SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY
Vol. 1, No. 1, 1993

THE KNIGHT'S MOVE IN THE PERIODIC TABLE:

a regularity amongst the d^{10} metals on the lower right-hand side

Michael Laing, University of Natal
DURBAN, South Africa.

ABSTRACT

This article describes a pattern of reactivity and properties of the d^{10} *metals in the bottom right-hand side of the periodic table. Pairs of metals such as Zn-Sn, Cu-In, Ag-Tl, Cd-Pb and Sn-Po, all related by the knight's move, are discussed taking into consideration their properties, electronic configuration and metallic state.*

RESUMO

Este trabalho descreve um padrão ou protótipo de comportamento das propriedades e reatividade dos metais com configuração d^{10} *na parte inferior da direita da Tabela Periódica. Pares de metais tais como Zn-Sn, Cu-In, Ag-Tl, Cd-Pb e Sn-Po, todos relacionados com o movimento do cavalo no jogo de xadrez, são discutidos em termos das suas propriedades, configuração eletrônica e estado metálico.*

All teachers of inorganic chemistry are familiar with the various patterns of regularities in the periodic table. There are the Triads of Dobereiner (1). For example, the properties of bromine are intermediate between those of chlorine and iodine. This applies to colour, physical state and atomic weight . Mendeleyeff based his predictions on this type of regularity when he predicted in detail the properties of the element eka-silicon, i.e., germanium (2). The chemical properties of an element were seen to be the "mean" of those of the elements above and below and to left and right of it.

On the top left of the periodic table there is yet another regularity, the so-called Diagonal Relationship. Here the chemical properties of an element are similar to those of an element one place to the right and one below it (3). For example, beryllium and aluminum and titanium have many properties

DOI: 10.48141/SBJCHEM.v1.n1.1993.38_1993.pdf

in common, particularly their solution chemistry and the behaviour of their oxides. This relationship is ascribed to a similarity in "ionic potential", the ratio of the charge to the ionic radius, of the two elements (3d).

The elements of Period 6 in the lower right hand side of the periodic table display the Inert Pair effect where the heaviest element in a group exhibits a stable oxidation state two less than the group number (4). The best known example is group IV where both tin and lead are found in oxidation states 2+ and 4+, but tin 2+ is a reducing agent and tin 4+ is inert, while lead in the 4+ state is an oxidiser and lead 2+ is inert. This effect is usually ascribed to the 6s pair of electrons being very firmly held to the nucleus.

Some time ago I was assigned the task of teaching descriptive inorganic chemistry to the freshman engineering students as a foundation for their course on materials. I covered the common trends in the periodic table and then, in an effort to emphasise the uses of the elements, I mentioned the common metals used for plating steel: tin plate used in cans for foodstuffs, and zinc plating to make galvanised iron for corrugated roofing and water tanks on farms (5).

I asked myself - why should these two metals so effectively plate steel? What is the link between them? I could not answer this question immediately except to say that tin is one down and two to the right from zinc in the periodic table. I wondered, was this Knight's Move a general regularity for the metallic elements on this side of the periodic table?

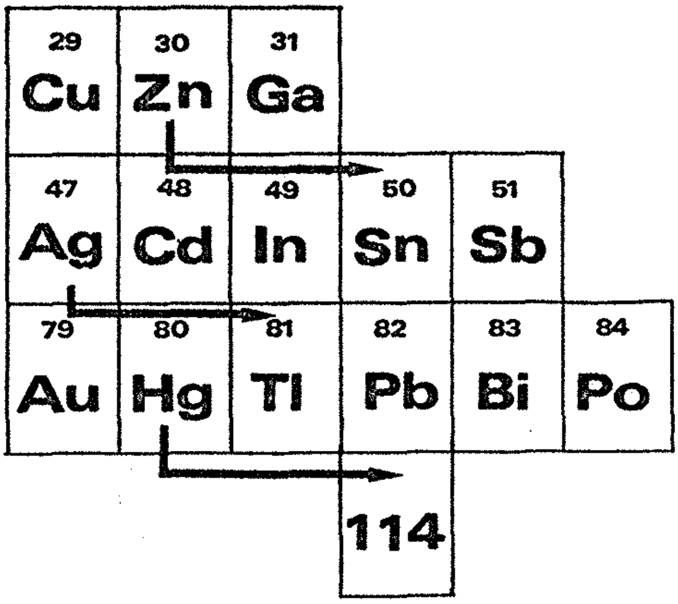

Figure 1. These metallic elements with d^{10} electron configurations show the Knight's Move relationship.

