
Predicting new, simple inorganic species by quantum chemical calculations: Some successes †

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A combination of ab initio calculations with the isoelectronic principle and chemical intuition is a useful way to predict new species. Some experimentally verified examples are 1) the transition-metal hydrides, MH_n ($n=4-12$), 2) new members of the multiply-bonded 2nd- or 3rd-Period species $A\equiv B$, $A=B=C$, $A=B=C=D$ or $A\equiv B-C\equiv D$, and $A=B=C=D=E$ classes, the last-mentioned class including the cations N_5^+ and $OCNCO^+$, 3) new members of the uranyl isoelectronic series, 4) actinyls where one of the oxygens is replaced by a 5d transition-metal (TM), 5) certain systems with noble-gas – noble-metal bonds, 6) the first argon compound HA_rF , 7) the cluster series of WAu_{12} , 8) TM-centred polyazide anions, 9) covalent molecules with a central -Zn-Zn- bond, 10) tetrahedral clusters of zinc and cadmium, 11) model systems for otherwise missing multiple bonds and 12) certain endohedral A@B systems. Further series of hypothetical species were used as a tool for developing recent sets of covalent radii, for studying the endohedral intermolecular interactions in A@B systems, or for finding examples of a 32-electron rule, corresponding to the well-known 8e- and 18e-rules. For obvious reasons, much of the molecular chemistry of the superheavy elements is based on studies of hypothetical model systems.

1 Introduction

In addition to being interpretative, Quantum Chemistry can be predictive. By pointing out that a certain molecule can exist, a theoretician can motivate the experimentalists to actually make it¹. In this Perspective we summarise several cases where this approach was successful. The only, brief earlier summary of our own attempts in this area was ref.³. Certain species in subsections 2.1, 2.4 and 2.8 were also already reviewed by Gagliardi⁴. From a purely experimental vantage point, an entire book on *Nonexistent Compounds* was published by Dasent⁵ in 1965. By now, many of them have been made.

A useful tool in searching for new molecules is the isoelectronic principle, introduced by Langmuir⁶ in 1919 as an 'isosteric principle'. His 21 'types' ranged from H^- to SeO_4^{2-} . The idea is to keep the number of electrons (and, as we now know, the approximate shape of the occupied molecular orbitals) constant, but to systematically vary the nuclear charges. For a diatomic of a given total charge, the pairs (Z_1 , Z_2) have one free variable. For a triatomic we have two variables, whose combinations can, for each total charge, be represented as in Fig. 1. For four atoms this can be generalized to a tetrahedron.

Another useful tool is the idea of *isobolality*. For instance a transition-metal M with its ligands L can form an $-ML_n$ group

that simulates in its chemical behaviour the σ hybrid of a $-CH_3$ group, see Hoffmann⁸. More recently, examples were found where similar bonds form with only M, without any ligands, L, a phenomenon termed *autogenic isobolality*⁹.

A third useful device are various electron-counting rules and their magic numbers. For one, central, main-group atom we have Lewis' octets. For a central transition-metal atom, Langmuir¹⁰ introduced both the well-known 18-electron (18e) rule and mentioned its possible 32e generalization. The first examples on the latter were recently identified¹¹⁻¹³ with actinides as the central atom. For a recent discussion on the interpretation of the 18e rule, see Pyykkö¹⁴ and references there. An estimate of the angular kinetic energies suggests that the ns and (n-1)d orbitals of the central atom typically contribute to bonding, but the np-type contribution can be dominated by ligand orbitals, only, with low or no metal character. For metal clusters we have the Wade-Mingos rules¹⁵.

A fourth general principle is that a group of atoms may, in its chemical behaviour, mimic a single atom of another element. The best established example are the pseudohalides, such as cyanide CN^- or cyanate OCN^- . The concept was introduced by Birkenbach and Kellermann¹⁶. For a treatise, see Golub et al.¹⁷. Obviously the idea can be generalized to pseudochalcogens¹⁸.

Similarly, sometimes unexpected, chemical analogies can occur between elements. Thus gold behaves as a halogen in solid $CsAu$ but the groups R_3PAu- mimic hydrogen, as first stated by Lauher and Wald¹⁹. Similarly, Pt may actually sim-

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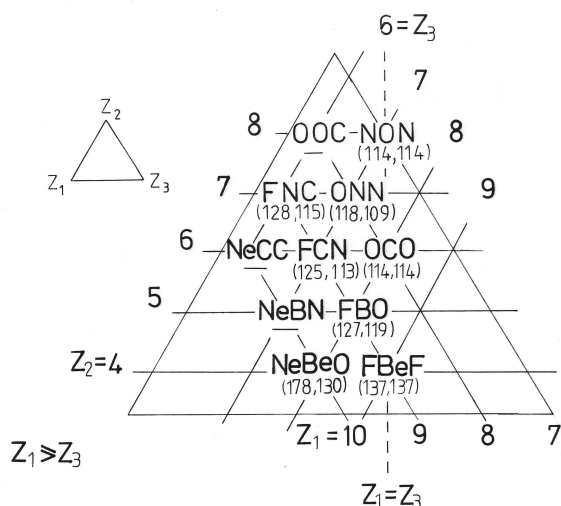


