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Analytical Chemistry of Metal Complexes with Nitrogen-containing Ligands of the 2,2′-bipyridyl Type

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A brief account is given of the analytical properties of complexes formed by metals with derivatives of 1,10-phenanthroline and 2,2′-bipyridyl, compounds that are widely used in chemical technology, biochemistry, and especially analysis. Detailed consideration is given to the possibilities and limitations of analytical methods based on various properties of these complexes (light absorption, luminescence, solubility, redox properties, etc). A list of 249 references is included.

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I. INTRODUCTION

The ability of the heterocyclic amines—1,10-phenanthroline and 2,2′-bipyridyl—to form complex compounds with various metals is widely used in many branches of chemistry and technology. The employment of these complexes in analysis is governed by their specific analytical properties.

The complexes formed with iron, copper, nickel, cobalt, and other metals tend to have high thermal and thermodynamic stability because of strong ligand fields and the formation of π-back bonding with the metals. The presence of a system of conjugated double bonds in these amines is responsible for the deep colour of the complexes, which enables them to be used in spectrophotometric analysis.

The present Review surveys the principal analytical properties of the metal complexes of 1,10-phenanthroline, 2,2′-bipyridyl, and their derivatives, which are widely used in analysis and several other fields of chemistry.

II. SPECTROPHOTOMETRIC METHODS

1. Effect of Substituents on Complex Formation with 1,10-Phenanthroline, 2,2′-Bipyridyl, and their Derivatives

The well known formation of a triphenanthrolineiron complex has long been used for the spectrophotometric determination of bivalent iron. The great stability of this complex is due to delocalisation of charge from the t_{2g} orbital of iron to the π-orbital of the ligand[1]. Iron(II) is known to form stable complexes with ligands having sufficiently strong fields to produce pairing of electrons in $3d$ orbitals. 1,10-Phenanthroline (phen) and 2,2′-bipyridyl (bipy), which form low-spin complexes with iron(II) contrasting with the high-spin ethylenediamine complexes[2], fall into this category of ligands. The lowest unoccupied levels in $[Fe\,phen_3]^{2+}$ and $[Fe\,bipy_3]^{2+}$ are antibonding molecular orbitals located between the ligands and the e_g orbitals of the metal, which explains the possibility of the formation of dative π-bonds. Oxygen-containing ligands (ethylenediaminetetra-acetic, citric, oxalic, tartaric acids), which form high-spin complexes with iron(II), bind it less firmly, and can therefore be used to mask other elements (aluminium, lead, bismuth, calcium, etc.) in the determination of iron with 1,10-phenanthroline[3,4].

On the other hand, manganese(II), zinc(II), cadmium(II), cobalt(II), nickel(II), and copper(I) form more stable complexes with phenanthroline than do aluminium, thorium, lead, bismuth, and calcium, which are characterised rather by bonding with oxygen- and sulphur-containing ligands. This property is exploited to mask the above metals in the complexonometric determination of aluminium, lead, bismuth, and other ions[5-7].

Complexes formed by metals with phenanthroline are usually more stable and more intensely coloured than are those with bipyridyl. The extension of conjugation by the incorporation of a further aromatic ring in the case of phenanthroline probably creates energetically more favourable orbitals for the establishment of π-back-bonding.

The stabilities of complexes of bivalent metals with phenanthroline and its methylated derivatives show that methyl groups in positions 2 and 5 have different effects on the properties of the ligands. The monocomplexes $[ML]^{2+}$ formed by phenanthroline, bipyridyl, and 5-methylphenanthroline have the stability sequence

$$Mn<Cd<Fe<Zn<Co<Ni$$

but the tricomplexes $[ML_3]^{2+}$ have the different sequence[8,9]

$$Mn<Cd<Zn<Co<Cu<Fe<Ni.$$

The variation in the position of iron in these series is due to the abnormally high stepwise stability constant K_3, which exceeds considerably the preceding two constants and the corresponding constant for nickel (Table 1).

The markedly higher stability of triphenanthrolineiron than of the diligand complex is due to the transition from a high-spin to a low-spin configuration.

A similar effect is not observed with the 2-methylphenanthroline complexes, where di- and tri-ligand complexes have the same stability sequence

$$Mn<Fe<Zn<Cd<Co<Ni<Cu$$

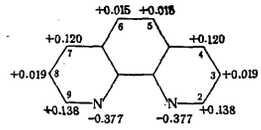
with the exception of univalent copper, which does not form a triligand complex. The position of copper in this

sequence is responsible for the use of 2,9-substituted phenanthroline derivatives for its analytical determination. In some cases the wavelengths and the molar absorption coefficients at band maxima for the iron and copper complexes of methylated phenanthrolines are additive functions [10-12] (see Table 2).

Table 1.

	Ni	Fe
lg K_1	8.6	5.8
lg K_2	8.1	5.2
lg K_3	7.6	10.0

The absorption of light by the iron complexes is most intense with the 4,7-substituted phenanthroline complexes. According to the diagram of the distribution of electron density [13]



(I)

positions 4 and 7, 2 and 9 in the phenanthroline molecule have a high positive charge (I), so that replacing the hydrogen atom at these positions by various donor groups produces a marked change in the properties of the complexes of metals with these ligands. Thus in the case of 4,7-diphenylphenanthroline (bathophenanthroline) the introduction at these positions of phenyl groups, possessing a greater donor power than methyl groups, doubles the sensitivity of the reaction with iron(II) ($\epsilon = 2.22 \times 10^4$) in comparison with phenanthroline. Bathophenanthroline is one of the most sensitive reagents for bivalent iron [14-16] (Table 3).

Table 2. Absorption of light by iron(II) complexes of methylated 1,10-phenanthrolines [10-12].

Positions of CH_3	λ, nm	$10^{-3}\epsilon$	Positions of CH_3	λ, nm	$10^{-3}\epsilon$
—	510	11.1	4,5	516	12.7
3	502	11.5	5,6	520	12.6
4	511	13.5	4,7	512	14.0
5	515	12.2	3,4,7	504	14.0
3,4	505	13.7	4,5,7	517	14.5
3,8	496	11.5	3,4,7,8	500	13.8
3,5	506	12.5	3,4,6,7	510	14.0

In 2,9-substituted phenanthrolines complex formation is influenced mainly by steric factors, owing to the nearness of the substituents to the nitrogen atoms. Thus 2,9-dimethylphenanthroline forms a stable, intensely yellow ($\epsilon = 7950$) dicomplex with copper(I) and the corresponding 2 : 1 iron complex (slightly coloured and unstable), but an iron tricomplex is not formed at all. This enables 2,9-dimethylphenanthroline (neocuproin) to be used as a highly sensitive reagent for copper(I) in the presence of iron(II), [11,17,18] titanium [19], tellurium [20], and plutonium [21].

The phenyl groups in 2,9-diphenylphenanthroline not only prevent the formation of tricomplexes of iron but also probably impede significantly the formation of a tetrahedral dicomplex of copper [13]. This is indicated by the halving of the molar absorption coefficient ($\epsilon = 3620$) in comparison with neocuproin.

Bipyridyl derivatives exhibit similar complexing properties. Positions 3,3′ (or 6,6′) in 2,2′-bipyridyl correspond to positions 2,9 in phenanthroline. Complex formation by bipyridyl with iron or copper leads to stabilisation of the rings in the same plane, and the optical density of such compounds, as a consequence of resonance conjugation, is little inferior to those of the phenanthrolinate complexes [22]. Thus, although 4,4′- and 5,5′-dimethyl derivatives of bipyridyl form tricomplexes with iron having the same absorption intensity [22] ($\epsilon = 8700$) as that of $[Fe\,bipy_3]^{2+}$, the absorption intensity of the iron complex with 3,3′-dimethylbipyridyl is only one-fifth of this value, owing to destruction of the planarity of the structure, which impairs the conditions of conjugation [23]. As in the case of neocuproin, the methyl groups do not prevent formation of a 2 : 1 copper(I) complex, but on the contrary they increase its stability, perhaps owing to enhanced basicity of the nitrogen atoms [22]. Probably for the same reason copper forms complexes [24-26] with bipyridyl-3,3′-diamine and 4,4′,6,6′-tetramethylbipyridyl, whereas iron does not yield complexes with these ligands. These reagents are highly specific for the determination of copper, but are little used owing to the difficulty of preparing them [27].

The presence of aromatic rings fused *ortho* to the nitrogen atoms produces the same effects as do methyl and phenyl groups, without yielding any analytical advantages (Table 3). Somewhat greater selectivity (for copper) in the case of 2-isoquinol-1′-ylquinoline is accompanied by a loss of reagent sensitivity ($\epsilon = 2550$). It is interesting that the introduction of a methyl group at position 3 of the quinoline ring in 2-pyrid-2′-ylquinoline and in 2,2′-biquinolyl diminishes only the sensitivity of the reagent, without affecting the stability or other properties of the complex [27]. Yet the copper complex of 3-phenyl-2,2′-biquinolyl even absorbs rather more strongly than does the corresponding biquinolyl complex, which probably indicates that steric hindrance is balanced by the high donor power of the aromatic ring [13]. In the case of 4,4′-diphenyl-2,2′-biquinolyl the donor properties of the phenyl groups are still more evident ($\epsilon = 9020$ in comparison with 5490 for the biquinolyl complex) [13,26,27]. A highly specific reagent for copper(I) is cuprotest—a derivative of bathophenanthroline containing aromatic groups *ortho* to the nitrogen atoms [28]: no anion (up to 1 M concentration) interferes with the determination of copper(I) with the exception of cyanide, thiosulphate, ethylenediaminetetra-acetate, and sulphide; the determination of microgram quantities of copper is not affected by 10 μg of any other metal. One of the most sensitive and selective reagents for copper(I) is 2,9-dimethyl-4,7-diphenylphenanthroline (bathocuproin), in which the selectivity of neocuproin is combined with the sensitivity of bathophenanthroline [29] and which can be used to determine copper in iron. While about half as sensitive as dithizone, this reagent is far superior in selectivity.

