# THE COÖRDINATING TENDENCY OF THE METALLIC IONS[1]

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The postulate of coördinate valence, conceived by Alfred Werner in 1893 and stated in terms of the electron theory by Sidgwick thirty years later, has now become one of the foundation stones of chemical thought. Originally devised to explain the existence of metal ammines and similar compounds, it is now used in every field of chemistry, and coördinate valence is recognized as one of the fundamental modes of atomic and ionic union. Yet there are many questions concerning coördination which the coördination theory does not explain. It is the purpose of this paper to call attention to a few of those questions, especially some involving coördinated metallic ions.

These "complex" ions are much more common than is usually realized. Many compounds ordinarily regarded as "simple" are in reality complex, as physical-chemical investigations amply show. For example, electrolysis of scandium sulfate solution shows that even in dilute solution part of the scandium is in the anion, so that the formula for the salt should evidently be written $Sc[Sc(SO_4)_3]$ (26). The parallel case of cadmium iodide is well known. Coördinated metal compounds vary in stability from those which are not decomposed at red heat (for example, some of the acetylacetonates) to those which exist only in the presence of excess of their components. The latter group is typified by the "double salts," which give analytical tests for the simple ions and at the same time give indications of complex ion formation. The interesting work of McBain and Van Rysselberghe (17) should be mentioned in this connection. These investigators reported that in the electrolysis of mixtures of salts, one of the metal ions frequently migrates to the anode, and must therefore be part of an anionic complex. For example, in a solution 0.95 molar in potassium sulfate and 0.05 molar in magnesium sulfate, the magnesium migrates toward the anode. In other cases the migration of the ion toward the

cathode is greatly hindered, but not reversed. Their interpretation has been criticized by Freed and Kasper (10) and by Houlton and Tartar (12). Freed and Kasper measured the magnetic susceptibilities of solutions of potassium sulfate and manganous sulfate and of mixtures of the two. On the assumption that complex formation would be accompanied by a decrease in magnetic susceptibility (an assumption which later work has been shown to be questionable (19)), they concluded that no complex ion was formed in the mixture, although transference experiments showed that the migration of the manganous ion toward the cathode was greatly surpressed. They attribute this effect to a clustering of sulfate ions around the manganous ion. Houlton and Tartar (12) studied the Raman spectra of solutions of potassium and manganous sulfates and mixtures of them, and found that the mixtures gave no Raman lines which were not given by the pure salts, from which they concluded that no complexes are formed between the two. In interpreting experiments like those of Freed and Kasper and of Houlton and Tartar it should be kept in mind that solutions of manganous salts do not contain the simple manganous ion, but a hydrated manganous ion, or possibly the $Mn(SO_4)_2^{--}$ ion, so that the manganese–oxygen coördinate bond is present before the other sulfate is added.

Werner supposed that each element and ion has a definite coördination number—that is, that it can surround itself with a definite number of coördinating groups. Werner's coördination numbers range from two to twelve, with six as the most common. While this assumption clears up many difficulties, it leaves many others completely unexplained. Compounds such as $ThCl_4 \cdot 20NH_3$ (29) and $Na_2CO_3 \cdot 10H_2O$ do not fit into the scheme at all. Werner made various assumptions to bring these exceptions into line with his theory—he assumed "double molecules" occupying one coördination position and molecules of solvent being held mechanically to a salt without definite chemical union—but in many cases even these assumptions failed to make the theory fit the facts. Some interesting work along this line has been done by Peters (20), who has shown from a large number of examples that when dry salts take up ammonia, the number of ammonia molecules held is frequently six or a multiple of six. In the latter case he assumes that both the cation and anion combine with ammonia. Spectral comparison of $CuCl_2 \cdot 6NH_3$ and $CuPtCl_6 \cdot 18NH_3$ indicates to him that only six molecules of ammonia are attached to the copper ion in the latter compound. The chloroplatinate ion must then hold twelve molecules. The spectral studies may be open to criticism because they were carried out in rather dilute aqueous solution, in which part of the ammonia might well have dissociated from the molecule. However, the solid salts are nearly the same color, the slight difference probably