Fig. 1 How to map all possible neutral chemical species in the OCO isoelectronic series. Reproduced from Pyykkö and Zhao⁷. Copyright American Chemical Society.

ulate O at the end of multiple bonds in molecules^{9,20}. The expected^{21,22} platinum anion, Pt^{2-} occurs in the newly synthesised²³ Cs_2Pt or the metallic BaPt_2 ²⁴.

As both SiH_4 and SiCl_4 exist and are tetrahedral, in the predicted²⁵ SiAu_4 , the Au could be seen as an analogue of either a halogen or a hydrogen. This aurosilane was made by Kiran et al.²⁶ in the gas phase.

A fifth general issue is that many of the new species suggested are highly-charged anions – in condensed matter, where the Coulomb field of the other ions stabilises them, making all electrons bound. A lump of calcium carbide, CaC_2 does not spontaneously spray out electrons. For stiff, strongly-bound anions, such those mentioned below in Table 2, ab initio calculations on the bare ion in vacuum, with small or moderate basis sets, in practise give bond lengths and vibrational frequencies, comparable with experiment. The two extremes of no crystal field, or only the nearest counterions were tested⁷ on C_2^{2-} and NCN^{2-} . The eigenvalues of the latter species are shown in Fig. 2. Also the calculated bond lengths were very similar with and without the crystal field and both were close to x-ray experiments. At high net charges, differences start to appear, for an example, see Fig. 3. The multiply-charged anions in vacuum are entirely different objects and do require special attention.

Once novel molecular structures have been found, with accessible energies and reasonable (positive) force constants, there are several options to make them. A short list with typical examples is: 1) Matrix isolation IR spectroscopy, usually including isotope shifts as a verification (HfH_4). 2) Mass spectroscopy for gas-phase species (NUO^+ , AuXe^+ , XeAuXe^+).

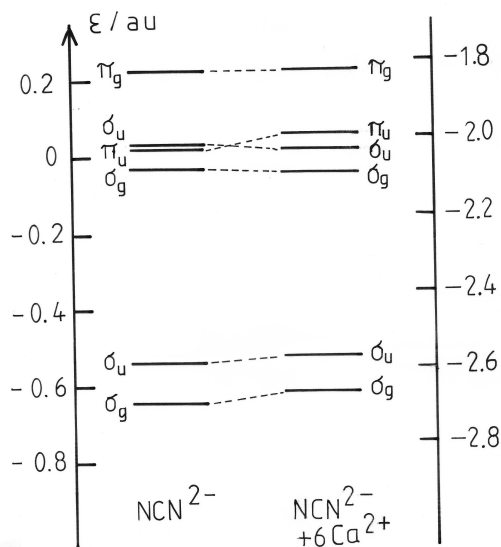


Fig. 2 The eigenvalue spectra for the NCN^{2-} anion at HF/6-31g* level at the two extremes of no crystal field (left) or an excessively attractive crystal field of the nearest counterations (right). Note the similarity⁷. Also the structural and vibrational differences are small. Reproduced with permission, from Pyykkö and Zhao⁷. Copyright American Chemical Society.

In this case, photoelectron spectra for a given m/e species can provide support for one or a few alternative structures (WAu_{12}). Also ion-mobility spectrometry (IMS) and trapped-ion electron diffraction (TIED) exist as further options. 3) For ions in solids, including occasional ones with a high formal charge, high-temperature melts provide a preparative route. In the simplest cases one just melts the elements together (PBP^{3-} in K_3PBP). 4) Naturally we have all classical, organic and inorganic synthetic methods (N_5^+ , OCNCO^+). 5) Finally we have the chances of finding new species playing a role in biology, possibly in low concentrations (OSCN^-).

2 Some experimentally verified examples

2.1 Metal hydrides, MH_n

It has been said that today's concrete World consists of the abstract thought models of yesterday. In a series of papers between 1974²⁹ and 1979³⁰, Desclaux and Pyykkö studied a broad series of MH_n hydride models of Groups 14²⁹, 11³¹, 13³², 4^{33,34}, 6³⁴, 2 and 12³⁵, or lanthanides and actinides^{30,34}. The purpose at the time was to study relativistic effects on chemical bonding. Most of the key conclusions still stand. The MH_n systems themselves were at the time regarded as unrealistic, but computationally doable model systems. Only

