

793. *Theoretical Basis of the "Rare-gas Rule."*

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The rare-gas rule for the electronic structure of metal carbonyls and other complexes is discussed in relation to changes in the electrostatic potential field of the metal caused by the ligands.

In the octahedral (d^6) and the tetrahedral (d^{10}) system the electrostatic potential of the carbonyl ligands is very nearly spherically symmetrical, up to 1.25 and 1.0 a.u., respectively, from the metal nucleus. It is in this region that the self-consistent field d -orbitals have a maximum charge density.

If electrons are transferred from a first-series transition metal to carbonyl groups in π -donor bonding, the reduced screening has the effect that the averaged potential approaches that of krypton in radial dependence as well as in spherical symmetry, in contrast to the situation for monoatomic ligands such as F^- .

Support is thus found for the view that, when the σ -bonds are formed by ligand lone-pair donation, the rare-gas rule will apply only if there is substantial electron transfer from the metal π -orbitals. Expansion of d -orbitals under the influence of ligand lone pairs is probably important in facilitating electron-withdrawal.

THE "rare-gas rule" expresses a feature of the electronic structures of a large number of complexes of transition metals, especially in low valency states. The rule asserts that the number of electrons from the metal added to the number of bonding electrons from the ligands equals the number of electrons in a rare gas. In complexes of first-row transition

metals the number of electrons is 36, equal to the number in krypton with filled $3d$, $4s$, and $4p$ orbitals. Thus nickel with 28 electrons attains the krypton configuration with eight electrons from the lone pairs of carbon monoxide molecules in $\text{Ni}(\text{CO})_4$, and cobalt has the rare-gas configuration in $\text{Co}(\text{CO})_3\text{NO}$, the nitroso-group contributing three electrons. The empirical fact is that with certain classes of ligands the most stable complexes have rare-gas configurations of the transition metals; the molecular compositions of stable molecules can be predicted by applying the rare-gas rule. In other cases such as $[\text{Co}(\text{NH}_3)_6]^{3+}$ a configuration of 36 electrons seems to be merely incidental to stability because other configurations such as that of square-planar Ni^{2+} complexes (34 electrons) are of comparable stability.

To put this in perspective it is well to have in mind that a similar rule, but one that applies more widely, is the octet rule for first-row elements, according to which the molecular compositions are determined by the attainment of the electronic configuration of neon. The main systematic exceptions are found in beryllium and boron compounds. In second-row elements there is an octet rule for the attainment of the argon configuration applying reasonably well to elements from silicon to chlorine so long as the attached elements are of low electronegativity. Exceptions are common with highly electronegative ligands where the octet is exceeded, as in numerous compounds of silicon, and in compounds such as phosphorus pentafluoride, sulphur hexafluoride, and chlorine trifluoride. In the first long period, terminating in krypton, there is a similar situation in the elements from germanium to bromine, but in the early part of the long period comprising the transition elements a large number of electrons have to be added to make up the krypton structure; this occurs only in rather special cases, mainly with $-\text{CO}$ and $-\text{NO}$ and other ligands capable of π -bonding. Even here there are exceptions showing that the energy relations are often only marginally in favour of the rare-gas configuration. Moreover, in transition-metal complexes of all kinds, the number of valency electrons is usually close to 18, almost always between 16 and 20, and we must expect examples of 18 valency-electron configurations, such as the diamagnetic hexamminecobaltic ion, that shed no light on the rare-gas rule because the ionic or molecular composition is determined by other factors.

The rare-gas rule thus reflects only one of the sets of conditions that can promote stability in transition-metal complexes and, while much progress has been made in delineating experimentally what these conditions are,^{1,2} the underlying causes are not well understood. The problem is to connect the facts about the rare-gas rule with the electronic structures of metal and ligand and, if possible, to give a basis from which its applicability to a particular case might be predicted.

Although the rare-gas rule is not to be taken literally in the full sense that the electron distribution about a transition element in a molecule should resemble that of krypton—for example, it obviously cannot do so near the nucleus—it should be useful to begin by comparing the potential fields in which the electrons move in the two situations. We begin with the electrostatic potential of a typical transition metal and calculate the extent to which it is modified by the potentials of surrounding carbonyl ligand groups. We then compare the resultant potential with the potential of krypton itself, consider how the potential might be changed in a way to stabilise the rare-gas configuration, and enquire whether such changes are likely in actual examples.

