THE ACID-BASE PROPERTIES OF COMPLEX IONS

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I. GENERAL

Although the term "complex" has been most often restricted to such particular classes of structures as the ammines, halides, etc. to which Werner gave the greater part of his attention, it is often useful to extend its meaning. Werner himself pointed out the essential similarity of such acids as H_2SO_4, HBF_4, and $H_2[PtCl_4(OH)_2]$, and even described HCl and KOH as merely the anhydro forms of the corresponding "true" or aquo acid and base concerned. Indeed, in attempting to discuss the protolysis of ions in water solution, one is inclined to include Fe^{+++} (as $[Fe(H_2O)_x]^{+++}$) and H^+ (as $[H_3O(H_2O)_x]^+$) on the same terms as $[Cr(NH_3)_6]^{+++}$ and NH_4^+. The difficulty is to find an ion to which the logically extended term "complex" does not apply. Probably such large and apparently slightly hydrated elementary ions as Cs^+ and I^- approach most nearly to this condition.

Present-day viewpoints permit a partial understanding of acid-base properties in terms of the same concepts as are necessary to account for the existence and relative stability of complex compounds,—indeed of compounds, radicals, and molecules in general. Adopting, for example, Mulliken's (30) formulation:—"Every nucleus (in a molecule) tends to be surrounded, by means of sharing or transfer of electrons, by an electron distribution corresponding to some stable configuration having a total charge approximately equal to or somewhat exceeding the charge of the nucleus";—it is evident that the vast majority of atoms have attained this state, some by the formation of "simple" ions (Na^+, Cl^-) or molecules (C_6H_6) and others by the formation of such typical *complexes* as $[Fe(CN)_6]^{---}$, $[Cu(NH_3)_4]^{++}$, HBF_4, HSO_4^-, $[S_x]^{--}$, $[Fe(H_2O)_x]^{+++}$, or R_3NH^+. The tendency of any particular complex to form is calculable in principle from a knowledge of the valence states of the atoms in the complex, the energies of these states, and like data for the atomic configuration which preceded the one we are studying. Tables of such valence state energies, and of relative electronegativities of atoms, have been given by Mulliken (30, 31) and others. The relative electronegativity of an atom depends equally on its ionization potentials and its electron affinity, and the same is true of molecules. Thus any molecule or atom will have some tendency to act as an electron donor (34) (and reductant) and also as an electron acceptor (and oxidant). The balance between these tendencies determines many of the most important properties of the molecule. Electron donation or reducing character naturally tends to increase quite regularly with the negative charge on the molecule, and to change in less simple ways with its pattern and the relative charges, sizes, and polarizabilities of the atoms it contains. For a discussion of these effects Ingold's (21) recent paper in this journal may be consulted. The same author has emphasized the point that protolytic reactions are also manifestations of the same mechanisms, so that in general, where one molecule is more of a donor or reductant than another, it may also be expected to be a stronger protophile or base. The general terms "nucleophilic" and "electrophilic" are proposed to designate these tendencies.

For the student of acid-base behavior the properties of the solvent are of paramount importance. This is seen, for example, both in the formation of acids in Brønsted's sense from molecules which in themselves contain no hydrogen (cf. $SO_3 + 3H_2O \rightarrow 2H_3O^+ + SO_4^{--}$ and $Fe^{+++} + nH_2O \rightarrow [FeOH(H_2O)_{n-2}]^{++} + H_3O^+$) and in other chemical respects, as well as in the influence it exerts through its dielectric properties on the thermodynamic properties of dissolved electrolytes.

In spite of Brønsted's success in giving to acid-base reactions a formulation sufficiently general to apply to all solvents, the great bulk of attention in this field, as in others, still remains centered upon water solutions.