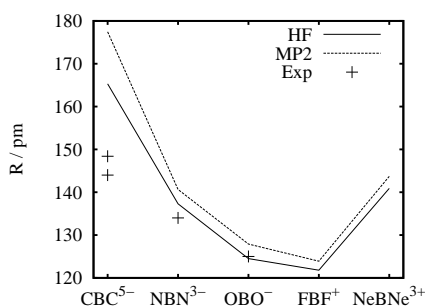


Fig. 3 The bond lengths for the series $[CBC]^{5-}$ to $[NeBNe]^{3+}$. 'Gas-phase' calculations using a 6-31g* basis are compared to experimental, solid-state values and agree down to about NBN^{3-} . The $[CBC]^{5-}$ references are Halet et al.²⁷ ($Sc_2(BC_2)$) and Hillebrecht et al.²⁸ (Al_3BC_3). For others, see ref.⁷.

a few decades later, many of them had been made using matrix spectroscopy, see Table 1.

Table 1 Some predicted MH_n species that were later experimentally made.

Group	Species	Prediction	Production
2	CaH ₂	35	36
	CaH ⁺ , SrH ⁺	35	37
	BaH ⁺	35,38	39
4	TiH ₄	33	40
	ZrH ₄ , HfH ₄	33	41
	ThH ₄	34	42
6	WH ₆	34 ^a	43
	WH ₁₂	44	45
12	HZnH	35	46,47
	HCdH	"	46
	HHgH	"	48
13	BiH ₃	49	50,51
14	PbH ₄ ^b	29	52

^a Original work done assuming O_h symmetry.

The molecule strongly distorts to C_{3v} .

^b For plumbane, PbH₄ there were earlier experimental claims. The relativistic calculations⁵³ went up to SnH₄.

In addition to PbH₄, another rather unstable main-group hydride is BiH₃. There had been theoretical calculations on it⁴⁹, but the first, clear spectroscopic characterization had to wait until Jerzembek et al.⁵¹ or Wang et al.⁵⁰ for gas-phase spectroscopic and matrix observations, respectively.

There was a further extension on store. Applying the H \leftrightarrow Au chemical analogy on WAu₁₂, Gagliardi and Pyykkö⁴⁴ predicted a species WH₁₂, actually having a structure of the type WH₄(η^2 -H₂)₄ with four classical W-H bonds and four side-on bonds to further H₂ units. Other valence isoelectronic species were also considered. This species was discovered in

matrix spectroscopy only four years later by Wang et al.⁴⁵.

Further molecular species with many hydrogens bound to a single metal were experimentally found for Th⁵⁴ and U⁵⁵, the UH_n, n=16 holding the record.

These structural principles inspired other workers to adapt them to potential hydrogen-storage systems based on scandium atoms on fullerene⁵⁶.

2.2 Multiply-bonded main-group species

For the author, this was the beginning of the systematic search for new species in some narrow classes. While teaching first-year chemistry at the University of Helsinki, I mentioned that the next member of the isoelectronic series BO₃³⁻, CO₃²⁻, NO₃⁻ would be a neutral OO₃, which led to the study⁵⁷. An independent ab initio study on OO₃ appeared in the same issue⁵⁸. An earlier semiempirical study had been published by Jubert and Varetti⁵⁹. This species is a local minimum at CASSCF level, but about 6.8 eV above 2O₂. It has not been experimentally found yet.

The only experimentally identified gas-phase O₄ species so far appears to be a weakly bound (O₂)₂ dimer, see Cacace⁶⁰.

The mentioned nitrate-like isoelectronic series was the beginning of a systematic mapping of possible new species. Simple as it may appear, already the map⁶¹ of triple-bonded, CO-like species (of 'Type 8' of Langmuir⁶) contained the later experimentally identified solid-state anions BN²⁻⁶² and BC³⁻⁶³. The possible salts of BO⁻ were also discussed⁶¹. For a later mapping, see Ehlers et al.⁶⁴. Diatomic species, containing the 3rd-Period elements S⁶⁵ and P⁶⁶ are discussed below, see also Table 2.

Table 2 Some predicted multiply-bonded main-group species that were later experimentally made. 'Type' refers to the Table I of Langmuir's 1919 paper⁶.

Series	Species	Prediction	Production	Type
A \equiv B	BN ²⁻	61	62	8
	BC ³⁻	"	63	
	CP ⁻	66	67,68	
A=B=C	O=O=O ²⁺	69	70,71	10
	ONS ⁺	65	72	
	NBC ⁴⁻	7	73	
	PBP ³⁻	66	74	
	OCP ⁻	"	75	
A \equiv B-C \equiv D	NBNN	76	77	
	CCCC ²⁻	"	78	
A=B=C=D	FCNF ⁺	76	79	
	OCNS ⁻	80	81	
A=B=C=D=E	OCNCO ⁺	82	(gas) ⁸³	
			(solid) ⁸⁴	
AB ₃	N ₅ ⁺	"	85	11
	PS ₃ ⁻	86	87	

