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Algebraic Characterization of Simple Transition-Metal Molecules*

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This work extends previous studies of molecules with main-group atoms to those also containing transition-metal atoms. The maximum oxidation states of group 3 to 7 atoms are succinctly described by the same algebraic equation that applies to ionically-bonded main-group atoms in molecules. Covalently bonded transition-metal molecules are characterized by the same equations that apply to main-group species, except that the octet rule is supplemented by the rule of 18, and a proposed rule of 12. Examples are given of organo-metallics with simple ligands and of transition-metal atoms in π -ring sandwiches. The solutions for a special case of the same equations apply to the gas-phase diatomic species which are of such importance in stellar and planetary atmospheres and in combustion devices.

»Replacing an explanation based on sound quantum mechanics with a numerical correlation seems like a step backward«

Prof. Kendall N. Houk

but

»Chemists who think about this problem will be enriched by considering both interpretations and 'We'll end up with a better understanding that we'll be teaching to undergraduates in the future'«

Prof. Andrew Streitwieser

Chemical and Engineering News, March 6, 2006, page 65.

INTRODUCTION

We seek to characterize simple transition-metal (TM) species by using Diophantine algebra and the stability rules familiar in chemistry. The idea is as follows: if analysis of the millions of known species in chemistry shows that the rule of 18 is widely applicable, then why not assume this rule (and one other) and find what species satisfy it (them)? Later on, quantum chemists and

experimentalists can be asked »How stable are the forecasted species?« or »In what environments are they stable or, at the very least, observable?«

The method of this paper is similar to that used for main-group (MG) molecules^{1–3} except, importantly, that in all but one section there is no limitation on the numbers of atoms in the molecules. We study organo-metallic molecules that possess one central TM atom with ionic,

* Dedicated to Professor Haruo Hosoya in happy celebration of his 70th birthday.

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TABLE I. A few of the many known period-4 rule-of-18 species

Atom	C_1	electrons needed	π -ring sandwiches ^{(a),(b)}	Species with :CO ligands ^(c)	Other species ^(b)
Sc	3	15			
Ti	4	14	Bis(π -cyclopentadienyl)titanium dichloride		
V	5	13	Vanadium, (η^6 -benzene)(η^7 -cycloheptadienyl)	$[\text{V}(\text{CO})_6]^{1-}$	
Cr	6	12	Chromium, bis(η^6 -benzene)	$\text{Cr}(\text{CO})_6$	$\text{Cr}(\text{PF}_3)_6$
Mn	7	11	Manganese, (η^6 -benzene)(η^5 -2,4-cyclopentadien-1-yl)		
Fe	8	10	Ferrocene (<i>i.e.</i> , $\text{C}_{10}\text{H}_{10}\text{Fe}$)	$\text{Fe}(\text{CO})_5$	
Co	9	9	Cobalt, (η^4 -cyclobutadiene- η^5 -cyclopentadienyl)	$\text{CoH}(\text{CO})_4$	
Ni	10	8		$\text{Ni}(\text{CO})_4$	$\text{Ni}(\text{PF}_3)_4$
Cu	11	7			$[\text{Cu}(\text{CN})_6]^{1-}$
Zn	12	6			$[\text{Zn}(\text{CN})_4]^{2-}$

^(a) Ref. 8; ^(b) Ref. 9; ^(c) Ref. 10.

or covalent and dative, bonds to atomic, functional-group, or π -ring sandwich ligands (the method could be extended to molecules with additional transition-metal atoms). We also study gas phase diatomic molecules that have one or two TM atoms (the method could easily be extended to triatomic or larger species).

ALGEBRAIC FORMULATION

Assumptions

1. Atoms will possess valence-shell electrons of their own plus (or minus) those due to the bonding that takes place with one or more neighboring ligands;

2. The bonds are atom-to-atom covalent, ionic, van der Waals, and/or dative and involve integer numbers of electrons;

3. The bond order may vary from 0 – a van der Waals bond – to a maximum of 3 including at most one dative bond (this assumption can be easily generalized to quadruple or higher-order bonds) – for covalent bonding – or more for ionic bonding;

4. Atoms with higher electronegativity will not donate an electron pair to form a dative bond with those of lower electronegativity.

