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Chemdex: quantification and distributions of valence numbers, oxidation numbers, coordination numbers, electron numbers, and covalent bond classes for the elements†

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The paper introduces Chemdex, a freely accessible web-based database of over 70 000 compounds characterised by crystallography from across the periodic table. Its software calculates for an atom of interest within each compound classifications including valence number, oxidation number, coordination number, electron number, several covalent bond classifications, and the attached atom set. Users may explore distributions of these classifications by percentages and heat map displays for individual elements or sets of elements, or in several cases for one classification plotted against a second. These properties often display clear periodicity. Based upon distributions across the periodic table of valence numbers, electron numbers, coordination numbers, and attached atom data suggestions are made regarding the placement of hydrogen in the periodic table, membership of group 3 in the periodic table, locations of the early actinoids in the periodic table, and assignments of certain elements as metalloids.

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Introduction

With experience, chemists tend to acquire at least subjective views of common chemical classifications such as valence or oxidation number. These views assist understanding of chemistry of the elements. However, trends for these classifications are, in general, not well quantified. This paper describes Chemdex,[1] a web-based project intended to provide a more quantified view of these classifications and others. Long-standing classifications of atom environments within compounds include oxidation number[2] (**ON**, also known as oxidation state[3]), valence number (**VN**),[4,5] coordination number (**CN**),[6] and electron number (**EN**). Key early publications contain tables or charts representing oxidation numbers for the elements.[7,8] Many books depict oxidation number trends, at least of metals, as part of sections on periodicity.[9,10] Entries in these tables or charts are sometimes identified as "important" or "common" without necessarily defining or quantifying those terms.

King described formal classification systems for d-block compounds[11] using the following ligand types:

X: one-electron donor ligands, examples include halides, pseudohalides, alkyl;

L: two-electron donor ligands (Lewis bases), examples include water, amines, phosphanes, carbon monoxide;

Z: zero-electron donor ligands (Lewis acids, two electron acceptor ligands), examples include boranes, gallanes, and many 16-electron metal fragments such as $W(CO)_5$.

King introduced charts representing three-dimensional matrices of **EN** against **CN**, of atomic number against **CN**, and atomic number against **EN** with in each case the third dimension being the overall charge q on the compound. More recently, Green introduced the MLXZ Covalent Bond Classification (CBC) based upon identification of attached groups or ligands as combinations of X, L, and Z on the atom of interest (usually denoted M, whether metal or not).[12] This leads to a $[MLXZ]^q$ designation (q is adjusted for remote charges on the ligands, if any). Green then provides a rules-based transformation of the $[MLXZ]^q$ designation into an equivalent neutral class (ENC) represented on two-dimensional MLXZ diagrams for each element (effectively heat map plots of **EN** against **VN**). The CBC is used mostly for d-block compounds but is also applicable to main group compounds.

One intention of the research described here was to create a database of atom environments within compounds with automatically calculated quantified values for these classifications. The Chemdex project described herein consists of a database

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† Electronic supplementary information (ESI) available: **VN–CN**, **VN–EN**, **ON–CN**, **ON–EN** plots for all elements printable at high resolution. Averages of **VN**, **CN**, **ON**, **EN**, **XN**, **LN**, **ZN**, and **BN** line graphs. Heat maps showing **VN**, **CN**, **ON**, **EN**, **XN**, **LN**, **ZN**, and **BN** for all elements. See DOI: **https://doi.org/10.1039/d3dt03738j**

that fulfils these requirements and a website that enable users to explore all these classifications and others for single elements or sets of elements.[1] An additional requirement is that for each found set of compounds the user may display a lists of compound formulae contributing to that set and to view a referenced entry for each and any individual compound.

Results and discussion

Entries within the Chemdex database are drawn from across the periodic table. In order to provide a consistent and high level of confidence in reported compound identities an early decision was to adopt mandatory criteria for inclusion of any compound within the database. The chosen criteria are:

a crystal structure with a crystallographic reference and coordinates available within the CSD at the Cambridge Crystallographic Data Centre (CCDC)[13] or the Inorganic Crystal Structure Database (ICSD),[14] and accessible through the CrystalWorks server (CDS/DL);[15]

a literature source for the crystal structure identified with a Digital Object Identifier (DOI).[16]

This does not exclude liquids and gases as many crystal structures of these are known. Once compounds are entered into the Chemdex database the software calculates for the atom of interest in each compound, and as appropriate, the classifications outlined in Table 1. The algorithms are outlined in the methodology section but some explanatory notes are appropriate. The valence number[4,12] of an element is not to be confused (as often happens) with oxidation number or coordination number; these terms are not the same and their purposes differ.[17–19] Other definitions of valence are not applicable here.[20] In practice, **ON** and **VN** values are often numerically equal for the atom of interest, especially for metals in complexes. All atoms in a compound may be assigned an oxidation number.[2] Similarly, in compounds with some degree of covalence, covalent classes such as $ML_lX_xZ_z$ and **VN** and may be assigned for all atoms.[4,12] This means **ON**, **VN**, and $ML_lX_xZ_z$ values may be assigned to C and H in methane as well as to Cr, C, and O in $[Cr(CO)_6]$.

Most of the covalent compounds within Chemdex are molecular but many are classed as oligomer, catena, or network. For instance, $[Mn_2(CO)_{10}]$ is entered as $[Mn(CO)_5]_2$, a dimer of $Mn(CO)_5$. Each manganese atom is surrounded by five L-type carbonyl groups and one $Mn(CO)_5$ X-type group attached by a Mn–Mn bond. The manganese compound $[Mn_2(\mu\text{-}Br)_2(CO)_8]$ is entered as $[Mn(\mu\text{-}Br)(CO)_4]_2$, a dimer of $MnBr(CO)_4$. Each manganese atom is surrounded by four carbonyl groups, one X-type Br group, and an additional L connection from the Br group on the adjacent $MnBr(CO)_4$ group. Catena structures, whether 1-, 2-, or 3-dimensional, are handled similarly and included so long as they can be represented as a unit connected to similar units through combinations of X, L, and Z connections. The network type is used principally for binary structures for which the difference in Allen electronegativities (the scale defined elsewhere for oxidation number calculations[2]) between the elements is less than 1.8. Covalent classes are calculated for these compounds. Compounds are entered as the lattice type when the difference in Allen electronegativity between the central atom and attached groups exceeds 1.8. In such cases **ON** and **VN** are calculated by the system, the **CN** is entered manually, and covalent classifications (**XN**, **LN**, **ZN**, **BN**, MLXZ, $[ML_lX_xZ_z]^q$) are not calculated. Some compounds identified in the literature with agostic interactions are within the database, but agostic interactions currently are not included (as an L-type function) within the calculated classifications. Some compound types are harder to classify using simple classifications such as **VN**, **ON**, and MLXZ.

Table 1 Common classifications associated with compounds

Classification	Comments
M	Atom of interest, used for metals and non-metals. The variable m denotes the number of valence electrons for an isolated neutral atom M.
QN	Overall charge number on the entity adjusted for remote charges on attached groups, if any, denoted q in equations.
ON	Oxidation number: the charge of an atom after its homonuclear bonds are divided equally and heteronuclear bonds assigned to the bond partners according to Allen electronegativity.[2]
CN	Coordination number: the number of attached group denticities given by the number of σ-bonds between the group and the atom of interest. Although both carbon atoms in ligated ethene are bound, the coordination number contribution of ethene is defined as one. Cyclopentadienyl and benzene each contribute three to the overall coordination number.[6]
LN	L number: the sum of attached L-type group values, denoted l in equations.[11,12]
XN	X number: the sum of attached X-type group values, denoted x in equations.[11,12]
ZN	Z number: the sum of attached Z-type group values, denoted z in equations.[11,12]
$[MLXZ]^q$	Constructed as $[ML_lX_xZ_z]^q$ from M, x, l, z, and q.[12]
MLXZ	MLXZ class or ENC (equivalent neutral class): derived from $[ML_lX_xZ_z]^q$ through a set of mapping rules.[12]
VN	Valence number: **VN** = $x + 2z$ from $ML_lX_xZ_z$.[4,12]
EN	Electron number: **EN** = $m + x + 2l - q$ from $[ML_lX_xZ_z]^q$ or **EN** = $m + x + 2l$ from the equivalent neutral class $ML_lX_xZ_z$.[12]
BN	Bond number (or ligand bond number): **BN** = $x + l + z$, denoted b.[12]
d^n	Number of primarily non-bonding d-electrons calculated from $d^n = m - v$ or from $d^n = m -$ **ON**.[2]

Compounds are built within the database by entering within their records at least: the central atom of interest, M and the number of M atoms where appropriate; the overall charge, q, on the compound, an integer (0, positive, or negative); the attached groups and the number of each; the compound type (molecular, oligomer, catena, network, lattice); the geometry around the atom of interest; if appropriate, additional X, L, and Z values to denote connections between formula units in oligomers, catenas, and networks.

Examples include some metal cluster compounds, boranes, some superficially simple binary compounds, and others.

The Chemdex set of atom environments is not claimed to be a pure statistical sample of all atom environments but is expected to be reasonably representative for each element. In general, compounds with simpler attached groups are selected over groups with very specialised or complex structures. While specific compound types were not sought out, where very few compounds of, for instance, the highest or lowest available valence or oxidation numbers are known these were indeed sought out and included, provided atom coordinates are available.

The Chemdex system allows users to explore its database through its web site. Users may select to view proportions for any of **VN**, **CN**, **ON**, **EN**, **XN**, **LN**, **ZN**, **BN**, and attached atom profiles as heat maps for individual elements or sets of elements. In addition, the system allows in several cases for the display of grids for one property displayed against a second property for individual elements or sets of elements. As examples, users may inspect grids showing **VN** plotted against **CN**, **ON** plotted against **CN**, **ON** plotted against **EN**, [MLXZ]^q plots, and MLXZ plots (effectively displays of **EN** against **VN**). All displays are generated live from the database and may change with time as additional structures are added.

Valence and oxidation number trends

The distributions of **VN** and **ON** for the elements extracted from Chemdex are shown as heat maps in Fig. 1. The **VN** distribution is also shown in periodic table format (discussed further later) in Fig. 2 and 3 allowing easier viewing of group and period trends. The highest and lowest values of **ON** are reminiscent of those in Mendeleev's early data table constructed using formulae of hydrides and oxides.[7–9] Elements to the top right of the p-block are associated with negative oxidation numbers. Some main group elements, and carbon in particular, form homonuclear bonds. Each homonuclear bond, if present, increases the valence by one but does not change the oxidation number. As an example, each carbon in ethane is tetravalent but C(−III). Consequently, although carbon shows the full range of oxidation numbers from C(−IV) to C(IV), **VN** = 4 predominates for carbon over all other values.