The symmetrical, linear O=C=O isoelectronic series⁶⁹ suggested the O=O=O²⁺ cation, later identified in the gas phase^{70,71}. The isoelectronic, asymmetrical A=B=C series⁷ soon led to the synthesis of NBC⁴⁻⁷³ in solid Ca₃Cl₂CBN. Of the predicted species, NCC³⁻, OCB³⁻, OBC³⁻ or OBN²⁻ remain unknown, despite short calculated intramolecular distances. Note that the 'pseudopnicogen' dimer OCBBCO was seen in matrices by Zhou et al.⁸⁸. It indeed has a central B≡B bond, as the pnicogen N≡N. An isoelectronic dianion to the neutral OCBBCO is [O≡B-B≡B-B≡O]²⁻, also with a central B≡B bond⁸⁹. For a theoretical analysis of the bonding in this isoelectronic series, see Ducati et al.⁹⁰.

Of the 3rd-Period elements, both phosphorus and sulphur can form good multiple bonds. Of the predicted species, PBP³⁻ occurs in K₃(PBP), which can be prepared by melting the elements together⁷⁴. That discovery was independent but simultaneous with the theoretical work, and the two papers could quote each other. The suggestion for an OCP⁻ anion⁶⁶ soon lead to syntheses of both its Li⁷⁵, and later, Ca⁹¹ and Na salts⁹². For a minireview on the new A=B=C species, isoelectronic to CO₂ and CS₂, see Klapötke⁹³. Solid compounds containing the phosphacyanide (or 'cyaphide') anion, C≡P⁻, were mentioned by us⁶⁶ and have later been prepared^{67,68}.

For a chain of four main-group atoms⁷⁶, two possible electron counts are the dicyan-, (N≡C-C≡N)-like 26e series and the OCCO²⁻-like 30-electron series. The latter can be prepared by reducing CO by K to yield the salt K₂(OCCO). Of the mapped species, FCNF⁺ was synthesized, and identified by Raman spectra by Klapötke⁷⁹, before the sample exploded. The closed-shell species CCCN⁻ and CCCP⁻ were found to be stable under the negative charge.

A particular four-atom chain of microbiological interest is the 'hypothiocyanite' anion. It is produced by lactoperoxidase and functions as an antibacterial agent in both saliva and milk. The traditional way of writing it was 'OSCN⁻'. Because it decomposes autocatalytically above about 0.1 mmol dm⁻³, there are no concentrated samples and no crystal structures. Our calculations⁸⁰ gave a lowest-energy linear OCNS⁻ structure, with ONCS⁻ over 140 kJ mol⁻¹ higher. Later Sundholm⁹⁴, using a different starting geometry, discovered the second-lowest, bent O-SCN⁻ structure. The ¹³C and ¹⁵N NMR shifts or the UV spectrum⁹⁵ support that, higher-lying, bent OSCN⁻ structure. Dua et al.⁸¹ calculate the CCSD(T) energy order OCNS⁻ < S-OCN⁻ < O-SCN⁻ < ONCS⁻, and produced mass-spectroscopic evidence for three of them. The bottom line is that the traditional 'OSCN⁻' appears to be the right structure, albeit not the lowest-energy one. The oxidation of thiocyanate by hydrogen peroxide⁹⁶ is another experimental way to reach it. For the latest summary on OSCN⁻/HOSCN chemistry, see Kalmár et al.⁹⁷.

The previously-known five-atom chain species included dicyanamide NCNCN⁻, carbon suboxide O=CCC=O and

cyanogen azide NC-NNN. Of those predicted⁸², the cation OCNCO⁺ was soon prepared, both as a gas-phase cation⁸³ and in crystalline [OCNCO]⁺[Sb₃F₁₆]⁻⁸⁴. The later gas-phase work on this cation includes Yang et al.⁹⁸, acting as a link to a broad further literature on OCNCO⁺ in mass spectroscopy. The bent structure of this ion, already calculated⁸² and crystallographically determined⁸⁴ later, was also rediscovered and debated in that literature. Seeing the OCNCO⁺ as two L = CO units, bridged by an N⁺ ion in a ¹D state, as suggested by Kerkines et al.⁹⁹, leads to an entire family of suggested L-(N⁺)-L' species, see Riedel et al.¹⁰⁰.

The 5-atom bent chain N₅⁺ was also treated, but not specially discussed by us⁸². Bulk compounds containing it were reported in 1999 by Christe et al.⁸⁵. They were strongly explosive.

It was also noted that the asymmetric structure NC-SCN for S(CN)₂ received no theoretical support in our calculations⁸². The inverted structure NC-NCS was already experimentally detected by King and Kroto¹⁰¹. Our bond lengths agree with the later experimental and high-level theoretical ones by Winnewisser et al.¹⁰², whose central bond angle was, however, bent.