Angular Dependence of the Potential.—We are concerned with two features of the potential field. One is the departure from spherical symmetry caused by the array of carbonyl ligands, namely, the angular dependence of the potential; and the other is the radial dependence. Both are, for the present purpose, important only in regions occupied by $3d$ -electrons.

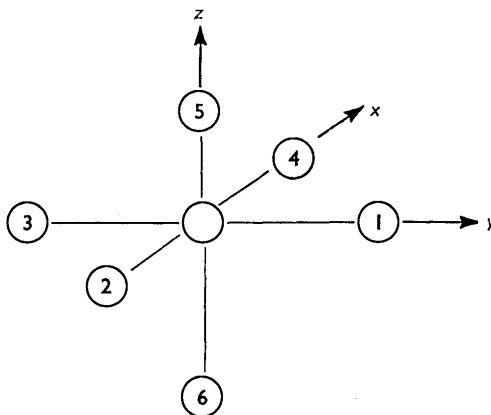
Let $V_1, V_2 \dots V_6$ be the electrostatic potentials of six carbonyl groups in a regular

¹ Chatt, *Ricerca sci.*, 1958, **28**, Suppl., 1.

² Nyholm, *Proc. Chem. Soc.*, 1961, 273.

octahedral arrangement, as in $\text{Cr}(\text{CO})_6$. The perturbing potential is given by expression (1).

$$V_{\text{oct}} = \sum_{i=1}^6 V_i \quad (1)$$



The potential V_i is simulated by the potential of a carbon atom in the digonal configuration $1s^2t_1^22p_x2p_y$, where t_1 is the carbon sp -hybrid lone-pair orbital directed toward the metal. If t_1 is given by

$$t_1 = (1 + \delta^2)^{-1/2}(s + \delta p_z).$$

it can be shown that the carbon potential V is:

$$V = (1 + \delta^2)^{-1}\{(1 - \delta^2)V_s + (\delta^2 - 1)V_{pz} + 4\delta V_{spz}\} + V(C), \quad (2)$$

where

$$V_s = \int 2s(1)2s(1)r_{12}^{-1}d\tau_1,$$

$$V_{pz} = \int 2p_z(1)2p_z(1)r_{12}^{-1}d\tau_1,$$

$$V_{spz} = \int 2s(1)2p_z(1)r_{12}^{-1}d\tau_1,$$

$V(C)$ being the potential of a carbon atom with the spherically symmetrical charge distribution $1s^22s^22p_x2p_y2p_z$. Self-consistent field (SCF) orbitals for carbon³ were at first used to calculate the potential V , but there is little loss of accuracy if Slater orbitals are used for V_s , V_z , and V_{spz} . There are convenient closed expressions for these three potentials in the literature.⁴ $V(C)$ is calculated from an analytical expression fitted to the potential based on Torrance's SCF wave functions.

By summing the individual potentials V_i at chosen points on spherical surfaces at different radii r we can display the deviations of the potential V_{oct} from spherical symmetry. We take four representative points defined by their distances from the origin and by the following angular co-ordinates. Type (a), $\theta = 90^\circ$, $\phi = 90^\circ$, lying in the bond direction; type (b), $\theta = 90^\circ$, $\phi = 30^\circ$, in the xy -plane 30° from a bond direction; type (c), $\theta = 90^\circ$, $\phi = 45^\circ$, in the xy -plane, midway between two bonds; and type (e), $\theta = 45^\circ$, $\phi = 45^\circ$, in the midpoint of a triangular face.

The potentials V_{oct} are given in Table 1 at radial distances important for $3d$ -orbitals in transition metals. The metal-carbon distance assumed is 3.5 a.u. (1.85 Å), and the hybridisation parameter δ in the carbon sp hybrid is given the two values 0.5 and 2.0. Jaffé and Orchin⁵ have given reasons for believing that the carbon lone pair in carbon

³ Torrance, *Phys. Rev.*, 1934, **46**, 388.

⁴ Barnett and Coulson, *Phil. Trans.*, 1951, *A*, **243**, 221.