The p-block elements are associated with greater valence numbers in cases where their lone pairs function as Lewis bases in complexes. For instance, nitrogen in amine complexes is pentavalent, trivalent in unbound amines, but N(−III) both cases. Similarly, oxygen is generally O(−II) and divalent, but tetravalent in aqua or ether complexes, for instance, when ligated through lone pair donation as a L-type ligand to metals. Consequently valence number distributions of carbon and some other p-block elements are quite different from their oxidation number distributions. Valence number distributions of p-block elements are characterised almost exclusively by either a single valence number or valence numbers separated by two units.

The d-block elements valence numbers vary from 0 up to a maximum of 8 (rare) but not necessarily separated by two valence units as is the norm for p-block elements. The most common valence number for lanthanoids is three but with a significant minority of two in many cases and four for cerium. Valence numbers of the first half of the actinoid block are characterised by much greater variability than the first half of the lanthanoid block and distributions are somewhat reminiscent of the early d-block elements. Values largely 3 after americium but data are scarce.

Valence and oxidation numbers are, in general, numerically similar for the s-, d-, and f-block elements within compounds. Differences are evident in at least four compound types including metal–metal bonded compounds, complexes of Z-type Lewis acid groups, complexes containing X-type ligands whose attached atom is less electronegative than the metal, and complexes of some strong π-acceptor ligands. As examples of the differences caused by metal–metal bonding, the **VN** of Re in $[Cl_4Re{\equiv}ReCl_4]^{2-}$ is 7, but **ON** = 3, while the **VN** of Re in $[(OC)_5Re{-}Re(CO)_5]$ is 1, but **ON** = 0. Metal complexes with Z-type ligands such as $InCl_3$ are rare but when present each Z-type ligand adds 2 to the **VN** relative to the **ON**. As an example, for Os in $[Os(GaCl_3)(CO)_4(PMe_3)]$ the **ON** is 0 while the **VN** is 2. Seemingly unusual oxidation numbers arise in metal complexes containing X-type attached groups where the group's attached atom, frequently another d-block metal or a main group metal, is less electronegative than the metal of interest. Examples include Re(−I) in $[(OC)_5Re{-}Mo(CO)_3(\eta^5\text{-}C_5H_5)]$ and Co(−III) in $[Co(SnCl_3)_2(CO)_3]^-$.

If π-backbonding in metal complexes is deemed significant there is an effect on the metal's **VN**. Backbonding is, in general, considerable for linear nitrosyl ligands. The current convention for oxidation number calculations is to regard linear nitrosyl ligands as NO^+ and bent nitrosyl ligands as NO^-(X). For a single linear nitrosyl ligand in the covalent bonding model three electrons (XZ) are required through backbonding to complete the population of the π* highest occupied molecular orbitals. Including the lone pair donation from nitrogen to the metal means a single NO ligand overall is therefore LXZ.[21] The three XZ electrons contributed by the metal are bonding and consequently the valence number of the metal increases by three. In oxidation number calculations, an electron is transferred to the metal resulting in NO^+; in that model four electrons are then involved in backbonding to the NO π* levels but that backbonding does not further affect the oxidation number of the metal. When more than one NO ligand is bound to the metal, molecular orbital calculations may be needed to determine an appropriate representation of bonding. For example, in the covalent model two NO ligands when *cis* in an octahedral environment are best treated as a composite group designated as L_2ZX_2.[21] In some cases the bonding of nitrosyl ligands is considered in further detail.[22] Backbonding is evident also for carbonyl complexes but the extent of backbonding is less than nitrosyl. If backbonding is not regarded as important then each CO ligand contributes two electrons to the metal and is treated as L. If backbonding is deemed important, perhaps for negatively charged carbonyl complexes, then further symmetry considerations are required

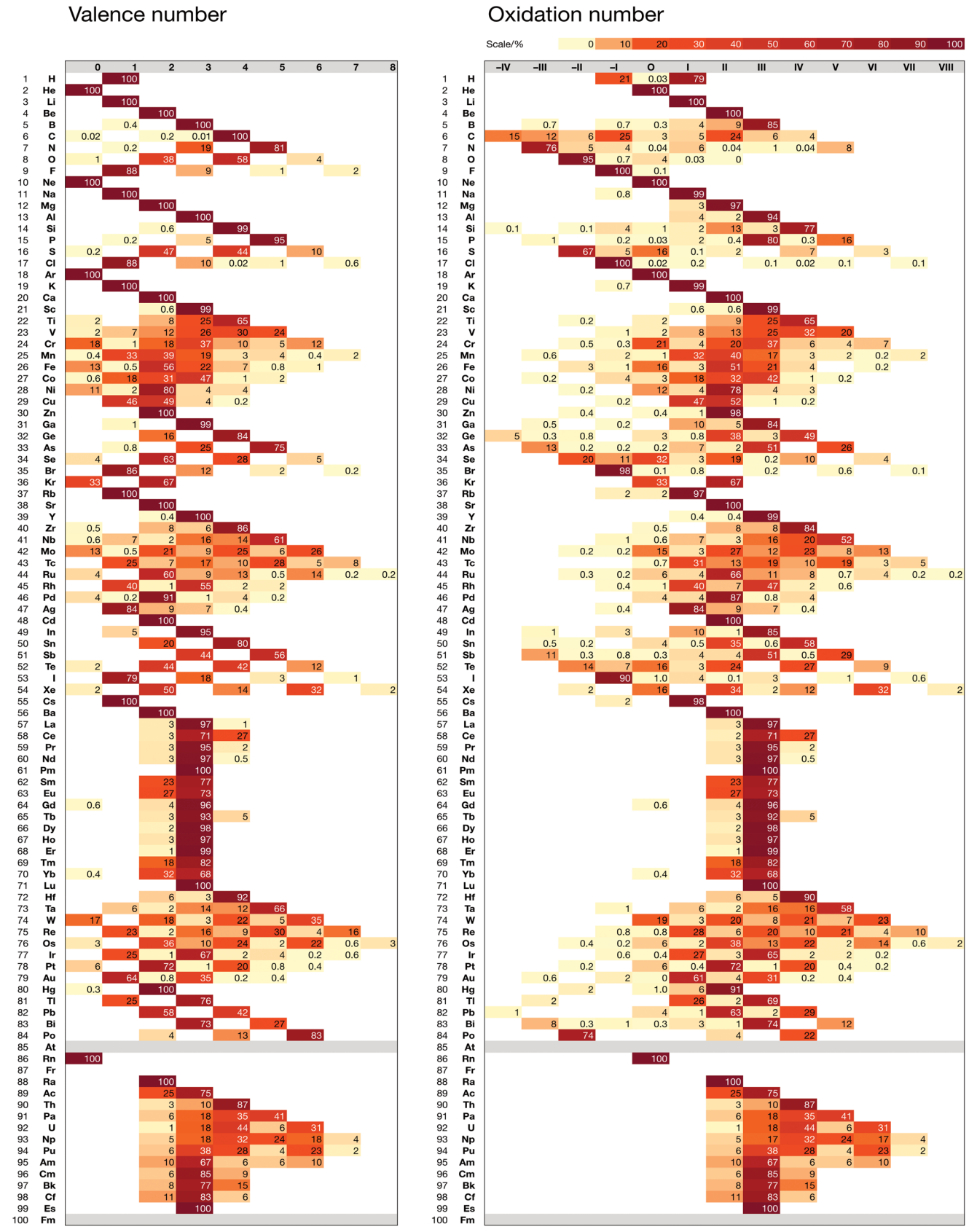

Fig. 1 Valence number (**VN**) and oxidation number (**ON**) proportions as percentages for the elements. There are no data for elements beyond einsteinium.

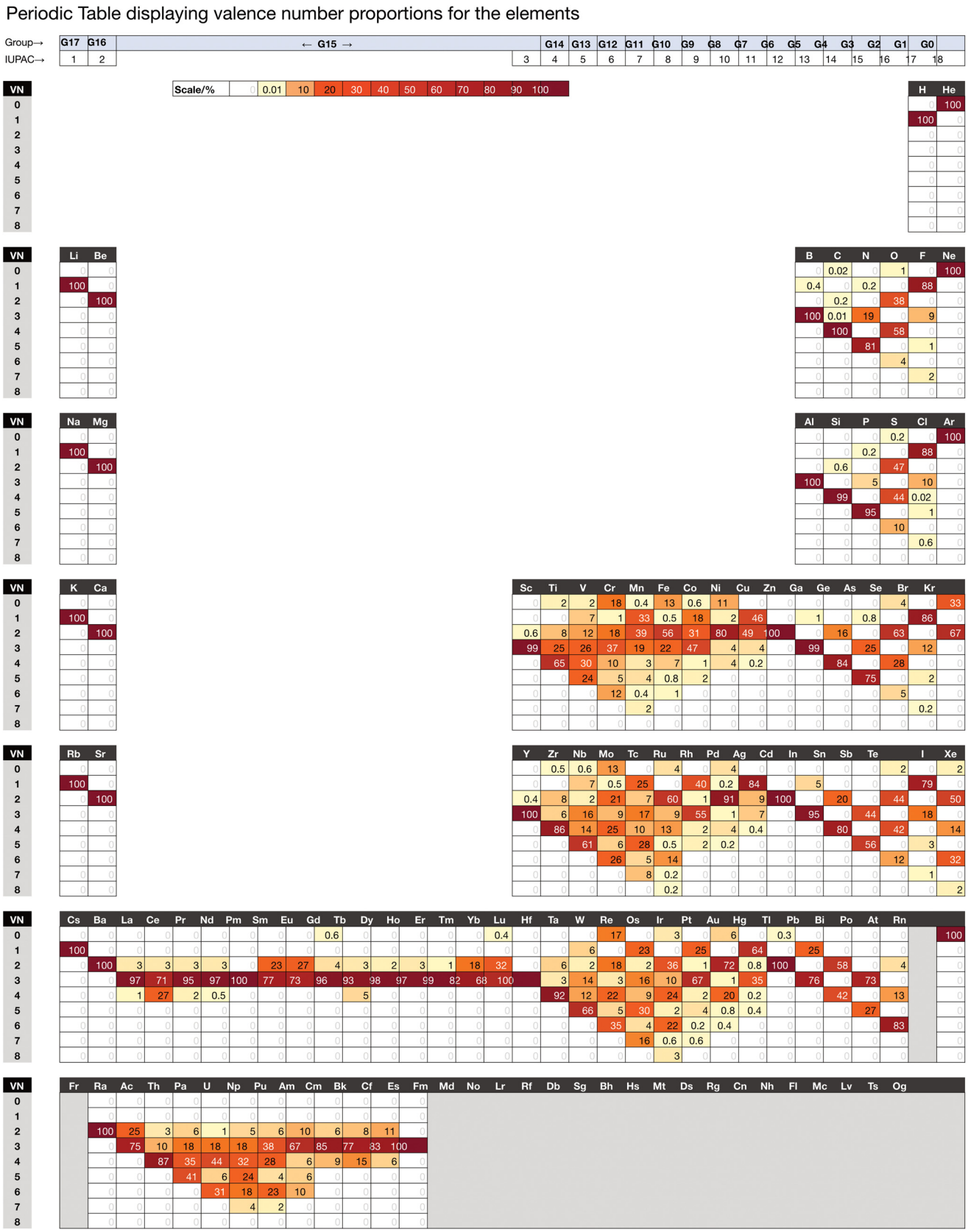

Fig. 2 Periodic tables displaying valence number proportions (%). There are few data for Pm and no data for Fr and elements beyond Es. The position of H and the group numbers are addressed below.