Very little investigation has been made of the effect of various acceptor substituents on the complexing properties

Table 3. Derivatives of 1,10-phenanthroline and 2,2′-bipyridyl in spectrophotometric analysis.

Reagent	Ion to be determined	λ, nm	$10^{-3}\epsilon$	Optimum pH	Solvents and extractants	Foreign ions and possible elimination of their effect	Ref.
1	2	3	4	5	6	7	8
1,10-Phenanthroline	Fe^{2+}	510	11.1 11.4	2—9 —	propylene carbonate —	Cu^{+} and ClO_4^- interfere —	47,67,242
	Cu^{+}	435	7.03	—	—	—	242
	Ru^{2+}	610 (fluorescence)		6—8	—	platinum metals (50 μg, but 20 μg of osmium) do not interfere	83,248
	Ag^{2+}	420	—	—	—	Ni^{2+}, Co^{2+}, Hg^{2+}, Tl^{+} interfere	236
	Mo	508	6.29	—	3 *N* HCl	Co^{2+}, Cu^{2+}, Al^{3+}, Cr^{3+} interfere; 1 mg Fe and 5 M SO_3^{2-}, NO_2^-, Ca^{2+}, Cu^{+} do not interfere, but the colour lasts only 30 s	166,167
	Ti^{3+}	410	0.80	1.8—2.8	bis-2-ethylhexyl hydrogen phosphate	Ti^{IV} not extracted by this extractant in presence of oxalic acid	156,216
2,2′-Bipyridyl	Fe^{2+}	552	8.7	3—9	—	—	242
	Cu^{+}	435	4.55		aqueous–alcoholic medium	—	242
	Ru^{2+}	450	14.5	—	—	—	10
		630 (fluorescence)		7	—	platinum metals (50 μg, but 20 μg of osmium) do not interfere	85—87,248
	Ti^{3+}	340	3.9	3.4	bis-2-ethylhexyl hydrogen phosphate	Ti^{IV} not extracted in presence of excess of reagent	156,216
Phenanthroline-3-sulphonic acid	Fe^{2+}	512	12.24	3—11	—	$HClO_4$ does not interfere	65
Phenanthroline-5-sulphonic acid	Fe^{2+}	517	10.84	—	—	$HClO_4$ does not interfere	65
4,7-Diphenylphenanthroline (bathophenanthroline)	Fe^{2+}	533	22.2	2—9	aqueous–alcoholic medium or extraction with nitrobenzene, propylene carbonate, isopentanol, or alcohol + chloroform	Cu^{+} does not interfere at pH ⩽ 4; Fe can be determined in Mo, W, Sn, Nb, and Ta of high purity	14—16, 69—71
	Ru^{2+}	460	27.0	4—5	hexanol	Ru can be determined in U on heating and with excess of the reagent	84
2,9-Dimethylphenanthroline (neocuproin)	Cu^{+}	454	7.95	3—10	hexanol or isopentanol	Fe does not interfere	11,17—21
Neocuproin + bathophenanthroline mixture	Cu^{+}	454	7.95	2—3	isopentanol in aqueous phase	Cu determined in organic phase, and Fe in aqueous phase, since Cu^{+} at pH < 4 does not form a complex with bathophenanthroline	235
	Fe^{2+}	535	22.0				
2,9-Dimethyl-4,7-diphenylphenanthroline (bathocuproin)	Cu^{+}	479	14.2	5	hexanol	Cl^-, ClO_4^-, NO_3^-, PO_4^{3-}, SO_4^{2-}, etc. do not interfere with determination of Cu in Fe	29
5,6-Dihydro-4,7-dimethyl-2,3,8,9-dibenzo-1,10-phenanthroline (cuprotest)	Cu^{+}	554	7.95	3—11	chloroform	hardly any metal (10 $\mu g\,ml^{-1}$) or anion up to 1 M (except $S_2O_3^{2-}$, CN^-, S^{2-}, edta) interferes	28
5-Nitrophenanthroline	Fe^{2+}	510	11.79	0 (HNO_3)	aqueous medium or extraction with mixture of higher alcohols	—	32,33
2,9-Dimethylnitrophenanthroline (nitroneocuproin)	Cu^{+}	455	7.92	5—6	aqueous medium or extraction with hexanol and with chloroform	Al^{3+}, Pb^{2+}, Zn^{2+}, Ni^{2+}, F^-, SO_4^{2-} do not interfere with determination in Pu	17
Phenanthroline-4,7-diol	Fe^{2+}	520	15.0 (4 M NaOH)	8—18 M NaOH	—	CN^- interferes	22
3,3′-Dimethyl-2,2′-bipyridyl	Cu^{+}	455	6.57	7—8	aqueous medium or extraction with isopentanol	Fe does not interfere in determination of Cu^{+} in Pu, Te	22
4,4′,6,6′-Tetramethyl-2,2′-bipyridyl	Cu^{+}	455	7.9	—	isopentanol, chloroform	Fe^{2+}, Co^{2+}, Ni^{2+} do not interfere	25
		454	6.7				
4,4′-Diphenyl-2,2′-bipyridyl	Fe^{2+}	552	21.1	—	—	—	221
	Cu^{+}	463	9.6				
2-Pyrid-2′-ylquinoline	Cu^{+}	490	5.78	—	isopentyl and benzyl alcohols, ethyl acetate and chloroform	neither Fe^{2+} nor Fe^{3+} interferes	11,13
2,2′-Biquinolyl (cuproin)	Cu^{+}	540	5.49	>3	chloroform	Ti(1 mg ml^{-1}) interferes; Fe^{2+}, Co^{2+}, Ni^{2+} do not interfere	11,13,27
		546	6.4		butanol		26
3-Methyl-2,2′-biquinolyl	Cu^{+}	525	4.12	3	chloroform	neither Fe^{2+} nor Fe^{3+} interferes	11,13,27
4,4′-Diphenyl-2,2′-biquinolyl	Cu^{+}	554	9.02	—	—	—	11,221
2,2′,2″-Terpyridine	Fe^{2+}	552	12.0	3—10	nitrobenzene used in $HClO_4$ medium	Co^{2+} interferes	45,242

Table 3 (continued).

Reagent	Ion to be determined	λ, nm	$10^{-3}\epsilon$	Optimum pH	Solvents and extractants	Foreign ions and possible elimination of their effect	Ref.
1	2	3	4	5	6	7	8
4,4″-Diethyl-4′-phenyl-2,2′,2″-terpyridine	Fe^{2+}	570	27.1	—	—	—	221
2-Pyrid-2′-ylbenzimidazole	Fe^{2+}	490	3.8	5.7	isopentanol	Ag^+, Hg^{2+}, and tartrates interfere strongly	91
2-Pyrid-2′-ylimidazoline	Fe^{2+}	560	7.8	9	isopentanol	Co^{2+}, Fe^{3+}, Cu^+ form yellowish complexes	91
4,4′,4″-Triphenyl-2,2′,2″-terpyridine (terrosite)	Fe^{2+}	583	30.2	3—8	alcohol–chloroform mixture	—	102
2,4,6-Tripyrid-2′-yl-1,3,5-triazine	Fe^{2+}	593	22.6	3—6	—	Fe can be determined in silicates;	102,103
		595	24.1	3—7	nitrobenzene or propylene carbonate	Cr^{3+}, Bi^{3+}, Hg^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}, $C_2O_4^{2-}$, NO_2^-, CN^- interfere	
4,6-Dipyrid-2′-yl-1,3,5-triazin-2-amine	Fe^{2+}	497	8.0	—	nitrobenzene	—	104,105
3-4′-Ethylpyrid-2′-yl-1,3,5-triazine	Fe^{2+}	605	24.37	—	aqueous–alcoholic medium	—	104,105
5,6-Diphenyl-3-pyrid-2′-yl-1,2,4-triazine	Cu^+	488	7.99	2—7	isopentanol	Fe determined after Cu, by decomposing complex of latter by means of NaCN;	109
	Fe^{2+}	555	23.5	—	—	Co^{2+}, Ni^{2+}, CN^- interfere, to a less extent also NO_2^-, $C_2O_4^{2-}$	
5,6-Diphenyl-3-4′-phenylpyrid-2′-yl-1,2,4-triazine	Fe^{2+}	561	28.7	4—7	isopentanol or nitrobenzene	Co^{2+}, Ni^{2+}, Cn^- interfere	102,108
1,10-Phenanthroline and Bromophenol Blue	Fe^{2+}	630	59.0	8.7—8.9	chloroform + isopentanol (4:1)	to determine Fe in especially pure hypophosphite it is first concentrated as ferroin iodide (pH 2–10)	117
1,10-Phenanthroline and Rose Bengal (tetrachlorotetraiodofluorescein)	Cu^{2+}	570 (fluorescence)	62.5	7—9	chloroform	Ag^+, Cd^{2+}, Co^{2+}, Mn^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+}, CN^- interfere;	126,127
		570 (fluorescence)	—	—	ethyl acetate	Cu first extracted with neocuproin to improve selectivity	
1,10-Phenanthroline and Bromopyrogallol Red	Cd^{2+}	620	10.0	7.8—8.1	—	Fe^{3+}, Al, Cr, Pb, Zn, Ni, Mo, Co interfere	128
	Ag^+	635	51.0	7	—	edta, Fe^{2+}, Au^{III}, Nb^V, Th^{IV}, UO_2^{2+}, CN^-, $S_2O_3^{2-}$ interfere	129
Silver(I) complex with Bromopyrogallol Red or Rose Bengal	CN^-	635	51.0	7	—	Fe^{3+}, Co^{2+}, Cu^{2+}, $S_2O_3^{2-}$, SCN^-, I^- interfere	130
		570	40.0	7	—		
1,10-Phenanthroline and sulpharsazen	Ag^+	600	—	5—7.5	—	Ag first extracted with dithizone in order to separate from Hg^{2+}, Cu^{2+}, Pd^{2+}, NO_3^-	131
		630	—	10.8	—		
1,10-Phenanthroline and galloin	Ag^+	630	40.0	—	—	pyridine and ammonia do not form a mixed complex	132
1,10-Phenanthroline and dithizone	Ni^{2+}	520	49.1	6.0	chloroform	—	118
1,10-Phenanthroline and catechol	Nb^V	360	18.0	3.5—4.5	chloroform	—	165
1,10-Phenanthroline and thiocyanate	Nb^V	400	24.0	3—5 *M* HCl	chloroform + tributyl phosphate (10:1)	—	165
Ferroin	CN^-	597	—	9.2—9.7	chloroform	Cu^{2+}, SO_4^{2-}, SCN^-, ClO_4^- do not interfere	79,243
	SCN^-	515	22.5	5—10	nitrobenzene	Co^{2+}, Cu^+, Ni^{2+}, Zn^{2+}, I^-, Br^-, NO_3^- interfere	75,244
	ReO_4^-	528	—	2—8	nitrobenzene	Mo and W (5 mg) do not interfere	241
	CrO_4^{2-}	516	—	3—4	nitrobenzene	Cr^{3+}, Ni, Cu, Zn, Mo, Cl^-, SO_4^{2-}, PO_4^{3-} do not interfere;	76
	HBF_4^-	510	12.0	4—8	dichloromethane	Fe^{3+}, Pb^{2+} interfere	73
	ClO_4^-	510	11.0	5(acetate buffer)	nitrobenzene or n-butyronitrile	can be used to determine Fe^{2+} in $HClO_4$ medium	74,245,247
	$HSal^-$	516	—	5.5—9.5	nitrobenzene	—	72
	PF_6^-	505	—	2.2—10.6	n-butyronitrile	—	246
	$PtCl_6^{2-}$	516	—	2—6	nitrobenzene	—	73
	AsF_6^-	505	—	2.2—10.1	n-butyronitrile	many anions interfere	237