Maximum Oxidation States

The maximum oxidation states of transition-metal atoms are 3 to 7 for groups 3 to 7 (in period 4) and 3 to 8 for groups 3 to 8 (in periods 5 and 6),⁴ though Shchukarev⁵ also allows Fe(VIII). (This phenomenon has led to occasions in which these maximum values are called valences⁶). The maximum values decrease thereafter. A simple algebraic expression is consonant with the maximum oxidation states of these five (six) groups of atoms:

$$C_1 - \sum_k^S q_k = 0 \quad (1)$$

C_1 is the group number of the transition-metal atom (3 to 7), q_k is the charge transferred to the S neighboring atoms or sites in polydentate neighbors, and zero indicates that the TM atom ends up with an argon configuration. For the special molecules to which this formula pertains, it can be said to articulate a »rule of zero«, though it really says that the oxidized atoms are described by the rule of 8.

The Rules of 18 and 12

The formulae are

$$C_1 + \sum_{i=0}^P v_{im} + 2 \sum_{j=0}^Q p_{jn} = R_1 \quad (0 \leq n \leq 1; \quad 0 \leq m + n \leq 3) \quad (2)$$

$$C_i + v_{im} = R_2$$

$$\begin{aligned} & \text{(if } m = 0 \text{ and } n = 0, \text{ then } C_k \rightarrow \text{Ne;} \\ & \text{if } m = 0 \text{ and } n = 1, \text{ then } C_k \rightarrow \text{any entity} \\ & \text{that has bound-pair electrons)} \end{aligned} \quad (3)$$

The group number C_1 can now vary from 3 to 12; v_{im} indicates that there is a covalent bond of order m between atom 1 and any of P ligands i ; p_{jn} means that some ligand j from among Q has contributed n (zero or one) dative bonds of two electrons each to atom 1. The sets of ligands i and j are not necessarily disjoint. C_i is the group number of an electronegative simple ligand i , or the group number that ligand i could have in view of the number of electrons it desires (*e.g.*, 17 for CN).⁷ R_1 is 18 (the rule of 18, which states that after bonding the period-4 TM atom shall have a krypton-like closed valence shell). R_2 is also 18, but for a totally different reason: it expresses the octet rule, which states that when bonded the period 2 main-group atom shall have a neon-like closed valence shell; this configuration, due to the numbering of atomic groups now in vogue, is 18. In Refs. 1 to 3, R_2 was 8 (or, for group-1 and group-2 atoms, 2).

The equations are solved by choosing the bonds and solving for the group numbers. In all the solutions given, atoms from the earliest possible period number are shown.

Example 1: If there are to be nine covalent single bonds and no dative bonds then $v_{2,1}$ to $v_{10,1}$ are 1, $C_1 = 9$ (i.e. Co), and C_2 to C_{10} are all 17. Having nine atoms surrounding the Co atom, providing these single bonds is not possible; however, they can be members of two π -rings, so the molecule can be η^4 -cyclobutadiene- η^5 -cyclopentadienyl cobalt, as listed in Table I and shown in Figure 1. The corresponding manganese π -ring sandwich cobalt and vanadium molecules are shown in Figures 2 and 3.

Example 2: If there are to be six covalent double bonds and no dative bonds then $v_{2,2}$ to $v_{7,2}$ are 2, $C_1 = 6$ (Cr), and C_2 to C_7 are all 6. Thus the molecule can be $\text{Cr}(\text{PF}_3)_6$, assuming that this radical provides double covalent bonds.

Example 3: If there are to be no covalent bonds but six dative bonds then $p_{2,1}$ to $p_{7,1}$ are 1, $C_1 = 6$ (Cr again), and C_2 to C_7 are all 18. The condition attached to Eq. (3) allows these ligands to be :CO, so the molecule can be $\text{Cr}(\text{CO})_6$ with chromium having a formal charge of zero, as listed in Table I.