It is therefore peculiarly gratifying that certain very important recent studies (2, 14, 39) have thrown new light on the peculiarities of this important solvent. Most liquids in the neighborhood of their freezing points seem to retain traces of crystalline order in the form of a "swarm" or "cybotactic" structure (38). This effect becomes much more marked when dipole interaction, hydrogen-bond formation, or resonance results in definite association into chains, as in alcohols, into polymers, as in carboxylic acids (36), or an actual tetrahedral (tridymite) structure of the swarm, as in cold water (2, 14, 39). This structure involves ionization at the ends only of any continuous chain running through the swarm, and explains the remarkably low conductivity of a substance so rich in mobile protons as water. The structure is thermolabile, so that conductance, hydrolysis, fluidity, and many other properties show a marked dependence on temperature, and is apparently also extremely sensitive to the depolymerizing effect of dissolved ions,—an effect that appears to extend over a considerable distance. According to Ulich (39) ions of sufficiently high ionic potential (Cartledge (11)) to be strongly solvated (H^+, Li^+, Na^+, etc.) show low mobility in all solvents because of the increase in their effective radii due to solvation. The large ions like Cs^+ and ClO_4^-, which are only slightly solvated, show normal mobilities in non-aqueous solvents, but high mobilities in water. The latter phenomenon is explained by the depolymerizing effect which the ion-dipole interaction with the solvent has on the exceptionally complete swarm structure of water, so that each ion becomes surrounded by a "private space," the viscosity of which corresponds to that of depolymerized water instead of to that of the solution as a whole. Many interesting relationships are given in Ulich's paper, which should be consulted for further details.

Although the structures of such hydrates as $CuSO_4 \cdot 5H_2O$ and $NiSO_4 \cdot 7H_2O$ in the solid state have recently been shown (3) to be in excellent agreement with such views as Sidgwick's (35), it is probably still impossible to give a physical meaning to the statement that the formula of the cupric ion *in water* is $[Cu(H_2O)_4]^{++}$, while that of the nickel ion is $[Ni(H_2O)_6]^{++}$ (29). Such definite formulas are not at all necessary to an understanding of acid-base behavior, but are definitely a convenience as will appear below.

In solvents other than water the problems of solvation and solvolysis are at least as difficult as in water solution and have been much less studied. Kraus (24) has discussed at length the nature of the ions in these solutions and clearly indicated the difficulties of the problem.

Within very recent years the work of Sir Harold Hartley and his associates has done much to supplement the earlier researches of Goldschmidt, Walden, Franklin, Kraus, etc. on the conductance of such systems, and writers such as Sidgwick and Davies have contributed interesting suggestions.

Fundamentally, as stated above (21), the effect of different solvents on a solute depends on the relatively electrophilic or nucleophilic character of the solvent, i.e., a solvent that can act as an electron donor, base, or reducer will compete for and promote the formation of possible cations of the solute in quite a different way from one which is only an acceptor, an acid, or an oxidizing agent. Hydroxylic and other amphiprotic solvents will also have a large self-buffering action (seen to the best advantage in H_2SO_4). Also dependent on this electronegativity balance will be the dielectric constant of the solvent, which will determine the tendency to ion-association (Bjerrum, Fuoss), and in the case of protolytic equilibria will determine the gross changes in the relative strength of acids which occur when acids of different charge type are transferred from one solvent to another (7). Wynne-Jones, (42) Schwarzenbach and Egli (33), and Hammett (41) have recently shown how the less striking but very important changes of relative strength among acids of the *same charge type* may be correlated with the structures of the acids, particularly with the electric moments of substituent groups.

A very interesting problem is presented in each solvent by the ions formed by the solvent itself. The fact that these ions have abnormal mobilities in water and some other solvents has led to two views: (1) that they are relatively little solvated, and (2) that they conduct in part by a Grotthuss chain mechanism. This latter view has been recently revived by Hückel (19) and by Fowler (2, 14) for aqueous solutions, but was adversely criticized by Kraus (24), and lately by others on the basis of results in deuterium oxide. Hammett (18), however, has redirected attention to the possibility (Latimer and Rodebush (28)) that whether or not "abnormal" mobility makes its appearance may depend on the basic strength of the solvent. Probably both the acid and basic strength of the solvent is involved, so that the phenomenon is striking in water, formic acid, and sulfuric acid (18) but less so in ammonia, pyridine, or the alcohols. The well-known effect of small quantities of water on the conductance of acids and some salts in the alcohols has recently been restudied by Hughes and Hartley (20), who give an interesting general discussion of these effects.