being due to the color of the chloroplatinate ion.  If we accept Peters'
conclusion, we must agree that the coördination number of platinum be-
comes eighteen, or that the twelve ammonia molecules are attached to
the chloride ions (thus expanding the chloride octet to ten or twelve), or
that they are held in place by some force as yet unexplained.  Peters' re-
sults, however, might also be explained by assuming that the cupric ion
can coördinate triple as well as single ammonia molecules without sensibly
changing the color of the complex, which is due to the linkage of the
copper with the nitrogen.

Pfeiffer and Tappermann (25) have carried out similar studies, using
the tridipyridyl and tri-ortho-phenanthroline complex ions of nickel, iron,
cobalt, zinc and cadmium.  Salts of these ions crystallize with large
amounts of water, at least part of which (usually six molecules) is attached
to the positive ion, although the normal coördination number of the metal
is satisfied by the three molecules of the organic amine.

Brintzinger and Osswald (2), by a study of dialysis coefficients, have
shown that hydration effects of this sort frequently occur in solution.
Thus, the triethylenediamine cobaltic ion seems to exist in solution as
$[Co\,en_3(H_2O)_{12}]^{+3}$.  Surprisingly, the closely related hexammine cobaltic
ion $[Co(NH_3)_6]^{+3}$ is not hydrated.

Using the same technique, Brintzinger and Ratanarat (3) found that
many of the "simple" ions are highly hydrated in solution.  Among the
cations are $[Al(H_2O)_{18}]^{+3}$, $[Fe(H_2O)_{18}]^{+3}$, $[Cr(H_2O)_{15}]^{+3}$, $[Th(H_2O)_{12}]^{+4}$,
and $[Be(H_2O)_{12}]^{+2}$, while some of the commoner anions are $[SO_4(H_2O)_2]^{-2}$,
$[C_2O_4(H_2O)_4]^{-3}$, $[PO_4(H_2O)_{24}]^{-3}$, and $[AsO_4(H_2O)_{24}]^{-3}$.

By means of dialysis experiments Brintzinger and his colleagues (4)
have determined ionic weights of many complex ions, and have shown that
they not infrequently are capable of forming super-complex ions.  Thus,
they write $\{[Cr\,pn_3](SO_4)_4\}^{-5}$, $\{[Co_2pn_6](HAsO_4)_4\}^{-2}$, and many others.
(The symbol "pn" represents propylenediamine.)

It seems quite evident that atoms and ions can have coördination
numbers much greater than Werner suggested, or that several concentric
coördination shells can be held around a single atom.  Such concentric
shells can be formed whenever the coördinating group can act both as
donor and acceptor.  In the hydrates and ammines this is accomplished
through hydrogen bonds.  The interesting compound $A \cdot 16BF_3$ discovered
by Booth and Willson (1a) is probably formed in an analogous way.

That real chemical union exists between such "extra" molecules and
the complex ion has been demonstrated by the stereochemical experiments
of Pfeiffer and Quehl (24).  They showed, for example, that the rotatory
power of zinc $\alpha$-bromo-$\pi$-camphorsulfonate is almost doubled by the addi-
tion of ortho-phenanthroline, which unites with the zinc to form a complex

ion, $[Zn(phen)_3]^{+2}$, in which the zinc is apparently coördinately saturated. Pfeiffer and Quehl say that asymmetry is "induced" in this ion by the presence of the optically active bromocamphorsulfonate ion in the solution. It does not seem possible that this can happen without some sort of union between the two ions. Several other examples of this effect have been reported (23).

Many factors must be taken into account in considering the stability of coördination compounds. The effect of temperature is obvious, and is illustrated by the decomposition of hydrates upon heating. Pressure is an important factor if the coördinating groups are volatile. The nature of the "central ion" of the complex is of extreme importance. In general, the tendency to form coördination compounds is shown most strongly by the transition elements, but is by no means limited to them. Attempts to predict coördinating tendency and coördination number on the basis of the periodic table are not entirely successful, as irregularities frequently appear. Thus the hydroxides of chromium, cobalt, and nickel dissolve in excess ammonium hydroxide, forming ammines, but those of manganese and iron do not. Platinous and palladous ions usually show a coördination number of four, but the nickelous ion, in spite of its smaller size, has a coördination number of six.