⁵ Jaffé and Orchin, *Tetrahedron*, 1960, **10**, 212.

monoxide is in a hybrid orbital of predominating p -character; if we accept this conclusion, and therefore take $\delta = 2$ to be the closer approximation, the results in the third column of Table 1 are the more significant. For a comparison with the field of a typical ionic ligand, values for F^- ($1s^2 2s^2 2p^6$) and neutral F ($1s^2 2s^2 2p^5$) are included; these are based on Froese's SCF results.⁶

TABLE 1.
Representative values of V_{oct} (in a.u.).

r (a.u.)	CO ($\delta = 0.5$)	CO ($\delta = 2$)	F ⁻	F	Type of point	r (a.u.)	CO ($\delta = 0.5$)	CO ($\delta = 2$)	F ⁻	F	Type of point
0.50	0.5317	0.7127	1.7122	-0.0641	b	1.0	0.5071	0.6809	1.7097	-0.0651	b
	0.5314	0.7130	1.7124	-0.0646	a		0.5026	0.6806	1.7138	-0.0729	a
	0.5318	0.7130	1.7120	-0.0642	c		0.5088	0.6808	1.7084	-0.0650	c
	0.5318	0.7128	1.7120	-0.0639	e		0.5097	0.6805	1.7071	-0.0601	e
	0.5219	0.7005	1.7114	-0.0650	b		0.4859	0.6519	1.7071	—	b
0.75	0.5307	0.7005	1.7130	-0.0665	a	1.25	0.4714	0.6472	1.7158	—	a
	0.5225	0.7003	1.7108	-0.0646	c		0.4902	0.6532	1.7040	—	c
	0.5230	0.7002	1.7102	-0.0643	e		0.4926	0.6532	1.7010	—	e

The potential of a carbon atom in the spherically symmetrical $sp_x p_y p_z$ configuration is attractive at all distances. In the configuration $t_1^2 p_x p_y$ the lone-pair repulsion makes the overall potential repulsive within the octahedron of ligands; and comparison of the $\delta = 0.5$ and $\delta = 2.0$ results in Table 1 show that the repulsion is greater the more p_z -character there is in the lone pair.

For $\delta = 2.0$ the potential is remarkably uniform (within 1%) over spherical surfaces out to a radius of 1.25 a.u., that is to say, to a radius within which most of the d -orbital is contained. Thus the electrostatic part of the potential field imposed upon a central atom by an octahedral set of carbonyl groups is essentially atomic in this region. However, this is not uniquely confined to carbonyl groups, because as also shown in Table 1 the results for the potential of six F^- ions show a similar character. With fluorine atoms, however, the departure from spherical symmetry is already marked at $r = 0.75$ a.u. It seems probable that near-spherical symmetry is produced in general by ligands with inward-facing lone pairs, and is not confined to those forming complexes with rare-gas electronic structures.

Effect on Metal Slater-type d-Electrons.—If the potential of the ligand groups is added to that of a transition metal we get a potential for the metal electrons modified both in angular and radial dependence. The change in the d -orbitals in the modified field can then be calculated. Initially we suppose the central metal atom to supply one d -electron in a Coulomb field of charge Z_a , and calculate the effect of the superposed ligand field as previously described.⁷ The total energy $W(k)$ of the d -electron in a Slater $3d$ -orbital is minimised with respect to the orbital exponent k . We have

$$\begin{aligned} W(k) &= \int \psi \left(-\frac{1}{2} \nabla^2 - Z_a/r + V_{\text{oct}} \right) \psi d\tau \\ &= w(k) + \int \psi V_{\text{oct}} \psi d\tau. \end{aligned} \quad (3)$$

Z_a is given the value 6, a representative value for first-row transition metals. The perturbation term in expression (3) is reducible to the sum of six ligand-metal interactions, each being a two-centre one-electron integral. The wave function ψ must be specified by its symmetry in the octahedral field as either d_ϵ or d_γ in type, and separate calculations must be made for each. Total energies for the perturbed d_ϵ - or d_γ -electron have been evaluated for a range of values of δ , the hybridisation parameter for the carbon monoxide lone pair, and of k . The results are given in Table 2 for a metal-carbon distance of 3.5 a.u.

⁶ Froese, *Proc. Camb. Phil. Soc.*, 1957, **53**, 206.

⁷ Craig and Magnusson, *J.*, 1956, 4895.

TABLE 2.

Total d -electron energy (a.u.) * as a function of k and δ : $Z_a = 6$.

