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Periodic patterns: the Group (n) and Group ($n + 10$) linkage

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Abstract The early Periodic Tables displayed an 8-Group system. Though we now use an 18-Group array, the old versions were based on evidence of similarities between what we now label as Group (n) and the corresponding Group ($n + 10$). As part of a series on patterns in the Periodic Table, in this contribution, these similarities are explored for the first time in a systematic manner. Pourbaix (Eh–pH) diagrams have been found particularly useful in this context.

Keywords Periodic table · Elements

Though studies of the Periodic Table traditionally emphasize groups and periods, there are other interesting and curious resemblances to be found. As part of a series examining these other relationships in detail, this author has reported on the chemical 'knight's move' relationship (Rayner-Canham and Oldford 2007); isoelectronic series (Rayner-Canham 2009); and diagonal relationships (Rayner-Canham 2011). Here the linkage between Group (n) and Group ($n + 10$) elements will be addressed by providing a selective discourse on each of the relevant pairs of Groups. In this way, additional linkages have been discovered to those previously reported.

The early periodic tables, such as one of Mendeléev's shown below (Fig. 1) were structured on a repetitive basis of eight (Scerri 2006). This made sense as there really are some similarities amongst the elements in each of the boxes. With the acceptance of the 18-Group array, the resemblances between the currently-labelled Group (n) and Group ($n + 10$) members has been 'written out' of most accounts of inorganic chemistry.

It was Laing who, in 1989, first reminded chemists of these similarities (Laing 1989a, b). He noted the resemblances between silicon and titanium compounds (such as the pair $SiCl_4$ and $TiCl_4$); phosphorus and vanadium compounds (such as $POCl_3$ and $VOCl_3$); sulfur and chromium polyatomic ions (such as SO_4^{2-} and CrO_4^{2-}); and chlorine and manganese compounds (such as Cl_2O_7 and Mn_2O_7). To emphasize the linkage, Laing

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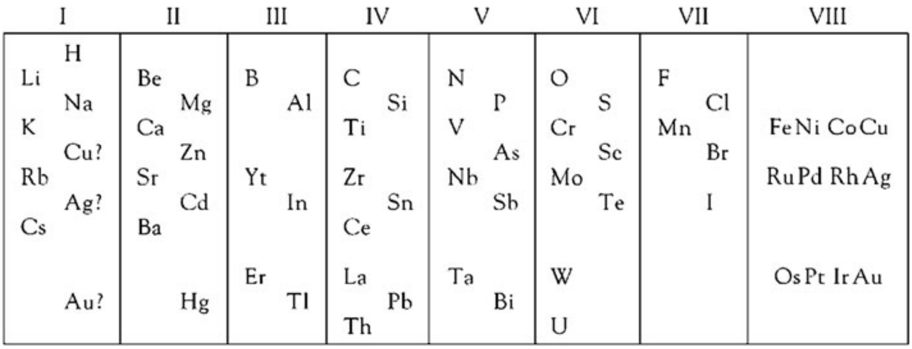


I	II	III	IV	V	VI	VII	VIII
H							
Li	Be	B	C	N	O	F	
Na	Mg	Al	Si	P	S	Cl	
K	Ca		Ti	V	Cr	Mn	FeNi CoCu
Cu?	Zn			As	Se	Br	
Rb	Sr	Yt	Zr	Nb	Mo		RuPd RhAg
Ag?	Cd	In	Sn	Sb	Te	I	
Cs	Ba		Ce				
		Er	La	Ta	W		OsPt IrAu
Au?	Hg	Tl	Pb	Bi			
			Th		U		

Fig. 1 One of Mendeléev's versions of the periodic table

proposed that the element 'boxes' of lithium to fluorine and sodium to chlorine be repeated above the corresponding transition metal column.

Rich (1991) proposed a modification to Laing's diagram: that oxygen and fluorine be deleted from the duplication as there are no similarities between those elements and the corresponding transition metals of chromium and manganese. In fact, there is little similarity between any of the Period 2 main group elements and the corresponding *d*-block elements. It is of note that all of Laing's examples compare Period 3 main group elements with the Period 4 *d*-group elements.