The interesting theory of Sidgwick (27) should be mentioned in this connection. It postulates that each ion tends to take up electrons from coördinating groups until it achieves the structure of the next noble gas. Thus the cobaltic ion, having twenty-four electrons, gains an additional twelve by coördinating six groups, and assumes the stable structure of krypton. However, there are several exceptions to the theory, and the tendency to build to a rare gas structure is overshadowed by other considerations. This has been discussed in detail by Mann (16).

The valence of a metal ion frequently influences its coördination tendency. Thus, $PtCl_2$ combines with four molecules of ammonia, but $PtCl_4$ combines with six. Palladous and palladic ions show the same variation. Hantzsch and Rosenblatt (11) have denied that the coördination number varies, suggesting instead that the platinous compound is a "pseudo-salt," $[PtCl_2 \cdot (NH_3)_4]$. In solution water molecules displace the chloride ions from the complex, giving $[Pt(H_2O)_2(NH_3)_4]^{+2}$ and $2Cl^-$. Upon crystallization the reverse reaction takes place. While the theory is supported by a considerable amount of evidence, it has not been tested enough to win widespread acceptance.

The coördinating power of a cation is greatly influenced by the anion with which it is united. This may be illustrated by the compounds of barium, of which the chloride and bromide form stable hydrates with two molecules of water, the iodide with six, and the hydroxide with eight.

The relative sizes of the ions are altered by hydration until a close-packed crystal lattice can be formed.

The nature of the anion may also influence the union of neutral molecules with metallic ions in another way. The anion may lose its ionic nature, in whole or in part, by coördinating with the cation, this occupying part of its coördination sphere and altering its properties. Thus, triethylenediamine chromic chloride is stable above 200°C., but the corresponding thiocyanate loses one molecule of ethylenediamine at 160°C., forming [Cr en₂(SCN)₂]SCN (22). Effects of this sort sometimes make it difficult to determine the true coördination number of a metallic ion.

The nature of the coördinating ("donor") group is one of the most important factors in determining the stability of coördination compounds. It is not possible, however, to arrange the various donor groups in a series in the order of their coördinating power, for this changes as the coördinated metal ion is changed. The cyanide ion forms very stable complexes with ferrous and ferric ions, and much less stable ones with nickel ion. On the other hand, ammonia coördinates much more readily with nickel than with ferrous or ferric ions. No satisfactory explanation of this has been advanced.

The nature of the donor group may even determine the coördination number of an ion, as Mann (16) has shown. Zinc, platinous, and palladous ions normally coördinate only four amine groups, but form very stable hexammine complexes with $\alpha,\beta,\gamma$-triaminopropane, utilizing all six of the amine groups from two triaminopropane molecules.

Almost any neutral or negative group which has a pair of unshared electrons may act as a donor group. The most important neutral groups are ammonia, organic amines, water, alcohols, and organic sulfides. However, hydrogen sulfide, phosphine, aliphatic phosphines and arsines, ketones, unsaturated hydrocarbons, and many other compounds can act as donor groups. Even phosphorus trichloride is known to form coördination compounds (7). Of the negative groups, cyanide, thiocyanate, hydroxide, and the halide ions are most frequently encountered, but almost any negative ion can function as a donor group.

If the donor group forms a chelate ring with the metal ion, the strength of the union is much enhanced. Ethylamine coördinates weakly, but ethylenediamine forms very stable compounds. Complex compounds of pyridine are much less stable than those of dipyridyl. This effect is shown, however, only if the chelate ring contains five or six members. Decamethylenediamine has very little tendency to coördinate. A complete discussion of the chelate rings may be found in the recent paper of Diehl (8).