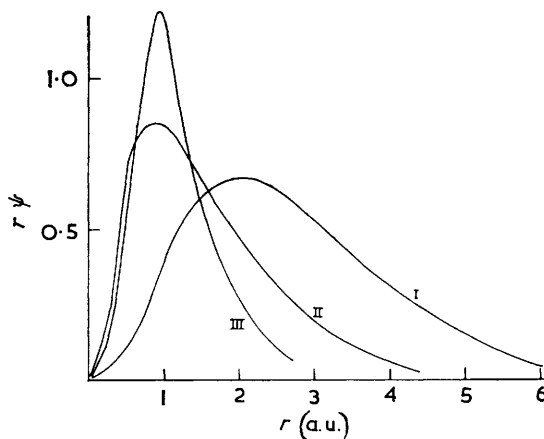
k	$\delta = 0$	$\delta = 0.5$	$\delta = 1$	$\delta = 2$	d -orbital
3	-1.7842	-1.0449	-0.7864	-0.8682	γ
	-1.7527	-1.0281	-0.7766	-0.8594	ϵ
2.5	-2.2017	-1.4737	-1.2211	-1.3043	γ
	-2.1353	-1.4309	-1.1893	-1.2737	ϵ
2	-2.4238	-1.7289	-1.4921	-1.5776	γ
	-2.2682	-1.6082	-1.3874	-1.4742	ϵ
1.5	-2.4910	-1.8981	-1.7049	-1.7902	γ
	-2.1393	-1.5827	-1.4064	-1.4937	ϵ
1	-2.2105	-1.8774	-1.7785	-1.8399	γ
	-1.6975	-1.3605	-1.2669	-1.3381	ϵ
0.5	-1.0634	-1.0111	-1.0430	-1.0310	γ
	-0.9350	-0.8974	-0.8907	-0.8716	ϵ

* 1 a.u. = 27.21 ev.

The energy minima for both $d\epsilon$ - and $d\gamma$ -orbitals occur for $k < 2$, showing that the d -orbital is made to expand by the ligand lone pairs. However, because exchange repulsions between the electrons of CO and the d -orbital are not included in the calculation,

FIG. 1. $3d$ Radial wave functions for $V^{2+}(3d)^3$.

(I) Slater orbital with exponent 1.43; (II) SCF orbital; (III) Slater orbital with exponent chosen to give a radial maximum at the SCF distance.



the splitting between $d\epsilon$ and $d\gamma$ is not a ligand-field splitting, but only an index of the departure of the electrostatic field of the ligands from spherical symmetry in the region occupied by the Slater $3d$ -orbital. Moreover, since the exchange terms have a much greater effect on the $d\gamma$ -orbital, which penetrates the carbonyl electron distribution far more than does the $d\epsilon$ -orbital, the results for $d\epsilon$ in Table 2 are a better guide to the extent of the d -orbital expansion. We conclude that the optimum exponent of a Slater $3d$ -electron is changed from a free-atom value $k = 2$ to about $k = 1.7$ by the ligands, corresponding to an expansion of the radial maximum from $r_M = 9/6 = 1.5$ a.u. (0.8 Å) to 1.76 a.u. (0.93 Å).

SCF d-Electrons.—It is well known that d -orbitals in transition metals are only poorly approximated in their radial form by Slater orbitals. Fig. 1 illustrates the comparison for V^{2+} ; in the Slater scheme the $3d$ exponent for V^{2+} in the $(3d)^3$ -configuration is 4.3/3. The Slater orbital for this exponent has its radial maximum much farther from the nucleus than the SCF orbital.⁸ Moreover, if the Slater exponent is to be adjusted to place the radial maximum correctly we require an effective charge of 10 units, more than double the Slater value, and the orbital then cuts off too fast at longer distances.

⁸ Hartree, *J. Opt. Soc. Amer.*, 1956, **46**, 350; Watson, *Phys. Rev.*, 1960, **118**, 1036; **119**, 1934.

Watson's SCF orbitals⁸ may be used for similar calculations of the influence of ligand fields. They have the radial factor (4):

$$R(r) = \sum_{m=1}^4 A_m \exp(-a_m r) \cdot r^2, \quad (4)$$

where A_m are numerical coefficients. These orbitals have radial maxima much closer in than the simple Slater form, as discussed above in connection with Fig. 1. Orbitals of the type (4) can be scaled to permit some treatment of the effects of molecule formation on orbital size by introducing a parameter α , analogous to the k parameter in Slater functions. We write

$$\alpha^{3/2} R(\alpha r) = \alpha^{7/2} \sum_{m=1}^4 A_m \exp(-a_m \alpha r) \cdot r^2 \quad (5)$$

and calculate the total energy as a function of α in the presence of the ligand field. The energy is then minimised with respect to α .