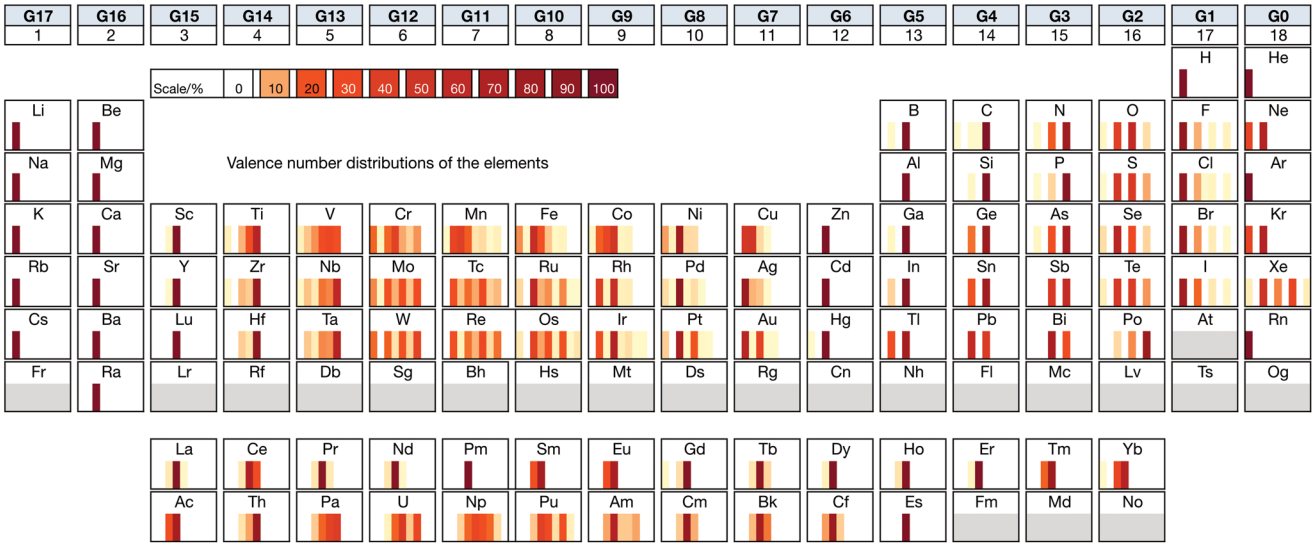

Fig. 3 Periodic tables displaying valence number proportions (%). There are few data for Pm and no data for Fr and elements beyond Es. The position of H and the group numbers are addressed below.

to determine the best value of **VN**. This requires the identification of one or more Z functions to denote backbonding and a consequential increase in the **VN** of two for each Z function.[21] Currently the only carbonyl complexes for which backbonding is taken into consideration in Chemdex are a few negatively charged homoleptic carbonyl species.

The differences in valence and oxidation numbers evident for these four specific compound types result in apparent discrepancies in the metal d^n number when calculated from $d^n = m - v$ and $m - \mathbf{ON}$ (Table 1). The d^n number is the number of approximately non-bonding d-electrons and may be useful, for instance, for understanding magnetic and spectroscopic features of d-block compounds. Discrepancies include values associated with compounds containing homonuclear metal–metal bonds, whether single or multiple. As an example the d^n value for Mn in $[Mn(CO)_5]_2$ is d^6 using $d^n = m - v$, but d^7 from $d^n = m - \mathbf{ON}$. For metal complexes with Z-type ligands such as $InCl_3$ the $d^n = m - v$ equation gives values 2 less than those from $d^n = m - \mathbf{ON}$ because the Z function does not alter the oxidation number.

Coordination number trends

The coordination number is not always unambiguous. By default, decisions upon connectivity are based upon a set of default covalent radii derived from empirical data.[23] Occasionally these are over-ridden when the original reports identify connected atoms at distances greater than their sum of default radii. This issue is discussed elsewhere.[24] As examples, from thallium onwards in the nether p-block region there may be ambiguities in assigning coordination numbers. Periodic trends are evident, if complex, for **CN** distributions (Fig. 4) but the periodicity of the average of coordination numbers is quite clear (Fig. 5). There is a decline for average **CN** across each period until the terminating noble gas which, in general, have **VN** = 0 and **CN** of 0. Xenon is the clearest exception, as a significant number of xenon compounds are known. Coordination geometries are assigned manually. Distributions of coordination geometries of d-block metals for different oxidation numbers using data from crystallographic databases are described elsewhere.[25]

Electron number trends

The electron number is often eight for main group compounds (Lewis's rule of eight or group of eight[26]) and is the origin of the octet terminology coined by Langmuir.[8] The octet rule is a classical concept that describes electron counts for p-block atoms in their compounds. The maximum number of electrons that can be accommodated in the valence shell of a first-row p-block element is eight given there are just four available orbitals. The 18-electron rule is an electron-counting rule analogous to the Lewis octet rule but applicable to d-block metals.[27] The octet and 18-electron rules are well known and the quantified data summarised in Fig. 4 and 5 show the tendency for average **EN** values to approach 8 and 18 for the p- and d-blocks respectively in particular, but there are many exceptions.

The average **EN** values are close to 8 for the lighter main group elements. For period 3 and main group elements in subsequent periods there are many apparent exceptions to this rule. In most cases, the **XN** and **LN** values for each compound are the sum of the individual x and l values for each attached group but sometimes the sum $(m + x + l)$ lead to **EN** values greater than 8. Participation by d-orbitals in bonding for these main group compounds is low and so hybridisation schemes such as dsp^3, d^2sp^3 that might explain such **EN** values are not good descriptions[28,29] while the concept of hypervalence is unnecessary.[30] Main group compounds with electron counts above eight are left as such in Chemdex to indicate that their

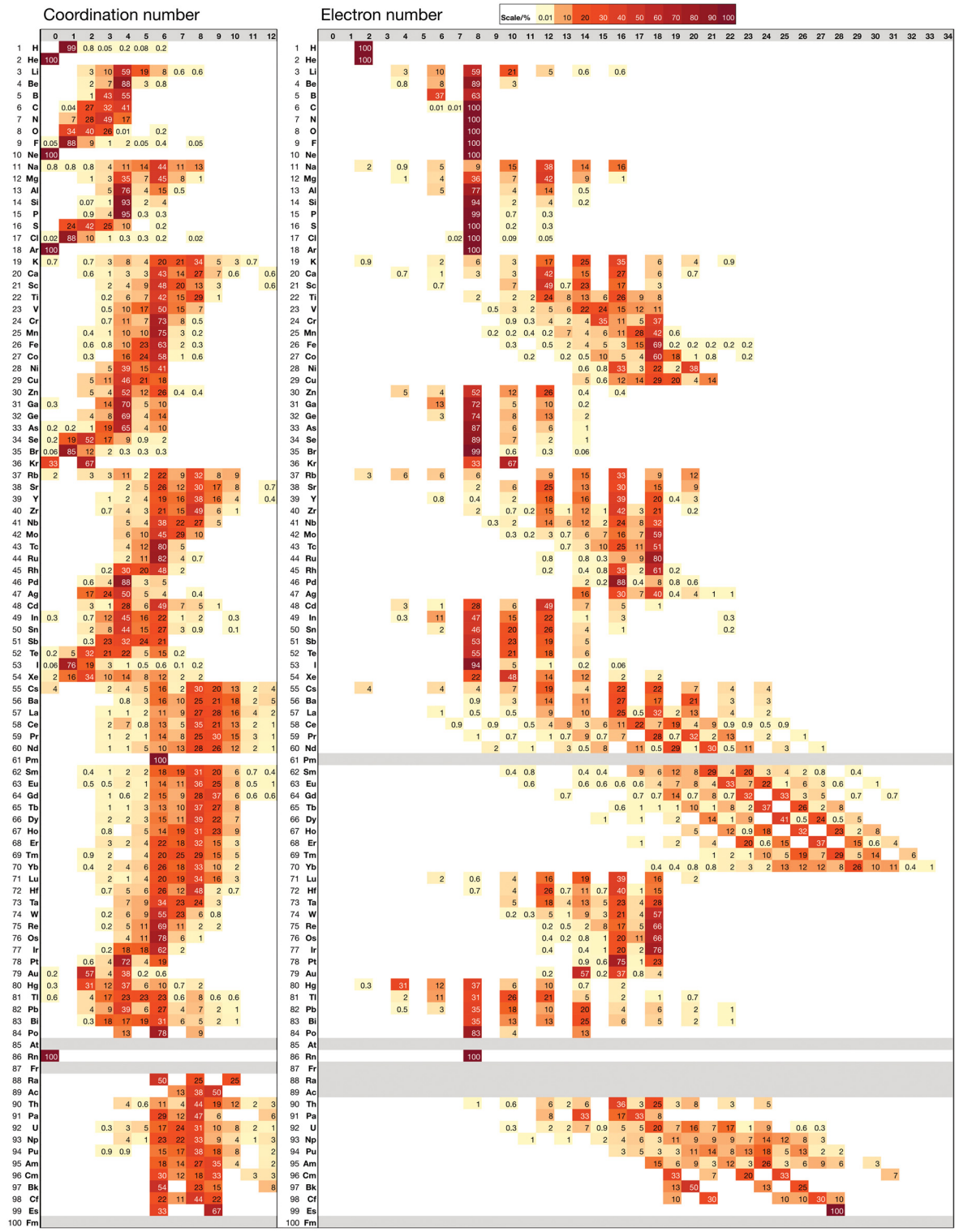

Fig. 4 Coordination number (**CN**) and electron number (**EN**) proportions for the elements. There are few data for Pm. There are no data for Fr and elements beyond Es.