The principle of 'interpseudohalogens', such as NC-NCO, was discussed by Jansen's group¹⁰³. Note that, just as Cl₂ is the dihalogen, corresponding to the halide Cl⁻, and dicyan, NC-CN is the di-pseudohalogen corresponding to the pseudohalide CN⁻, one can form neutral dimers of the more complex pseudohalides, including mixed dimers.

2.3 The uranyl isoelectronic series

The uranyl cation O≡U≡O²⁺ is one of the most common species in the chemistry of uranium. It is best written with two triple bonds, as deduced from the U-O distance by Pauling¹⁰⁴, from spectroscopy by Denning¹⁰⁵, from ab initio quantum chemistry by us¹⁰⁶ and from the experimental electron density by Pinkerton's group¹⁰⁷. The electron configuration is σ_g²π_g⁴π_u⁴σ_u², and the *g* and *u* electrons bond to U 6d and 5f, respectively, making six bonds.

A mapping of the possible isoelectronic species was done¹⁰⁶. Of the studied species, NUO⁺ (and the valence isoelectronic NUS⁺) were soon afterwards reported in mass-spectroscopy¹⁰⁸ (see Table 3). An observation in neon matrices followed five years after the calculation¹⁰⁹. The neutral CUO and NUN were already spectroscopically known in 1994. It might be noted that those spectroscopic observations on terminal, triple N≡U bonds preceded the similar observations in the bulk¹¹⁰ by 34 years. Fox and Cummins¹¹¹ recognise this in their paper on U(VI) nitridoborates.

A curious point about NUO⁺ was that the calculated N-U bond length was shorter than the U-O one¹⁰⁶, see also Table 4. Several further cases with the same trend are shown there.

Table 3 Other predicted multiply-bonded species that were later experimentally made. 'SS' refers to a subsection of the present paper.

SS	Species	Prediction	Production
2.3	NUO ⁺	106	108
2.4	OUIr ⁺	112	113
2.11	AuC ⁺	114	115

Table 4 Examples on multiply-bonded species where $R(N-M) < R(O-M)$. The stretching a_1 vibrational frequencies, ν , reflect the same trend. ¹⁴N assumed.

Compound	R/pm		ν/cm^{-1}		Method
	N-M	O-M	N-M	O-M	
NUO ⁺	163.1	171.5	1293	1059	HF ¹⁰⁶
			1118.6	969.6	Exp ¹⁰⁹
NCIO ₂ ²⁻	146.6	156.1	1313	833	MP2 ¹¹⁶
			1267	829	Exp ¹¹⁷
NOsO ₃ ⁻			1021	897	Exp ¹¹⁷

2.4 Species with actinide–transition-metal multiple bonds

Using the chemical analogy between O and Pt (or N and Ir, etc.)^{9,20}, Gagliardi and Pyykkö¹¹² tried to use it for finding new actinyl derivatives. It was found that one end atom could be substituted. If both were substituted, the molecule went open-shell. A map of such systems was given. Of the species predicted, OUIr⁺ has so far been identified in mass-spectroscopy¹¹³. No properties have been measured but the calculated U≡Ir distance is very short, 215 pm¹¹². Here we have, not only a new species, but a new type of bond *viz* a short U≡Ir triple bond between an actinide and a 5d transition metal. NUIr had a similar bond length. Further members of the metalloactinyl series, EThM and MThM' (E=N-F; M=Ir-Au) were studied by Hrobárik et al.¹¹⁸.

Short, open-shell multiple U-U bond lengths were calculated for both the experimentally known diatomic U₂¹¹⁹ and the predicted U₂²⁺¹²⁰. The values were 243 and 230 pm, respectively.

2.5 Noble-metal–noble-gas chemical bonds

Knowing that [ClAuCl]⁻ is a stable bulk anion, and that the isoelectronic anions [SAuS]³⁻ and [PAuP]⁵⁻ occur in crystals, Pyykkö¹²¹ asked, whether, instead of one or two steps left in the Periodic Table, one could go one step right. The predicted XeAuXe⁺ ion and also the diatomic AuXe⁺ were mass-spectroscopically identified by Schröder et al.¹²². The improved CCSD(T) calculations gave for AuXe⁺ a D_0 of 30.1 kcal/mol. These were perhaps the first *noble-metal* – *noble-*

gas covalent bonds. The later calculations on NgAu⁺ include Belpassi et al.¹²³. The valence isoelectronic NgMNg; M=Pd,Pt were considered by Taketsugu et al.¹²⁴ For a gas-phase observation of [ClAuCl]⁻, see Schröder et al.¹²⁵.

Seppelt's group produced, quite unexpectedly, the first bulk compounds with Au-Xe bonds^{126,127}. Moreover, the oxidation state of gold in the approximately D_{4h} [AuXe₄]²⁺ cation was Au(II). A perspective on the work was also published¹²⁸.