Table 3 (continued).

Reagent	Ion to be determined	λ, nm	$10^{-3}\epsilon$	Optimum pH	Solvents and extractants	Foreign ions and possible elimination of their effect	Ref.
1	2	3	4	5	6	7	8
	$[Sn(C_2O_4)_3]^{2-}$	—	—	—	nitrobenzene	Ag^+, Hg^{2+}, Ti^{IV}, Mo, W interfere	239
	$[AuCl_4]^-$	511	—	—	chloroform	Co, Cu, Ni, Fe, Mn, Pt, Pd, Ir, Os, Hg do not interfere	177
	I^-	500 516	— —	4.5 —	— nitrobenzene	ClO_4^-, SCN^- interfere strongly; Cl^- ions do not interfere even in large excess	75
Iron Bathophenanthrolinate	$HSal^-$	536	—	2.5—4.5	butyl acetate	—	73
Tris-2,2′-bipyridyliron(II) complex	SCN^-	518	21.7	—	4-methylpentan-2-one	I^-, Br^-, NO_3^- interfere	75,243,244
	$HgBr_4^{2-}$ (HgI_4^{2-})	526	—	6.5	dichloromethane	Sn^{2+}, Cu^{2+} interfere; they are masked by nitrilotriacetic acid	73
	CCl_3COOH	516	—	4	nitrobenzene	PO_4^{3-}, SO_4^{2-} do not interfere	240
	$TlBr_4^-$	524	—	4.5	dichloromethane	Hg^{2+}, Au^{III}, I^-, edta interfere; Fe^{3+}, Cu^{2+}, Zn^{2+}, Pb^{2+} do not interfere	238

of phenanthroline and bipyridyl. The latter ligand is made unreactive towards iron(II) by carboxyls at positions 3,3′ and 5,5′.[22] Phenanthroline-2-carboxylic acid forms a series of mixed complexes with copper and cadmium as well as dicomplexes with iron, cobalt, nickel, manganese, zinc, and cadmium in which it acts as a terdentate electronegative ligand. Iron forms either a dinuclear complex or a six-coordinate complex, a chloroform solution of the latter exhibiting weak absorption ($\epsilon = 2500$).[30,31]

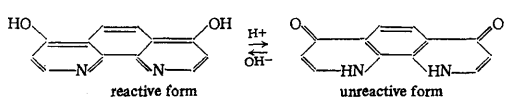
5-Nitrophenanthroline can be used to determine iron at pH 0; the sensitivity of the reaction depends on the nature of the acid, but is unaffected by the nitro-group. Conditions for the determination of iron are best in nitric acid. Phenanthroline behaves as a monobasic acid $phenH^+$ with $K_{diss,25^\circ} = 1.1 \times 10^{-5}$. Because of the high equilibrium constant

$$K_{eq:25^\circ} = \frac{[Fe\ phen_3^{2+}][H^+]^3}{[Fe^{2+}][phen.H^+]^3} = 2{,}5 \cdot 10^6,$$

the phenanthrolinate complex is formed quantitatively at pH 3–9; the complex already begins to be decolorised at pH < 2.[32,33] Probably the nitro-group in nitroferroin, by diminishing the basicity of the nitrogen in phenanthroline, increases the stability of the complex, which makes possible the determination of iron in more acid media.

Similarly, copper(I) can be determined at a lower pH with nitroneocuproin than with neocuproin[17].

In acid and neutral medium phenanthroline-4,7-diol exhibits very little complexing power for iron(II), but in strongly alkaline solutions it becomes an extremely sensitive reagent for iron ($\epsilon = 1.5 \times 10^4$)—as a consequence of the equilibrium



reactive form unreactive form

postulated[22] by analogy with 4-hydroxyquinoline[34].

2. Kinetics of Reactions Involving Metal Complexes of 1,10-Phenanthroline and 2,2′-Bipyridyl

In the analytical application of various phenanthroline derivatives and in the assessment of the stability of complexes formed by various metals, the pH of the medium must be taken into account not only in connection with the acid–base properties of the ligands but also in relation to hydrolysis and aquation, reactions which affect complex formation and the stability of complexes in solution.

Kinetic investigations of the aquation and hydrolysis of various substituted ferroins[35–39] have shown that donor substituents—methyl, phenyl, and amino—in positions 4,7 and 5,6 confer the greatest stability towards these reactions. Acceptor groups—nitro and chloro—in contrast, by diminishing the electron density on iron atoms in tricomplexes, facilitate attack by hydroxide ions on the central atom during hydrolysis, and promote the replacement of ligands by water molecules. Therefore both aquation and hydrolysis occur most rapidly in 5-nitro-, 5-chloro-, and 5-methyl-6-nitro-ferroins, and with greatest difficulty in 4,7- and 5,6-dimethylferroins, as well as in 5-aminoferroin. The kinetic characteristics of ferroin itself are intermediate between those of the two kinds of derivatives. The only exception is the 4,7-dihydroxyphenanthrolinate complex of iron, which readily undergoes aquation in acid medium, while being very stable in alkaline medium.

Solutions in aqueous organic solvents and also various masking ions are very often used in analytical practice to improve the solubility of reagents and enhance the stability of complexes. Therefore planned kinetic investigations of aquation, dissociation, and other reactions involving complex ions will give extremely valuable information on the influence of the ionic strength, the polarising properties of the medium, and the chemical nature of the solvent on the state of these ions in solution.

Thus polarographic studies have revealed a specific effect of methanol on the stability of various bipyridyl complexes of copper[40]. Complex formation between platinum(II) and phenanthroline or bipyridyl is considerably more rapid in the presence of alcohols[41-43]. In this connection it is noteworthy that $\lg(k_w/k_b)$ (where k_w and k_b are the rate constants for the aquation of 5-nitroferroin in aqueous solution and in aqueous butanol respectively) is an extremal function of the mole fraction of the alcohol[44]. This may be due to changes in the structure of the solution, so that structural factors must be considered when organic additives are used.

Study of the racemisation of triphenanthroline-iron and -nickel complexes yields interesting results enabling the stability of complexes to be assessed[45]. Whereas the rates of racemisation and dissociation are the same for $[Ni\,phen_3]^{2+}$ (which is consistent with several known facts), the rate of racemisation of ferroin far exceeds the rate of dissociation, which can be explained by postulating a complicated mechanism of intramolecular rearrangement occurring in a solution of the complex.

The reactivity of such complexes undergoes great changes in the presence of electrolytes[46]. Thus the large cations of strychnine, quinine, and brucine accelerate the dissociation and the racemisation of $[Fe\,phen_3]^{2+}$ and $[Ni\,phen_3]^{2+}$ (probably by diminishing the electron density in the bond between the central metal atom and a ligand nitrogen atom). On the addition of acids, on the other hand, the rate of dissociation decreases, to a far greater extent for $[Fe\,phen_3]^{3+}$ than for ferroin.

Kinetic differences in the rates of formation of complexes with phenanthroline can be used for the simultaneous determination of iron(II) and iron(III).[47] In determinations with phenanthroline iron(III) is usually reduced to the bivalent state by means of ascorbic acid, hydroxylamine, or sodium sulphite[48]. This method can be used to determine iron in vanadium (in weakly acid medium vanadium(IV) gives a colourless complex with phenanthroline[49]).

Tervalent iron gives the most stable complexes with oxygen- and sulphur-containing ligands, in which it is present in a high-spin state owing to the energetic advantage of the d^5 configuration. For this reason the dark blue triphenanthroline complex $[Fe\,phen_3]^{3+}$ is less stable than ferroin, and is obtained by oxidising the latter[13]. Many studies indicate[50-55] that direct reaction between iron(III) and a solution of phenanthroline produces polynuclear complexes of presumed structure[54]

$$[phen_2(X)Fe-O-Fe(X)phen_2]^{2+},\ \text{where } X = Cl^-, SCN^-\ \text{etc.}$$

Polynuclear complexes are formed with phenanthroline not only by iron but also by copper[56-60], chromium[61], rhodium[62], molybdenum[63], and palladium[64], but inadequate study has been made of their complicated structure, conditions of formation, and analytical properties.