bonding requires further consideration, many of which involve multicentre bonds (leading to eight electron counts),[31] but also because of the usefulness of the higher number to VSEPR shape predictions.[32]

The **EN** for the metal is the sum of the number of metal approximately non-bonded electrons and the number of electrons in the metal–ligand bonds. Assuming some covalence, the maximum **EN** should be 18, corresponding to occupancy

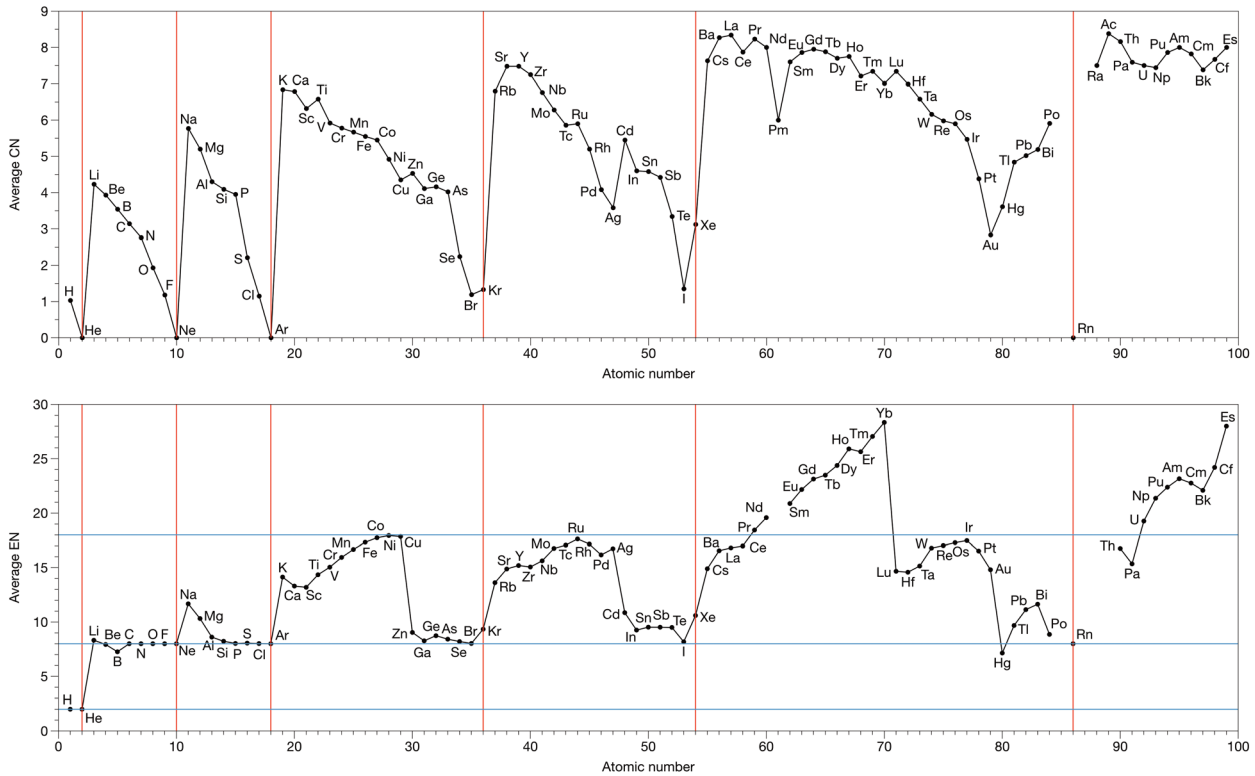

Fig. 5 Periodicity of average coordination number, **CN**, and electron number, **EN**, plotted against atomic number. There are few data for Pm. There are no data for Fr and elements beyond Es.

of the nine available valence orbitals. The calculated **EN** is fewer than 18 for many d-block metal compounds. Many of these possess ligands with π-donor capabilities in addition to σ-bonding. Examples include complexes containing one or more or F, Cl, Br, I, NR_2, NR, OR_2, and OR groups, together with analogues from lower in the periodic table. Although X values for attached groups are often clear, this may not be true of L values for such ligands arising from possible π interactions. Such ambiguities are best not ignored but not necessarily easy to resolve. As one example, azanyl NR_2 ligands are X when the N is pyramidal but possibly XL when planar.[12,33] It is not always clear without the benefit of more detailed analysis what the most appropriate value of **EN** is in some such examples, but sometimes values of **EN** reported in Chemdex as less than 18 may be higher than reported, but not necessarily 18.[12]

In other cases, a simple additive approach gives values such as 20 rather than 18 for d-block complexes with a considerable degree of covalent bonding, apparently problematic given that only nine metal valence orbitals are available for bonding. This phenomenon is analysed elsewhere for compounds using molecular orbital approaches including $[M(L)(RC{\equiv}CR)_3]$,[34] $[ME_4]^{n-}$ (E = O, S, Se),[12] $[M(NR_2)_5]$ (M = Nb, Ta),[35] pentalene complexes $[M(\eta^8\text{-}C_8R_6)_2]$ (M = Ce, Zr, Hf),[36] various tris-cyclopentadienyl complexes $[ML_i(\eta^5\text{-}C_5R_5)_3]$ containing the $M(\eta^5\text{-}C_5R_5)_3$ fragment (M = Y, Zr, Hf, Lu, lanthanoids, and actinoids),[37] and various bent metallocene complexes $[ML_i(\eta^5\text{-}C_5R_5)_2]$ in the presence of some π-donor ligands.[38] These compounds are reported in Chemdex as 18-electron compounds by constructing sets of ligands in the attached atom database with appropriate values of X and L derived from these publications.

Cycloheptatrienyl and analogues are perhaps problematic. Formal oxidation numbers for η^7-cycloheptatrienyl complexes may be based upon formal charges associated with either $C_7H_7^{3-}$ (the default in Chemdex, XL_3Z, reduces to X_3L_2) or $C_7H_7^{+}$, both of which are associated with Hückel aromatic π-electron numbers.[33,39]

The Zn, Cd, and Hg group elements are strictly divalent (**VN** = 2) and their 10 d-electrons complete the d-subshell; however these electrons are poor participants in covalent bonding. Those 10 electrons are therefore discounted from **EN** values for this group and these elements regarded as main-group metals. Zinc in $[Zn(NH_3)_6]^{2+}$ is therefore assigned an **EN** value of 12 rather than 22.

Two- and three-dimensional grids

Green's MLXZ classification (Table 1) is a covalent classification, but one that frequently provides classes that have use even when bonding is not strongly covalent, such as [Li(Br)(12-crown-4)]. Green classifies reaction classes such as oxidative addition and reductive elimination as translations on these equivalent neutral class two-dimensional MLXZ plots.[12] Chemdex displays MLXZ (effectively plots of **EN** against **VN**)

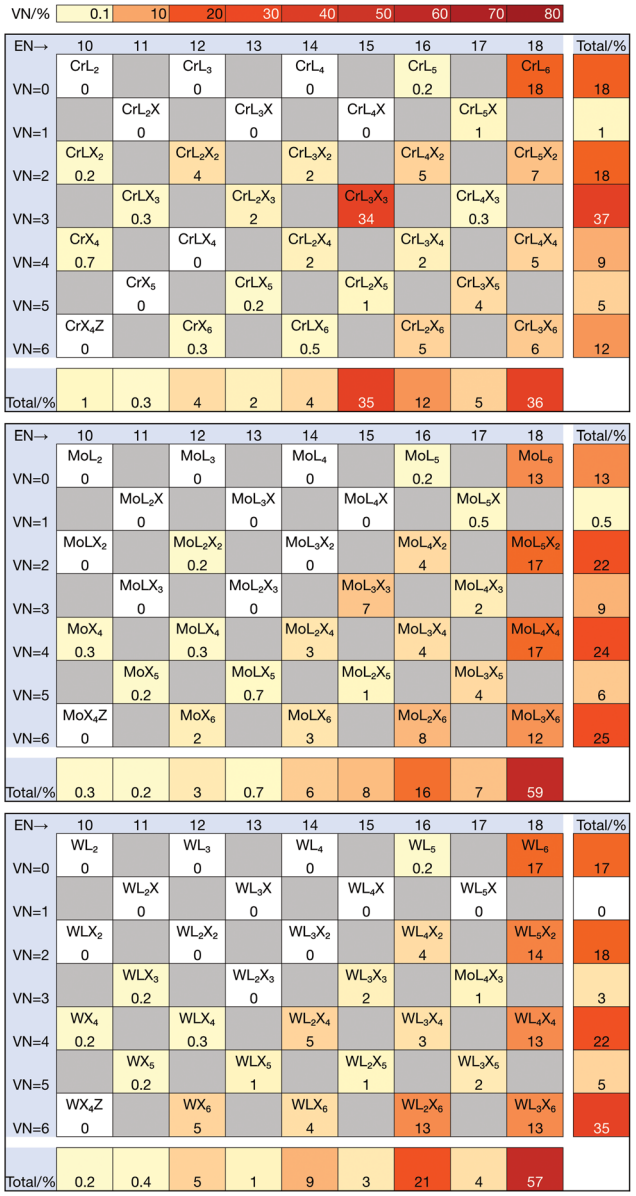

Fig. 6 Comparison of MLXZ grids extracted from Chemdex for Cr, Mo, and W.

and $[MLXZ]^q$ grids. As examples, MLXZ plots for IUPAC group 6 elements (Fig. 6) are illustrated. The proportions for each cell are broadly similar to those first published.[12,31] but compounds used for the Chemdex plots are not restricted to organometallic structures.

Some compounds located above and to the left of the diagonal $[MX_6]$–$[ML_6]$ in Fig. 6 correspond to the "bulky ligand" region[12] but are not adjusted for close contacts such as agostic (L-type) interactions that when deemed present would move those entries towards the right in the grid. The MLXZ plots for molybdenum and tungsten are quite similar but notably different from that of chromium. The same can be said for many other d-block groups where the 3d elements show different MLXZ profiles to the corresponding 4d and 5d elements. Another feature of the 4d and 5d element profiles is a tendency for the 5d elements to show slightly higher valence numbers overall than the 4d elements.

