

MAIN GROUP CLUSTERS OF GROUPS 4, 5, AND 6A

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Structurally, clusters may be viewed as intermediate forms between bulk elements and their isolated atoms or ions. Because of the great degree of direct atomic bonding, they create polycyclic systems. Clusters are found of most all the elements and may be neutral, cationic, or anionic [1]. The neutral clusters may be a link between the structures of solid materials and known isolated molecules, while the anionic and cationic clusters can be viewed as "frozen" models for the stepwise oxidation and reduction of the elements [2].

These main group clusters may be separated conveniently into two categories, homonuclear and heteronuclear systems. Both categories are well known with the Te_4^{2+} ion first synthesized by Klaproth in 1798 [3] and P_4S_3 (the common ingredient in "strike anywhere" match heads) discovered by Lemoine in 1864 [4]. Since that time many more clusters have been prepared and characterized using a variety of synthetic and physical techniques. Most recently, main group clusters have been used as ligands for various transition metals and exhibit several modes of coordination [5].

Early work by Zintl and co-workers [6,7] was the first to accurately characterize a number of homoatomic polyanions. Their work included characterization of polyanions of tin, lead, arsenic, antimony, bismuth, sulfur, selenium, and tellurium. Using potentiometric titrations of sodium-liquid ammonia solutions and extractions of alkali metal alloys of post-transition elements, both cluster size and charge were determined. No crystalline solids could be isolated, however, because the ammoniated sodium cation loses ammonia at room temperature, leading to polyanion decomposition.

The smallest homonuclear cluster system is one containing four atoms. For groups 4, 5, and 6A, the P_4 and Si_4^{4-} clusters [8] exist as tetrahedra, while Si_4^{6-} [9] assumes a butterfly configuration. The isoelectronic species Bi_5^{3+} [10], Pb_5^{2-} and Sn_5^{2-} [11] represent pentanuclear clusters and provide an insight into the synthesis of many larger clusters of Groups 4, 5, and 6A. The trigonal prismatic structure of Te_6^{4+} [12] represents a breakdown in rationalizing bonding with two-center, electron pair bonds. Starting with an A_4 tetrahedral core, the isostructural and isoelectronic clusters As_7^{3-} [13], Sb_7^{3-} [14], and P_7^{3-} [15] can be assembled by the addition of an A^- unit to each of three edges. The P_7^{3-} case exhibits an exchange process giving rise to equivalence of all phosphorus in the ^{31}P NMR at 80°C . The nonanuclear clusters Bi_9^{5+} [16], Sn_9^{4-} [17], Ge_9^{2-} , and Ge_9^{4-} [18] point out the close relationship between the tricapped trigonal prism and the capped square antiprism. The structure of the Sn_9^{4-} cluster in solution has been studied by ^{119}Sn NMR [19] and show rapid intramolecular exchange similar to that seen in the P_7^{3-} molecule. In higher nuclearity clusters, P_{10}^{6-} [20] may be viewed as a derivative of the P_4 tetrahedron, isoelectronic clusters

As_{11}^{3-} [21] and P_{11}^{3-} [22] although complicated at first appearance, may be broken down into derivatives of smaller simpler clusters. However, the Se_{10}^{2+} [23] species fails to fit into any logical pattern.

Heteronuclear clusters can be visualized as derivatives of homonuclear species by addition or substitution of atoms or iso-electronic units to these homonuclear clusters. Examples of this relationship are the P_4 to $\alpha-P_4S_4$, Te_6^{4+} to As_4Se_4 , S_8 to S_4N_4 [24] and As_7^{3-} to $As_3Se_4^+$ [25] pairs.

A primary goal of main group cluster chemistry of groups 4, 5, and 6A is the development of a scheme to interpret the bonding and predict the structure of these clusters. Lauher's molecular orbital treatment of transition metal clusters [26] is reasonably successful when applied to these main group clusters, for it deals with a localized bonding approach. The optimized syntheses of new and existing clusters are continually being sought. With the synthesis of substituted clusters and their use as ligands for transition metals, relatively new areas of chemistry are being explored including the use of chiral cluster ligands in selective synthesis [1].

References

1. von Schnering, H. G. Angew. Chem. Int. Ed. Engl. 1981, 20, 33.
2. Reingold, A. L. "Homoatomic Rings, Chains and Macromolecules of Main Group Elements," Elsevier, Amsterdam, 1977.
3. Bucholz, C. F. Gehlen's Neues J. Chem. 1804, 3, 7.
4. Lemoine, G. Bull. Soc. Chim. Fr. 1864, 1, 407.
5. Haiduc, I. Chem. in Brit. 1981, 17, 330.
6. Zintl, E.; Goubeau, J.; Dullenkopf, W. Z. Phys. Chem. 1931, A154, 1.
7. Zintl, E.; Harder A. Z. Phys. Chem. 1931, A154, 47.
8. White, J.; von Schnering, H. G. Z. Anorg. Allg. Chem. 1964, 327, 260.
9. Eisenmann, B.; Janzon, K. H.; Schäfer, H.; Weiss, A. Z. Naturforsch. 1969, B24, 457.
10. Burns, R. C.; Gillespie, R. J. Luk, W. C. Inorg. Chem. 1978, 17, 3596.
11. Edwards, P. A.; Corbett, J. D. Inorg. Chem. 1977, 16, 903.
12. Burns, R. C.; Gillespie, R. J.; Luk, W. C.; Slim, D. R. Inorg. Chem. 1979, 18, 3086.

13. Schmettow, V. W.; von Schnering, H. G. Angew. Chem. 1977, 89, 895.
14. Adolphson, D. G.; Corbett, J. D.; Merryman, D. J. J. Am. Chem. Soc. 1976, 98, 7234.
15. Baudler, M.; Ternberger, H.; Faber, N.; Hahn, J. Z. Naturforsch. 1977, B34, 1690.
16. Friedman, R. M.; Corbett, J. D. Inorg. Chem. 1973, 12, 1134.
17. Edwards, P. A.; Corbett, J. D. J. Am. Chem. Soc. 1977, 99, 3313.
18. Belin, C. H. E.; Corbett, J. D.; Cisar, A. J. J. Am. Chem. Soc. 1977, 99, 7163.
19. Rudolph, R. W.; Taylor, R. C.; Young, D. C. "Fundamental Research in Homogeneous Catalysis 3," Tsutsi, M., Ed.; Plenum Press, New York, 1977, p. 997.
20. Hönle, W.; von Schnering, H. G. Z. Krist. 1980, 153, 339.
21. Belin, C. H. E. J. Am. Chem. Soc. 1980, 102, 6036.
22. Wichelhaus, W.; von Schnering, H. G. Naturwissenschaften 1973, 60, 104.
23. Burns, R. C.; Chan, W. L.; Gillespie, R. J.; Luk, W. C.; Sawyer, J. F.; Slim, D. R. Inorg. Chem. 1980, 20, 1432.
24. Gillespie, R. J. Chem. Soc. Rev. 1979, 8, 315.
25. Christian, B. H.; Gillespie, R. J.; Sawyer, J. F. Inorg. Chem. 1981, 20, 3410.
26. Lauher, J. W. J. Am. Chem. Soc. 1978, 100, 5305.