The coördinating ability of acetylacetone deserves special mention. Not only does acetylacetone coördinate with a very large number of positive

ions, including its own enolic hydrogen ion, but some of its compounds are characterized by an unparalleled degree of stability. This may be due to resonance of the carbon–carbon double bond in the chelate ring.

Tables 1 to 7 have been compiled to indicate the coördinating power of some of the more common donor groups. Those elements whose symbols are set in bold-face type form definite linkages with the group in question, while those elements whose symbols are set in italics form unstable or questionable compounds. Elements not so designated may form such linkages, but the literature seems to contain no mention of them. Water, the simpler alcohols, ammonia, and the halide ions coördinate with practically all of the metals, so tables were not prepared for them. Naturally, these coördination compounds vary greatly in stability, but quantitative measurements of stability have been made in very few cases. The ammines of some of the Group VIII metals are remarkably stable; thus, hexammine cobaltic chloride can be recrystallized from concentrated hydrochloric acid or warmed with sodium hydroxide solution without decomposition.

Among the halide ions the fluoride ion is the most interesting, because the metals usually show their highest coördination number when in union with fluorine.

The complex cyanides (table 1) present a compact group when arranged according to the Bohr periodic table. The metals in the center form the most stable cyanides, the stability decreasing rather uniformly as we proceed in either direction. Molybdenum and tungsten show a coördination number of eight toward the cyanide ion; for vanadium, chromium, and the metals of Groups VII and VIII this drops to six, and for the elements of the copper and zinc groups it is only four. It is hardly safe to generalize, but many examples could be cited to indicate that the coördination number of these transition elements tends to decrease as we proceed toward the right. This agrees qualitatively with Sidgwick's theory. There are so many exceptions, however, that it can hardly be taken as support of the theory.

Most of the metallic ions form compounds with the aliphatic amines (table 2). The simpler primary amines coördinate as firmly as ammonia itself (21), the stability of the union decreasing as the length of the carbon chain increases. Diamines coördinate more firmly than monoamines if they form suitable chelate rings. Secondary amines have less tendency to coördinate than primary amines; in tertiary amines (except heterocyclics) the tendency is almost lost. It appears very strongly with pyridine, ortho-phenanthroline, and similar bases (table 3).

The nitrite ion forms many very stable complexes (table 4). In most of these we have a nitrogen -metal bond rather than an oxygen–metal

## TABLE 1
### *Cyanides*

| | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | H | | | | | | | | | | | | | | | | | He |
| 2 | Li | Be | | | | | | | | | | | Be | B | N | O | F | Ne |
| 3 | Na | Mg | | | | | | | | | | | Al | Si | P | S | Cl | A |
| 4 | K | Ca | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn | Ga | Ge | As | Se | Br | Kr |
| 5 | Rb | Sr | Yt | Zr | Cb | Mo | Ma | Ru | Rh | Pd | Ag | Cd | In | Sn | Sb | Te | I | X |
| 6 | Cs | Ba | RE* | Hf | Ta | W | Re | Os | Ir | Pt | Au | Hg | Tl | Pb | Bi | Po | | Nt |
| 7 | | Ra | Ac | Th | U$^x$ | U | | | | | | | | | | | | |

*RE = rare earths.

## TABLE 2
### *Aliphatic amines*

| | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | **H** | | | | | | | | | | | | | | | | | He |
| 2 | **Li** | **Be** | | | | | | | | | | | **B** | C | N | O | F | Ne |
| 3 | Na | **Mg** | | | | | | | | | | | Al | *Si* | P | S | Cl | A |
| 4 | K | Ca | Sc | Ti | V | Cr | Mn | **Fe** | **Co** | Ni | **Cu** | Zn | Ga | **Ge** | As | Se | Br | Kr |
| 5 | Rb | Sr | Yt | **Zr** | Cb | Mo | Ma | **Ru** | **Rh** | **Pd** | **Ag** | **Cd** | **In** | **Sn** | **Sb** | Te | I | X |
| 6 | Cs | Ba | RE | Hf | Ta | W | Re | Os | **Ir** | **Pt** | **Au** | **Hg** | **Tl** | **Pb** | **Bi** | **Po** | | Nt |
| 7 | | Ra | Ac | **Th** | U$^x$ | U | | | | | | | | | | | | |