Chemdex allows plots of a number of other pairs of properties, currently including **VN–CN**, **VN–EN**, **VN–ON**, **ON–CN**, **ON–EN**, **XN–CN**, **LN–BN**, **VN–BN**, **ON–BN**, and **CN–BN** plots. These all have uses but examination of the **VN–CN** plots are particularly instructive as both properties are clearly periodic (Fig. 1–5). Valence numbers are preferred over oxidation numbers for this exercise largely because, as noted earlier, valence numbers take into consideration homonuclear element–element bonding and L/Z Lewis base/Lewis acid interactions, which oxidation numbers do not. This is particularly relevant for main group compounds. The electron number, **EN**, while also useful, is perhaps less useful as a second classification because of uncertainties in assigning **EN** described earlier and because **EN** values tend to approach 8 or 18 appears according to the element's block in the periodic table (Fig. 5).

King introduced three-dimensional matrices for coordination compounds of a given metal or type:[11]

CEQ-matrix – a grid for which **CN** and **EN** are plotted together for each charge number;

ACQ-matrix – a grid for which atomic number and **CN** are plotted together for each charge number;

AEQ-matrix – a grid for which atomic number and **EN** are plotted together for each charge number.

Chemdex allows plots of these matrices but currently not with separate layers for the charge number. King classified reaction classes including isoelectric exchange, positive-moving and negative-moving exchanges, oxidation/reduction, and oxidative addition/reductive elimination as translations within these three-dimensional matrices.

Plots of **VN** against **CN** for the periodic table groups headed by titanium, vanadium, and chromium are shown in Fig. 7. Plots for thorium, protactinium, and uranium are included for comparison. Plots for all elements are available as ESI† but can be generated online by users. As for the MLXZ plots it is notable that in each group the appearances of the 3d element plots differ somewhat from the 4d and 5d elements. The 4d and 5d element plots for each group are quite similar apart, again, for the tendency towards higher valences for the 5d elements. For all three groups the average **CN** of the 5d elements are slightly lower than those of the corresponding 4d elements (Fig. 7). The corresponding data for Th, Pa, and U differ in that low valences (**VN** = 0, 1, 2) are completely absent or rare while their average coordination numbers are higher than the 5d elements. A colour-coded periodic table plot of **VN** against **CN** is shown in Fig. 8 for all elements.

Metal and non-metals

The elements are often classified as metals or non-metals with an additional small group of elements regarded as metalloids. There is no precise definition of the term metalloid but they are elements for which properties of interest are said to be intermediate between metals and non-metals. Properties used

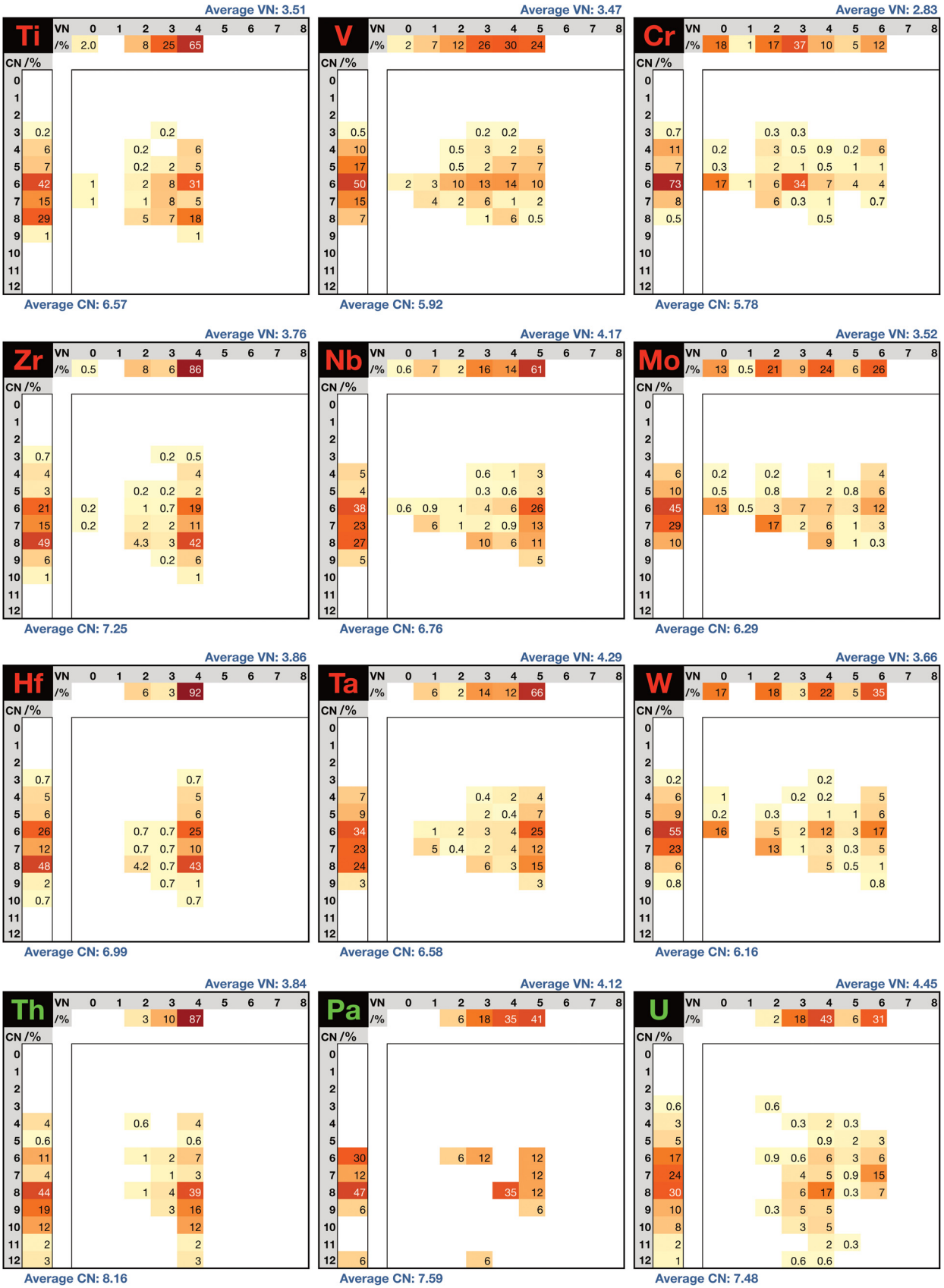

Fig. 7 Plots of valence number (**VN**) against coordination number (**CN**) proportions for the periodic table groups headed by Ti, V, and Cr. Data for Th, Pa, and U are included for comparison.

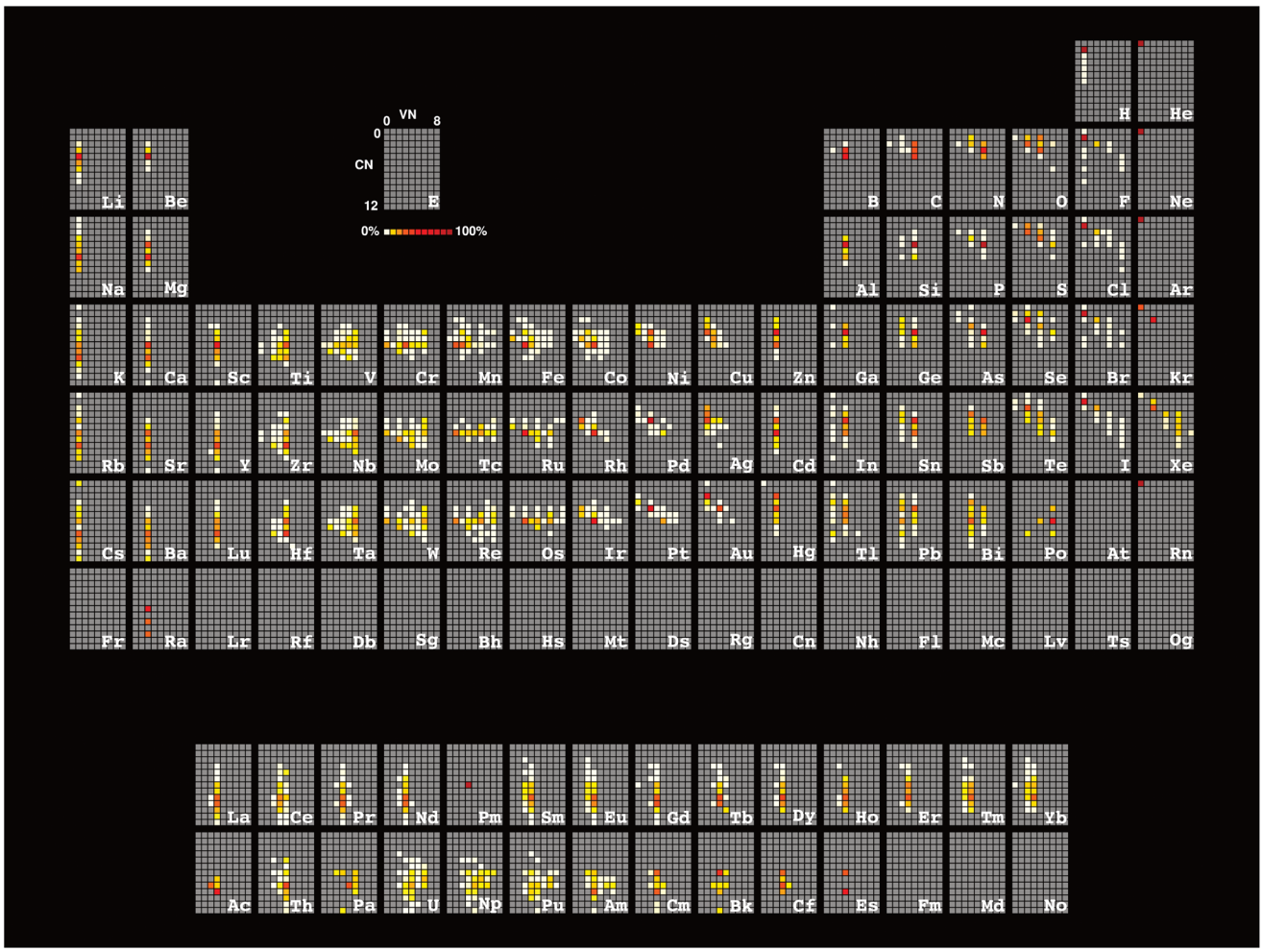

Fig. 8 Colour-coded heat map diagram showing percentages of **VN** (0–8)/**CN** (0–12) pairs for each element. Each square denotes the percentage of **VN** (left to right) and **CN** (top to bottom). The element key shows the 0–100% coding while grey squares denote no value for that **VN**/**CN** pair.

to identify metalloids include electronegativity, appearance, and electrical resistivity. A characteristic chemical tendency of metals is coordination of Lewis base (L) ligands, often in addition to X ligands. On the other hand, non-metals such as carbon show virtually no tendency to possess L values greater than 0 in their equivalent neutral classes. Fig. 9 shows the percentages of compounds in the Chemdex database for which $l > 0$ in their $ML_lX_xZ_z$ equivalent neutral classifications. It is clear that elements to the top right of the periodic table very rarely have $l > 0$ in their $ML_lX_xZ_z$ equivalent neutral classifications whereas almost all compounds of elements on the left of the periodic table are invariably have $l > 0$ in their equivalent neutral classifications. The tendency for attachment to L-type groups for IUPAC groups 12–18 increases down the groups and decreases from left to right within the lower main group elements.