II. COMPLEX METAL CATIONS

Complex ions first made their appearance in chemical theory to explain (1) the virtual disappearance of the properties of, for example, Fe^{++} ion in ferrocyanide solution, and (2) the anomalous results of transference studies in which certain usually positively charged elements apparently migrated toward the positive electrode. The real heyday of the complex compounds only began, however, with Werner's studies of the hydrates and ammines. The remarkable stability of the latter led Werner to develop a powerful new theory of valency, and to enrich almost every department of chemistry with his ideas. The subject of acids and bases was often uppermost in his mind. Thus we find that his attention was attracted by a group of compounds (40) whose behavior could be explained by assuming that they contained the ten series of cations shown in table 1. On examination he found that: (1) Only the first series are able to precipitate silver oxide from silver nitrate. (2) Only the first three series liberate ammonia from NH_4^+ in the cold. (3) Only the first five series absorb carbon dioxide. (4) The first eight series react alkaline to litmus, the other two neutral. (5) The first eight series are more soluble in acetic acid than in water. From solutions of 1, 2, and 3, metallic salts precipitate aquo salts, but from solutions of 4, 5, 6, 7, and 8, hydroxo salts are precipitated. (6) All the series appear to form aquo salts with mineral acids, which are usually precipitated as such by metallic salts, but from the last two series only hydroxo salts are reprecipitated.

This beautiful group of semiquantitative results interpreted in the light of later knowledge shows: (1) The central atom confers acid strength in the diminishing order Pt^{IV}, Ru^{IV}, Cr^{III}, Co^{III}. (2) As would be expected, the total charge of the strongest base is low (+1) while the weakest has a charge of +2, but constitutive influences seem to overcome the effect of the charge in several cases. (3) The presence of aquo groups seems to increase the acid strength of the corresponding acids to an extent roughly proportional to their number. (4) The equilibrium constant (no concentrations are given) for the reaction

$$\text{aquo-cation} + H_2O \rightleftharpoons \text{hydroxo-cation} + H_3O^+$$

may be roughly estimated from the results reported below:

series	*constant*
1	10^{-6}
2–3	10^{-6} to 10^{-5}
4–5	10^{-4} to 10^{-3}
6–8	10^{-2} (*circa*)
9–10	10^{-2} to 10^{0}

TABLE 1

Werner's series of basic cations

SERIES	CATION	SERIES	CATION
1	$[Co(NH_3)_4(NO_2)OH]^+$	6	$[Cr(NH_3)_2H_2O)_3OH]^{++}$
2	$[Co(NH_3)_5OH]^{++}$	7	$[Cr(NH_3)_2(H_2O)_2(OH)_2]^+$
3	$[Co(NH_3)_4(H_2O)OH]^{++}$	8	$[Co(NH_3)_2py_2(H_2O)OH]^{++}$
4	$[Coen_2(H_2O)OH]^{++}$(1,2-)	9	$[Ru(NH_3)_4(NO)OH]^{++}$
5	$[Coen_2(H_2O)OH]^{++}$(1,6-)	10	$[Pt(NH_3)_4(OH)_2]^{++}$

Largely guided by these results, Werner proposed his hypothesis that equilibria exist in solution between water, the hydroxo salts, and the corresponding aquo compounds, and later broadened this conception into a new comprehensive theory of acids and bases. The equilibria postulated by Werner may be written

$$\text{hydroxo-cation} + H_2O \rightleftharpoons \text{aquo-cation} + OH^-$$

and

$$\text{hydroxo-cation} + H_3O^+ \rightleftharpoons \text{aquo-cation} + H_2O$$

It was natural that these mechanisms should seem to Werner of great significance and that he should have concluded that *all* metallic hydroxides are anhydro bases, becoming "true" or aquo bases only on solvation, while acids like hydrochloric he also assumed were anhydro acids. These ideas shocked the convinced followers of Arrhenius at the time, and Lamb in

1921 could write (27), "this theory has apparently found such scant acceptance that only a brief discussion of it . . . is required." Indeed, in the form proposed, Lamb was able to show that it involved "gratuitous and arbitrary assumptions" in many cases. I think it is fair to say now that the special form of the theory has no particular appeal, while many of its substantial ideas are wholly consistent with present views.

