THE CHEMISTRY OF COMPLEXES CONTAINING 2,2′-BIPYRIDYL, 1,10-PHENANTHROLINE, OR 2,2′,6′,2″-TERPYRIDYL AS LIGANDS

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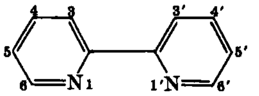
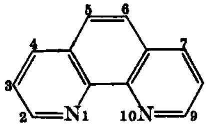
I. Introduction

The organic molecules 2,2′-bipyridyl (or α,α′-bipyridyl), 1,10-phenanthroline (or *o*-phenanthroline) and 2,2′,6′,2″-terpyridyl are well-known, and frequently used, ligands. Their structure and the numbering of their ring positions is shown in (**1**)–(**3**). Throughout this review we shall adopt the abbreviations bipy, phen, and terpy for these ligands, and an



Bipy

(1)



Phen

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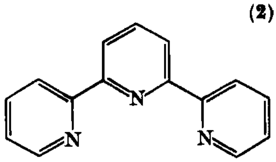


Terpy

(3)

analogous set of abbreviations for their substituted derivatives, e.g., 4,7-dimethyl-1,10-phenanthroline will be designated 4,7-Me_2-phen. When used, the symbol L will be taken to mean bipy or phen.

Since Brandt, Dwyer, and Gyarfas (*94*) reviewed the complex chemistry of these and related ligands in 1954, many more reports of their chemistry have appeared, largely in new fields of interest, some of which have been reviewed elsewhere (*482*). We attempt here to present a review giving emphasis to these new fields, and to this end as much material as possible has been subdivided under the headings of the various techniques and types of information. As a result of the chosen subdivision, certain aspects, such as the nature of the metal-to-ligand bonding, are discussed in more than one section.

Little mention will be made of the analytical uses of these ligands, which have recently been reviewed separately (*711*), of the synthesis of ring-substituted derivatives of the parent ligands, although a potentially useful method using transition-metal complexes has been reported (*505*); or of related species such as 4,4′-bipyridyl. Our coverage of the literature is complete up to the end of 1967, and usually to the end of April 1968; and although many publications have regretfully not been mentioned, we have attempted to discuss the great majority of those papers which we believe to be of special importance.

Very recently a book on the analytical application of these ligands (*622a*) and two reviews of relevance to parts of this article (*42a*, *428a*) have appeared.

II. Structural Information

Although we represent bipyridyl in (**1**) as having a cis-planar conformation, as is usual in its complexes, the free ligand exists in a trans-planar conformation in the solid state, as shown by X-ray studies (*81*, *249*, *485*, *527*). Dipole moment studies (*180*, *255*) show that the molecule is still transoid—rather than cisoid—in benzene solution, but that there now appears to be a net interplanar angle of between 20° and 30°. Ultraviolet and NMR spectroscopy have also been used to study the conformation of the ligand in solution. These results, whose interpretation is less reliable, are discussed in Sections V, B and C. An attempt has been made to study this molecule in the gaseous state by electron diffraction, but the results are ambiguous (*13*). It seems likely that terpyridyl will exhibit similar characteristics. In contrast to these two ligands, phenanthroline is rigidly held in a cis conformation, and is almost always found as a planar ligand (see Rund, *607*). The dipole moment is therefore larger, being 3.64 *D* as compared to 0.69 *D* for bipyridyl in benzene at 25°C (*180*), and the stable monohydrate usually obtained exhibits solely intramolecular hydrogen bonding between both protons of the H_2O moiety and the ligand N atoms (*204*). The only information available for terpyridyl is conformational deductions in various pH ranges, based on UV data (*553*).

Occasionally, a trans-bridging bipyridyl ligand has been suggested in complexes of rhodium (*475*), zirconium (*267a*), and tin (*423*, *523*, *545*), but no definite evidence in support of this suggestion is available. Such evidence might be obtained from studies of X-ray and NMR data, or from optical activity data if the bridging ligand is not planar, but behaves as do substituted biphenyls. In Table I we present a representative sample of the available crystallographic data which is relevant here. The internal dimensions of the ligands may also be found from these references.

