert the d into the l-form.

VI. Cobaltous chloride--dimethylsulfoxide, $\text{CoCl}_2[(\text{CH}_3)_2\text{SO}]_3$

(with Joel M. Klein)

Crystals of this compound can be obtained easily from a solution of CoCl_2 in purified dimethylsulfoxide. The substance has been described by Cotton e.a. (9), who first prepared it and reported its I.R. spectrum (10). The crystals are deep blue and exceedingly hygroscopic. The color indicates that the cobalt ions--at least in part--are tetrahedrally surrounded, since cobalt (II) in its (normal) octahedral environment is pink.

Because of the hygroscopic nature of the compound it was difficult to keep crystals long enough for the required X-ray exposures, even when the crystals were sealed in thin-walled pyrex capillaries. Furthermore, there is a strong tendency for twinning. The crystal was found to be tetragonal with axes $a=b=19.04\text{\AA}$, $c=8.61\text{\AA}$. There are 8 formula units in the cell. The space group is $P 4/n$ or $P 4/n mm$, the former being the one used in all subsequent calculations.

Complete intensity data were collected on a precession camera with $\text{MoK}\alpha$ radiation, from a crystal along the b-axis. Intensities were read using a photoelectric, integrating densitometer developed in our laboratory. 5000 observations were made, resulting in a total of about 2900 individual reflections. The Lorentz and polarization corrections were applied in the usual manner, but for the time being absorption corrections were omitted.

Two- and three-dimensional Patterson functions have been calculated. On these maps the Co-Co vectors show up quite clearly, which is not surprising since the Co-atoms must be in special positions and constitute the strongest scatterers in the structure. The sites of the Co-atoms

(9) F.A. Cotton and R. Francis, J.A.C.S., 82, 2986 (1960)

(10) F.A. Cotton, R. Francis and W.D. Horrocks, Jr., J.Phys.Chem. 64, 1534 (1960)

are such, however, as not to allow the expected (and most likely) structure: $\text{Co}[\text{DMSO}]_6^{+2} \cdot \text{CoCl}_4^{-2}$. Different configurations are presently being tried. The best R-factor obtained so far is 0.28, indicating that the main features are probably correct but that changes still have to be effected.

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I. Eriks, K.
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Boston University

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