In the case of a chromium $3d$ -orbital the values of the parameters are as follow:⁸

$$\begin{array}{ll} A_1 = 0.1708692 & a_1 = 1.0505 \\ A_2 = 2.607979 & a_2 = 2.1494 \\ A_3 = 22.53086 & a_3 = 4.0812 \\ A_4 = 46.86990 & a_4 = 7.7963 \end{array}$$

and the necessary one-centre integrals are listed in Table 3 for several values of the scale parameter α . To ensure that the virial theorem is satisfied for a single $3d$ -electron in a Coulomb field it is necessary to choose Z_a equal to 9.

By using equation (3) the total energy of the perturbed d -electron may be calculated as before. At the energy minimum, expansion of both $d\epsilon$ - and $d\gamma$ -orbitals again occurs, confirming the view that the effect of the ligands is to move the radial maximum away from the nucleus.

The results of the calculations are given in Table 4.

TABLE 3.
One-centre integrals in the basis of scaled Watson orbitals.

α	Kinetic energy	Potential energy ($\times Z_a^{-1}$)	α	Kinetic energy	Potential energy ($\times Z_a^{-1}$)
0.6	1.5129	-0.5462	1.0	4.2023	-0.9103
0.7	2.0592	-0.6372	1.1	5.0845	-1.0012
0.8	2.6894	-0.7282	1.2	6.0510	-1.0922
0.9	3.4036	-0.8192			

TABLE 4.
 d -Electron energy for $Z_a = 9$, $\delta = 2$.

	$\alpha = 0.6$	$\alpha = 0.7$	$\alpha = 0.8$	$\alpha = 0.9$	$\alpha = 1.0$
$W(\gamma)$	-3.2984	-3.4723	-3.5763	-4.1996	-3.5771
$W(\epsilon)$	-3.0414	-3.2556	-3.3964	-4.0620	-3.4528

The expansion of the SCF orbital, in terms of the change in radial maximum, is in about the same proportion as for the Slater orbital, but the splitting is now quite small, because the penetration by the SCF $d\gamma$ -orbital into the core of the carbon atoms is much less. As before, the splitting itself is of no interest physically on account of the lack of exchange terms in the energy, giving a splitting of the wrong sign.

We conclude from these studies that the ligands cause a considerable expansion of the metal $3d$ -orbitals; the expansion is of significance in increasing overlap with ligand π -orbitals, and facilitates double-bonding.

Radial Dependence of the Potential.—For a calculation of the radial dependence of the complete potential, the field of the ligands must be added to that of the metal atom in a chosen configuration. In the case of octahedral carbonyl ligands, the appropriate first-transition-series metal is chromium (d^6), as in $\text{Cr}(\text{CO})_6$. To get the average radial dependence of the potential the six $3d$ -electrons are distributed equally amongst the five d -orbitals, giving a spherically symmetrical charge distribution from which the potential may readily be calculated by double integration of the Poisson equation with the appropriate SCF wave functions. This gives the potential illustrated in Fig. 2 as a plot of Vr against the radial distance r .

To test the hypothesis that the 18-electron rule is obeyed when the potential acting on the $3d$ -electrons resembles that in krypton itself, the potential of chromium plus that of the ligands is compared with the krypton potential in the range $r = 0.5$ — 2.5 a.u., within which