Example 4: If there are to be one single bond and separately four dative bonds then $c_{2,1}$ is 1, $p_{3,1}$ to $p_{6,1}$ are 1, $C_1 = 9$ (Co again), C_2 is 17 (e.g. F), and C_3 to C_6 are 18 (e.g. :CO again). Thus the molecule can be $\text{CoF}(\text{CO})_4$. If R_2 is set to 2 then C_2 can be 1 (H in column 1) and the molecule is $\text{CoH}(\text{CO})_4$ as listed in Table I. A further example of prediction from the equations is in a later section.

It is not being claimed that *all* transition-metal atoms will have 18 or 12 valence-shell electrons when present in molecules, but that note should be taken of the many that do.

Isolated zinc, cadmium, and mercury atoms have closed s and d subshells. They behave somewhat like rare gas

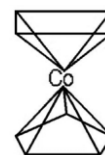


Figure 1. Cobalt, (η^4 -cyclobutadiene- η^5 -cyclopentadienyl).

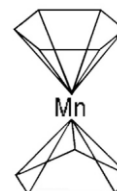


Figure 2. Manganese, (η^6 -benzene)(η^5 -2,4-cyclopentadien-1-yl).



Figure 3. Vanadium, (η^6 -benzene)(η^7 -cycloheptadienyl).

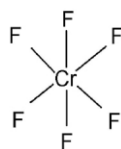
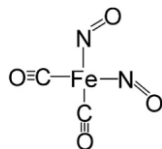
atoms (the more so in the order listed), as manifested in their dissociation energies, vibration frequencies, and internuclear separations. This behavior suggests that a »rule of 12« might be worth investigating in molecules as well.¹² The general formulae for these molecules are the same as those above except that in Eq. (1) $R_1 = 12$; the method of solution is similar to that described above, including the combinatorial development that can be built up starting with such formulae as CrX_6 . Table II shows a very few of the known molecules that can obey this »rule«. One chromium and one iron molecule are shown in Figures 4 and 5.

TABLE II. A few of the many known period-4 »rule-of-12« species

Atom	electrons needed	Group 16 ligands	Group 17 ligands	Other species ^{(a),(b)}	Other species ^(b)
Sc	9				
Ti	8				
V	7			$\text{VC}_{12}\text{H}_9\text{Cl}_3\text{N}_3\text{O}_4$	$\text{VC}_6\text{H}_{12}\text{NO}_4$
Cr	6	$\text{CrO}_3^{(c)}$	$\text{CrX}_6^{(c)}$	$\text{Cr}(\text{CO})_6$	$\text{CrC}_5\text{H}_5\text{NO}_5$
Mn	5			$\text{MnC}_{12}\text{H}_{31}\text{N}_2\text{O}_2\text{P}_2$	
Fe	4			$\text{Fe}(\text{CO})_2(\text{NO})_2$	
Co	3		$\text{CoX}_3^{(c),(d)}$		
Ni	2	$\text{NiO}^{(e)}$	$\text{NiX}_2^{(c),(d)}$		
Cu	1		CuX^{13}		

^(a) Carbonyls in these molecules attach with a single covalent bond; ^(b) Ref. 11; ^(c) Ref. 10;

^(d) X, any halide, can be replaced by OH, NO_3 , or many other functional groups; ^(e) Ref. 13.

Figure 4. CrF₆.Figure 5. Fe(CO)₂(NO)₂.

The vacancy for scandium in both tables is consistent with the conclusion of Ref. 14 that group 3 and 4 metals usually bond ionically, and the CuX entry is consistent with its conclusion that Cu(I) much prefers covalent bonding.

Gas Phase Diatomic Molecules with a Row-4 TM Atom and Row-2 MG Atom

The molecules to be discussed here are primarily of interest in gas-phase chemistry, and scores of them are listed in data bases.¹³ The Lewis dot rules are less pervasively relevant for these species; nonetheless, we shall proceed to see where the method leads. The equations for covalent and dative bonding between one TM and one MG atom are special cases of Eq. (2) and (3):

$$C_1 + v + 2p = R_1 \quad (4)$$

$(0 \leq p \leq 1; < +p \leq 3)$

$$C_2 + v = R_2 \quad (5)$$

(if $< = 0$ and $p = 0$, then $C_2 \rightarrow \text{Ne}$;
if $< = 0$ and $p = 1$, then $C_2 \rightarrow$ any entity
that has bound-pair electrons)