TABLE I

X-RAY CRYSTALLOGRAPHIC DATA

Complex	Angle NMN (°)	M–N separation (Å)	Ref.
$Ti(bipy)_3$	72.8 ± 1.5	2.09 ± 0.03	(*5*)
$V(bipy)_3$	73.6 ± 1.5	2.10 ± 0.03	(*5*)
$Cr(bipy)_3$	74.7 ± 1.5	2.08 ± 0.03	(*5*)
$[Cu(bipy)_2I]I$	81, 83	1.96, 2.00, 2.03, 2.10	(*41*)
$Cu(2,9\text{-}Me_2\text{-}phen)_2Cl_2 \cdot H_2O$	79.5	1.98, 2.23	(*590*)
$Zn(terpy)Cl_2$	73, 74	2.24, 2.09, 2.18	(*227*)
$Zn(phen)Cl_2$	80.4	2.07, 2.05	(*596*)
$[Hg_2(phen)](NO_3)_2$	78	2.30, 2.48	(*228*)
$Me_2(phen)Tl(ClO_4)$	63	2.57	(*86*)

With the exception of the mono-2,9-Me_2-phen complex of Cu(II), where steric factors are important, variations in the dimensions of first-row transition-metal complexes on changing the metal ion, ligands, or the coordination number of the metal are not marked. The values determined for the NMN angles are all appreciably less than 90°, and therefore tris chelate complexes should show appreciable trigonal distortion. Similar values for metal-to-ligand bond lengths are quoted for *cis*-$[Co(phen)_2Cl_2]Cl \cdot 3H_2O$, whose conformation is also confirmed (*3*). X-Ray techniques have also been used to show that $Ni(bipy)_3SO_4$ and $Cu(bipy)_3SO_4$ are isomorphous (*402*), as are $[Co(phen)_2X_2]X \cdot 3H_2O$ where X = Cl and Br (*425*).

Several 5-coordinate complexes, both cationic and neutral, have been prepared and studied. The coordination number has been demonstrated both by conductivity (*318*) and X-ray techniques. The initial crystallographic results of Corbridge and Cox (*175*) for $Zn(terpy)Cl_2$ have been refined (*227*) and extended by the study of unit cell dimensions and isomorphism to $M(terpy)X_2$, where M = Mn, Fe, Co, and Ni and X = Cl, Br, and I, to $Cu(terpy)Cl_2$ and its dihydrate, and to $Cd(terpy)Cl_2$ (*175, 317, 412, 603*). With the exception of $Fe(terpy)Cl_2$ where there is some doubt (*412, 603*), these complexes are believed to be both isomorphous and isostructural. Except for M = Mn, the paramagnetic complexes exhibit moments appreciably above the "spin-only" values. The structures of the 7-coordinate $[Cr(O)(O_2)_2(phen)]$ (*664*) and the highly distorted octahedral ion $[Me_2SnCl(terpy)]^+$ in $[Me_2SnCl(terpy)][Me_2SnCl_3]$ (*226*) have also been reported. As would be expected from a consideration of complex formation, complexes of type $[ML_2X_2]$, where X is a monodentate ligand, usually have a cis conformation. When M = Rh and X = Cl or Br, a trans conformation has been postulated; but these complexes are now believed to be cis complexes (see Section VII).

Theoretical treatments have been applied to derivations of the relative net charges on the various atoms of the free phenanthroline molecule (*490*) and to discussions of the absorption spectrum of bipyridyl in both cis and trans conformations (*290*).

Recently, the cis-distorted octahedral complex $[Cu(bipy)_2(ONO)]NO_3$ has been discussed and compared with the copper complexes listed in Table I (*590a, 590b*). The bipyridyl ligand in $IrI_2(OOC \cdot CH_3)(CO)(bipy)$ has been found to be nonplanar (*4a*).

III. Thermodynamic Data

A. The Basicity of the Ligands

Bipyridyl, terpyridyl, and phenanthroline behave as weak bases, usually forming monoprotonated species. Typical values for the first stability constant (i.e., pK_a) are to be found tabulated in Charton (*152*). Further data may be found elsewhere (*17*, *154*, *239*, *448*, *492*, *615*). The data of McBryde (*492*) tabulated in Table II can be taken as representative.