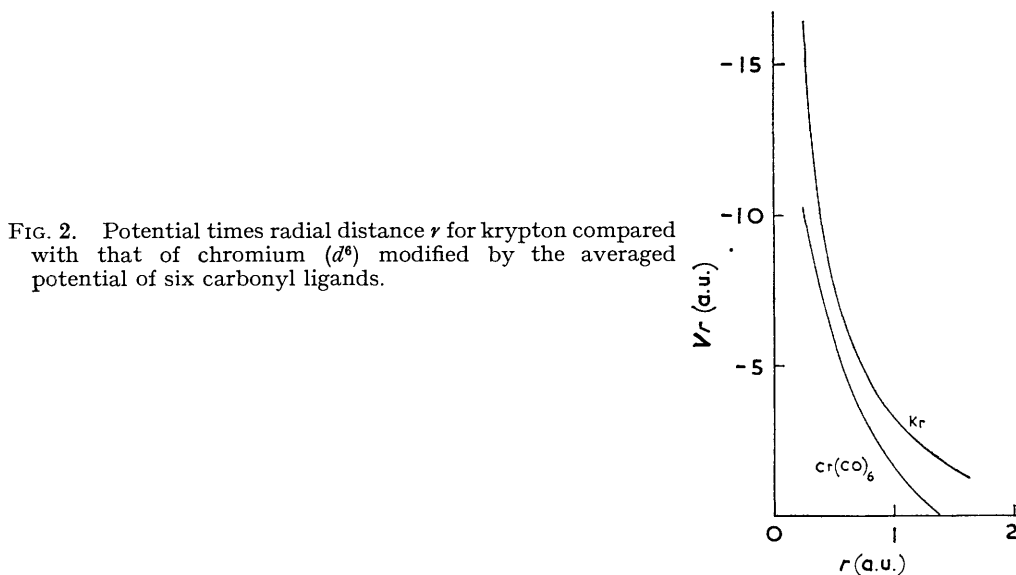


FIG. 2. Potential times radial distance r for krypton compared with that of chromium (d^6) modified by the averaged potential of six carbonyl ligands.

the d -electrons lie. The krypton potential may be calculated in the same way from SCF wave functions of Miss Worsley.⁹

The comparison in Fig. 2 shows that the composite potential of metal plus ligands does not resemble that of krypton at all closely, and we must consider what environmental changes might be made that would make the resemblance closer, particularly in the region near 1 a.u. where the greatest d -electron density occurs. This may be achieved in one or perhaps both of two principal ways. One is by withdrawing charge from the ligand atoms so that their potentials become more attractive. In carbonyls this could only be done by removing π -electrons from carbon and placing them on oxygen. This brings the potential closer to that of krypton in the important range of r . However, the added electronic charge on the oxygen atoms produces an opposing change in the potential due, roughly speaking, to the surrounding "sphere" of negative charge, and when this is taken into account the movement of charge within each carbonyl group from carbon to oxygen required to give a krypton-like potential is increased to $0.8e$. This seems unreasonably large and incompatible with theories of carbonyl binding.

The alternative mechanism is the withdrawal of $d\pi$ (*i.e.*, $d\varepsilon$) metal electrons by delocalisation into the carbonyl groups. To test the scale of change produced in this way, we calculate the decreased shielding corresponding to removal of two electrons from the

⁹ Worsley, *Proc. Roy. Soc.*, 1958, *A*, **247**, 390; 1962, *A*, **267**, 146; Mayers, personal communication.

metal (averaged over all d -orbitals), giving a net gain of $\frac{1}{3}$ electron by each carbonyl group. This proves to be enough to raise the potential approximately to that of krypton in the region of r near 1 a.u., as is shown in Fig. 3, in which the differences of the products Vr are plotted as a function of r .

The calculation of the potential resulting from withdrawal of two electrons is made quite straightforwardly by adding the potential of Cr^{2+} in the configuration d^4 to that of six octahedral carbonyl groups carrying a total of two negative charges. The partition of the surplus negative charge on the carbonyl groups between carbon and oxygen has some influence on the results. Supplementary molecular-orbital calculations of the π -electron population¹⁰ suggest a partition corresponding to the formula $\text{Cr}(d^4)(\text{C}^{\alpha+}\text{O}^{\beta-})_6$, $\alpha = 0.16/6$, $\beta = 2.16/6$, and this has been adopted.

Fig. 3 shows that the resemblance to the krypton potential is confined to a fairly narrow range of r ; but the increased potential in the d -electron zone owing to charge withdrawal is the important point, and suggests that substantial electron delocalisation into the ligands may be the condition required for stabilising configurations with a filled d -shell. The

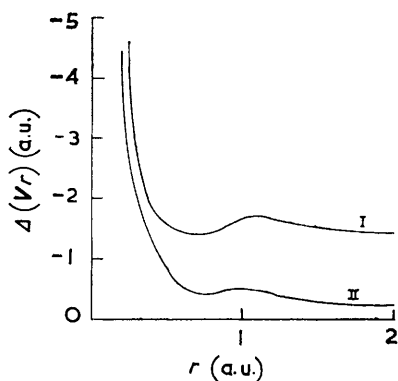


FIG. 3. Difference between the products Vr of potential and radial distance for krypton and $\text{Cr}(\text{CO})_6$ calculated for (i) chromium in the d^6 -configuration, (ii) $\text{Cr}(d^4)$, corresponding to the withdrawal of two $d\epsilon$ -electrons by double-bonding to the carbonyl ligands. The curves for $\text{Ni}(\text{CO})_4$, with nickel in the d^{10} - and d^8 -configurations, are very similar.

importance of double bonding in carbonyls and similar complexes has, of course, long been recognised; these calculations focus attention more specifically on the significance of the corresponding electron withdrawal.