I suddenly remembered my lecturer of 30 years ago talking of thallium and saying that its stable oxidation state was +1, that its chloride was insoluble in water, and that it was photo-sensitive like silver chloride (6). Thallium and silver also were related by the Knight's Move!

Could the Knight's Move predict the properties of a rare element such as polonium? For example, what would be its melting point? That of tin is 232°C; if the pattern is true then the melting point of polonium might be similar. To my amazement it turned out to be 254°C, almost too good to be true (7). Now I asked myself the question - Why should these similarities be? What are they trying to tell us?.

The similarity in melting point for tin and polonium implies that the forces between the atoms in the solids must be comparable in magnitude. Examination of the crystal structures shows that both metals have the same coordination number of six and a similar pattern of M-M bonds (ideally octahedral in polonium, but distorted in tin) (8), in spite of the electron configuration of tin being $d^{10}s^2p^2$ while that of polonium is $d^{10}s^2p^4$. (But do these electron configurations have any reality in the metallic state? They were, after all, deduced from atomic spectra at infinite dilution in the gas phase). The s^2 pair on the polonium atom seems to be acting as an "Inert Pair", leaving the four p electrons to participate in the bonding; while the s^2 pair on tin seems to be promoted and joins with the p^2 electrons in the bonding.

I returned to the metals zinc and tin; what other similarities were there? Of course: brass is an alloy of zinc and copper, while bronze is an alloy of tin and copper (9). Both alloys have been known since antiquity. The relationship was there again. To be sure there are also intermetallic compounds with well-defined atom ratios such as CuZn and Cu_3Sn (10) whose bonding fits the Hume-Rothery ratios (11). But these Hume-Rothery rules require that the zinc contribute two electrons while the tin has to be a four-electron donor. I checked another book about alloys. Although miscible as liquids, zinc and tin are insoluble in each other as solids (12)! They form neither alloys nor intermetallic compounds; yet they are mutually soluble in copper to give the alloy of approximate compsoition 96 Cu, 2 Sn, 2 Zn which is used in British bronze 1p coins.

As may be expected, their crystal structures differ greatly (13). Zinc is distorted hexagonal close-packed with a $^c/a$ ratio of 1.856 compared with 1.633 for an ideal HCP structure. This gives the Zn atom a total coordination number of 12, with 6 atoms at 2.64 A^0 in a close-packed layer, and a further six, three above and three below, at 2.91 A^0. On the other hand, tin has the unusual structure with coordination number 6 mentioned above.

The atomic volume of zinc is 15.2 Å^3 while that of tin is almost double, 27.0 Å^3. Nevertheless, iron with its body-centered cubic sturcture senses something similar about the two solid metals that allows them to plate onto iron so successfully. Copper also feels some similarity in the individual zinc and tin atoms as they dissolve into it to form brass and bronze. Yet the atoms of the pure metals will not interact enough to give mutual solubility (14): a puzzlement. The only faint ray of light is that both iron and copper have the identical atomic volume of 11.8 Å^3.

I looked at other properties. Zinc and tin are non-poisonous. Zinc occurs in many enzymes necessary for biochemical processes in the human body, and it is commonly taken by mouth as a trace element supplement (15). Tin is used in medicines and is taken orally as both metal and oxide (in Metinox) for the treatment of acne. The harmless nature of tin can easily be deduced from its ubiquitous presence as stannous fluoride in toothpaste to combat caries.

Compare this with their congeners, the pair cadmium and lead, both of which are poisonous if ingested. Generally speaking, the heavy metals that form insoluble sulphides are toxic e.g. mercury, thallium, lead, cadmium.

It is interesting to note that bismuth is not toxic, and that each year over 100 tons are used in the manufacture of phar- maceuticals (16). Bismuth is taken orally in the form of the basic nitrate (in Bisodol) for minor digestive problems, and the oxide and subgallate are used in suppositories (such as Anusol and Anugesic) for the treatment of haemorrhoids. Antimony also is used as a medicant in the form of the well-known compound tartar emetic.

