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The chemical 'Knight's Move' relationship: what is its significance?

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Abstract Similarities in properties among pairs of metallic elements and their compounds in the lower-right quadrant of the Periodic Table have been named the 'Knight's Move' relationship. Here, we have undertaken a systematic study of the only two 'double-pairs' of 'Knight's Move' elements within this region: copper-indium/indium-bismuth and zinc-tin/tin-polonium, focussing on: metal melting points; formulas and properties of compounds; and melting points of halides and chalcogenides. On the basis of these comparisons, we conclude that the systematic evidence for 'Knight's Move' relationships derives from similarities in formulas and properties of matching pairs of compounds in the same oxidation state. Physical properties, such as melting points, do not provide consistent patterns and trends and hence should not be considered as a common characteristic of this relationship.

Keywords Periodic table · Periodic patterns · Knight's move · Copper · Indium · Bismuth · Zinc · Tin · Polonium · Chemical formulas · Melting points

Introduction

There are a number of patterns that we find in the Periodic Table, including the traditional Group and Period trends, the diagonal relationship in the upper left corner of the Periodic Table, and the similarities between the Group (n) and Group (n+10) elements.

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In 1999, Laing reported the discovery of a previously overlooked pattern, one involving the metallic elements in the lower right portion of the Periodic Table (Laing 1999). As the linkage related an element and a corresponding element one Period down and two Groups to the right, he dubbed it the ‘Knight’s Move’ relationship by comparison to the chess move of the same manner. On the basis of that one article, the ‘Knight’s Move’ has become accepted as a genuine periodic relationship, having been included in such resources as: a conference proceedings on the Periodic Table (Rouvray and King 2004); a text on descriptive inorganic chemistry (Rayner-Canham and Overton 2004); and a definitive work on the history and structure of the Periodic Table (Scerri 2007).

An over-riding and oft-forgotten point about the chemical elements is that each element is unique. It is this individuality that makes inorganic chemistry such an interesting but, at the same time, gargantuan field of study. Thus, in looking for relationships, one should not expect total congruence among the elemental behaviours; on the other hand, one should be hoping to find consistent patterns that are more than simple probability. For this reason, the ‘Knight’s Move’ concept needs to be tested by looking systematically and comprehensively at one or more pairs of elements.

It is the purpose of this paper to report such a study, and from this study, to provide our views on the validity of the ‘Knight’s Move’ as a true periodic relationship. We chose two unique sets of elements: Copper–Indium-Bismuth, and Zinc–Tin–Polonium, in which each central element has two other elements linked by potential Knight’s Move relationships. We are not aware of anyone having commented previously on the uniqueness of these double-pairs of potential ‘Knight’s Move’ relationships. There are three features on which we will focus: metal melting points, compound formulas and properties, and compound melting points.

The Knight’s move

Laing identified the sets of elements having atomic numbers: 29–31, 47–51, and 79–84, as marking the boundaries of the ‘Knight’s Move’ (Fig. 1). These limits provide the following pairs of related elements: copper–indium, zinc–tin, and gallium–antimony, of Periods 4–5; and silver–thallium, cadmium–lead, indium–bismuth, and tin–polonium, of Periods 5–6.

To summarize Laing’s discovery, he proposed that the following specific features indicate the existence of a ‘Knight’s Move’ pattern:

1. Similarities of metal melting points;
2. Patterns in compound formulas and solubilities;
3. Parallels in melting and boiling points of compounds of the same formulation.

In addition, he noted for certain pairs:

Group 11	Group 12	Group 13	Group 14	Group 15	Group 16
Cu	Zn	Ga			
Ag	Cd	**In**	Sn	Sb	
		Tl	Pb	**Bi**	Po

Fig. 1 Metallic elements of the ‘Knight’s Move’ block. Of the two sets studied here, one double-pair is in bold and the other in outline

4. Toxicity or essentiality of some corresponding elements;
5. Structural and colour similarities among a few compounds of corresponding formulation.

He also reported some specific curious parallels, such as the use of both zinc and tin to plate steel and to form alloys with copper.

As to the cause of these similarities, Laing was unable to propose a clear answer. He raised the possibility of the so-called 'inert-pair' effect and relativistic effects but found any single theory lacking credibility.

Metal melting points

Laing noted in his paper the similarity in melting points between tin (232°C) and polonium (254°C). Looking at the melting and boiling points of our first double-pair of zinc–tin–polonium (Table 1), there does seem to be a similarity of melting points (tin–polonium) and boiling points (zinc–polonium), though no systematic pattern involving all three metals.

However, the matching table for the copper–indium–bismuth double-pair indicates that low melting points are characteristic of all the lower *p*-block metallic elements (Table 2). In fact, the closest match in melting and boiling points does not come from 'Knight's Move' pairs but from the Periodic Table 'nearest neighbours' of bismuth (Table 2) and polonium (Table 1). Therefore, metal melting points and boiling points, in our opinion, are not a defining feature of the 'Knight's Move.'