These remarks apply to ligands supplying a lone pair to form the σ -bond: in other cases, in which the ligand supplies one electron per atom as in the cyclopentadienyl complexes, the electrostatic field of the ligand is attractive at all distances, so that the potential of metal plus ligand becomes more strongly attractive even without electron-withdrawal.

According to the view we have been developing, the rare-gas rule for lone-pair-bound ligands ought to be relevant to questions of stability only in cases where substantial electron withdrawal can take place into the ligand's π -orbitals, so reducing inner screening by metal d -electrons, and providing a potential which, in the electrostatic approximation, approaches that of krypton. The effectiveness of $-\text{NO}$ as well as $-\text{CO}$ is understandable on this basis; also, for example, that of the PX_3 ligands, of which the most strongly held is PF_3 . In these cases the $3d$ -orbital of phosphorus is the acceptor.

The situation must be carefully distinguished from that in which the potential cannot be made to resemble that of krypton. Energetic factors other than attainment of the rare-gas configuration must then dominate and the number and type of ligands, and with them the number of valency electrons, are settled by these other factors. We do not expect, for example, that ligands such as ammonia and water will stabilise the rare-gas configuration.

Other Stereochemical Arrangements.—Calculations entirely similar to these may be made for other stereochemical arrangements of ligands about a central metal atom. We have

¹⁰ Doggett, Thesis, University of London, 1961.

treated the tetrahedral $M(\text{CO})_4$, with special reference to nickel, with very similar results to those for octahedral $\text{Cr}(\text{CO})_6$. The metal wave functions are those of Watson,⁸ and the derived potential is added to that of tetrahedrally arranged carbonyl groups with Ni-C distance of 3.5 a.u. and then compared with that of krypton. Withdrawal of a total of two d -electrons, and consequent reduction of inner screening, leads to a change of potential essentially the same as that of Fig. 3.

Application.—If it is concluded from this analysis of the potentials that the rare-gas rule has an application only in cases where d -electrons are withdrawn substantially from the central metal, several conclusions may be drawn about the cases to which the rule should be relevant. If a transition metal has a low nuclear charge, and correspondingly only a small number of d -electrons, π -bonding ligands cannot modify the potential enough to stabilise the rare-gas configuration. Thus the rule is not expected to apply at the beginning of the first transition series.

In the elements near the end of the series the rule will also fail for the following reason. The withdrawal of metal electrons by the ligand depends on the extent of the overlap between the metal $d\varepsilon$ -orbitals and the acceptor $p\pi$ - or $d\pi$ -orbitals; since the d -electrons

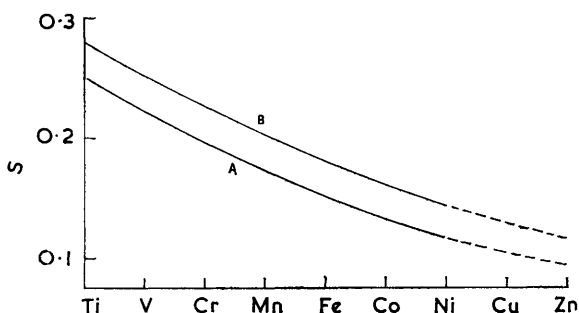


FIG. 4. $d\varepsilon$ - $2p\pi$ Overlap integrals for metals in the d^n -configuration with carbon $2p\pi$ -orbitals (exponent 1.625) at a distance 3.46 a.u. (A) Free-atom d -orbital exponents. (B) d -Orbitals expanded to $\alpha = 0.9$. The broken regions apply to the $d^{10}s^1$ - and $d^{10}s^2$ -configurations of Cu and Zn, the values for the latter being extrapolated.

become steadily more contracted in the heavier metals, the overlap of $d\varepsilon$ -orbitals with ligand π -orbitals becomes less, and π -electron withdrawal is reduced and the rare-gas rule will not apply. This is illustrated in Fig. 4 giving the $d\varepsilon$ - $p\pi$ overlap for first-series transition metals with carbonyl groups. The d -orbitals are the simpler two-parameter analytical fits to the SCF wave functions.¹¹

Values for Fig. 4 are calculated both for free-atom parameters, and for d wave functions expanded according to a common scale factor $\alpha = 0.9$, which is the value calculated for chromium, as explained earlier. The expansion should be separately calculated for each case, and would certainly be less in the heavier metals, leading to an even more rapid drop in overlap. Thus the overlap falls sharply towards the end of the series, and is negligible in zinc. The rare-gas rule should apply best in the middle of the first transition series. Departures from the rare-gas rule, in compounds formed with ligands of the carbonyl type, should be in the sense of having fewer electrons than the rare gas in the early transition elements: in the later elements compounds exceeding the rare gas configuration may be expected, because the greater nuclear charge should increasingly stabilise the σ -bonds, as π -donation by the metal is reduced.