It is notable that the elements with L values in their $ML_lX_xZ_z$ equivalent neutral classes between about 5 and 35 (Si, Ge, As, Se, Sb, Te, and Po) correspond very closely to those identified as metalloids by other definitions. It is evident that there is no sharp border between metals and non-metals.

Implications for the periodic table

The periodic table underpins much of chemistry; its story is well documented.[40] IUPAC publishes a periodic table but states clearly that it not the definitive table.[41] There are many published variants of the periodic table, also well documented.[9,42] Most recent tables tend to be medium or long format with s, p, d, and f-blocks. In general, these are perhaps more focussed on the atomic structure of neutral atoms or properties of the elements themselves rather than properties of compounds.

Some of the periodic table variants referred to earlier[7–9] refer to the positions of (a) hydrogen, (b) helium, (c) lutetium and lanthanum, (d) the early actinoids, and (e) beryllium and magnesium. It is appropriate to consider these variants in the context of the Chemdex data, using in particular the **VN** and **CN** values.

Position of hydrogen. The percentage of hydrogen environments containing an L value in its ENC values is zero (Fig. 9), the same as fluorine and a value expected for a non-metal. This contrasts strongly with the metal lithium for which that

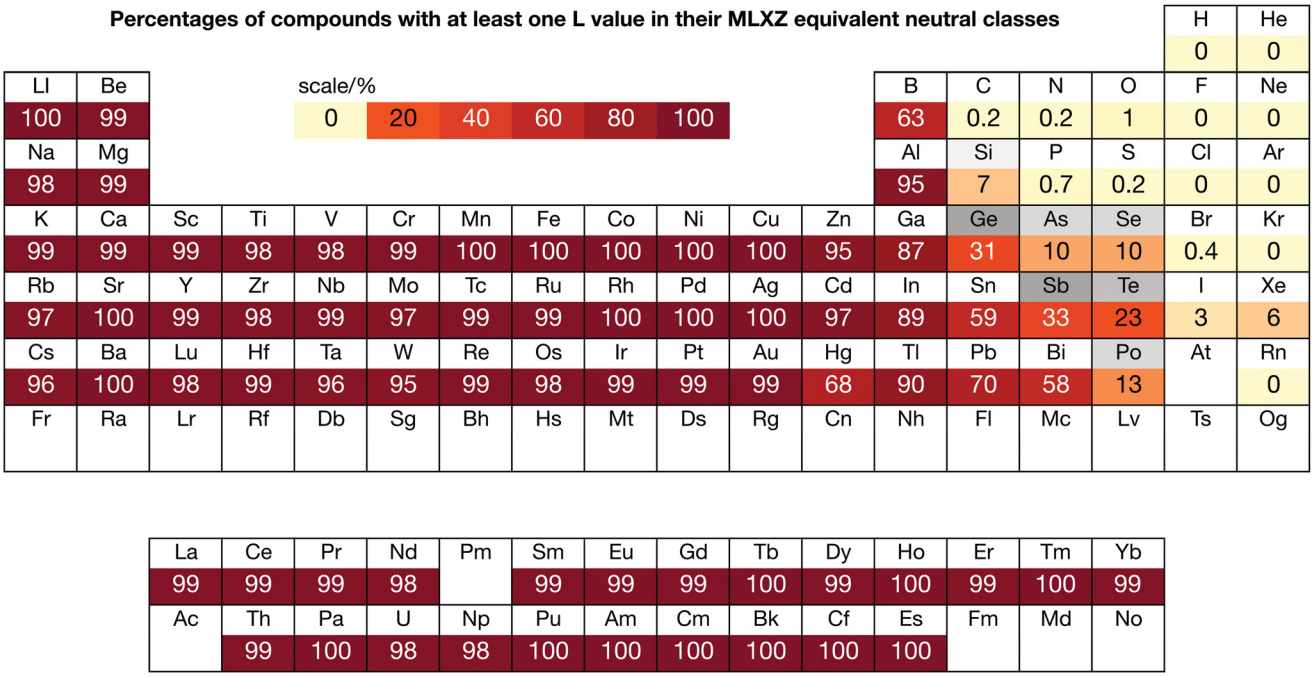

Fig. 9 Percentages and heat map of compounds for each element for which $l > 0$ in their equivalent neutral class ($ML_lX_xZ_z$).

value is 100%, immediately suggesting that hydrogen in its compounds is very different from those of the IUPAC group 1 metals. Chemdex contains a feature allowing extraction of proportions of attached atoms for each element (Fig. 10). These data show that both H and F bind to most elements across the period table while Li compounds largely feature only Li-p-block element interactions. Similarly, Cl, Br, and I bind to nearly all elements across the periodic table.

The Chemdex data show hydrogen is strictly monovalent (**VN** = 1) with an average **CN** value barely above 1 (1.03, Fig. 11). Relatively rare coordination numbers are known including two or three when bridging, and six in salts such as sodium hydride and interstitial hydride metal cluster compounds. Fluorine is broadly similar; 88% of entries are **VN** = 1 and **CN** = 1 with the remainder showing **CN** values of >1 for lattice structures and oligomer or catena species with μ-F groups. Lithium is also strictly monovalent but with a **CN** range of up to 8, never 1 in the solid state, and predominantly **CN** = 4 or 5. The average **CN** values of hydrogen shown within Fig. 10 are similar to the halogens rather than the IUPAC group 1 metals.

It is clear, so far as the proportions of attached L groups, attached atoms profiles, and coordination numbers are concerned, H is a better match with F than Li. Placement of H above F is therefore suggested in a chemical periodic table. This does not imply hydrogen is a halogen, which are defined as F, Cl, Br, I, and At,[5] or that reactions of elemental hydrogen and fluorine are similar, which they are not. What it does mean is that the proportions of attached L groups, the attached atom profiles, the **CN** profiles, and the **VN** profiles of H, F, Cl, Br, and I are very similar.

In the majority of periodic tables, hydrogen is placed above lithium at the left of the table. Hydrogen is located above fluorine in some chemical-based periodic tables including that proposed by Newlands in 1865 [9,43] and a later one proposed by Remy.[44] Some suggest hydrogen be placed over other groups,[45] over both Li and F,[46] or in no group at all.[47]

Helium above beryllium or neon. Helium does not form any compounds characterised by X-ray crystallography other than clathrates and is therefore always zerovalent. Beryllium forms many compounds and is always divalent, but neon forms none (also zerovalent). Therefore helium is best placed over neon rather than beryllium in any chemical periodic table despite both He and Be having s^2 electronic structures for their atoms in the gaseous phase.

Lutetium or lanthanum below yttrium. The membership of IUPAC group 3 elements (Sc, Y, La, Ac or Sc, Y, Lu, Lr) is the subject of discussion[48–50] and an IUPAC group is concerned with a recommendation.[51] Both lutetium and lanthanum are predominantly trivalent and the average coordination number of lutetium (7.3) based upon Chemdex data matches that of yttrium (7.5) quite closely (Fig. 12), perhaps not surprisingly given the similarity of ionic radii of these two elements.[52] The corresponding average coordination number for lanthanum is larger (8.3) and no doubt related to its larger ionic radius. The trends for the corresponding average **CN** values of groups 4–7 elements are reminiscent of the Sc–Y–Lu trend and on that basis Lu is better placed beneath Y rather than La in a chemical periodic table based upon **VN** and **CN**. This is reinforced by a comparison of attached atoms for Y with La and Lu (the most common in the Chemdex data are C and O for all three elements). Yttrium compounds in the dataset show overall

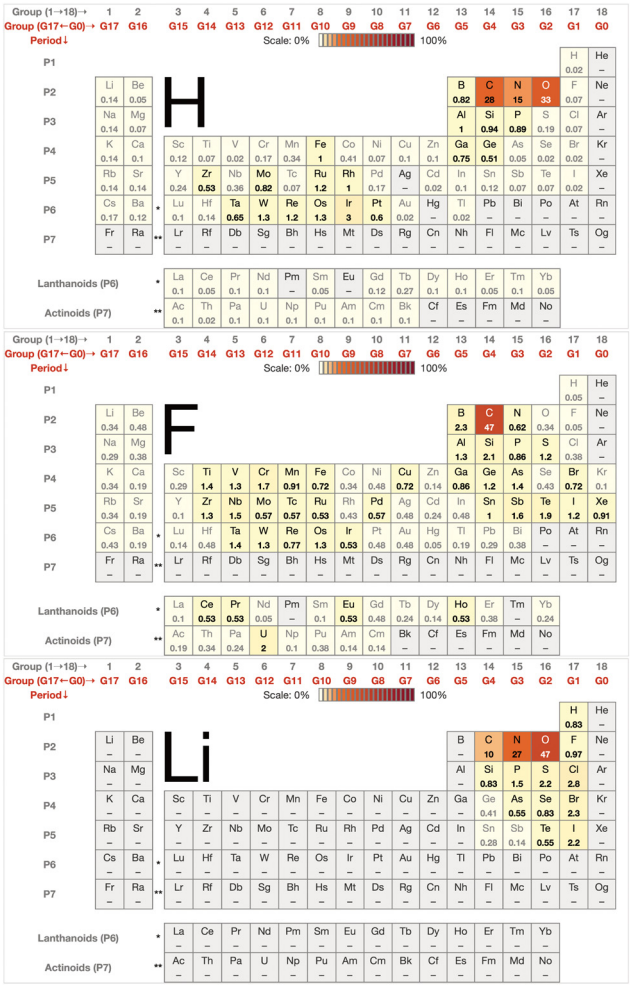

Fig. 10 Proportions of elements attached to H, F, and Li.