Stepping back the Knight's Move from bismuth and antimony, one comes to indium and gallium, about which toxicological information is rather sparse (17). However, gallium appears to be innocuous, while indium is less toxic than cadmium, thallium and lead.

I looked at the melting and boiling points of some pairs of metal halides (18): see Table 1.

These values showed that the Knight's Move pattern of regularity was more widespread than I had originally thought. Similarities of melting point will occur if the crystal structures and intermolecular forces in both solid and liquid are similar. This suggests that there will be similarities between pairs of chlorides and bromides which are mainly covalently bonded and therefore are molecular in nature. On the other hand, the picture must change for fluorides because the bonding in these compounds is predominantly

TABLE 1

Melting and Boiling Points of Metal Chlorides and Bromides

	Melting Point °C		Boiling Point °C
AgCl	445	$CdCl_2$	980
TlCl	429	$PbCl_2$	954
AgBr	430	$GaCl_3$	200
TlBr	456	$SbCl_3$	221
CdI_2	385	$GaBr_3$	279
PbI_2	412	$SbBr_3$	280
$ZnCl_2$	275	$ZnBr_2$	650
$SnCl_2$	247	$SnBr_2$	619
$GaCl_3$	77	$CdBr_2$	863
$SbCl_3$	73	$PbBr_2$	916

ionic in character, with structures (and therefore lattice energies) strongly dependent on the ionic radius of the metal cation as well as on its charge (19). For example, the melting point of CdF_2 is 1110°C, while that of PbF_2 is 822°C, in line with the radii of 0.92 Å for Cd^{2+} and 1.21 Å for Pb^{2+}.

I returned to the behaviour of thallium. That TlCl should be insoluble in water indicates that the lattice energy must be similar to the analogous value for silver chloride. However, AgCl will dissolve in ammonia while TlCl is insoluble. This is easily explained by the formation of the $[Ag(NH_3)_2]^+$ cation, in which the bonding picture invokes the use of two collinear sp orbitals (20). This is impossible for Tl^+ because the cation already has a pair of tightly held (presumably) s electrons. However, an analogous linear species $[TlL_2]^+$ should exist in which the two L groups are one-electron donors. Such cations do exist: e.,g. $[Tl(CN)_2]^+$ and the stable linear complex $[Tl(CH_3)_2]^+$, formal derivatives of Tl(III), which are isoelectronic with the other wellknown linear species $Hg(CN)_2$ and $[Au(CN)_2]^-$ (21).

Applying the Knight's Move to copper suggests that indium should be in various ways similar to it. The melting point of indium is only 157°C, in keeping with its crystal structure which is not close packed and very different from the crystal structure of copper (22).

However, In(I) with its $d^{10}s^2$ electron configuration may be expected to form compounds analogous to those of the d^{10} Cu(I) species. These compounds exist, e.g. InI and $InClO_4$, and, like those of Cu(I), are easily synthesised in CH_3CN as solvent (23). A conventional examination of the periodic table would not have led to such a prediction.

The same approach can be used in the qualitative analysis scheme (24). $PbCrO_4$ is a yellow insoluble species, therefore (a Knight's Move away) $CdCrO_4$ should also be yellow and insoluble in water, and now a classical Mendeleyevian approach requires that $ZnCrO_4$ will be similar. It is, and $ZnCrO_4$ is the corrosion inhibitor in the paint used as an undercoat on steel (25), which was of interest to my engineers who started all this!

Sb_2S_3 is wellknown as the bright orange sulphide precipate in Group II of the qualitative analysis scheme. The Knight's Move suggests that Ga_2S_3 should be in some way similar. Ga_2S_3 is a yellow solid, but it hydrolyses in water as Al_2S_3 does. The similarity between the compounds Ga_2S_3 and Sb_2S_3 turns out to be in the complexity of their crystal structures, neither of which is as simple as the stoichiometry would suggest. That of Ga_2S_3 is a derivative of the Wurtzite structure but with vacancies at the metal positions, while the structure of Sb_2S_3 is unique and quite complex (26).