Compound formulas

From our investigations, it is the compounds of the same oxidation states that provides the 'Knight's Move' with its main validity. In fact, this matching of oxidation states seems to be the key feature of the linkages (Fig. 2). As an example, for silver and thallium, the +1 state is stable and preferred in aqueous solution while both these elements also exhibit the +3 oxidation state. Among their matching compounds are the chromates, Ag_2CrO_4 and Tl_2CrO_4, both of which are insoluble and brick-red in colour (the only two chromates to have this colour). Silver and thallium(I) halides are whitish except for the iodides which are yellow, while AgF and TlF are water-soluble and all other silver and thallium(I) halides are insoluble. A particularly intriguing example for the silver–thallium linkage is the thallium-containing mineral, *crookesite*, $Cu_7(Ag,Tl)Se_4$, in which silver and thallium occupy the same lattice sites.

The following two sections highlight some chemical similarities for compounds of each of the four pairs: copper(I)–indium(I) and indium(III)–bismuth(III); zinc(II)–tin(II) and tin(IV)–polonium(IV). Four main sources of information have been used (Bailar et al. 1973; Cotton et al. 1999; Greenwood and Earnshaw 1997; Massey 2000).

Table 1 The phase change temperatures for the Zn–Sn–Po double-pair

Element	Zinc	Tin	Polonium
Melting point (°C)	420	232	254
Boiling point (°C)	907	2623	962

Table 2 The phase change temperatures for the Cu–In–Bi double-pair

Element	Copper	Indium	Bismuth
Melting point (°C)	1083	157	271
Boiling point (°C)	2570	2073	981

Cu (+1), +2	Zn +2	Ga +3			
Ag +1, (+3)	Cd +2	In (+1), +3	Sn +2, (+4)	Sb +3, (+5)	
		Tl +1, +3	Pb +2, (+4)	Bi +3, (+5)	Po +2, +4

Fig. 2 The common oxidation states of the 'Knight's Move' elements with the less common oxidation state indicated in parentheses

Copper–indium and indium–bismuth compounds

For double-pairs, as can be seen from Fig. 2, it is always the lower oxidation state of the element of Period 5 that matches an oxidation state of the Period 4 element while the higher oxidation state of the Period 5 element matches the lower oxidation state of the Period 6 element. Thus in this section, we will be comparing the existence of corresponding compounds of copper(I) and indium(I) and then corresponding compounds of indium(III) and bismuth(III).

The usual aqueous oxidation state for copper is +2 while that for indium is +3. For both copper and indium, the +1 oxidation state is a comparative rarity found mostly in insoluble solid-state species, though in itself, the existence of this matching oxidation state is notable in the context of the 'Knight's Move'. Table 3 shows some of the simple copper(I) and corresponding indium(I) compounds known. Also of note, fluorides are unknown for both copper(I) and indium(I).

The comparative chemistry of indium(III) and bismuth(III) is more extensive. All of the tripositive halides and chalcogenides are known for both elements. Indium(III) and bismuth(III) also form corresponding tetra- and hexa-coordinate halo-complex ions: MX_4^- and MX_6^{3-}. The parallels between indium(III) and bismuth(III) are particularly strong as +3 is the more common oxidation state for both elements. Bismuth exemplifies the phenomenon that the elements of the later Period 6 tend to favour the lower oxidation states over the highest.

There are some notable specific similarities, for example, the formation of alums: $M^IM^{III}(SO_4)_2 \cdot 12H_2O$, where M^I is a large monopositive ion and M^{III} is indium(III) or bismuth(III). More persuasive of a linkage, both indium and bismuth readily form stable oxo-halides of matching formula, such as InOCl and BiOCl.

Table 3 Some corresponding copper(I) and indium(I) compounds

Copper(I)	CuCl	CuBr	CuI	Cu_2O	Cu_2S
Indium(I)	InCl	InBr	InI	In_2O	In_2S

Zinc-tin and tin-polonium compounds

Though here we focus on ‘Knight’s Move’ resemblances, it is important to note that an element in this region can also possess similarities to elements elsewhere in the Periodic Table. Zinc may hold the record in this context. Laing has related zinc to magnesium by the (*n*) and (*n*+10) relationship (Laing 1989); while Massey has pointed out similarities of zinc with beryllium in compound formulas (Massey 2000, p. 174) and zinc with gallium in chemical behaviour (though not formula) (Massey, 2000, p. 208). Here we are reporting on the fourth link, that of zinc with tin(II).

The comparative chemistry of this pair certainly provides several similarities. Zinc and tin(II) exhibit amphoteric behaviour, their hydroxides dissolving in excess hydroxide ion to form zincates and stannates, respectively. The species are pH and concentration dependent but at high pH values they can be represented as tetracoordinate $[Zn(OH)_4]^{2-}$ and hexacoordinate $[Sn(OH)_6]^{4-}$ (tin being significantly larger than zinc). Aqueous solutions of their divalent chlorides hydrolyse to give insoluble Zn(OH)Cl and Sn(OH)Cl, respectively. In the presence of high chloride ion concentrations, the chlorides give parallel chloro-complex ions: $ZnCl_3^-$ and $SnCl_3^-$; and $ZnCl_4^{2-}$ and $SnCl_4^{2-}$. Also, the elements both form dialkyls of the form R_2M (where M = Zn or Sn), though the zinc series tend to be monomeric while the tin(II) compounds are polymeric.