and the equations for ionic and dative bonding are

$$C_1 - q + 2p = R_1 \quad (6)$$

$(0 \leq p \leq 1; 1 \leq q \leq 3 \text{ if period number} = 4)$

$$C_2 + q = R_2 \quad (7)$$

$(1 \leq q \leq 3 \text{ if period number} = 4)$

The solutions of Eqs. (4) and (5) are not as trivial as it may appear, because row 4 contains not only TM, but also MG, atoms, and so many solutions are void. The italicized values of R show which atoms are specified as from period 4, whether they be s, p, or d. On the other hand, a simplifying factor is that the TM atom in a covalently-bonded diatomic molecule cannot accumulate the number of electrons needed for a Kr configuration,

and so it can only be described by the rule of 12. The solutions follow.

- $(R_1, R_2) = (12, 12)$: there can be a van der Waals bond (Zn_2) or covalent bonds of order 1 (Cu_2), 2 (Ni_2), and 3 (Co_2). No dative bonding will take place. This series is analogous to the series Ne_2 , F_2 , O_2 , N_2 for molecules with two rule of 8 (18) atoms.
- $(R_1, R_2) = (12, 2)$: a van der Waals bond gives $ZnBe$, and no dative bond will be given. A single covalent gives $CuLi$; a dative bond given by Cu would cause atom 2 to be below row 2. The abnormal notations are in the same order as the solutions to Eqs. (4) and (5).
- $(R_1, R_2) = (2, 12)$: the reverse of the preceding case; the same molecules (but in standard notation). The reversal invites for Li in $LiCu$ to form a dative bond, but Li has no bound pair.
- $(R_1, R_2) = (12, 0)$ and $(0, 12)$: the only solution is van der Waals bonded $ZnHe$.
- $(R_1, R_2) = (12, 18)$: a van der Waals bond yields $ZnNe$. Covalent bonds of orders 1, 2, and 3 yield FCu , ONi , and NCo ; in the first two instances, dative bonds are forbidden due to electronegativity considerations; in the third the dative bond is disallowed because the bond order would exceed 3. $ZnNe$, CuF , NiO , and CoN are the analogs of Zn_2 , Cu_2 , Ni_2 , and Co_2 .
- $(R_1, R_2) = (18, 12)$: the same four molecules appear in reverse notation, however, now Cu and Ni can donate a dative bond to make CuN and NiC . Co cannot make CoB because a quadruple bond would be involved.
- $(R_1, R_2) = (18, 2)$, $(2, 18)$, $(18, 0)$ and $(0, 18)$: there is no molecule with a TM atom.

The solutions for ionic bonding, Eqs. (6) and (7), are even fewer in number. TM atom in a diatomic molecule cannot give away enough electrons to achieve an argon configuration, so again it can only be described by the rule of 12. The solutions follow.

- $(R_1, R_2) = (0, 12)$: Li loses one electron to resemble He and Cu gains one to resemble Zn ($LiCu$); Be loses two electrons to resemble He and Ni gains two to resemble Zn ($BeNi$). Neither Li^+ nor Be^+ are able to donate a dative bond. $CuLi$, from $(R_1, R_2) = (12, 2)$, and $BeNi$ are analogs of LiF and BeO for molecules with two rule of 8 (18) atoms.
- $(R_1, R_2) = (0, 18)$: Sc loses three electron to resemble Ar, and N gains three to resemble Ne (ArN).