It follows also that the rare-gas rule is less likely to hold in positively charged ions. The d -orbitals in the positive ion are more contracted and their overlap with ligand orbitals is less. A correspondingly increased C-O π -bonding is shown by an increased infrared stretching frequency in the positive ion $[\text{Mn}(\text{CO})_6]^+$ of 2090 cm^{-1} ¹² compared with the isoelectronic neutral molecule $\text{Cr}(\text{CO})_6$ of 1984 cm^{-1} . One can expect, therefore, that positive ions with the rare-gas structure will be confined to the middle and earlier elements

¹¹ Richardson, Nieuwpoort, Powell, and Edgell, *J. Chem. Phys.*, 1962, **36**, 1057.

¹² Fischer and Öpele, *Angew. Chem.*, 1961, **73**, 581.

of the first transition series. Excess negative charge, on the other hand, should increase $d\pi-p\pi$ overlap, and should give rise to rare-gas configurations more commonly. The decreased carbonyl stretching frequency in the negative ions $[\text{Fe}(\text{CO})_4]^{2-}$ and $[\text{Co}(\text{CO})_4]^-$ of 1788 and 1883 cm^{-1} , respectively, compared with $\text{Ni}(\text{CO})_4$ 2046 cm^{-1} agree with this point of view.

The calculations suggest that penetration by the ligand's lone pair into the electron cloud of the metal causes an expansion of the $d\varepsilon$ -orbitals, so increasing overlap with the ligand π -orbitals; it thus facilitates electron-withdrawal. In a comparison of different ligands the nature of the lone-pair hybrid orbital, and the bond distance between the metal and the ligand are likely to be important among the conditions for the rare-gas rule. The results in Table 2 show that $d\varepsilon$ -orbitals are expanded more when the carbon lone pair electrons have a large amount of p -character. It may readily be shown that the overlap integrals with metal $d\gamma$ -orbitals also increase with increasing p -character in the lone pairs, confirming the view that the degree of orbital expansion is greater the more penetration there is by the lone pair.

A comparison of the same kind can be made between different ligands, by calculating the overlap integrals of the lone-pair orbitals available with the $d\gamma$ metal orbital directed towards it. For this purpose we assume a Slater d -orbital with an effective nuclear charge of 7.5 units. The precise value taken is not of importance to the order in which the various overlap integrals fall. We then find that the overlap integral for an sp -hybrid of carbon at the observed M-C distance in $\text{Ni}(\text{CO})_4$ is 0.20. Essentially the same value would apply to an alkyl isocyanide as ligand. For an sp^3 lone pair of nitrogen in ammonia as ligand it is 0.17, for an sp nitrogen lone pair in nitric oxide it is 0.22, and for an sp^3 oxygen lone pair in water (H_2O) it is 0.12. The lone pair overlaps in systems where there is also π -bonding are increased because the bond lengths are shortened, and the difference between the values for ammonia and nitric oxide reflects the change in bond length as well as a change in hybridisation. One can see that there is a sensitive mutual influence of the σ - and π -bond components. π -Bonding is increased by the effect on metal $d\varepsilon$ -electrons of the penetration by the ligand σ -bonding lone pair; this replaces the usual statement that lone pair donation in a σ -co-ordinate bond facilitates back-donation in π -bonding.

Conclusions.—Our conclusions may be summarised as follows:

(i) In complex-formation by σ -lone-pair ligands attainment of a rare-gas configuration is expected to be a significant factor in the energetics determining which complexes will or will not be formed only if the ligands, or some of them, are capable of withdrawing d -electrons from the transition-metal core. The possibilities of such a withdrawal are less both at the beginning and at the end of the transition series than at the centre.

(ii) The conditions in which the rule holds for positive ions are more restrictive than for neutral molecules. Examples should be limited to the early part of the transition series. The conditions for negative ions are less restrictive.

(iii) The relative ability of different ligands in giving complexes with the rare-gas configuration should depend mainly on two factors, (a) the power of the lone pair used in σ -bonding to expand the $d\varepsilon$ -orbitals, which increases with increasing p -character in the hybrid, and (b) their electron-withdrawing power into π -orbitals.

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