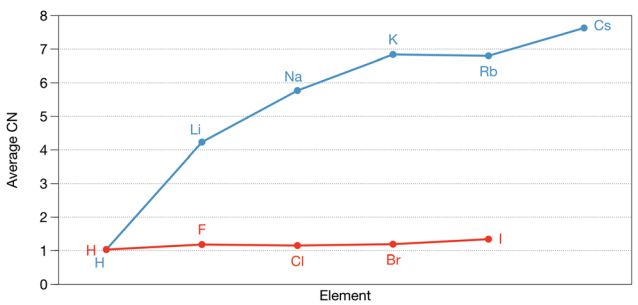

Fig. 11 Average coordination numbers for hydrogen when placed above Li–Cs and F–I.

36% C and 39% O attached atoms, very similar to lutetium (39% C and 38% O) but somewhat different from La (22% C and 47% O). This propensity for La–O binding corresponds to results from a related study involving oxygen affinity of lanthanoids that concludes Lu is closer in properties to the adjacent d-block elements rather than La.[49] On the other hand a different study based upon sets of Sc, Y, La, and Lu compounds concludes there is no chemical basis for placing Lu beneath Sc and Y. There are few characterised compounds of Lr and Ac, but by convention these remain placed below Lu and La respectively.

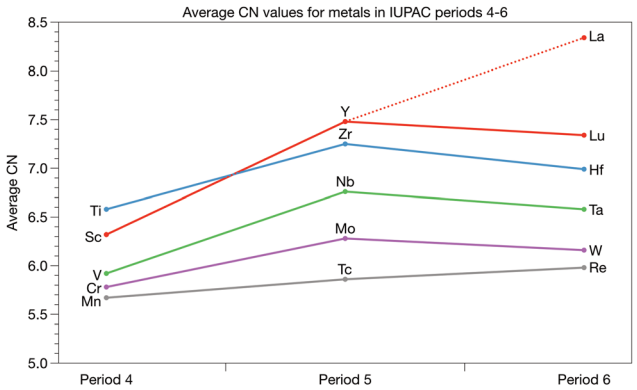

Fig. 12 Average coordination numbers for groups 3–7 elements comparing La and Lu beneath Y.

Early actinoids below period 6d-block elements or early lanthanoids. The actinoids are grouped below the lanthanoids in most modern periodic tables but the earlier actinoids are placed below the earlier d-block elements in some early tables.[9,45,49] For instance, Remy's table shows the actinoids Th–U placed below the d-block elements Hf–W so it is appropriate to consider the placing of the early actinoids based upon the Chemdex data.[49] Structural data for the later actinoids are sparse, understandable because of scarcity of samples and difficulties of handling.

The lanthanoid metals in compounds are largely trivalent (Fig. 1–3) although a minority are divalent and a significant minority (27%) of cerium compounds are tetravalent. There is little correspondence of early actinoids valence number distributions with those of the early lanthanoids. Early actinoids as far as americium differ from the lanthanoids in the sense that their compounds show maximum valences from three to seven (for a few compounds of Np and Pu). These higher valence numbers are more reminiscent of the earlier d-block elements Lu–Ir than the lanthanoids La–Eu. Valence trends considered in isolation might suggest that Ac–Am might be better placed beneath Lu–Ir in groups 3–9 in an empirical chemical periodic table. This would place Pu beneath Ru and Os, which are octavalent in a few compounds. There are no crystallographically characterised octavalent plutonium complexes but Pu(VIII) may exist in solution.[53] However, the virtual absence of low-valent (**VN** = 0–2) compounds is notable. In addition, the early actinoids do not display alternating peaks and troughs of valence abundances shown by the corresponding 4d and 5d elements (Fig. 1 and 2). It is known that lanthanoids and actinoids in their compounds have at least some access to d orbitals in bonding.[54] Relativity is significant for some actinoid complexes; the metals show relativistically "activated" 5f and 6d shells in their higher valence states.[55] This may account for the higher valence numbers from three for Ac up to seven for

Np and Pu. Valence numbers above three are not very evident for the lanthanoids as relativistic effects are less, but clearly four valence electrons are available to some extent, in particular for cerium for which tetravalent structures are present to about 27% in the dataset. The majority of the few known later actinoid compounds are trivalent corresponding to those later actinoids being placed below the later lanthanoids. However the absence of higher valence numbers for the later actinoids may be because of difficulties in accessing and characterising higher valence number compounds within the short lifetimes of these synthetic elements.

Coordination numbers of representative actinoid compounds are compared (Fig. 13) with the corresponding lanthanoids and the lower d-block elements (Ac–Am beneath Lu–Ir). Average coordination numbers for the lanthanoids and actinoids appear more related to each other and are higher than those of the corresponding d-block elements. Attached atom data within Chemdex suggest the early actinoids have an excess of attached oxygen atoms relative to the corresponding 5d metals but similar to lanthanoid attached atom profiles. Part of this excess is because of the large number of *trans*-actinyl (actinoid compounds containing the *trans*-MO_2 unit) complexes for which there is no match in either the corresponding lanthanoids or the corresponding d-block metals.[56] Additionally, the actinoids and lanthanoids both show relatively few attached P, S, and other lower groups 15 and 16 atoms as compared to the 5d metals. Again, this may be because of experimental difficulties resulting in fewer data.

There is a clear mismatch of valence distributions involving the early lanthanoids and actinoids. However **CN** and attached atom profiles for the early lanthanoids and actinoids are quite similar but distinct from the 5d Lu–Ir elements. Therefore perhaps the early actinoids best remain beneath the corresponding lanthanoids and so distinct from the early d-block elements.

Beryllium and magnesium above zinc. Most current periodic tables place beryllium and magnesium above calcium in IUPAC group 2 but Werner and others place them above zinc (or both calcium and zinc), in IUPAC group 12.[57,58] Both IUPAC group 2 and 12 elements are strictly divalent so there is no discrimination there but the coordination number distributions (Fig. 14) and attached atom profiles do discriminate to some extent.

CN	Be	Mg	Ca	Sr	Ba	Ra
0	0	0	0	0	0	0
1	0	0	0	0	0	0
2	2	1	1	0	0	0
3	7	3	1	0	0	0
4	88	35	3	2	1	0
5	2	7	3	5	3	0
6	1	45	43	26	16	50
7	0	8	14	12	10	0
8	0	1	27	30	25	25
9	0	0	7	17	21	0
10	0	0	1	8	18	25
11	0	0	0	0	2	0
12	0	0	1	1	5	0
Av→	3.9	5.2	6.8	7.5	8.3	7.5

CN	Be	Mg	Zn	Cd	Hg
0	0	0	0	0	0.3
1	0	0	0	0	0
2	2	1	5	3	31
3	7	3	4	1	12
4	88	35	51	28	37
5	2	7	12	6	6
6	1	45	27	49	10
7	0	8	0.4	7	0.7
8	0	1	0.4	5	2
9	0	0	0	1	0
10	0	0	0	0	0
11	0	0	0	0	0
12	0	0	0	0	0
Av→	3.9	5.2	4.5	5.5	3.6

Fig. 14 Comparison of proportions of Be and Mg coordination numbers (%) when placed above Ca (left) and Zn (right). Average **CN** values are shown in the bottom row.

When Be and Mg are placed above calcium in IUPAC group 2 there is a fairly steady increase for the average coordination number down the group (the value for Ra is not significant as there are few data points). However, the average **CN** for Mg is greater than that of Zn, not less. Oxygen predominates as attached atom for the Be–Ba series whereas for the Zn–Hg series nitrogen predominates over oxygen. Therefore on balance, if a choice has to be made, Be and Mg seem better placed over Ca, as is the current convention. On the other hand, recent calculations show that $(n-1)$d orbitals are involved to some extent in covalent metal–ligand interactions of the heavier alkaline earth metals and that Ca, Sr, and Ba could be regarded as transition metals.[59] Any such involvement of d-orbitals in bonding does not appear to cause any significant discontinuity in the **CN** trend down the IUPAC group 2 but perhaps encourages the notion that Be and Mg could be placed over Zn (a main group metal) as that creates a d-block or transition series 10 elements wide headed by Ca–Cu.

The chemical periodic table. The structures of medium and long form chemical periodic tables based upon the Chemdex data described above are shown in Fig. 15. The medium

CN	Zr	Hf	Ce	Th
0	0	0	0	0
1	0	0	0	0
2	0	0	0	0
3	1	1	2	0
4	4	5	7	4
5	3	6	1	1
6	21	26	13	11
7	15	12	5	4
8	49	48	35	44
9	6	2	21	19
10	1	1	13	12
11	0	0	2	2
12	0	0	1	3
Avg:	7.2	7.0	7.9	8.2

CN	Nb	Ta	Pr	Pa
0	0	0	0	0
1	0	0	0	0
2	0	0	0	0
3	0	0	1	0
4	5	7	2	0
5	4	9	1	0
6	38	34	14	29
7	22	23	8	12
8	27	24	25	47
9	5	3	30	6
10	0	0	15	0
11	0	0	3	0
12	0	0	1	6
Avg:	6.8	6.6	8.2	7.6

CN	Mo	W	Nd	U
0	0	0	0	0
1	0	0	0	0
2	0	0	0	0
3	0	0.2	1	0.6
4	6	6	1	3
5	10	9	5	5
6	45	55	10	17
7	29	23	13	24
8	10	6	28	30
9	0	1	26	10
10	0	0	12	8
11	0	0	2	2
12	0	0	1	1
Avg:	6.3	6.2	8.0	7.5

CN	Tc	Re	Pm	Np
0	0	0	0	0
1	0	0	0	0
2	0	0	0	0
3	0	0.2	0	0
4	4	5	0	4
5	12	11	0	1
6	80	69	100	23
7	5	11	0	22
8	0	2	0	33
9	0	2	0	9
10	0	0	0	4
11	0	0	0	1
12	0	0	0	3
Avg:	5.9	6.0	6.0	7.4

CN	Ru	Os	Sm	Pu
0	0	0	0	0
1	0	0	0	0
2	0	0	0.4	0
3	0	0	1	1
4	2	4	2	1
5	11	11	2	0
6	82	78	18	15
7	4	6	19	17
8	1	1	31	38
9	0	0	20	18
10	0	0	6	9
11	0	0.0	1	0
12	0	0	0.4	2
Avg:	5.9	5.9	7.6	7.9

CN	Rh	Ir	Eu	Am
0	0	0	0	0
1	0	0	0	0
2	0	0	0.5	0
3	0.2	0.2	0.5	0
4	30	18	2	0
5	20	18	1	0
6	48	62	14	18
7	2	2	11	14
8	0	0	36	27
9	0	0	25	35
10	0	0	8	4
11	0	0	0.5	0
12	0	0	1	2
Avg:	5.2	5.5	7.9	8.0

Fig. 13 Comparison of coordination numbers (%) in the bottom rows of the tables for some elements of the d-block with some lanthanoids and actinoids. There are few data for Pa and Pm.