3. Enhancement of Selectivity of Determination by Extraction

The sensitivity to metals of many phenanthroline reagents, especially those containing phenyl substituents, is limited by the sparing solubility of the reagents themselves in water. The solubility of triphenanthrolineiron in perchlorate media is increased by introducing a sulphogroup at position 3 or 5. The spectral characteristics of the complex remain almost unchanged[65]. The solubility of complexes of copper with bathocuproin has been increased in this way[64].

However, a decrease in the solubility of reagents and complexes in water is usually accompanied by an improvement in their solubility in organic solvents. The application of extraction methods greatly enhances the selectivity and the sensitivity of reactions. Whereas long-chain alkyl sulphates and alkanesulphonates (Teepol) are required for the extraction of ferroin[67], bathophenanthrolineiron is extracted very well by chloroform and by pentanol[16], which enables 0.25 μg of iron to be determined in the presence of $H_2PO_4^-$. However, the kinetic stability of the iron complex in chloroform [with an iron(III) content of 25 mg and above] is debatable[68].

More often a more polar extractant (nitrobenzene[69,70]) or a less toxic one (propylene carbonate[15]) is used. When isopentanol is used to extract the iron complex, the presence of cobalt, whose complex is not extracted at pH 2–9, does not interfere with the determination[11]. Iron has been determined in tin, molybdenum, tungsten, niobium, and tantalum of high purity by an extraction–photometric method using isopentyl alcohol[71]. Such methods for determining anions are based on the ability of ferroin and $[Fe\,bipy_3]^{2+}$ to form insoluble precipitates with many anions. The most stable and insoluble adducts are usually given by large anions—both organic[72,73] (salicylate, picrate, pentachlorophenoxide) and inorganic[74-76] (SCN^-, ClO_4^-, CrO_4^{2-}, $PtCl_6^{2-}$, $HgBr_4^{2-}$, etc.) (Table 3)—which is consistent with the low hydration energies calculated for large ions by means of Born's equation. Thus the use of nitrobenzene to extract adducts of ferroin with chloride, bromide, iodide, thiocyanate, and perchlorate ions showed that the difference ΔH between energies of solvation in water and in the solvent was most negative with the last three anions, zero for bromide, and positive for the chloride ion, which agrees with their stability and extractability[75,77].

Very sensitive methods for determining iron have been based on the formation of adducts of ferroin with dioctyl sulphosuccinate[78] and with cyanides[79]. The latter method enables iron to be determined in the presence of copper, since the colourless copper complex $Cu(CN)_3^{2-}$ is more stable than the corresponding complex with phenanthroline, and on extraction with chloroform in the narrow pH range 9.2–9.7 most anions do not interfere with the determination of iron.

Like ferroin, nickel(II), cobalt(II), zinc(II), copper(I), and cadmium(II) form[80,81] the compounds $M\,phen_3X_2$ ($X = I^-$, SCN^-, ClO_4^-), which can be used for the extractive spectrophotometric determination of the metals, but these methods are insufficiently specific. Several such compounds are suitable for gravimetric determination.

A rapid method for determining nickel in the presence of iron and cobalt is based on formation of the complex of nickel(II) with phenanthroline and trichloroacetic acid, which is extracted with dichloroethane. In the presence of cerium(IV) as oxidant iron and cobalt are not extracted[82].

Ruthenium(II)—an electronic analogue of iron—forms when heated with phenanthroline a yellow tricomplex, which is suitable for its spectrophotometric determination[83]. However, a more sensitive method is to extract tribathophenanthrolineruthenium with hexanol ($\epsilon = 2.7 \times 10^4$), which is inferior in sensitivity only to the 4-phenylthiocarbazide method[84].

4. Luminescent and Catalytic Properties of Metal Complexes of 1,10-Phenanthroline and 2,2′-Bipyridyl

Since preliminary separation of ruthenium from osmium and other platinum metals is required by most—including catalytic—methods, a certain advantage attaches to those based on the specific fluorescence of the bipyridyl [85], 4,4′-dimethylbipyridyl, and 5,6-dimethylphenanthrolinate complexes of ruthenium [86-88]. None of the platinum metals (up to 50 μg—osmium up to 20 μg) interferes with the determination of 0.02–0.07 μg of ruthenium. The strength of emission by the osmium complex is one-sixtieth of that due to the ruthenium complex.

Luminescence has been discovered in triphenanthroline-iridium(III) complexes in dimethylformamide solution [89].

Since transition metals usually quench luminescence by the ease of $d-d$ transitions, ruthenium(II) and iridium(III) are evidently exceptional in having a sufficiently large energy difference between filled and vacant orbitals in their tricomplexes.

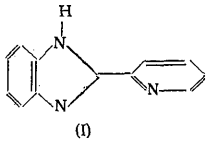
The fluorescent properties of mixed phenanthroline complexes of samarium, europium, terbium, dysprosium, etc. are very important for the development of methods for the analysis of rare-earth metals.

Many complex compounds of transition metals with phenanthroline and bipyridyl exhibit catalytic properties. Thus $[Fe\,bipy_3]^{3+}$ catalyses the chain decomposition of hydrogen peroxide [46]. Bipyridyl complexes of copper(II) actively influence the luminol–hydrogen peroxide system, widely used in luminescent analysis, the catalytic activity increasing in the sequence [90]

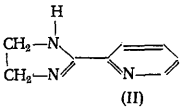
$$Cu\,bipy_3^{2+} < Cu\,bipy_2^{2+} < Cu\,bipy^{2+}.$$

5. Photometric Reactions Involving Ligands Containing One or More N.C:C.N Groups

2-Pyrid-2′-ylbenzimidazole (I) and 2-pyrid-2′-ylimidazoline (II)

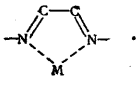


(I)

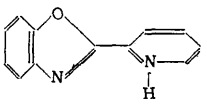


(II)

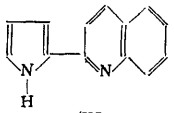
have been used [91] as reagents containing the ferroin grouping N.C:C.N. The tricomplex of iron(II) with (II) absorbs considerably more strongly than does that with (I) (ϵ = 3800 and 7800 respectively), probably owing to the unfavourable steric influence of the aromatic ring in (I), as with reagents of the type 2,2′-biquinolyl and 2-pyrid-2′-ylquinoline [11,92]. Although possessing no advantages over other reagents, (I) and (II) have found wide application in the pharmaceutical industry for the production of various derivatives substituted at the NH group, whose acidic properties are greatly dependent on the nature of the metal—iron, cobalt, nickel, zinc, copper, or manganese—coordinated into the ring



It is interesting that iron(II) does not form complexes with 2-pyrid-2′-ylbenzoxazole (III) and 2-pyrrol-2′-ylquinoline (IV)



(III)



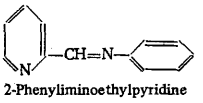
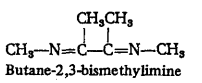
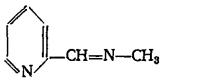
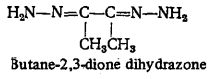
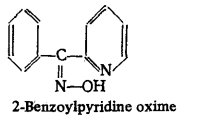
(IV)

perhaps owing to diminished basicity of the nitrogen atom in the five-membered ring [93]. Furthermore, formation of a complex with (IV) is sterically hindered, as with copper and cobalt.

Bipyridyl *NN′*-dioxide forms seven-membered cyclic complexes, resembling complexes of pyridine *N*-oxide in the character of the bond with the metal [94]. However, they are relatively unsuitable for spectrophotometry owing to insufficient intensity of absorption.

Comparison of the structure of reagents for iron and for copper indicates the presence of two specific groups [13]—for iron(II) the N:C.C:N group, and for copper(I) R.CH.N:C.C:N.CH.R, where R = CH_3, C_6H_5, NH_2.

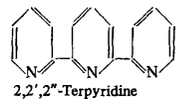
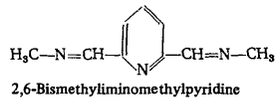
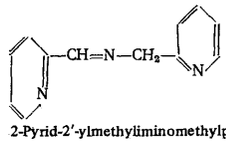
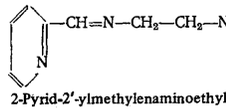
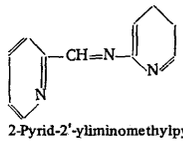
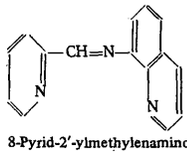
Table 4. Spectral characteristics of complexes of iron(II) with ligands containing a ferroin group [95,96].

No.	Ligand	λ, nm	$10^{-3}\epsilon$
1	 2-Phenyliminoethylpyridine	578	—
2	 Butane-2,3-bismethylimine	568	10.7
3	 2-Methyliminomethylpyridine	551	11.15
4	2,2′-Bipyridyl	522	8.7
5	1,10-Phenanthroline	510	11.5
6	 Butane-2,3-dione dihydrazone	444	7.0
7	 2-Benzoylpyridine oxime	560	15.6

The character of complex formation between the ligand and iron(II) may vary depending on the nature of the groups directly adjacent to the nitrogen atoms of the ferroin grouping. This is evident from the spectral characteristics of complexes of iron with ligands containing different groups directly attached to the nitrogen atoms [95,96] (Table 4). Thus the tricomplex of iron with butane-2,3-dione dihydrazone is sharply distinguished in its visible and ultraviolet spectra from the remaining complexes, which probably indicates that the nature of the ligand changes

under the influence of complex formation. The charcter of complex formation between different metals and 2-benzoylpyridine oxime is determined, as with all oxime and dioxime reagents, by the ability of the hydroxyl hydrogen to be replaced by the metal [97].