Though Laing's study focussed on the formula similarities of the Period 3 main group elements with the corresponding Groups of the transition series, Mingos (1998) showed that such parallels in formula existed in other (n) and ($n + 10$) pairs. For example, chromium forms compounds of formula: CrF_6, CrO_2F_2, and $CrO_4{}^{2-}$; while selenium forms parallel compounds of formula: SeF_6, SeO_2F_2, and $SeO_4{}^{2-}$. Mingos also contrasted the parallel, and not-so-parallel, chemistry of vanadium and arsenic over each of their respective oxidation states.

The Group (n) and Group (n + 10) relationship

The linkage in chemical formulas and chemical behaviour between each Group (n) member and the corresponding Group (n + 10) member is quite specific. The relationship is between compounds and polyatomic ions of the highest oxidation state of the main group elements and those of the same oxidation state of the matching transition elements. A general definition for this relationship is:

> There are some similarities in chemical formulas and structures of compounds and polyatomic ions of the highest oxidation state of Group (n) elements with compounds and polyatomic ions of the highest oxidation state of the corresponding Group (n + 10) elements.

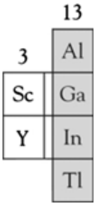
In the study on isoelectronic series (Rayner-Canham 2009), it was pointed out that the (n) and (n + 10) linkage for highest oxidation states comes about through electronic structural similarities. That is, the (n) element in its highest oxidation state has a noble-gas electron configuration while the corresponding (n + 10) element in its highest oxidation state has, in addition, a filled d^{10} set. For the elements lower in the respective groups, there is also a filled f^{14} electron set. It was proposed that such parallel pairs be referred to as *pseudo-isoelectronic*. In this paper, then, some evidence of the (n) and ($n + 10$) relationship comes from the existence of such pseudo-isoelectronic pairs or trios of compounds and polyatomic ions. Also, parallels in high-oxidation state aqueous species across the pH range provide a separate strand of evidence of the (n) and ($n + 10$) relationship.

The focus in previous published studies on this linkage has been the specific resemblance of the chemistry of the Period 2 main group elements with the corresponding Period 3 transition metal. However, here a wider range of matches of Group (n) elements with corresponding Group ($n + 10$) elements will be reported.

Like the diagonal relationships discussed previously (Rayner-Canham 2011), there does not seem to be a standard pattern in these linkages from one group-pair to the next. Instead, each group-pair has to be examined separately for commonalities (see below). Though as a generality, there seem to be similarities between the Period 4, Group (n) element and the Periods 3 and 4, Group ($n + 10$) elements; together with some similarities between the lower members of each corresponding pair of groups.

Group 3 and Group 13

In this pair of groups, Greenwood and Earnshaw (1997) have discussed the way in which aluminum can be considered as belonging to Group 3 as much as to Group 13, particularly in its physical properties. The Canadian geochemist, Habashi, has suggested that there are so many similarities between aluminum and scandium that aluminum's place in the Periodic Table should actually be shifted to Group 3 (Habashi 2010). In terms of the electron configuration of the tripositive ions, one would indeed expect that Al^{3+} (electron configuration, [Ne]) would resemble Sc^{3+} (electron configuration, [Ar]) more than Ga^{3+} (electron configuration, [Ar]$3d^{10}$).



In terms of their comparative solution behaviour, scandium(III) resembles both aluminum(III) and gallium(III). For each ion, the free hydrated cation exists only in acidic solution. On addition of hydroxide ion to the respective cation, the hydroxides are produced as gelatinous precipitates. Each of the hydroxides re-dissolve in excess base to give an anionic hydroxo-complex, $M(OH)_4^-$. The similarities are summarized in Table 1.