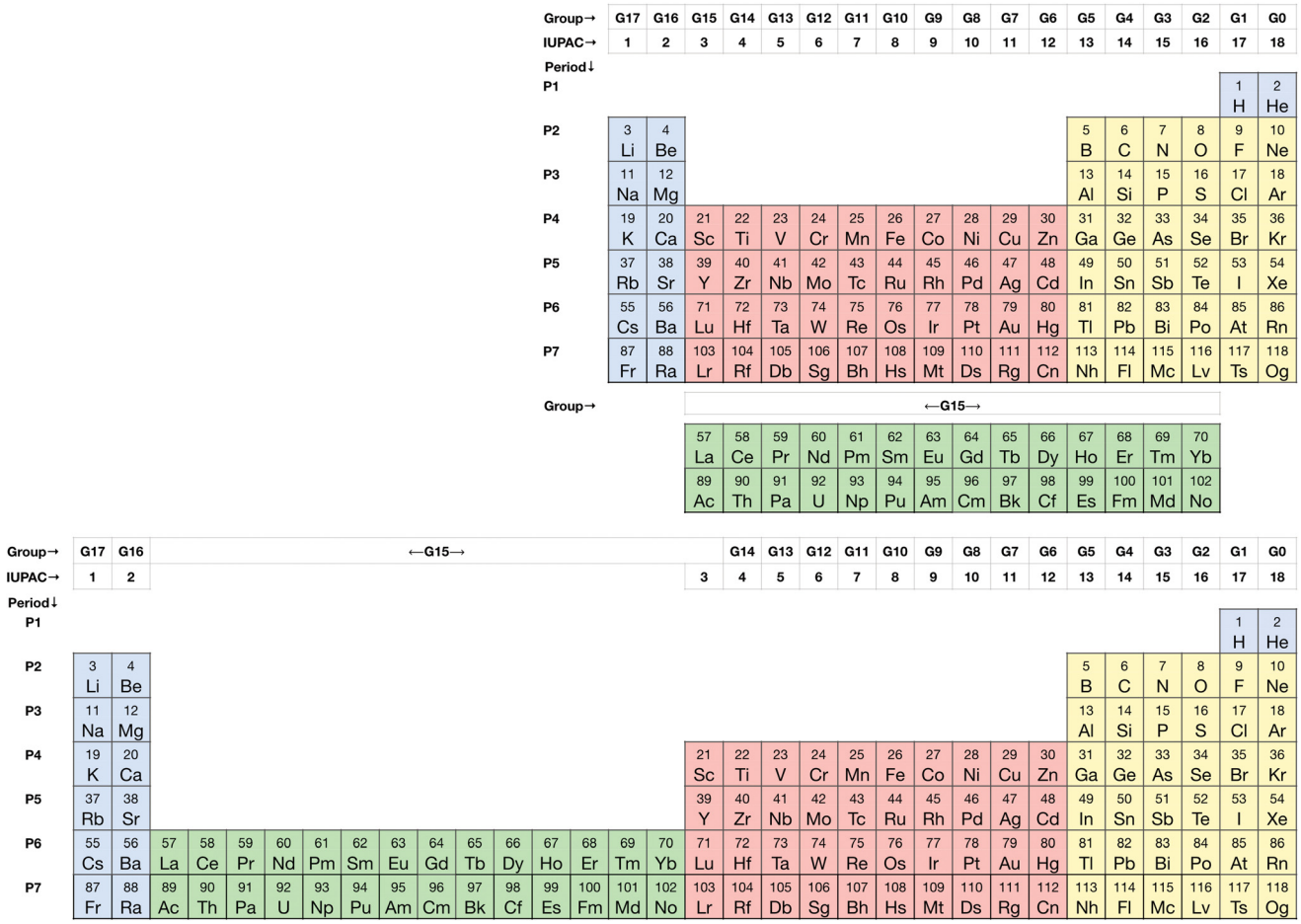

Fig. 15 Medium and long formats of the empirical chemical periodic table.

format table in Fig. 2 and 3 shows associated **VN** proportions for each element using the medium format.

Electron number and periodic table group numbering. The IUPAC group numbering scheme for the periodic table (Fig. 15) is 1–18 from left to right. The first 11 group numbers correspond with the number of valence electrons but for group 12 elements onwards the group number meaning are perhaps less obvious. What is the relevance or meaning of the numbers 17 to fluorine or 18 to helium? An alternative numbering scheme G17–G0 with the group number increasing from right to left (Fig. 2, 3, and 15) corresponds to the number of electrons required for the element to acquire an **EN** value of 2, 8, or 18 as appropriate. The aim of this scheme is to improve the chemical information imparted by group labels. This scheme emphasises the overall number of electrons commonly acquired by the element to form compounds, rather than the number of valence electrons associated within the groups for each element at least as far as IUPAC group 11. Thus, hydrogen and fluorine in group G1 require one electron to reach the requisite 2 and 8 respectively. Nitrogen in group G3 requires 3 electrons to make the octet found in NH_3 and Cr in group G12 requires 12 electrons from six CO ligands to make the 18-electron count in $[Cr(CO)_6]$.

Methodology

Software. The Chemdex system is built upon the Drupal open-source content management system for web sites.[60] Data for the compounds are embedded within the Drupal database. The Drupal system is extensible using custom plug-in modules written using the PHP programming language.[61] Custom modules were created to enable Chemdex to handle chemical calculations, to determine element classifications (Table 1), and to display data.

Inclusion of any compound within the database requires a crystallographic record including atom coordinates available within the CSD at the Cambridge Crystallographic Data Centre (CCDC)[13] or the Inorganic Crystal Structure Database (ICSD).[14] Compounds are associated with literature sources identified by their Digital Object Identifier (DOI) allowing users to validate data.[16]

Data for attached groups are available to the Chemdex system through a separate database. That database stores information for attached groups including overall charge (and any charges remote from the attached atom or atoms), **X** class, **L** class, **Z** class, denticity, attached atom set, an atom used to identify the Allen electronegativity value of the attached atom, formula, and a

name. Attached group entries may include, as appropriate, π-interactions involving **X**, **L**, and **Z** functions but generally exclude metal–ligand π–**Z** interactions (π-back bonding).

Calculation of oxidation number. Oxidation numbers are calculated using an algorithm based upon the definition that **ON** "equals the charge of an atom after its homonuclear bonds are divided equally and heteronuclear bonds assigned to the bond partners according to Allen electronegativity, except when the electronegative atom is bound reversibly as a Lewis-acid group, in which case it does not obtain that bond's electrons".[2] Oxidation numbers are integers, but as is the convention, represented by Roman numerals, even when negative.

Calculation of X, L, Z, [MLXZ]^q and MLXZ classes. The **X** number corresponds to the sum of all individual ligand **X** values and denoted in equations as x. Similarly the **L** number and **Z** number correspond respectively to the sum of all individual ligand **L** and **Z** values and denoted respectively in equations as l and z. The $[MLXZ]^q$ class is constructed using the individual values x, l, and z values where M denotes the element of interest and q the overall charge number on the entity (adjusted for remote charges on attached groups, if any). The MLXZ class or ENC is derived from $[ML_lX_xZ_z]^q$ through mapping rules described elsewhere.[12,31]

Calculation of valence number. The valence number is calculated using an algorithm based upon the definition of absolute valence given by Sidgwick: "…numerically equal to the number of electrons of their atoms 'engaged' in attaching the other atoms" or "…equal to the change in number of unshared electrons caused by the combination".[4,5] This is given by **VN** = $x + 2z + q$ from $[ML_lX_xZ_z]^q$ or **VN** = $x + 2z$ from $ML_lX_xZ_z$ (Table 1). The **VN** is always zero or a positive integer and denoted in equations as v.[12,31]

Calculation of coordination number. Coordination number is a common term in metal chemistry but used here for compounds of all elements in the periodic table. The **CN** is calculated from an algorithm based upon the definition that the **CN** equals the number of attached group denticities given by the number of σ-bonds between the attached group and the central atom.[6] Therefore ammonia is monodentate but diaminoethane is bidentate. Nitrato, carboxylato, carbonato, *etc.* for which two oxygen atoms are coordinated are classed as bidentate.

Calculation of electron number. The electron number is calculated using an algorithm based upon the sum of the number of electrons associated with the element of interest and the bonding electrons provided by its attached atoms. It is given by the equation **EN** = $m + x + 2l - q$ from $[ML_lX_xZ_z]^q$ or **EN** = $m + x + 2l$ from $ML_lX_xZ_z$.[12,31]

Calculation of bond number. The bond number is the sum of the number of bonds associated with the element of interest. It is calculated from the equation **BN** = $x + 2l + z$ using $ML_lX_xZ_z$ class.[12,31]

Conclusions

The aims for Chemdex described herein include the development of a freely accessible database of atom environments characterised crystallographically and whose software calculates oxidation number, valence number, coordination number, electron number, bond number, the covalent bond classifications $[MLXZ]^q$ and MLXZ, and attached atoms. This was achieved for the Chemdex database.[1] The Chemdex web site enables users to explore quantified distributions of these classifications for the elements and so research distributions of common and uncommon values for each of these classifications. Additionally, distributions of one property plotted against a second property for several pairs of properties may be analysed by users.

Metals form a high proportion of compounds attached to at least one Lewis base group whereas non-metals do not. On that basis, while also taking coordination number and attached atom data into consideration, hydrogen is better placed above fluorine rather than lithium in the periodic table. Average coordination number data suggest that lutetium rather than lanthanum is better placed below yttrium in IUPAC group 3. The valence number trends of the actinoid elements Ac–Am are somewhat more related to those of the d-block elements Lu–Ir than the early lanthanoids La–Eu. Notwithstanding that, coordination number and attached atom data suggest on balance that the early actinoids remain better placed beneath the early lanthanoids.

Chemdex contains many compound entries denoted as a "compound" content type and which contain formal classifications for each compound's properties. Work is proceeding on development of additional content types within Chemdex including a "reaction" content type that links compound entries as reactants and products. These reactions will be classified automatically as "oxidative addition", "substitution", *etc.* A further content type will link reaction content types together to create reaction sequences (including cycles). It will be interesting to consider the implications of such data to reaction mechanisms including catalytic cycles.

Work is also required to allow user contributions and validation of those contributions to the Chemdex database.

Conflicts of interest

There are no conflicts to declare.

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