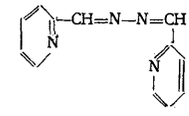
Table 5. Spectral characteristics of dicomplexes of iron(II) with ligands containing a terpyridine grouping N : C.C : N.C.C : N. [98]

No.	Ligand	λ, nm	$10^{-4}\varepsilon$
1	 2,2′,2″-Terpyridine	552	—
2	 2,6-Bismethyliminomethylpyridine	585	—
3	 2-Pyrid-2′-ylmethyliminomethylpyridine	568	1.1—1.2
4	 2-Pyrid-2′-ylmethylenaminoethylamine	592	—
5	 2-Pyrid-2′-yliminomethylpyridine	667	0.75
6	 8-Pyrid-2′-ylmethylenaminoquinoline	659	0.65

The most crucial sites for selectivity towards iron and copper are the 2,9-positions in phenanthroline and the 3,3′-positions in bipyridyl. A 2-carboxyl converts phenanthroline into a terdentate ligand, while bipyridyl and phenanthroline completely lose their ability to form complexes with iron(II) when methyl, phenyl, and amino-substituents are present in these positions. This is explained by steric hindrance to the coordination of iron, which does not develop on complex formation with copper(I); this may be connected with the size of the cations. Replacement of methylimino by ethylimino deprives both substituted phenanthrolines and aliphatic imines (e.g. No. 2 in Table 4) of their ability to yield tricomplexes [96] with iron(II). The appearance of aromatic rings and the increase in their number on passing from butane-2,3-bismethylimine to phenanthroline are accompanied by a shift in the absorption maxima of the iron(II) complexes to shorter wavelengths, but the lengthening of the chain of conjugated double bonds in 2-phenyliminomethylpyridine produces a bathochromic shift owing to the delocalisation of π-bonds. A similar bathochromic displacement is observed in a series of iron(II) dicomplexes with Schiff bases containing a terpyridine grouping N:C.C:N.C.C:N (Table 5). [98] The replacement of aliphatic double bonds (2, 3) by single bonds (4) or double bonds in an aromatic ring (5, 6) leads to a bathochromic shift in the spectrum of the iron(II) complexes, which is especially marked in the last case.

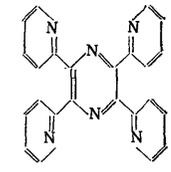
2,2′,2″-Terpyridine, like 2,2′-bipyridyl, is a planar ligand, as is confirmed both by X-ray examination and by the absence of optically active bisterpyridine complexes, e.g. with ruthenium(II) and nickel(II). [46] The formation of octahedral complexes produces some strain in the terpyridine molecule owing to the inevitable distortion of the angles between the pyridine rings. Since such deformation should be still greater with quaterpyridine, four coordination cannot be achieved with this compound. As a reagent, terpyridine has no advantages over bipyridyl, but its derivatives are widely used in analysis, and compounds containing terpyridine and bipyridyl groupings find application in biology. Their complexes with metals—iron, cobalt, nickel, ruthenium, osmium—are intensely coloured and possess biological activity.

Certain difficulties in studying complex formation are created by multidentate ligands [99]. Thus terdentate pyridine-2-carbaldehyde azine forms strongly coloured octahedral complexes with iron(II) and nickel(II). However, dinuclear compounds of the type $[M_2A_3]^{4+}$ are also known, where A represents



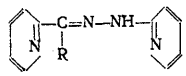
and is a bisbidentate ligand. This reagent forms also the iron complex $[FeA_3]^{2+}$. As with phenanthroline and bipyridyl, the presence of any substituent in position 2 of the pyridine ring strongly affects the coordinating properties of such ligands.

It is interesting that 2,3,5,6-tetrakispyrid-2′-ylpyrazine



is a terdentate ligand like terpyridine, since simultaneous coordination of all six nitrogen atoms is impossible without destroying the planarity of the structure. Furthermore, the coordination of one nitrogen atom of the pyrazine ring causes a marked diminution in the donor properties of the other, which is confirmed by the fact that pyrazine does not form diquaternary ammonium bases. However, unsubstituted pyrazine forms compounds with copper(I), nickel(II), and cobalt(II), in which both nitrogen atoms of the pyrazine ring are coordinated with the metal [100].

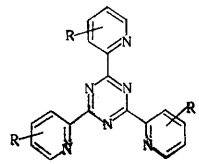
In the terdentate hydrazine derivatives of general formula



either three donor nitrogen atoms may be coordinated depending on the pH (to form the complex cations $[MA_2]^{2+}$) or (in alkaline medium) all four nitrogen atoms may be coordinated to form neutral dicomplexes [101]. The reversibility of such transformations can be utilised for the technical purification of metals, since in alkaline solution these neutral complexes are readily extracted.

Terpyridine forms complexes not only with iron(II) and cobalt(II) but also with quadrivalent platinum [$PtCl_3$terpy].Cl, as well as five-coordinated complexes of the type [MX_2terpy] (M = Co, Cu, Cd), the mechanism of whose formation has not been adequately clarified [45].

One of the most sensitive reagents for iron(II) is 4,4′,4″-triphenyl-2,2′,2″-terpyridine (terrosite) [102] ($\epsilon_{583} = 3.02 \times 10^4$), but the sparing solubility and poor extractability of the complexes obtained restricts its analytical application. The search for highly sensitive reagents whose complexes could be readily extracted has involved the study of numerous hydrazine and triazine derivatives, data on which are briefly summarised in Tables 3 and 4. The most sensitive reagents for the determination of iron(II) were 2,4,6-derivatives of 1,3,5-triazine of general formula

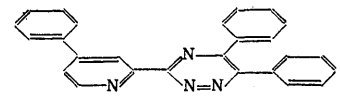


the complexes of which have values of $10^{-4}\epsilon$ of 2.26, 2.44, and 2.52 respectively depending on whether R = H, 4-C_2H_5, 4-C_6H_5. The comparative availability of 2,4,6-tripyrid-2′-yl-1,3,5-triazine has been responsible for its widespread use to determine iron in various materials [104].

The presence of amino-groups in the triazine ring strongly diminishes the complexing power of the ligand, the decrease being an additive function of the number of such groups. Whereas the extinction coefficient for the iron complex of 4,6-dipyrid-2′-yl-1,3,5-triazin-2-amine is more than halved ($\epsilon_{497} = 8000$) in comparison with tripyrid-2′-yl-1,3,5-triazine, we have $\epsilon_{455} = 300$ for 6-pyrid-2′-yl-1,3,5-triazine-2,4-diamine, and 1,3,5-triazinetriamine (melamine) does not form an iron(II) complex at all. The introduction of ethyl and phenyl substituents into the pyridine ring slightly increases the extinction coefficients of the complexes, as was to be expected. Use of the polar extractant nitrobenzene also enables the intensity of absorption of the complexes to be raised [105]. Values calculated for the extinction coefficients from refractometric data were then rather higher than the observed values, which was shown to be due to the involvement of water in formation and extraction of the complex.

Calculation of the most important sites of association in the complexing molecule will probably permit the planned introduction of substituents to obtain extractable complexes having specified properties [106,107].

Among other triazine derivatives the most effective was found to be the bidentate ligand 5,6-diphenyl-3,4′-phenyl-pyrid-2′-yl-1,2,4-triazine



which is inferior in the sensitivity of its reaction with iron(II) ($\epsilon_{561} = 2.87 \times 10^4$) only to terrosite, but possesses considerably better solubility in organic solvents [102,108].

Complexes of *N*-heterocyclic amidrazones, containing the ferroin grouping, are usually unstable even with a large excess of the reagent. In several cases, however, they can be used as acid–base indicators, since they contain a hydrogen atom which can be detached in alkaline medium [101].

A combined method has been worked out for the simultaneous determination of copper and iron by means of 5,6-diphenyl-3-pyrid-2′-yl-1,2,4-triazine and the ability of copper to form a stable complex with cyanide ions in the presence of this reagent [109]. The concentration of copper was found from the decrease in optical density at the wavelength of absorption by its complex with the reagent ($\epsilon_{488} = 7900$), and that of iron(II) from the optical density of the solution after the addition of sodium cyanide ($\epsilon_{555} = 2.35 \times 10^4$). Use of the above reagents to determine cobalt(II) was relatively ineffective, because of inadequate sensitivity.

Isomeric phenanthrolines and bipyridyls used in spectrophotometric methods are 6-hydroxy-1,7-phenanthroline (an analogue of 8-hydroxyquinoline) to determine iron and vanadium [110,111] and 2,3′-bipyridyl to determine niobium and titanium as mixed complexes with salicylic acid and catechol [112], germanium [113], and uranyl [114].

4,4′-Bipyridyl, in contrast to the 2,2′-isomer, forms with metals of the platinum group microcrystalline precipitates suitable for their microcrystalline detection [115]. The arrangement of the nitrogen atoms in 4,4′-bipyridyl favours the formation of polynuclear compounds with many metals [116].

6. Physicochemical Properties of Mixed Complexes and Their Application to Extractive Photometric Analysis

The sensitivity and the specificity of the extractive photometric analysis of metals can in many cases be considerably increased by the use of phenanthroline (or bipyridyl) mixed with various oxygen-, sulphur-, and nitrogen-containing ligands, since the stability and the light absorption of the mixed complexes are frequently far greater than those of the simple complexes. Thus the adduct of ferroin with a sulphophthalein dye molecule (bromophenol Blue) is intensely coloured [117] ($\epsilon_{630} = 5.9 \times 10^4$) and is readily extracted by a mixture of chloroform and isopentanol (4 : 1) within a narrow pH range (8.7–8.9). Traces of iron in hypophosphite (~10^{-8}%) are determined in this way. Dithizone (Dz) is an extremely sensitive but relatively unspecific reagent. Nickel, like many other metals, gives an intensely coloured dithizonate ($\epsilon = 3.4 \times 10^4$), but in the presence of phenanthroline a chloroform-extractable blue complex $NiDz_2$phen is formed, which is more intensely coloured ($\epsilon = 4.91 \times 10^4$) than is the dithizonate [118].