There does seem to be a triangular relationship between these three elements. However, scandium does more closely resemble aluminum rather than gallium in its chemistry. If hydrogen sulfide is bubbled through a solution of the respective cation, scandium ion gives

Table 1 A comparison of aluminum, scandium, and gallium species under oxidizing conditions

	Acidic	Mid-to-basic pH range	Very basic
Aluminum	$Al^{3+}(aq)$	$Al(OH)_3(s)$	$Al(OH)_4^-(aq)$
Scandium	$Sc^{3+}(aq)$	$Sc(OH)_3(s)$	$Sc(OH)_4^-(aq)$
Gallium	$Ga^{3+}(aq)$	$Ga(OH)_3(s)$	$Ga(OH)_4^-(aq)$

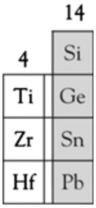
a precipitate of scandium hydroxide, while aluminum ion gives a precipitate of aluminum hydroxide. By contrast, gallium ion gives a precipitate of gallium(III) sulfide. Also, scandium and aluminum both form carbides, while gallium does not.

Not previously identified, there are similarities in the chemistry of yttrium and indium. For example, their aqueous chemistry is dominated by the soluble 3+ cation in acid and by the insoluble hydroxide at neutral and basic pH (Table 2).

As a final note, the bottom member of Group 13, thallium, has very different chemistry to either yttrium or indium. The chemistry of thallium is more appropriately linked to that of silver through the ‘knight’s move’ relationship (Rayner-Canham and Oldford 2007).

Group 4 and Group 14

This Group seems to be unique in that, although there are similarities between titanium(IV) and silicon(IV), there is a much greater resemblance of titanium(IV) with tin(IV), further down Group 14.



In some ways, the chemistry of titanium(IV) resembles that of all the Group 14 elements in their +4 oxidation state. In particular, all five form tetrahedrally-coordinated chlorides which are hydrolysed to give the dioxide and hydrogen chloride:

$$\mathrm{MCl_4}(l) + 2\,\mathrm{H_2O}(l) \rightarrow \mathrm{MO_2}(s) + 4\,\mathrm{HCl}(g)$$

Interestingly, even though they have significantly different molar masses, the chlorides of titanium(IV) and tin(IV) have remarkably similar melting and boiling points (Table 3). By contrast, both zirconium(IV) chloride and hafnium(IV) chloride are high-melting solids with a polymeric, six-coordinate structure.

As another example of the similarity of titanium(IV) and tin(IV), the most common form of crystal structure of titanium(IV) oxide is rutile, and tin(IV) oxide adopts the same structure. Also, titanium(IV) oxide and tin(IV) oxide share the rare attribute of thermochroism by turning from white to yellow reversibly on heating.

Group 5 and Group 15

In this group-pair, the major resemblance seems to be between vanadium(V), phosphorus(V), and arsenic(V). There is also a similarity in aqueous species between niobium and antimony.

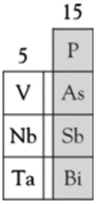


Table 2 A comparison of yttrium and indium species under oxidizing conditions

	Acidic	Mid-pH range	Basic
Yttrium	$Y^{3+}(aq)$	$Y(OH)_3(s)$	
Indium	$In^{3+}(aq)$	$In(OH)_3(s)$	

Table 3 The comparative physical properties of the silicon, titanium(IV), and tin(IV) chlorides

Compound	Molar mass (g mol^{-1})	Melting point (°C)	Boiling point (°C)
Titanium(IV) chloride	190	−24	136
Silicon tetrachloride	170	−70	57
Germanium(IV) chloride	214	−52	87
Tin(IV) chloride	261	−33	114
Lead(IV) chloride	349	−15	Dec

Table 4 A comparison of aqueous vanadium, phosphorus, and arsenic species in dilute solution under oxidizing conditions

	Very Acidic	Acidic	Basic	Very Basic
Vanadium	VO_2^+	$H_2VO_4^-$	HVO_4^{2-}	VO_4^{3-}
Phosphorus	H_3PO_4	$H_2PO_4^-$	HPO_4^{2-}	PO_4^{3-}
Arsenic	H_3AsO_4	$H_2AsO_4^-$	$HAsO_4^{2-}$	AsO_4^{3-}