With Larson in 1920, Lamb (26) determined the relative stabilities of several cobaltic ammines, finding that the dissociation into simple cobaltic ions, ammonia, and other products decreased in the order shown in table 2. The concentration dissociation constants are very small ($K_c = 2.2 \times 10^{-34}$ in the case of the hexammine), as is indicated by the well-known stability of these groups in ordinary chemical operations. It is, of course, to be expected that those cations with the greatest tendency to liberate ammonia should be the weakest acids and this is in general the case, as indicated in table 6. The same authors also determined the dissociation constant of *cobaltous* hexammine, and give the list shown in table 3 for comparison. These complexes, being much more highly dissociated, should evidently be still weaker acids.

TABLE 2

Relative stabilities of cobaltic ammines

(1) $[Co(NH_3)_4(NO_2)_2]^+$(1,6-)	(4) $[Co(NH_3)_4(NO_2)_2]^+$(1,2-)
(2) $[Co(NH_3)_6]^{+++}$	(5) $[Co(NH_3)_4(H_2O)_2]^{+++}$
(3) $[Co(NH_3)_5(NO_2)]^{++}$	(6) $[Co(NH_3)_5(H_2O)]^{+++}$

TABLE 3

Dissociation constants of ammines

AMMINE	K_c
$Ag(NH_3)_2^+$	6.8×10^{-8}
$Cu(NH_3)_2^+$	1.5×10^{-9}
$Cd(NH_3)_4^{++}$	1.0×10^{-7}
$Zn(NH_3)_4^{++}$	2.6×10^{-10}
$Co(NH_3)_6^{++}$	1.25×10^{-5}

Much work has been done on the vapor tensions of ammines, and a particularly interesting series of results is given by Spacu and Voichescu (37). In a study of certain ammoniates of the thiocyanate, formate, acetate, chromate, glycolate, and other salts of Cu^{++}, the strength of the bond between the metal ion and ammonia was found to be inversely proportional to the base strength of the anion of the salt, under otherwise comparable conditions, while many other structural influences were also apparent.

Bjerrum (4), in 1906, gave 0.89×10^{-4} as the constant at 25°C. of the reaction

$$Cr(H_2O)_6^{+++} + H_2O \rightleftharpoons Cr(H_2O)_5OH^{++} + H_3O^+$$

and Denham (12), in 1908, gave a value about twice as great. With Fonda (25), Lamb made several determinations of this quantity, arriving at an average value of 1.58×10^{-4} at 25°C. The later determination by Brønsted and Volqvartz (9) lies in the same range.

A broader attack on the acidity problem was made in collaboration with Victor Yngve (27). Lamb and Yngve determined the conductance ratio $\alpha = \frac{\lambda_v}{\lambda_0}$ for a series of hydroxides of cobaltammine cations at 0°C., finding that many of the bases were apparently as highly ionized as the hydroxides of the alkalis. Their series is presented in table 4. These values are for the hydroxides of the cations as written. If the more probable assumption (rejected by Lamb) is made, that the aquo-cations are transformed to hydroxo compounds in Werner's sense, the more useful figures (α') in the third column are obtained.

TABLE 4

Conductance ratio of a series of hydroxides of cobaltammine cations

NO.	CATION	α (PER CENT) ($1.33 \times 10^{-3}M$)	α' (PER CENT)
1	$[Co(NH_3)_4CO_3]^+$	97.6	
2	$[1,6\text{-}Co(NH_3)_4(NO_2)_2]^+$	95.0	
3	$[Co(NH_3)_6]^{+++}$	89.5	
4	$[Co(en)_3]^{+++}$	88.6	
5	$[1,2\text{-}Co(NH_3)_4(NO_2)_2]^+$	81.2	
6	$[Co(NH_3)_5(H_2O)]^{+++}$	53.5	82.9
7	$[Co(NH_3)_3(H_2O)(NO_2)_2]^+$	36.0	
8	$[Co(en)_2(H_2O)_2]^{+++}$	27.3	84.8
9	$[Co(NH_3)_4(H_2O)_2]^{+++}$	24.6	74.0

Brønsted (8) has called attention to the importance on the one hand of the number of dissociable protons in the acid and on the other of the number of possible points of attachment on the conjugate base. This "statistical factor" appears useful in harmonizing the results of catalytic studies with bases of different charge type (10), although it is not sufficient to explain the whole difference in strength found in a series of otherwise similar trivalent cation acids (Brønsted and Volqvartz (9)).