By the same token, the structures of ZnS and SnS should be related. They are, in the sense that the metal atoms in both cases have coordination number four, despite the two extra electrons on the Sn(II) (27).

Similarly, the structures of ZnO and SnO are expected to be related. Once again, the common factor is a coordination number of 4 for the metal but, as might be predicted, the coordination about Sn is distorted with four short Sn-O contacts in a square on one side, and no close contacts on the other side. The Pb(II) cation in PbO has the same environment. (Figure 2, below). This in turn is almost identical with the coordination geometry around the Sb(III) cation in tartar emetic which is non-spherical, being coordinated to four oxygen atoms in a square on one side of the cation (28). The two non-bonded electrons on the antimony atom seem to have the steric attributes more closely associated with an orbital of p-character. The distortion of the Pb(II) cation from sphericity is not the behavior expected from a cation with a spherically symmetrical "inert lone pair" of electrons! Simarly, in Pb_3O_4 the coorindation about the Pb(IV) cation is nicely octahedral, while that about the Pb(II) ion is very irregular. The Pb(II) ion is clearly not "spherical". This is hardly what one would expect for a cation with a spherically symmetrical inert s-pair.

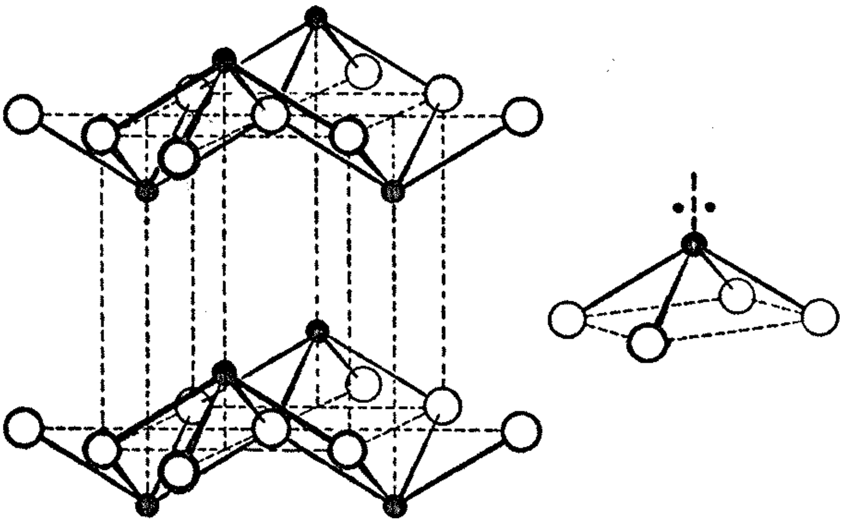

Figure 2. The crystal structure of PbO (and SnO). The solid circles represent the metal cations. The arrangement of the four close M-O contacts is shown on the right hand side; the two dots represent the "inert" pair of electrons.

The "lone" pair of electrons on Pb(II) seems also to be sterically "active" in various xanthate and thioate complexes (29), where the coordination sphere is an irregular pentagonal bipyramid with the "lone pair" occupying an equatorial position. Nevertheless, the mean Pb-S bond length in the thioate complex is little different from the Pb-S distance of 2.97 Å found in cubic galena (30).

Is the Knight's Move merely a special case of the Inert Pair effect applied to metals with a d^{10} electron configuration? The electron configuration of the metal at the upper left is $d^{10}p^{X}$ or $d^{10}s^{2}p^{X}$ while that at the end of the move is $d^{10}s^{2}p^{X}$ or $d^{10}s^{2}p^{X+2}$. But to invoke an inert s^2 pair is too facile. In fact the lower right-hand metals of the linked pairs often behave as if the electron pairs were not inert s^2 but rather p^2 i.e. a sterically active "inert lone pair" with p-character! e.g. the non-spherical nature of the Pb(II) cation. There is more behind the Knight's Move than meets the eye.

We are dealing here with an extremely complex phenomenon, not easy to explain. The macroscopic observable is the result of a complicated balance of factors including: covalent bonding within the species; intermolecular forces between the species in the solid as well as in the liquid state; the size of the metal cation; the ratio of charge to cationic radius; and the stability of the $6s^2$ pair of electrons (arising from relativistic effects) (31). Or as Dr. Johnson might have said: "I have found you an argument; it is a little more difficult to find you an under-standing" (32).