Table 5 Some parallel compounds and ions of vanadium(V) with phosphorus(V) and arsenic(V)

Group 7	Group 17
V_2O_5	P_4O_{10}, As_2O_5
VO_4^{3-}	PO_4^{3-}, AsO_4^{3-}
$V_4O_{12}^{4-}$	$P_4O_{12}^{4-}$
$VOCl_3$	$POCl_3$, $AsOCl_3$
VF_5	PF_5, AsF_5
VF_6^-	PF_6^-, AsF_6^-
VOF_4^-	POF_4^-(unstable)

In terms of the simple oxo-anions, vanadium resembles both phosphorus and arsenic. Vanadate, phosphate, and arsenate are all strong bases with similar pKa values. The only significant difference is that at low pH, vanadium forms the vanadyl ion, not the undissociated acid as do phosphorus and arsenic (Table 4).

There are a significant number of parallel compounds between vanadium, phosphorus, and arsenic, as can be seen from Table 5. Of the two, vanadium more closely resembles phosphorus as there are several examples, two of which are listed below, for which there is no known arsenic analogue.

Table 6 A comparison of aqueous antimony and niobium species under oxidizing conditions

	Acidic	Mid-pH range	Basic
Niobium	$Nb_2O_5(s)$		isopolyniobates(*aq*)
Antimony	$Sb_2O_5(s)$	isopolyantimonates(*aq*)	

Table 7 A comparison of aqueous chromium, sulfur, and selenium species under oxidizing conditions

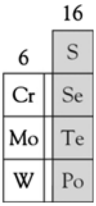
	Very Acidic	Acidic	Basic	Very Basic
Chromium	H_2CrO_4	$HCrO_4^-$	CrO_4^{2-}	
Sulfur	HSO_4^-	SO_4^{2-}		
Selenium	$HSeO_4^-$	SeO_4^{2-}		

There is also an interesting parallel in aqueous species between antimony and niobium as is shown in Table 6. Though the aqueous antimonate ion is usually represented as $[Sb(OH)_6]^-(aq)$ and the aqueous niobate ion as $[NbO_3]^-(aq)$, Greenwood and Earnshaw (1997) have pointed out that for both of them, isopolymeric species predominate over most of the soluble range.

By contrast, tantalum forms insoluble tantalum(V) oxide across the full pH range, while bismuth(III) dominates that element's aqueous chemistry.

Group 6 and Group 16

Just as vanadium(V) resembles phosphorus(V) and arsenic(V), so chromium(VI) resembles both sulfur(VI) and selenium(VI).



Again there are parallels in the acid–base behaviour of the oxo-anions, the only difference in this case being that chromic acid is a weaker acid than either sulfuric acid or selenic acid (see Table 7).

There are also several formula similarities between chromium(VI) and both sulfur(VI) and selenium(VI). A few examples are given in Table 8.

Group 7 and Group 17

Once again, there seem to be a triangular relationship, this time between manganese(VII), chlorine(VII), and bromine(VII). There are also parallels in formulas between rhenium(VII) and iodine(VII).

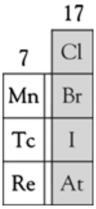


Table 8 Some parallel compounds and ions of chromium(VI) with sulfur(VI) and selenium(VI)

Group 7	Group 17
CrO_3	SO_3, SeO_3
CrO_4^{2-}	SO_4^{2-}, SeO_4^{2-}
$Cr_2O_7^{2-}$	$S_2O_7^{2-}$, $Se_2O_7^{2-}$
CrO_2Cl_2	SO_2Cl_2
CrF_6	SF_6, SeF_6
$CrOF_4$	SOF_4, $SeOF_4$
CrO_2F_2	SO_2F_2, SeO_2F_2

Table 9 Some parallel compounds and ions of rhenium(VII) and iodine(VII)

Group 7	Group 17
Re_2O_7	I_2O_7
ReF_7	IF_7
$ReOF_5$	IOF_5
$ReO_2F_4^-$	$IO_2F_4^-$