The last paper referred to is almost the only serious modern attempt that has been made to determine accurately the relative strength of a series of multiply charged cation acids. The substances studied with their dissociation constants at 15°C. are supposedly the tripositive ions (see

TABLE 5

Brønsted and Volqvartz's series of tripositive acids

NO.	ION	$K_a \times 10^6$	NO.	ION	$K_a \times 10^6$
1	$\left[\mathrm{Co}\begin{matrix}\mathrm{H_2O}\\(\mathrm{NH_3})_5\end{matrix}\right]$	2.04	5	$\left[\mathrm{Rh}\begin{matrix}\mathrm{H_2O}\\(\mathrm{NH_3})_5\end{matrix}\right]$	1.38
2	$\left[\mathrm{Co}\begin{matrix}(\mathrm{H_2O})_2\\(\mathrm{NH_3})_4\end{matrix}\right]$	6.03	6	$[\mathrm{Al(H_2O)_6}]$	11.2
3	$\left[\mathrm{Co}\begin{matrix}(\mathrm{H_2O})_3\\(\mathrm{NH_3})_3\end{matrix}\right]$	18.8	7	$[\mathrm{Cr(H_2O)_6}]$	126.
4	$\left[\mathrm{Co}\begin{matrix}(\mathrm{H_2O})_4\\(\mathrm{NH_3})_2\end{matrix}\right]$	400.	8	$[\mathrm{Fe(H_2O)_6}]$	6300.

TABLE 6

Summary of results on the acid strength of the ammino cations

ACID	pK_a (Lamb (0°C.))	pK_a (Werner)	pK_a (Brønsted (15°C.))
$[\mathrm{Co(NH_3)_4CO_3}]^+$			
$[\mathrm{Co(NH_3)_4(NO_2)_2}]^+$(1,6-)			
$[\mathrm{Co(NH_3)_6}]^{+++}$			
$[\mathrm{Coen_3}]^{+++}$			
$[\mathrm{Co(NH_3)_5OH}]^{++}$			
$[\mathrm{Co(en)_2(OH)_2}]^+$	(13)		
$[\mathrm{Co(NH_3)_4(NO_2)_2}]^+$(1,2-)			
$[\mathrm{Co(NH_3)_4(OH)_2}]^+$	(12)		
$[\mathrm{Co(NH_3)_3(NO_2)_2(H_2O)}]^+$	(11)		
$[\mathrm{Co(NH_3)_4(NO_2)(H_2O)}]^{++}$		(6)	
$[\mathrm{Rh(NH_3)_5(H_2O)}]^{+++}$			5.86
$[\mathrm{Cr(H_2O)_4Cl_2}]^{++}$	5.72 (20°C.)	5.42 (Bj.)	
$[\mathrm{Co(NH_3)_5(H_2O)}]^{+++}$		(5–6)	5.69
$[\mathrm{Co(NH_3)_4(H_2O)_2}]^{+++}$		(5–6)	5.22
$[\mathrm{Co(en)_2(H_2O)_2}]^{+++}$(1,2-)		(3–4)	
$[\mathrm{Co(en)_2(H_2O)_2}]^{+++}$(1,6-)		(3–4)	
$[\mathrm{Al(H_2O)_6}]^{+++}$(?)			4.95
$[\mathrm{Co(NH_3)_3(H_2O)_3}]^{+++}$			4.73
$[\mathrm{Cr(H_2O)_6}]^{+++}$(?)	3.80 (25°C.)	4.05 (Bj.) 3.75 (D.)	3.90
$[\mathrm{Co(NH_3)_2(H_2O)_4}]^{+++}$			3.40
$[\mathrm{Cr(NH_3)_2(H_2O)_3OH}]^{++}$		(2–3)	
$[\mathrm{Cr(NH_3)_2(H_2O)_4}]^{+++}$		(2–3)	
$[\mathrm{Co(NH_3)_2py_2(H_2O)_2}]^{+++}$		(2–3)	
$[\mathrm{Ru(NH_3)_4NOH_2O}]^{+++}$		(2)	
$[\mathrm{Pt(NH_3)_4(H_2O)_2}]^{+++}$		(2)	
$[\mathrm{Fe(H_2O)_6}]^{+++}$(?)			2.20

* In this table (Bj.) refers to Bjerrum (4) and (D.) to Denham (12).

table 5). It will be noted that Nos. 1 and 2 relate to Werner's series 2 and 3 (table 1) and that the constants actually determined in these cases fall within the limits indicated by Werner's work.