Further noble-metal–noble-gas bonds that should have a very good chance of being made are the diatomic NiXe, PdXe and PtXe¹²⁹.

2.6 Other new noble-gas compounds

The argon compound HARf was reported by Khriachtchev et al.¹³⁰. It could rather be characterized as a 'hydridoargon fluoride', [(HAr)⁺F⁻]. The point in the present context is that the authors knew what they were looking for. There were theoretical calculations in that original paper and lower-level calculations¹³¹ were published before the experimental observation.

2.7 New clusters

In 2002 we suggested that an icosahedral WAu₁₂ cluster could be particularly stable for the three complementary reasons of having an 18e structure, relativistically strengthened radial covalent bonds, and numerous (dispersion-type) *metallophilic* interactions between the gold atoms¹³². The valence isoelectronic analog MoAu₁₂, as well as the anions MAu₁₂⁻; M=V,Nb,Ta were also mentioned. The suggestion was communicated to Dr. Lai-Sheng Wang, whose group produced both the two neutrals¹³³ and the three anions¹³⁴, also verifying the icosahedral geometry. The molecules form spontaneously when tungsten and gold are vapourised into a helium carrier gas. Electron attachment and time-of-flight mass-spectroscopy preceded the photoelectron spectroscopic study. See also the review by Wang¹³⁵.

As quoted in our original paper¹³², a similar electron count was already reached in the organometallic compound [Au₁₃(PMe₂Ph)₁₀Cl₂](PF₆)₃ of Briant et al.¹³⁶. It might be added that of its $(a_{1g})^2(t_{1u})^6(h_g)^{10}$ 18e system, Mingos¹³⁷ only thought of the octet, neglecting the bonding h_g contribution of the 18e.

Later computational work on these systems comprises a study on their properties¹³⁸, and a temperature-dependent molecular dynamics study¹³⁹, demonstrating surface melting to 'a small spherical liquid' between 366 and 512 K, while the radial W-Au bonds remained intact.

As the -Au ligand is isolobal with the -Hg-R group, or its analogues, it is logical, that a series of [M(ER)₁₂] (M = Cr, Mo, W; E = Zn, Cd, Hg) compounds has been synthesised and theoretically modelled¹⁴⁰. An earlier example, synthesised in

R. A. Fischer's group¹⁴¹, was $[\text{Mo}(\text{ZnMe})_9(\text{ZnCp}^*)_3]$. A review on this class of compounds has been published¹⁴². See also Molon et al.¹⁴³.

The theoretical model¹⁴⁴ $[\text{WAu}_{12}(\text{CO})_{12}]$ is isoelectronic with the experimentally observed¹⁴⁵ $[\text{Pt}_{13}(\text{CO})_{12}]^{8-}$ group in solids.

2.8 New polynitrogen systems and the 5d character of barium

The case of N_5^+ was already mentioned in 2.2. Three further classes consist of the use of aromatic N_n rings to model their $(\text{CH})_n$ analogues, of polyazide systems and of systems with pentazolide anions.

It was first noted by Gagliardi and Pyykkö¹⁴⁶ that the C_{7v} ScN_7 formed a locally sturdy molecule. Combining two rings, the axially symmetric series $(\text{N}_5)\text{M}(\text{N}_7)$, $\text{M} = \text{Ti-Hf}$ was the next step. The seven-ring was also used to model the study of d-character of the Group-2 metals for $\text{Cs}(\text{N}_7)\text{Ba}$ ¹⁴⁷. (Note here that in a species, like BaH^+ (see Table 1), there is more 5d character than 6s character, although the latter is the official valence orbital of barium³⁸. In that sense Ba is a *pre-d element*¹⁴⁸.)

While studying theoretically the dissociation of $\text{Cs}(\text{N}_7)\text{Ba}$, Gagliardi¹⁴⁹ found CsNBa with a multiple N-Ba bond. A bond of the same type was confirmed using microwave spectroscopy by Ziurys' group¹⁵⁰ in the linear BaNH . The experimental Ba-N bond length in BaNH and the computed one in BaNCs were 207.7(2) and 204.7 pm, respectively. The calculated value for diatomic BaN^- was 217 pm. All three systems exhibit a triple bond to the alkaline earth barium, convincingly demonstrating its 5d character.

Moreover it was noted that $5+7=3\cdot4$, which yielded the study on the tetra-azides, $\text{M}(\text{N}_3)_4$, $\text{M}=\text{Ti-Hf,Th}$ ¹⁵¹. Experimentally, Haiges et al.¹⁵² synthesized both $[\text{Ti}(\text{N}_3)_4]$, as well as the penta- and hexa-azido anions with a Ti central atom. The Ti-N₁-N₂ angles were bent, not linear as found theoretically¹⁵¹. Note that the bending frequencies were small. Finally, Straka and Pyykkö¹⁵³ found energy minima for complexes of one Group-5 metal atom, M, and up to eight pentazole rings, N_5^- . Thus one metal atom would be theoretically capable of maintaining at place forty nitrogen atoms.