Nevertheless, application of the idea of the Knight's Move amongst the metals with d^{10} electron configurations on the bottom right hand side of the periodic table leads to many correct predictions that would not be made easily by the conventional application of the usually accepted trends in the Periodic Table. The Knight's Move also acts as a useful aide-memoire when dealing with the chemistry of these heavy metals.

As a final exercise in prediction I asked the question : which of the superheavy yet-to-be-discovered elements has the best chance of being found in isolable amounts? The answer is element 114, eka-lead (33). And what will be its physical and chemical properties? Apply the Knight's Move and the element on which to base prediction is Mercury. One concludes then that element 114 will be a metal of moderate density, about 16, having a very low melting point, possibly liquid at room temperature. Its stable oxidation states will be 0 and +2. Its chloride will have the formula MCl_2 and its oxide, MO, will be thermally unstable (34). We must now await the production of macroscopic amounts of element 114 to test these predictions which could have been made by any undergraduate with the aid of the Knight's Move in the Periodic Table.

REFERENCES

1. Weeks, M. E. Discovery of the Elements, 6th ed.; J. Chemical Education: Easton, 1956; pp. 653 and 747.

2(a) Moeller, T. Inorganic Chemistry; J. Wiley : New York, 1982; p.107.

(b) Nekrasov, B.V. Osnovy Obshchei Xhimii; Xhimiya: Moscow, 1969; Vol. 1, p.217.

3(a) Huheey, J. E. Inorganic Chemistry; Harper and Row : New York, 1972; pp. 87 and 604.

(b) Hanusa, T. P. J. Chem. Educ. 1987, 64, 686.

(c) Ref. 2, p.247.

(d) Cartlege, G.H., J. Amer. Chem. Soc., 1928, 50, 2855; 1930, 52, 3076.

4(a) Cotton, F. A.; Wilkinson, G. Advanced Inorganic Chemistry, 4th ed.; J. Wiley : New York, 1980; pp. 327 and 380.

(b) Ref. 3(a), p. 620-622.

5. Street, A.; Alexander, W. Metals in the Service of Man, 8th edition; Penguin: Harmondsowrth, U.K., 1982; p.191 (Tin plating), p.196 (Zinc plating).

6. Partington, J.R. A Text-book of Inorganic Chenmistry, 5th edition; Macmillan: London, 1947; p.887, 888. (Dumas called thallium the "platypus" among the elements).

7. Bagnall, K. W. Chemistry of The Rare Radioelements; Butterworths : London, 1957; p.47.

8. Donohue, J. The Structures of the Elements; J. Wiley: New York, 1974; pp. 274-276, 391.

9. Van Vlack, L.H. Elements of Material Science, 2nd edition; Addison-Wesley: Reading, MS, 1970; pp.266, 269.

10(a) Hume-Rothery, W. Electrons, Atoms, Metals and Alloys, 3rd edition; Dover: New York, 1963; pp.205, 206 (inert pair), pp.276, p.315 (brass), p.300 (bronze).

(b) Remy, H. Treatise on Inorganic Chemistry; Elsevier: Amsterdam, 1956; Vol. 1, p.574; Vol. 2, pp.16-22, 372.

11(a) Evans, R.C. Crystal Chemistry, 2nd edition; C.U.P.: Cambridge, 1964; p.328.

(b) Seitz, F. The Modern Theory of Solids; McGraw-Hill: New York, 1940; pp.30-32.

(c) Barret, C.; Massalski, T.B. Structure of Metals, 3rd edition; Pergamon: Oxford, 1980; p.159 (brass), pp.249-252 (Hume-Rothery ratios).

12(a) See ref. 5, p.187.

(b) Metals Handbook; Anmerican Society for Metals; Cleveland, 1948; p.1240 (Sn/Zn phase diagram), p.1265 (Cu, Sn, Zn phase diagram).

13\. See ref. 8, p.225.

14\. Further details of the phase diagrams and solubility characteristics are available in:

(a) ref. 12b. pp.1217, 1218 (Fe/Sn); pp.1220, 1221 (Fe/Zn).