Table 10 Some parallel compounds of osmium(VIII) and xenon(VIII)

Group 8	Group 18
OsO_4	XeO_4
OsO_3F_2	XeO_3F_2
OsO_2F_4	XeO_2F_4

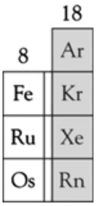
The most obvious similarity between the three at the top of their Groups are the strongly oxidizing oxoanions: permanganate, perchlorate, and perbromate. All three elements form corresponding trioxofluorides: MnO_3F, ClO_3F, and BrO_3F. There seems to be a slightly greater similarity between manganese(VII) and chlorine(VII) in that only those two form oxides in the +7 oxidation state: Cl_2O_7, and Mn_2O_7, both of which are highly explosive liquids at room temperature.

Equally interesting in this group-pair are the similarities of rhenium with iodine.

Some of the parallel compounds are shown in Table 9. Of note, $ReOF_5$ has a melting point of 44 °C while that of IOF_5 is 45 °C.

Group 8 and Group 18

Somewhat surprisingly, there are two elements near the bottom of each group, that share several similarities in chemical formulas: ‘noble metal’ osmium(VIII) and ‘noble gas’ xenon(VIII).



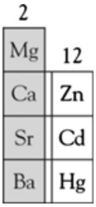
Some parallels in formula are shown in Table 10. Similarities even extend to chemical behaviour: osmium(VIII) oxide, OsO_4, is a yellow solid and strongly oxidizing, while xenon tetraoxide, XeO_4, is a pale yellow explosive compound.

Group 1 and Group 11

Group 1 and Group 11 are the most problematic of the group-pairs. While the alkali metals always exhibit an oxidation state of +1, for the Group 11 metals, copper's common higher oxidation state is +2 and there are even compounds of oxidation state +3. Though the oxidation state of silver is often +1, that element, too, can have higher oxidation states of +2 and +3. Many gold compounds have a metal oxidation state of +3. Thus using the definition above for the Group (n) and ($n + 10$) relationship, it is preferable to regard this group-pair as being an exception to the patterns.

Group 2 and Group 12

All of these elements have +2 as the sole common oxidation state, except for mercury for which it is the higher oxidation state. Thus there are some resemblances for all of the Group 2 elements with zinc and cadmium. For example, all six of these elements form hygroscopic anhydrous metal chlorides. However, the closer link seems to be between cadmium and calcium.



The hydroxides of zinc and cadmium are insoluble, and in that respect, resemble the insoluble magnesium hydroxide and somewhat insoluble calcium hydroxide, rather than the soluble hydroxides of strontium and barium. Cadmium oxide has the NaCl structure, as do the Group 2 oxides, while in zinc oxide, the ions are tetrahedrally arranged. Zinc is also different in that zinc hydroxide is the only one of the hydroxides to dissolve readily in excess hydroxide ion to form a soluble anion. Of particular biochemical note, high levels of calcium(II) ion inhibit the toxicity of cadmium(II) ion, suggesting that the two ions share the same cellular pathway (Michibata, Sahara and Kojima 1986). Thus overall, cadmium and calcium seem to have the closer resemblance.

Commentary

Here it has been demonstrated that there are numerous links in formula of compounds and polyatomic ions of elements of Group (*n*) with pseudo-isoelectronic species of elements of the corresponding Group ($n + 10$). The similarities pertain to the highest oxidation state in each case. As the metal is in a high oxidation state, the bonding in each compound is predominantly covalent. It has been pointed out in a previous part of this series (Rayner-Canham 2009) that covalent bonding can transcend bonding type and lead to some interesting isostructural compounds. In addition, there are similarities in the pH dependence of aqueous species in the highest oxidation state for some of the (*n*) and ($n + 10$) pairs.

There seems to be a general (with exceptions) similarity of the element of Period 4, Group (*n*) with both Period 3 and 4 members of Group ($n + 10$), though the stronger link seems to be with the Period 3 main group member. In addition, there are several interesting parallels between lower members of the group-pairs.

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