Whereas Cu^+, as a consequence of stereochemical uniformity is characterised by simple complexes with polarised ligands such as phenanthroline and bipyridyl, the easily deformable Cu^{2+} ions readily form mixed complexes by establishing stable covalent bonds with different ligands. Examples are complexes of copper(II) with bipyridyl and glycine, pyridine-2-carboxylic acid, 8-hydroxyquinolinesulphonic acid, pentane-2,4-dione,[119-123] biguanidine, and diacid Schiff bases[124,125]. These are of especial interest, since they are readily soluble in such organic solvents as dimethyl sulphoxide, pyridine, dimethylformamide, and ethanol, and possess high molar absorption coefficients—$\epsilon = (5-12) \times 10^3$.

One of the most sensitive photometric methods for determining copper is based on the fluorescence of the mixed complex CuRBE$phen_2$ (where RBE represents the xanthen acid dye Rose Bengal—tetrachlorotetraiodofluorescein), which can be extracted by chloroform and by ethyl acetate ($\epsilon_{570} = 7.8 \times 10^4$). This method enables 1 μg of copper to be determined in 500 ml of solution on extraction with 25 ml of chloroform. Iron is masked by excees of phenanthroline, since it forms a more stable complex with the latter. Sometimes copper is first extracted as its neocuproin complex in the presence of ethylenediaminetetra-acetic acid in order to improve the selectivity[126]. Since many metals form complexes of this type with phenanthroline and Rose Bengal[127,128] (Table 6), masking agents must be used to enhance the selectivity of this method.

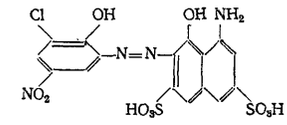
Table 6. Comparative absorption intensities by metal dithizonates by their mixed complexes [M$phen_2$RBE].[127]

Cation	Absorption $10^{-4}\epsilon$		Extractant
	dithizonate	mixed complex	
Cd^{2+}	8.8	9.2	ethyl acetate
Co^{2+}	5.9	9.2	ethyl acetate
Cu^{2+}	4.5	7.8	ethyl acetate
		6.25	chloroform
Mn^{2+}	3.2	6.5	ethyl acetate
Ni^{2+}	3.4	5.0	chloroform
Ag^+	—	4.0	chloroform
Pb^{2+}	7.2	7.0	nitrobenzene
Zn^{2+}	9.4	9.5	ethyl acetate

A highly sensitive method has been developed for determining silver(I) by means of other fluorescein derivatives: the intensity of absorption of the mixed complex Ag$phen_2$BPR is fivefold that of the simple Bromopyrogallol Red complex AgBPR ($\epsilon_{635} = 5.1 \times 10^4$ and $\epsilon_{390} = 1.0 \times 10^4$ respectively). In the presence of excess of phenanthroline iron(II) does not interfere with the determination[129].

Stable cyanide complexes of silver are easily formed in the presence of phenanthroline and either dye (Bromopyrogallol Red or Rose Bengal), a fact which is utilised to determine cyanide ions at concentrations of 0.1–0.00001 M. The end-point of the titration is determined either photometrically or visually from the fluorescence of the mixed complex Ag$phen_2$BPR or Ag$phen_2$RBE.[130] Silver concentrations of 0.2–15 μg ml^{-1} are determined as a mixed complex with bipyridyl and sulpharsazen (the sodium salt of 2-arsono-4′-*p*-nitrophenyltriazenoazobenzene-4-sulphonic acid), which is tribasic[131]. Preliminary extraction with dithizone eliminates the effects of the cations Hg^{2+}, Cu^+, and Pd^{2+}, and of the anions SO_4^{2-}, Cl^-, NO_2^-, and CH_3COO^-.

Galloin, a hydroxylated aromatic sulphonic acid



(H_3R), has also been suggested as a third component for the mixed complex. The formation of (Ag$phen_2$)$_3$R can be used to determine silver[132] ($\epsilon_{630} = 4.0 \times 10^4$). Pyridine and ammonia are stated not to form analogous ternary compounds with galloin. The stepwise complex formation, depending on the pH of the solution, rather complicates the choice of optimum conditions.

Since most of the above methods for determining copper and silver have approximately the same sensitivity, the choice of reagent must obviously depend on the presence of intefering ions in the specimen[133] (brief data on the effect of foreign ions are given in Table 3).

The widespread use of mixed complexes in chemistry led to a series of studies on the influence of the electronic structure of metals, the nature of ligands, and the interaction of coordinated groups on the stability, solubility, redox behaviour, and other analytical properties of these complexes. The combined application of physicochemical and physical methods to solve these problems enables laws of complex formation to be established, which stimulates the further development of analytical methods using mixed complexes.

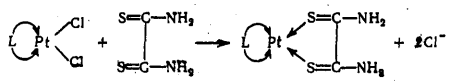
The effect of the nature of the amines on the stability of the mixed compounds has been studied with nickel(II) as example. Thus the replacement of pyridine by ammonia occurs more easily in complexes of this metal with ethylenediamine and pyridine than in those with phenanthroline and pyridine. Complexes in which the ligands are both heterocyclic or both aliphatic are more stable than mixed complexes, in which the π-bonds are regarded as destroying the symmetry of the complexes[134], which diminishes their stability. These results are consistent also with the fact[135] that complexes with 8-hydroxyquinoline or with bipyridyl are more stable than the mixed compounds with these ligands[136]. Nevertheless, the stability of the mixed compounds of cobalt(II) and zinc(II) is the same, while with copper the mixed complexes are the more stable.

Whereas the character of the bond in the copper complexes changes little on passing from bipyridyl to biquinolyl (biqu), while steric factors play the main part with iron, favourable conditions for increasing covalency of the bond are created in gold(III) complexes with biquinolyl. This is apparent, for example, in the fact that the complexes [AuX_2bipy]$^+$ are electrolytes[136], whereas [AuX_3biqu] are non-electrolytes[137]. Study of complex formation between monocomplexes of nickel with phenanthroline and its derivatives on the one hand, and with diethylenediamine and nitrilotriacetic acid on the other, showed[138] that, although the rate of formation of the mixed complex is affected by the nature of the substituent in the phenanthroline, the rate-determining stage of the process is dehydration of the cation [Ni phen]$^{2+}$. The infrared spectra of the complexes $Fe(CN)_2$(5-Xphen)$_2$ (where X = Cl, NO_2, CH_3, C_6H_5) indicate that the presence of acceptor substituents strengthens the Fe–NC bond and diminishes the electron density on the nitrogen atoms in the phenanthroline molecule[139]; donor groups have the opposite effect. The degree of π-bonding of cyano-groups with the

central metal atom in this series of compounds intensifies from iron(II) through ruthenium(II) to osmium(II).[140] Increase in covalency of the metal–ligand bond and in the stability of the bivalent state in the same sequence is characteristic also of compounds[141] of the type MCl_2bipy_2, and in the sequence $Ni^{2+} < Pd^{2+} < Pt^{2+}$ of the compounds $[MX_2amin]$, where amin = phen, bipy.[42,142,143]

In most cases substitution of a ligand in platinum complexes takes place according to the equation[144,145] $k = k_1 + k_2[Y]$, where k_1 is the aquation [rate] constant and k_2 a constant depending on the nature and the three-dimensional structure of the ligands, while Y is the attacking ligand.

Kinetic study of the exchange interaction between dithio-oxamide and dichlorodiamineplatinum complexes with bipyridyl, pyridine, and ethylenediamine (L)



has shown[146] that the bipyridyl complex is the most reactive, although infrared spectroscopy indicates the most stable platinum–chlorine bond in this particular complex[147]. Obviously, the peculiarities of the metal–ligand (L) bond develop in this case only at the instant of attack on the complex by the second ligand (i.e. at the instant of the transition state).

Salt isomerism has been found among mixed complexes[148] of palladium(II) and platinum(II) of the type $[MX_2bipy]$, where $X = SCN^-$, $SeCN^-$. In aqueous solution thiocyanates in which the metal is coordinated with the nitrogen atom are the more stable, and selenocyanates in which coordination is effected between the metal and the selenium atom.

Mixed complexes with phenanthroline and bipyridyl are used for the analytical determination of scandium, rare-earth metals, and uranyl. Many eight-coordinate compounds of scandium and rare-earth metals with phenanthroline and 4,4,4-trifluoro-1-thienylbutane-1,3-dione[149], pentane-2,4-dione[150], cupferron, and 5,7-dibromo-8-hydroxyquinoline[151] are readily extracted by benzene and other solvents in acid media. These complexes are usually slightly coloured, but differences in extractability associated with the ionic radii of rare-earth metals can probably be used for extractive determinations with the application of isotopes. Several mixed complexes of europium, samarium, terbium, and dysprosium with bipyridyl and 4,4,4-trifluoro-1-thienylbutane-1,3-dione, dibenzoylmethane, etc. fluoresce, generally more strongly than do the simple complexes[152,153]. The bipyridyl molecules probably create asymmetric fields that favour f–f transitions[154]. The complex of uranyl with phenanthroline and 4,4,4-trifluoro-1-thienylbutane-1,3-dione is also extracted well by benzene, and its solutions fluoresce in long-wavelength ultraviolet radiation[155].

Highly charged cations generally form unstable complexes with ligands such as phenanthroline, which usually stabilise the lowest oxidation states—iron(II), copper(I), ruthenium(II), and titanium(III). The stabilisation of tervalent titanium, which is extremely unstable under normal conditions, enables it to be determined in the presence of titanium(IV) and a hundredfold excess of phenanthroline or bipyridyl as the tricomplex. In the presence of oxalic acid, quadrivalent titanium bound into an anionic complex is not extracted by bis-2-ethylhexyl hydrogen phosphate, but the complex of tervalent titanium is readily extracted[156] ($K_{distrib} \simeq 1000$). A metal indicator method has also been used to study the stability of phenanthroline complexes of titanium and zirconium[157,158].

Mixed complexes of highly charged cations are more stable. An alcoholic solution of bipyridyl is used with iron(III) chloride to detect phenols in paper chromatography[159]. Many complexes are known[160–163] of vanadyl with phenanthroline and anionic ligands (4,4,4-trifluoro-1-thienylbutane-1,3-dione, chromotropic acid, collidinic acid, tiron, etc.), which are of interest in connection with their extractability and their electrical conductivity.