## TABLE 3
*Pyridine, phenanthroline, etc.*

| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | **H** | | | | | | | | | | | | | | | | | He |
| 2 | Li | **Be** | | | | | | | | | | | **B** | C | N | O | F | Ne |
| 3 | Na | **Mg** | | | | | | | | | | | **Al** | Si | **P** | S | F | A |
| 4 | K | *Ca* | Sc | **Ti** | V | **Cr** | **Mn** | **Fe** | **Co** | **Ni** | **Cu** | **Zn** | Ga | Ge | **As** | Se | Cl | Kr |
| 5 | Rb | Sr | **Yt** | **Zr** | Cb | **Mo** | **Ma** | **Ru** | **Rh** | **Pd** | **Ag** | **Cd** | **In** | **Sn** | **Sb** | Te | Br | X |
| 6 | Cs | Ba | **RE** | Hf | **Ta** | *W* | **Re** | Os | **Ir** | **Pt** | **Au** | **Hg** | **Tl** | **Pb** | *Bi* | Po | I | Nt |
| 7 | | Ra | Ac | **Th** | Uˣ | **U** | | | | | | | | | | | | |

## TABLE 4
*Nitrites (nitro)*

| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | H | | | | | | | | | | | | | | | | | He |
| 2 | Li | Be | | | | | | | | | | | B | C | N | O | F | Ne |
| 3 | Na | Mg | | | | | | | | | | | Al | Si | P | S | Cl | A |
| 4 | K | *Ca* | Sc | Ti | V | **Cr** | **Mn** | **Fe** | **Co** | **Ni** | **Cu** | *Zn* | Ga | Ge | As | Se | Br | Kr |
| 5 | Rb | *Sr* | Yt | Zr | Cb | Mo | Ma | **Ru** | **Rh** | **Pd** | Ag | **Cd** | In | Sn | Sb | Te | I | X |
| 6 | Cs | *Ba* | RE | Hf | Ta | W | Re | **Os** | **Ir** | **Pt** | Au | **Hg** | Tl | Pb | *Bi* | *Po* | | Nt |
| 7 | | Ra | Ac | Th | Uˣ | U | | | | | | | | | | | | |

## TABLE 5
*Unsaturated hydrocarbons*

| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | H | | | | | | | | | | | | | | | | | He |
| 2 | Li | Be | | | | | | | | | | | **B** | C | N | O | F | Ne |
| 3 | Na | Mg | | | | | | | | | | | **Al** | Si | P | S | Cl | A |
| 4 | K | Ca | Sc | Ti | V | Cr | Mn | **Fe** | Co | *Ni* | **Cu** | Zn | Ga | Ge | **As** | Se | Br | Kr |
| 5 | Rb | Sr | Yt | Zr | Cb | Mo | Ma | Ru | Rh | **Pd** | **Ag** | Cd | In | Sn | **Sb** | Te | I | X |
| 6 | Cs | Ba | RE | Hf | Ta | W | Re | Os | **Ir** | **Pt** | Au | **Hg** | Tl | Pb | Bi | Po | | Nt |
| 7 | | Ra | Ac | Th | Uˣ | U | | | | | | | | | | | | |

## TABLE 6
*Amino acids*

| | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | *H* | | | | | | | | | | | | | | | | | He |
| 2 | *Li* | Be | | | | | | | | | | | B | C | N | O | F | Ne |
| 3 | *Na* | *Mg* | | | | | | | | | | | Al | Si | P | S | Cl | A |
| 4 | *K* | *Ca* | Sc | Ti | V | **Cr** | Mn | Fe | **Co** | **Ni** | **Cu** | **Zn** | Ga | Ge | As | Se | F | Kr |
| 5 | *Rb* | *Sr* | Yt | Zr | Cb | Mo | Ma | Ru | Rh | Pd | Ag | *Cd* | In | Sn | *Sb* | Se | Br | X |
| 6 | *Cs* | *Ba* | *RE* | Hf | Ta | W | Re | Os | Ir | **Pt** | *Au* | **Hg** | Tl | Pb | Bi | Po | I | Nt |
| 7 | | Ra | Ac | Th | U× | U | | | | | | | | | | | | |