Pentazole rings also occurred in the model study on the sandwich complexes $[\text{Ti}(\eta^5\text{-E}_5)_2]^{2-}$, $\text{E} = \text{CH, N-Sb}$ by Lein et al.¹⁵⁴, and in similar model studies with a central Fe^{155,156} atom.

A substantial literature exists on hypothetical N_n isomers. Particularly noteworthy are the IR spectroscopic observation¹⁵⁷ of tetrahedral N_4 and the theoretical result (see Nguyen¹⁵⁸) that N_6 prefers a diazide structure $\text{N}_3\text{-N}_3$ to an aromatic N_6 ring. The result was confirmed by Tobita and Bartlett¹⁵⁹.

2.9 Covalent molecules with a -Zn-Zn- bond

The searches for new metal hydrides MH_n were discussed in subsection 2.1. During the matrix spectroscopic search for ZnH_2 , also other species were formed. One was H-Zn-Zn-H (or its deuterated forms)⁴⁶. This was the first experimentally observed -Zn-Zn- bond in a molecule. Later, bulk compounds such as $(\text{Cp}^*)\text{Zn-Zn}(\text{Cp}^*)$ ¹⁶⁰ have been synthesised and theoretically studied.

2.10 Tetrahedral clusters of zinc and cadmium

Johansson and Pyykkö¹⁶¹ studied the stability of tetrahedral M_n clusters, $\text{M}=\text{Zn,Cd}$; $n=4, 10, 20, 35, 56$ at DFT level. These valence electron numbers of 8-112 correspond to magic numbers for particles in a tetrahedral box¹⁶². The species were, indeed, found to be tetrahedral at the DFT level.

Later experimental studies also showed abundance maxima for Zn_n ¹⁶³ and Cd_n ^{163,164}, $n = 10, 20, 35$.

2.11 Model systems for multiple bonds

Multiple bonding appears to be more common in the Periodic Table than was previously thought. One consequence was the development of new sets of additive covalent radii for both triple¹⁶⁵ and double¹⁶⁶ bonds, up to superheavy elements. Many of the species used were initially theoretical models and some of them have later been synthesised. An example is the simple diatomic species $\text{Au}\equiv\text{C}^+$, predicted by Barysz and Pyykkö¹¹⁴ and experimentally observed two years later¹¹⁵.

2.12 Endohedral A@B systems

To combine two parts to a new species, we do not necessarily need chemical bonds. A sterical hindrance may suffice. Then the interaction energy will be a combination of both sterical repulsion and attractive dispersion and other terms, enumerated from a one-centre multipolar point of view by us^{167,168}. London-like formulas were derived for the leading, attractive, dispersion terms in this situation where formally the distance between A and B, $R = 0$. This involves the usual dipole polarisability for the inner system A (such as $\text{A} = \text{He-Xe; Zn-Hg; H}_2, \text{CH}_4$ etc.) but a new, 'irregular' polarisability for the outer subsystem $\text{B} = \text{C}_{60}$. For further calculations of the interaction energies, see Korona and Dodziuk¹⁶⁹.

Note here that precise spectroscopic information is available for the hydrogen isotopes of $\text{H}_2@\text{C}_{60}$ ¹⁷⁰. In that sense, they are very well-characterised species.

2.13 Some further work by others

A review under the present title would not be complete without mentioning that the long search for a Hg(IV)F₄ molecule finally was brought to fruition in 2007¹⁷¹. The evidence consists of one infrared line. The secret was to use just the right amount of light in a photochemical reaction, that first makes and then breaks the product. This was, not only a new species, but a new oxidation state.

3 Some predictions waiting to be discovered

3.1 Superheavy elements

As already said, the chemistry of the not yet made superheavy elements must rest on a purely theoretical basis. A list of some possible molecules was given¹⁷² for the range E121 to E164. We reproduce it here as Table 5. To mention one such species, the (E125)X₆ hexahalides are suggested to be the first 5g¹ species, thus occupying the 5g shell^{172,173}. The situation would be analogous to NpF₆, which is 5f¹.

The already prepared noble gas E118 was predicted to have an electron affinity^{174,175}, due to the relativistic stabilisation of the next, vacant 8s shell. It would be the first noble gas with an EA.

Table 5 Some possible molecules, containing the 5g, 6f and 7d elements E121-E164. X is a halogen, O oxygen. Reproduced from ref.¹⁷².