Niobium(V) and titanium(IV) form anionic complexes which, with aliphatic and aromatic bases in weakly acid solution, yield precipitates extractable by chloroform[164]. Fairly sensitive methods have been developed for determining niobium as mixed complexes with phenanthroline and catechol or thiocyanate ions[165]. No definite relations could be detected between the pK values of the bases and the stability and extractability of the mixed adducts, since these properties are subject to the simultaneous influence of many factors (the basicity of the ligands, the polarising properties of the medium, the dipole moments of the molecules, etc.), which cannot be allowed for because of the absence of systematic investigations on the combined effect of these factors on the properties of complexes of this type.

Study of the mechanism of complex formation is considerably complicated by the tendency of multivalent cations to undergo hydrolysis in solution and form polynuclear compounds, by their enhanced affinity for oxygen. Therefore an empirical method must frequently be used to standardise the reaction conditions.

For example, the addition of phenanthroline and a solution of tin(II) chloride in 3–5 N hydrochloric acid to a solution containing molybdate ions produces a fairly intense coloration ($\epsilon_{508} = 6290$). However, although this reaction is quite sensitive, its application is extremely restricted owing to the instability of the coloration (~0.5 min). The reaction mechanism has not been elucidated, but it has been established that the most intense colour is observed with the ratio $[Mo^{VI}]/[Mo^{V}] = 1:5$ and the use of phenanthroline. Derivatives of phenanthroline cause the absorption to diminish; with terpyridine $\epsilon_{508} \simeq 880$; and bathophenanthroline forms an insoluble white precipitate. The same reaction is used as a spot test for the detection of 0.2 μg of molybdenum in 0.5 ml of solution, from the colour of a benzene extract[166,167].

Chromium(III) forms complex dinuclear compounds with phenanthroline[61,168], but the mechanism of these processes has also remained univestigated.

III. GRAVIMETRIC AND TURBIDIMETRIC METHODS

In the presence of alkali and alkaline-earth metals, ammonium, aluminium, chromium, beryllium, and scandium, the bivalent metals—cobalt, zinc, nickel, copper—and also bismuth(III) form insoluble mixed complexes with phenanthroline and thiocyanate ions, which are suitable for the gravimetric determination of these metals[169–171].

Milligram quantities of phosphorus are determined by means of the reaction of dodecamolybdophosphoric acid with phenanthroline, which yields an insoluble yellow crystalline precipitate $phen_4H_3PMo_{12}O_{40}$, of high molecular mass and therefore an ideal form for weighing[172]. Uranyl is determined by a combined method involving preliminary precipitation of a mixed complex with phenanthroline and m-aminobenzoic acid $UO_2(m\text{-}NH_2C_6H_4COO)_2phen_4$ and subsequent titration of the complex with nitrite[173]. Mixed complexes, but more soluble, are formed also by p- and o-amino-acids.

The heterometric titration of tungstophosphoric acid with phenanthroline[174] enables 0.0025 M heteropoly-acid or 0.001 M phenanthroline to be determined. The structure of the resulting complex has not been studied. Methods have been worked out also for the heterometric titration of palladium, platinum, and gold as mixed complexes with phenanthroline and thiocyanate or chloride ions[175]. A gravimetric method for determining lead is based on the formation of an insoluble precipitate by the interaction of the bulky quadruply charged anion $[Pb(S_2O_3)_3]^{4-}$ with ferroin[176]. The insolubility of the mixed complexes of scandium and vanadyl with phenanthroline and 4,4,4-trifluoro-1-thienylbutane-1,3-dione forms the basis of turbidimetric methods[149,163] for their determination in aqueous solution. Mercury(I) forms with phenanthroline the insoluble compound[177] $Hg_2(NO_3)_2$phen (solubility product 10^{-24}).

Table 7. Gravimetric methods using 1,10-phenanthroline and 2,2′-bipyridyl

Reagent	Species estimated	Quantity	Error, %	Ref.
Ferroin	$[Pb(S_2O_3)_3]^{4-}$	0.007—0.024 g	0.7	176
1,10-Phenanthroline (or 2,2′-bipyridyl) and thiocyanate	Cu^{2+}	0.0005—0.003 g	0.1—0.6	169
	Zn^{2+}	0.0005—0.003 g	0.1—0.6	169
	Ni^{2+}	0.0005—0.003 g	0.1—0.6	169
	Co^{2+}	0.0001 g	—	170
	Bi^{3+}	0.005—0.020 g	1.5	171
1,10-Phenanthroline and *m*-aminobenzoic acid	UO_2^{2+}	0.01 g	0.2	173
1,10-Phenanthroline and Na molybdate	$H_2PO_4^-$	0.001—0.01 g	—	172
1,10-Phenanthroline	tungstophosphoric acid	$2.5 \cdot 10^{-3}$ M	—	174
$K_2[FePhen(CN)_4]$	Zn^{2+}	10^{-5} M	0.4	249

The sparing solubility of certain compounds of metals with phenanthroline is utilised for their preliminary concentration, after which the metals are determined by spectrophotometric or redox methods. For example, this procedure is used to determine iron with Bromophenol Blue[146]. Since the adduct of ferroin with this dye is extracted over the narrow pH range 8.7—8.9, the iron is first precipitated as ferroin iodide. An indirect method[80] for determining lithium involves precipitation of $KLiFeIO_6$ followed by decomposition and the determination of iron with phenanthroline.

A method[178] for recovering phenanthroline (up to 86%) from ferroin complexes is based on precipitating $CuSO_4$. .phen, decomposing it with ammonia, and extracting the phenanthroline with chloroform.

A turbidimetric method[179] for determining cadmium(II) is based on the insolubility of CdI_2phen. Gravimetric methods have been proposed also for determining cadmium(II) and uranyl with 2,3′-bipyridyl.[143]

Differences in the solubility of ruthenium and osmium complexes in different oxidation states are of industrial interest[180,181]. The optical *D*- and *L*-isomers of osmium(II), ruthenium(II), and nickel(II) triphenanthrolinates not only differ in biological activity but also give compounds with antimonyl *d*-tartrate differing very markedly in solubility, a property which is used for their separation[182].

While considerably less sensitive than other methods, gravimetric methods using various complexes of phenanthroline and bipyridyl derivatives can be applied in combined procedures to enhance the selectivity of reagents. Table 7 gives examples of the most widely used gravimetric methods involving complexes with phenanthroline.

IV. ANALYTICAL METHODS BASED ON THE REDOX PROPERTIES OF METAL COMPLEXES OF 1,10-PHENANTHROLINE AND 2,2′-BIPYRIDYL

The use of solvents varying in donor power—dioxan, alcohols, oxolan, formamide, dimethylformamide, sulpholan, etc.—in preparations and in electrochemical investigations[183-186] enables several compounds of phenanthroline and its derivatives with transition metals to be obtained in different oxidation states. Besides their theoretical interest these complexes are of great practical interest as catalysts. All this leads to the development of methods for determining the different valency forms of metals and use of the redox properties of such complexes for analytical purposes. Among well known examples is the ability of phenanthroline and bipyridyl to stabilise the lower states of oxidation of metals, which has enabled titanium(III) to be determined in the presence of titanium(IV)[156] and various anions to be estimated by means of ferroin $[Fe\,phen_3]^{2+}$, whose redox potential is $E_0 = -1.06$ V, whereas

$$E_{0Fe(H_2O)_6^{2+}/Fe(H_2O)_6^{3+}} = -0.77 \text{ V}.$$

2,3,4-Substituted phenanthrolinates of iron and copper(II) exhibit a linear relation between the redox potential and the dissociation constant of the ligand[187]. Use of substituted phenanthroline complexes has enabled a series of oxidimetric indicators (Table 8) to be produced[22].

Table 8.

Indicator	E_0 in 1 M H_2SO_4, V
$[(5\text{-}NO_2phen)_3Fe]^{2+}$	1.25
$[(5\text{-}SO_4phen)_3Fe]^{2+}$	1.20
$[Fe\,phen_3]^{2+}$	1.06
$[(5\text{-}CH_3phen)_3Fe]^{2+}$	1.02
$[\{5,6\text{-}(CH_3)_2phen\}_3Fe]^{2+}$	0.97
$[\{4,7\text{-}(CH_3)_2phen\}_3Fe]^{2+}$	0.88
$[\{3,4,7,8\text{-}(CH_3)_4phen\}_3Fe]^{2+}$	0.81

The stable vanadium complex $[V\,phen_3]^{2+}$ is also used as a redox indicator[188] in the titration of iron trichloride with bivalent chromium. The corresponding bipyridyl complex is not suitable for this purpose, since its rate of dissociation depends on the acidity of the medium.

Many compounds of tervalent titanium with bipyridyl have been prepared. In view of their low electrical conductivity in non-aqueous solutions, they are assumed to have a bridged structure[189].

The rhenium compound $Na_2[Re(CN)_4bipy]$ is extremely stable in aqueous solution, although the metal is present in the uncharacteristic bivalent state. The acid $H_2[Re(CN)_4bipy]$ is very strong ($pK_2 = 2.23$); it gives

insoluble precipitates with many cations [190]—iron(II), iron(III), copper(II), silver(I), cobalt(II), nickel(II), zinc(II), cadmium(II), mercury(II), etc. Compounds of rhenium with bipyridyl in which the metal is present in its lower oxidation states have typically a dinuclear structure [191]. The number of compounds with phenanthroline and bipyridyl in which the metals—manganese, technetium, rhenium—are present in higher states of oxidation increases in this sequence, which is consistent with the known tendency for the stability of such compounds to increase in the same sequence.