## TABLE 7
*d-Tartaric acid*

| | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | H | | | | | | | | | | | | | | | | | He |
| 2 | Li | **Be** | | | | | | | | | | | **B** | C | N | O | F | Ne |
| 3 | Na | Mg | | | | | | | | | | | **Al** | Si | P | S | Cl | A |
| 4 | K | Ca | Sc | **Ti** | V | Cr | **Mn** | **Fe** | **Co** | Ni | Cu | Zn | Ga | Ge | **As** | Se | F | Kr |
| 5 | Rb | Sr | Yt | **Zr** | **Cb** | **Mo** | Ma | Ru | Rh | Pd | Ag | Cd | In | Sn | **Sb** | **Te** | Br | X |
| 6 | Cs | Ba | **RE** | **Hf** | Ta | W | Re | Os | Ir | Pt | Au | Hg | Tl | **Pb** | **Bi** | Po | I | Nt |
| 7 | | Ra | Ac | **Th** | U× | U | | | | | | | | | | | | |

bond, and the group is properly referred to as a "nitro" group. This has been proven by Chernyaev, who has reported that platinous nitro compounds can be reduced to platinous ammines by zinc and either hydrochloric or acetic acid (5). The metal–nitrogen bond must be present before reduction takes place, as ammonia will not coördinate with the metal ion in an acid solution.

Jorgensen prepared "nitrito" cobaltic complexes (13), containing an oxygen–cobalt bond. These are not stable, however, and rearrange to the isomeric nitro compounds.

The coördination of unsaturated hydrocarbons with metal ions (table 5) is of great theoretical interest, because electrons have to be withdrawn from the double bond before coördination is possible. (See, for example, the work of Anderson (1) and of Kharasch and Ashford (14).) This, however, leaves one of the carbon atoms with only a sextet. It is possible in some cases that this carbon atom is coördinated to the metal, in which case the metal is the "donor," rather than the "acceptor." Most of the theoretical work has been done on the platinum–olefin complexes, but many of the others are equally stable. Anhydrous aluminum and iron chlorides catalyze the Friedel–Crafts reaction through the formation of compounds of this type. Gallium chloride also catalyzes this reaction (28) and probably in the same way. No compounds have been isolated, however. The mercury–olefin compounds are of interest as intermediates in organic syntheses.

Other unsaturated organic groups may also coördinate with metal ions. The azo dyes unite with the mordant through the nitrogen–nitrogen double bond (9).

The amino acids (table 6) may coördinate with metal ions through the —$NH_2$ groups, or through the amino and carboxyl groups simultaneously. In the latter case, $\alpha$-amino acids give extremely stable chelate rings. Cobalt alanine, for example, can be recrystallized from hot 50 per cent sulfuric acid (15). The interesting stereochemical possibilities offered by these compounds have been studied to some extent in the cases of cobalt and chromium. They offer a fertile field for research.

The hydroxy acids also form chelate rings. Tartaric acid (table 7) has found several applications as a coördinating agent. Its use in Fehling's solution is well known. It has recently been shown (18) that beryllium can be separated from aluminum, iron, copper, and chromium by precipitating it from a tartrate solution with ammonium hydroxide. The other metals do not precipitate. Still a third application is that of deBoer and Emmens (6), who have developed an interesting polarimetric method of determining the relative amounts of zirconium and hafnium in a mixture

through the formation of optically active complex ions with dextrotartaric acid.

Tables might be prepared for many other donor groups, but the ones given suffice to bring out most of the periodic regularities and to indicate points at which research can profitably be undertaken.

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