Class	Molecules	Analogs
8s ⁰ 5g ⁰	(E121)X ₃	LaX ₃ ¹⁷⁶
	(E122)X ₄	
	(E123)X ₅	
	(E124)X ₆ ,...	
	(E126)O ₄	
8s ⁰ 5g ¹	(E125)X ₆ ^a	
8s ² (8p*) ⁰ 6f ⁰ 5g ¹⁸	(E142)X ₄	ThF ₄
	(E144)X ₆	UF ₆
	(E144)O ₂ ⁺	UO ₂ ⁺
8s ⁰ (8p*) ⁰ 6f ⁰ 5g ¹⁸	(E144)F ₈	PuF ₈ ¹⁷⁷
	(E144)O ₄	PuO ₄ ¹⁷⁷
	(E148)O ₆	UO ₆ ^{178,179}
	(E142)X ₆	
	(E158)X ₆	WF ₆ , SgF ₆
8s ² (8p*) ⁰ 7d ⁰ 6f ¹⁴ 5g ¹⁸	(E160)O ₄	OsO ₄ , HsO ₄
	(E158)X ₈	
8s ⁰ (8p*) ⁰ 7d ⁰ 6f ¹⁴ 5g ¹⁸	(E158)O ₄	
	(E164)X ₂	HgX ₂
8s ² (8p*) ⁰ 7d ¹⁰ 6f ¹⁴ 5g ¹⁸	(E164)X ₄	HgF ₄ ¹⁷¹

^a Theoretically studied by Makhyoun¹⁷³.

3.2 Further possible noble-gas molecules

The next member of the perchlorate, ClO₄⁻, isoelectronic series would be ArO₄³⁻. It remains a local minimum in later theoretical studies^{116,180}, but has not been observed yet. We also considered the substitution of the ArO₄ oxygens by NCN²⁻ groups.

Curiously, if one of the four oxygens is substituted by nitrogen, that bond in NSO₃³⁻, NClO₃²⁻ or NArO₃⁻ is calculated to become the shorter one¹¹⁶ in these anions, as already stated in Table 4. The substituted perchlorate is experimentally known but only the average bond length is reported¹⁸¹. The observed Cl-N A₁ stretching frequency is higher than the Cl-O one by a factor of 1.53¹¹⁷.

Our maps also show local minima for species, like SBeNe, SBNe⁺ and SCNe²⁺⁶⁵. They have been later theoretically confirmed¹⁸², including other noble gases, but not yet experimentally observed.

An entire class of mass-spectroscopically observed helium species are the *helides*, such as VHe³⁺. A CASSCF calculation¹⁸³ revealed a predominant charge(V³⁺)-polarisability(He)R⁻⁴ interaction, but also traces of further interactions. Other possibilities, such as AlHe³⁺¹⁸⁴ or ThHe⁴⁺ were mentioned. For the latest review on helium species, see Grandinetti¹⁸⁵.

The xenon trioxide and tetroxide are well-known bulk compounds. A theoretical study on a molecular XeO₂ showed it to be a local minimum¹⁸⁶. The recently synthesised, solid XeO₂ actually has four, bridging, oxygens bonding to each xenon, as found by Brock and Schrobilgen¹⁸⁷.

3.3 Oxygen-bridged main-group systems

Seeing a sulphate anion as a pseudochalcogenide, it is easy to imagine the corresponding pseudochalcogen dimer (SO₄)₂¹⁸⁸. Similarly, a (PO₄)₂ would be a pseudopnicogen dimer. Note that such multiple peroxide bridges occur in boron-containing detergents ('Persil'), and have been proposed for beryllium¹⁸⁹.

The other species, contained single, bridging, oxygen- or sulphur atoms include species like a D_{2h} O=C(μ-O)₂C=O, already discovered theoretically four times^{188,190-192} (Pyykkö quoting Lewars, and Tassone quoting Frapper), but not yet experimentally made.

3.4 Predicting new solids

Here our predictions have not yet resulted in experimental results. One idea was to predict new, dense, high-pressure forms of solid SO₃¹⁹³. Another was to start from solid AuCN but to entirely reshape its known structure, which consists of a hexagonal packing of linear -Au-CN-Au- chains, to a sheet structure of triaurotriazine units C₃Au₃N₃^{194,195}, having

a comparable energy. A third idea was to make nanostrips¹⁹⁶ of quinoline-type spacers, bridged by gold atoms. They also could be bent to nanorings, thus treating the bending energies or deformation vibrations of such molecules as those of elastic bodies¹⁹⁷.

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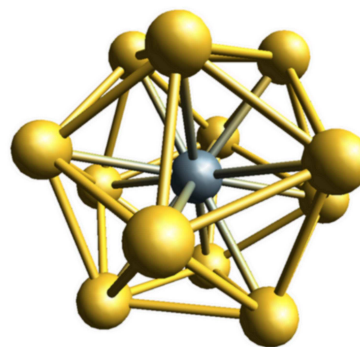


Fig. 4 Graphical Abstract: The combination of ab initio calculations with the isoelectronic principle and chemical intuition is a powerful tool to discovering new, simple inorganic species, such as WAu₁₂.