(b) Metals Handbook, 8th edition; American Society for Metals: Ohio, 1973; Vol. 8 p.293 (Cu/Fe), p.299 (Cu/Sn), p.301 (Cu/Zn), p.306 (Fe/Sn), p.308 (Fe/Zn), p.336 (Sn/Zn), p.431 (Cu/Sn/Zn).

(c) Hansen, M. Constitution of Binary Alloys, 2nd edition; McGraw-Hill: New York, 1958; pp.580-582 (Cu/Fe), pp.633-636 (Cu/Sn), pp.649-653 (Cu/Zn), pp.718-719 (Fe/Sn), pp.737-740 (Fe/Zn), pp.1217-1218 (Sn/Zn).

15(a) Hughes, M.N. The Inorganic Chemistry of Biological Processes; J. Wiley: Chichester, 1984; pp.89-115, 297.

(b) Stryer, L. Biochemistry, 2nd edition; Freeman: New York, 1981; pp.148-153.

16\. Greenwood, N.N.; Earnshaw, A. Chemistry of the Elements; Pergamon: Oxford, 1984; p.640.

17\. Sax, N.I. Dangerous Properties of Industrial Materials; Van Nostrand Reinhold: New York, 1975; p.504 (cadmium), p.783 (gallium), p.829 (indium), p.861 (lead), p.1160 (thallium).

18. Sanderson, R. T. Inorganic Chemistry; van Nostrand Reinhold : New York, 1967; pp. 318, 319, 344 and 357.

19. Parish, R.V. The Metallic Elements; Longmans: London, 1977; p.184.

20. Huheey, J.E. Inorganic Chemistry; Harper and Row: New York, 1972; pp.371, 372.

21(a) Greenwood, N.N.; Earnshaw, A. Chemistry of the Elements; Pergamon: Oxford, 1984; p.293.

(b) Ford-Smith, M.H. The Chemistry of Complex Cyanides; H.M.S.O.: London, 1964; pp.48, 64, 66, 68, 69.

22. See ref. 8, pp.220, 244, 245.

23. Cotton, F.A.; Wilkinson, G. Advanced Inorganic Chemistry, 5th edition; J. Wiley: New York, 1988; p.230.

24. Brady, J.E.; Holum, J.R. Fundamentals of Chemistry, 3rd edition; J. Wiley: New York, 1988; pp.1076, 1078.

25(a) Thompson, R., Editor, Speciality Inorganic Chemicals, Special Publication No. 40; Royal Society of Chemistry: London, 1981; pp.333, 334.

(b) Austin, G.T. Shreve's Chemical Process Industries, 5th edition, McGraw-Hill: New York, 1984; p.436.

26. Naray-Szabo, I. Inorganic Crystal Chemistry; Akademiai Kiado: Budapest, 1969, pp.179, 180, 284, 285.

27(a) Bokii, G.B. Introduction to Crystal Chemistry; USAEC: Washington, 1960 (English translation), Moscow, 1954 (Russian original), Vol. 2, pp.375, 382.

(b) Krebs, H. Fundamentals of Inorganic Crystal Chemistry; McGraw-Hill: London, 1968; pp.198, 204.

28. Cotton, F.A.; Wilkinson, G. Advanced Inorganic Chemistry, 5th edition; J. Wiley: New York, 1988; p.421.

29. Lawton, S.L.; Kokotailo, G.T. Inorg. Chem. 1972, 11, 363.

30. Wells, A.F. Structural Inorganic Chemistry, 5th edition; O.U.P.: Oxford, 1984; pp.752, 1186; see also pp. 557 to 559.

31(a) McKelvey, D.R. J.Chem. Educ. 1983, 60, 112.

(b) Pitzer, K.S. Acc. Chem. Res. 1979, 12, 271.

(c) Pyykko, P.; Deslaux, J.P. Acc. Chem. Res. 1979, 12, 276.

32(a) Bartlett, J. Familiar Quotations, 15th edition; Macmillan: New York, 1980; p.357.

(b) Cohen, J.M.; Cohen, M.J. The Penguin Dictionary of Quotations; Penguin: 1960; p.210.

33. Ref. 2, p.114.

34. Fricke, B. Superheavy Elements in Structure and Bonding; Springer-Verlag : New York, 1975; Vol. 21, p.89.