There is a clear equivalence between the two pairs of equations if $p = 0$ in equation (4) and if $v = q = p$. Thus, in Eqs. (4) and (5) if $(R_1, R_2) = (12, 18)$ and $v = 1$, then $(C_1, C_2) = (11, 17)$ and the molecule is CuF . Cor-

C_2	Zn	12	ZnHe		BeZn												ZnNe
	Cu	11		LiCu	BeCu ⁺	CuB	CuC ⁺	CuN	CuO ⁺	CuF							
	Ni	10			BeNi		NiC	NiN ⁺	NiO								
	Co	9		LiCo	BeCo ⁺			CoN									
	Fe	8			BeFe												
	Mn	7															
	Cr	6															
	V	5															
	Ti	4						TiN ⁺									
	Sc	3						ScN									
			0	1	2	13	14	15	16	17	18						
			He	Li	Be	B	C	N	O	F	Ne						
																	C_1

Figure 6. Neutral and ionized diatomic molecules containing one period-4 TM molecule and one period-2 MG molecule. Standard nomenclature (lower electronegativity first) is used even though it hides from which values of (R_1, R_2) the molecules come in the calculations. Cations in the figure are positioned by finding the molecule with the same electronegative atom and with the other, more electropositive, atom having an atomic number larger by one unit.¹ The cations that are isoelectronic to lithium molecules are at right; those isoelectronic to Be and higher molecules are above except in those cases where the replacement would be a closed-shell species. These placements have the curious result that BeCu⁺ is related both to LiCu and BeNi; there are two other similar cases.

respondingly, in Eqs. (6) and (7) $q = 1$ and $p = 1$, then again $(C_1, C_2) = (11, 17)$ and again the molecule is CuF (as demonstrated in Figure 6). If $v = q = p = 2$ then the molecule is NiO; if $v = q = p = 3$ then it is CoN; neither molecule is in Figure 6 due to the imposed limitations. Eqs. (6) and (7) are not redundant; they allow for BeNi and ScN and for the molecules discussed in Section Maximum oxidation states.

Figure 6 shows all of the molecules in the entire solution set except for $(R_1, R_2) = (12, 12)$ and $(0, 18)$. Several interesting features are seen in this figure – for instance the absence of neutral radicals; the series NeZn, FCu, ONi, CoN that exactly parallels the series Ne₂, F₂, O₂, N₂ for MG molecules; the absence of FeC, which would like C_2 require a quadruple bond; and van der Waals species, NeZn and ZnHe. The comparable plot for MG molecules is given in Ref. 1.

The situation differs somewhat for diatomic molecules where both atoms are transition metals. The molecules Zn₂, Cu₂, Ni₂, and Co₂ go down the diagonal from the upper right to lower left.

PREDICTIONS

Many more species that satisfy the rule of 18 can be forecasted from the concepts of Section The rules of 18 and

12. To illustrate, consider nickel, to which eight covalent bonds are allowed. In combinatorial fashion one can begin with six single bonds, one double bond and four single bonds, two double bonds and two single bonds, and so on, giving for example the series CrF₆, CrOF₄, CrO₂F₂, CrO₃, CrNF₃, CrNOF, and CrN₂. Higher period-number TM atoms should not lightly be substituted for period-4 TM atoms without further investigation.

COMMENT

Froeyen and Herdewijn¹⁵ have also used algebraic methods, but to opposite effect: the atoms are given and the bond orders are found. Their paper shows that additional non-trivial restrictions, such as bond angles and »adjacent charges,« could be included in further development of our model. On the other hand, Vukičević and Graovac^{16,17} use set theory to determine whether a molecular graph can exist when the covalent bonds are given: the goal is similar but the mathematics differs.

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SAŽETAK**Algebarska karakterizacija molekula prijelaznih elemenata****Ray Hefferlin i Ken Luk**

U radu su ranija istraživanja molekula s atomima glavne skupine proširena na one prijelaznih elemenata, pri čemu su najveća oksidacijska stanja atoma skupina 3 do 7 opisana istom algebarskom jednadžbom koja vrijedi i za ionski vezane atome glavnih skupina. Kovalentno vezane molekule prijelaznih elemenata opisane su jednadžbama koje vrijede i za one glavne skupine osim što se oktetno pravilo zamjenjuje pravilom 18 i ovdje predloženim pravilom 12, što je ilustrirano primjerima organo-metalnih spojeva s jednostavnim ligandima i na atomima prijelaznih elemenata u sendvič-molekulama. Rješenja iste jednadžbe za posebne slučajeve vrijede i za plinski fazu dvoatomskih molekula važnih u atmosferi zvijezda i planeta te u uređajima za spaljivanje.