The calculated influence of the statistical factor is in direct agreement with the first four values given, but is insufficient to account for the gradations found. The authors estimate the residual "chemical" effects on the strength as increasing in the ratio 1:1.5:3.3:50. If the statistical factor proves to be universally important, it may later be possible from such results as these to calculate back from the observed strength or catalytic constants of a series of hydrates and determine the relative number of water molecules bound in the coördination complex. Thus in the present case better agreement would be secured by assuming a structure $[Al(H_2O)_4]^{+++}$ for the Al^{+++} ion. Brønsted and Volqvartz (9) also determined the salt effects on the constants listed and found them very large in agreement with prediction.[1]

Table 6 gives an attempt to summarize the results of the work reported above on the acid strength of the ammino-cations. A few hydrate complexes are included for comparison.

It is evident that the usual influences such as charge and size of the complex, charge of the central atom, and the statistical factor are operating here. No certain conclusions can be drawn concerning the relative effect of the different anions within the complex, although the weakest acid of the whole list contains the very strong base CO_3^{--}. The ammino-cations are in general far less acid than the corresponding aquo-cations, as well as far more stable.

Quite recently (15) it has been found that of the isomeric complexes $[Pt(NH_3)_2(OH)_2]$, the *trans* isomer is much the stronger base, and that the difference between the first and second hydroxyl is much sharper than in the *cis* complex.

III. THE ACIDITY OF HYDRATES

It has not seemed worth while to present a complete table of results on the hydrolysis of metallic salts, because (1) the results are relatively familiar, (2) the exact structure of the acids concerned is for the most part unknown, and (3) there is a fairly satisfactory qualitative theory of the effects concerned.

Many authors have discussed the effect of charge and size of a simple cation on the acidity of its oxide and hydroxide, and Cartledge (11) has developed an expression for the ionic potential which has been applied by Brintzinger (6) to the hydration of cations in solution. This and other aspects of Brintzinger's work have, however, been destructively criticized by Schmitz-Dumont (32).

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[1] A recent modification by Pedersen of the theory of the statistical factor seems to be controverted by recent studies in heavy water (43).

The hydrolysis of a great many salts in solution has been measured by a variety of means, and the results are to be found in tables such as those of Landolt-Börnstein. Some of the best work in this field has been done by Bjerrum. A large number of rare earth cations were studied at the University of Illinois by Kleinheksel and Kremers (22).

IV. ONIUM SALTS AS ACIDS

Since the great work of Bredig (5) on the hydrolysis of the organic ammoniums, little of fundamental importance has been done on the relation of structure to acid strength of these groups in water solution. Hall and Sprinkle (16) called attention to a few new regularities in this field, and two extremely interesting contributions by Hammett have greatly extended the possibilities of further advance. In one (17) he showed how the acid strength of extremely strong indicator acids could be quantitatively studied, and in the other (13) extended the method to colorless substances by the use of ultra-violet colorimetry. The special properties of the hydronium ion $H^+(H_2O)_n$ are discussed by Rodebush in another paper in this symposium.

That the onium compounds may be acids not only in solution, but also in the fused state has been emphasized in valuable papers by Audrieth (1).

V. COMPLEX ANIONS

While a few anions of low charge are acidic in water, the overwhelming majority are either neutral or distinctly basic. Since structural influences on the strength of the uncharged acids have been so often discussed, only brief mention of them will be made here.

Many of the common anions contain a central atom, such as chlorine or iron, and varying numbers of atoms or groups coördinated with it.

Hantzsch remarked that among the oxygen acids those with the most oxygen were in general the strongest, and that, as a rule, complex anions tend to be weak bases. Since the mechanism of solvation and solvolysis is different with anions and cations, it is reasonable to expect those anions whose central atoms are coördinatively saturated to attract the hydrogen of water relatively weakly and to undergo less basic hydrolysis, just as the ammines and similarly saturated cations show but slight acid properties. Of course, the influence of the charge is as usual all important. In two recent papers Kolthoff and Tomsicek (23) have brought to light the striking fact that while $[Fe(CN)_6]^{---}$ and $[Mo(CN)_8]^{----}$ are very weak bases, $[Fe(CN)_6]^{----}$ is about as strong a base as benzoate ion.

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