Manganese can be determined by a combined method [192], involving preliminary extraction as $Mn(SCN)_2phen_2$ followed by titration of this complex in acid medium with potassium permanganate. Although the Mn^{2+} ion is very stable in acid solution as a consequence of its d^5 configuration, in the presence of phenanthroline this titrant [193,194] oxidises it in concentrated hydrochloric acid to Mn^{3+}. In ammonium acetate buffer manganese(II) is more firmly bound by ethylenediaminetetra-acetic acid than by phenanthroline, a property that is used to mask manganese [5] in the determination of nickel and cobalt.

Redox systems often catalyse reactions between two other systems if they have an intermediate redox potential. Thus the system $[Co\,bipy_3]^{2+} \rightleftharpoons [Co\,bipy_3]^{3+} + e$ ($E_0 = -0.91$ and -1.2 V in 50% alcohol and in water respectively) is a catalyst for the reduction of aromatic nitro-compounds by sodium tetrahedroborate [195]. The trisbipyridyliron complex catalyses the chain decomposition of hydrogen peroxide [46], and copper complexes act as catalysts of chemiluminescence [90].

The complex $[Fe(C_2H_5)_2bipy_2]^{3+}$ has been prepared by the interaction of iron acetylacetonate and diethylaluminium ethoxide in ether. This is a very active catalyst of the cyclopolymerisation of butadiene, acetylene, and acrylonitrile [196]. Polymerisation has been shown to involve the intermediate formation of a bond between the substrate and the iron atom.

Establishment of the mechanism of the oxidation–reduction reactions of these compounds may be of great value for elucidating the nature of their catalytic action [197]. Thus it has been shown by an isotope method that hydrogen peroxide is formed when the cation $[Cu\,bipy_2]^+$ undergoes oxidation by oxygen: water molecules play no part in the reaction [198]. This fact is very important for understanding the role of this complex cation in chemiluminescence.

In the presence of phenanthroline, cobalt(II) chloride acts as an oxygen carrier [199]. The high rate of electron transfer in complexes of metals with ligands of this type is responsible also for the high rates of redox reactions involving such complexes. This is evidently due to the small difference in size between reduced and oxidised cations, which requires no considerable reorientation of the solvate structure; furthermore, the π-character of the metal–ligand bond also facilitates electron transfer [22,200]. The rates of electron transfer in such complexes far exceed those of complex formation [46].

Study of the optical properties of the D-$[Os\,bipy_3]^{2+}$–L-$[Os\,bipy_3]^{3+}$ system showed that loss of optical activity and electron transfer take place simultaneously and at the same rate [201,202].

The large difference in potential between the Co^{2+}/Co^{3+} and Fe^{3+}/Fe^{2+} systems in the presence of phenanthroline and also the stabilisation of the cobalt(III) and iron(II) states by this ligand, so that a clear end-point is obtained (Δv = 600 mV), are exploited in the potentiometric titration of cobalt(II) with tervalent iron [203]. Cobalt can be determined in metallic nickel by this method. The ferroin that is formed is determined spectrophotometrically or by back-titration with cerium(IV). [204] It is possible also to titrate a bivalent cobalt salt directly with a quadrivalent cerium salt in the presence of ferroin as redox indicator [205]. Similar indirect methods using iron(III) chloride in the presence of phenanthroline have been employed also in determining uranium(IV), [206] niobium [207], vanadium [208], and vitamin E. [209]

A sensitive method [210] for determining traces of hydrogen peroxide is based on its reactions with ferroin or with iron bathophenanthrolinate.

The low potentials of the transition $Cu^{2+} \rightleftharpoons Cu^{+} \rightleftharpoons Cu^{0}$ are responsible for the use of complexes of copper with biquinolyl and 2,9-disubstituted phenanthrolines for the determination of oxidants and reductants (glucose, creatine, ascorbic and uric acids [211]).

Table 9. Combined methods of analysis based on photometric and redox properties of complexes with 1,10-phenanthroline

Reagent	Species determined	λ, nm	$10^{-3}\varepsilon$	pH	Sensitivity	Ref.
Ferroin	H_2O_2	510	11.1	2—9	10^{-5} M	210
Fe bathophenanthrolinate	H_2O_2	533	22.4	4	10^{-6} M	210
	Reductants				μg/100 ml	
$H[Fe(CN)_4Phen]$	quinol	462	—	2	60—300	212
	ascorbic acid				100—500	
	tannin				16—190	
	hydroxylamine				30—300	
	hydrazine				4—50	
	$Na_2S_2O_3$				130—550	
	$K_4[Fe(CN)_6]$				400—1800	
	Oxidants				μg/100 ml	
$K_2[Fe(CN)_4Phen]$	Ce^{IV}	462	—	2	60—560	212
	Cr^{VI}				10—70	
	MnO_4^-				30-120	
	IO_4^-				110-460	206
1,10-Phenanthroline and $FeCl_3$	U^{IV}	510	11.1	1.5—5	—	

The pair of complexes—$K_2[Fe(CN)_4phen].4H_2O$ (I) and $H[Fe(CN)_4phen].H_2O$ (II)—is most suitable for the determination of oxidising and reducing agents. The potential of this system ($E_{0,I/II}$ = 0.656 V) is almost independent of pH. The first complex has a sharp absorption maximum at 462 nm; the second hardly absorbs in this region. Many substances can be determined (Table 9) by measuring the optical density at this wavelength in solutions of complex (I) or (II) in the presence of oxidants or reductants respectively. The only limitation of this method is that the rate of redox processes may not be high enough in the determination of a particular substance [212]. The nature of a substituent has an appreciable influence on the kinetics of the oxidation of ferroins by quadrivalent cerium [46]: 5-nitroferroin is oxidised more slowly than ferroin itself by several orders of magnitude.

The rate of oxidation of ruthenium(II) by tervalent thallium is considerably lower in deuterium oxide than in water, which probably indicates that the proton plays a part in the oxidation [213].

Phenanthroline and bipyridyl accelerate the oxidation of malic and lactic acids [214] by chromic acid. It is important to study the mechanism of this reaction in order to elucidate the part played by these acids in biochemical processes.

A kinetic study of the reduction of platinum(IV) by the trisbipyridyl complex of bivalent chromium has established [215] that in aqueous solution stable platinum(IV) compounds usually contain two hydroxy-groups.

We may note in conclusion that redox processes involving complexes of metals with ligands such as phenanthroline and bipyridyl cannot be adequately characterised because of the lack of sufficient quantitative data.

V. VALUE OF 1,10-PHENANTHROLINE AND 2,2′-BIPYRIDYL DERIVATIVES IN ANALYSIS AND IN APPLIED CHEMISTRY

Analysis and technology make widespread use of the ability of 1,10-phenanthroline and 2,2′-bipyridyl to stabilise various oxidation states of metals and also of the catalytic properties of the complexes formed by these ligands with metals [3,4,90,156,188,216–218].

The use of non-aqueous solutions for inorganic preparations has yielded several complexes of metals with these ligands possessing valuable catalytic properties. Thus $[Fe(C_2H_5)_2bipy_2]^{3+}$ effectively catalyses the cyclopolymerisation of butadiene and acetylene [196]. Many complexes of Group VIII metals with ligands containing bipyridyl and imino-groups are also effective biological catalysts. The biological activity of these compounds depends on the nature of the coordinated metal, which is utilised in the production of pharmaceutical preparations [219]. The ability of the imino-hydrogen atom in such ligands to be replaced reversibly by a metal can be used for the technical purification of metals and in analysis [219].

The analytical possibilities are considerably extended by the use of phenanthroline and bipyridyl derivatives containing various donor and acceptor substituents, which have an active influence on the sensitivity and the selectivity of these reagents. The application of non-aqueous solvents and extractants also assists the controlled variation of the analytical properties of the metal complexes [44].

Metal complexes are becoming increasingly widely used in analysis as a consequence of the growing application of non-aqueous solutions in chemistry and technology. Thus dicyanodiphenanthrolineiron(II) (ferrocyphen) and the corresponding ruthenium(II) complex, because of their rapid and reversible protonation accompanied by a sharp change in spectral properties, serve as indicators for acid–base titration in non-aqueous media (acetic acid, chloroform, chlorobenzene, etc.) [220,221]. It is interesting that diethylzinc can be determined selectively (in the presence of its hydrolysis products) with phenanthroline in toluene (spectrophotometrically or thermometrically) [222].

The simultaneous application of different methods using various properties of complexes is acquiring increasing importance in analysis. In iodometric titration, for example, a complex of ruthenium with phenanthroline or a methyl derivative is used as fluorescent indicator, since at the equivalence point the red–orange fluorescence of the initial complex disappears owing to formation of an insoluble iodide complex [223].

Traces (10^{-7}%) of iron have been separated from nickel, chromium, manganese, tin by adsorption of an iron complex on silica gel, and then determined spectrophotometrically [224].

The determination of organic compounds is a separate problem in analysis, for which various methods are used. Thus microgram quantities of phenol are determined in alcoholic solution with bipyridyl and iron trichloride by paper chromatography [159]. Phenanthroline and bipyridyl derivatives themselves are most often determined by gravimetric or spectrophotometric methods using various metal cations [221].

Phthalic acid (10^{-5} M) can be determined by an indirect atomic adsorption method with preliminary extraction of the complex neocuproincopper(I) phthalate with 4-methylpentan-2-one. [225]

The brown dinuclear complex of iron(III) with phenanthroline has found practical application in radiodosimetry. Under the influence of γ-rays it decomposes with the formation of a definite quantity of ferroin proportional to the radiation dose [226].

The number of investigations involving new physical methods has grown considerably during recent years [227–230]. In several cases the use of the results of nuclear magnetic and electron spin resonance, mass spectroscopy, and quantum-chemical calculations enables the effects to be elucidated of electronic and structural factors, the nature of the solvent, the temperature, and the pressure on the analytical properties of the systems formed by metals with these ligands [231–234]. The establishment of relations between the kinetic and thermodynamic parameters of these systems and their analytical properties will make it possible to elucidate the mechanisms of many analytical reactions, to find correlations between the structure of the ligands and the state of the complex ions in solution, and to predict the physicochemical properties of novel complexes as functions of the nature of the ligands and the solvent.

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