Though some compounds of polonium(VI) are known, polonium, like bismuth, prefers lower oxidation states. There are a wide range of compounds of polonium(IV) together with some compounds of polonium(II). It was noted by Brasted over 45 years ago (Brasted 1961) that polonium bore little resemblance in its chemistry to tellurium and instead, that polonium(II) behaved more like lead(II) of Group 14. However, we found more similarities between polonium and tin than polonium and lead. For example, there are numerous formula correspondences between tin(IV) and polonium(IV), such as $SnCl_4$ and $PoCl_4$, and the complex ions, $[SnCl_6]^{2-}$ and $[PoCl_6]^{2-}$. In addition, the only solid stable nitrates of both metals correspond: $Sn(NO_3)_4$ and $Po(NO_3)_4$. There are matching oxides in the +4 oxidation state: SnO_2 and PoO_2; and in the +2 state: SnO and PoO.

Melting points of some copper–indium–bismuth compounds

Laing (Laing 1999) noted close-matching melting points or boiling points among specific halide pairs involving the metal combinations of: Ag(I)–Tl(I), Cd(II)–Pb(II), Zn(II)–Sn(II), and Ga(III)–Sb(III).

In this and the next section, we look systematically at melting point series for the two double-pairs. Boiling points were also examined for potential patterns but incomplete data were available and correlations showed no better correspondence than those of melting points. The values of the melting points have all been obtained from the WebElements® on-line site for consistency (Winter 2006). Table 4 shows the melting points of the

Table 4 Melting points of corresponding copper(I) and indium(I) halides

	MCl	MBr	MI
Copper(I)	422	504	606
Indium(I)	211	285	364

corresponding copper(I) and indium(I) halides. There does not seem to be any significant correlation.

For the indium(III) and bismuth(III) pair, the melting points of both the halides and the chalcogenides are tabulated (Tables 5 and 6). The halides do not show close matches. However, though the melting points of In_2O_3 and Bi_2O_3 differ significantly, melting points of pairs among the other chalcogenides are somewhat similar.

Melting points of some zinc–tin–polonium compounds

Laing [Laing 1999] used the similarity in melting points of the $ZnCl_2$–$SnCl_2$ pair as an example of the 'Knight's Move' linkage. Surveying the complete series of zinc and tin(II) halides (plus the two known polonium(II) analogs) in Table 7, $ZnCl_2$–$SnCl_2$ are, in fact, the only strong matches to be found. There are no melting point similarities between the pairs of tin(IV) and polonium(IV) halides (Table 8).

Commentary

We set out in this study to provide a more systematic reinforcement for the concept of the 'Knight's Move' relationship. However, instead, our findings for the two double-pairs seem to point out the limitations of the relationship. We could find no systematic patterns

Table 5 Melting points of corresponding indium(III) and bismuth(III) halides

	MF_3	MCl_3	MBr_3	MI_3
Indium(III)	1170	583	435	207
Bismuth(III)	649	234	219	409

Table 6 Melting points of corresponding indium(III) and bismuth(III) chalcogenides

	M_2O_3	M_2S_3	M_2Se_3	M_2Te_3
Indium(III)	1913	1050	660	667
Bismuth(III)	817	850	710	580

Table 7 Melting points of corresponding zinc, tin(II), and polonium(II) halides

	MF_2	MCl_2	MBr_2	MI_2
Zinc	872	275	394	446
Tin	213	247	216	320
Polonium	–	355	270	–

Table 8 Melting points of corresponding tin(IV) and polonium(IV) halides

	MF_4	MCl_4	MBr_4	MI_4
Tin	subl.	−33	31	143
Polonium	–	300	330	>200

for metal melting points, nor for the melting points of the corresponding halides and chalcogenides in the series studied here.

The validity of the 'Knight's Move' linkage is far more convincing in terms of parallels in compound formulas of the same oxidation state. Thus, in our view, the 'Knight's Move' effect correlates with the increasing stability of lower oxidation states with the later Period 5 and Period 6 elements. In addition, there seems to be closer resemblance between 'Knight's Move' pairs from Periods 5 and 6 than between pairs from Periods 4 and 5.

The indication of a periodic pattern is the consistent applicability of a phenomenon to a sub-set of the Periodic Table of Elements. We suggest that the justification of the 'Knight's Move' relationship should be made primarily on the basis of similarities in formulas and chemistry of compounds of 'Knight's Move' pairs of metallic elements in the lower-right quadrant of the Periodic Table. Though there are a few specific resemblances in melting and boiling points among pairs of 'Knight's Move' compounds, we consider that they are not widespread and consistent enough to be regarded as evidence of a systematic relationship. Thus, in our opinion, it is the chemical rather than the physical properties, which should be emphasized as evidence for this relationship.

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