TABLE II

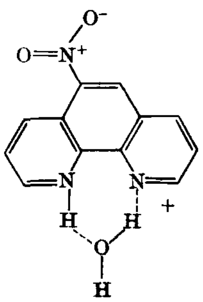
STABILITY CONSTANTS FOR THE SPECIES LH^+ AND LH_2^{2+}

Ligand	Log (K_1)	Log (K_1K_2) estimated
Bipy	4.5	−0.5
Phen	4.98	−1.7
5-Me-Phen	5.26	−1.6
5,6-Me_2-Phen	5.60	−1.6
4,7-Me_2-Phen	5.95	−1.0
2,9-Me_2-Phen	5.85	−0.3

Charton (*152*) has successfully applied the extended Hammett equation to these data and discussed the macroconstant, pK_a, in terms of the tautomerism

$$[LH^1]^+ + H_2O = L + H_3O^+ = [LH^{10}] + H_2O$$

where the superscript refers to the ligand site to which the proton is attached. Even when the substituent effects are assumed to be additive and interaction terms negligible, a good fit between observed and calculated values is found, thus suggesting that the addition of one proton may be described by a tautomerism process. Discrepancies between the observed and calculated values are found for the 2-Me-, 5-Cl-, and 5-NO_2-substituted and the 5,6-disubstituted phenanthrolines. In the first case



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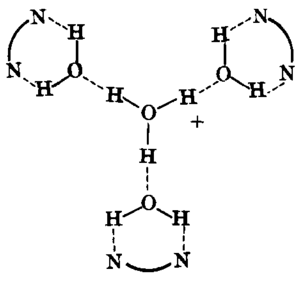

(5)

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this is ascribed to errors in the estimated constants, while the other deviations are rationalized by postulating protonation not on N but on coordinated H_2O, as shown in (**4**).

Diverse pieces of evidence suggest that a change in protonation site is unlikely.

Fahsel and Banks (*239*) reasonably propose similar structures, e.g., (**5**), to that in (**4**) to account for such species as $[H(phen)_3]^+$, thus implying the participation of H_2O for all the protonated phenanthroline molecules.

Comparison of entropy and enthalpy data for the protonation of bipyridyl (*18*, *189*, *447*), phenanthroline (*18*, *469*), and 5-NO_2-phenanthroline (*468*) suggests that the effect of protonation varies little between these species.

Thermodynamic data (*268*) for the process

$$L \cdot H_2O\ (s) \rightarrow L\ (s) + H_2O\ (g)$$

where L = phen, 5-Br-phen, and 5-Me-phen, do not suggest any marked change in interaction between L and H_2O on replacing Me by Br.

The anomalous data for the alkaline fission of $Fe(5\text{-}NO_2\text{-phen})_3^{2+}$ have been explained by postulating lability for the 6-proton (*115*) which, if correct, casts doubt on the estimated constants used by Charton.

Carman and Hall (*138*) observed by NMR spectroscopy an effect, the "buttressing effect," for adjacent methyl groups, thus rendering the assumption that for the 5,6-disubstituted phenanthrolines substituent effects are additive invalid. The Hammett equation has also been applied to 4,4′-disubstituted bipyridyls (*691*).

There is considerable evidence that at high acid concentrations these ligands may pick up a second proton (*448*, *492*, *730*) and the agreement between values of the second stability constant for $[bipyH_2]^{2+}$ is good. This species has also been shown by NMR spectroscopy to occur in solution (*143*). The mono- and diprotonated species both have transoid skew conformations. The enforced cis geometry of the phenanthrolinium ions may account for the difficulty, relative to the bipyridylium ions, of adding a second proton, as shown in Table II.

Fahsel and Banks (*239*) report that the logarithms of the stability constants for $[H(phen)]^+$, $[H(phen)_2]^+$, and $[H(phen)_3]^+$ are 5.11, 7.22, and 9.03, respectively. On the basis of the data for the phenanthroline monohydrate (*56*, *268*) they suggest the structure illustrated in (**5**) for the tris-phenanthroline ion.

B. STABILITY CONSTANTS OF METAL COMPLEXES

Many publications may be found concerning the stability constants of metal complexes of these ligands. Irving and Mellor (*398*) and McBryde

(*493*) compare the various techniques used and criticize some published results; the method of pH balance is especially liable to yield incorrect results for this family of ligands. In Table III we give data obtained at an ionic strength of 0.1 *M* taken from the papers of Irving and Mellor (*398*), Anderegg (*17*), and Dale and Banks (*181*), and at an ionic strength of 0.3 *M* taken from Crabtree *et al.* (*178*). Data obtained at other ionic strengths (*23*, *154*, *189*, *584*, *616*), in mixed solvents (*46*, *154*, *404*, *579*), for 5-Me-phen (*494*), and for other metal ions (*17*, *154*, *181*, *454*, *455*) are also available. Data derived kinetically may be found in Section IV, A. The changes in enthalpy (kcal/mole) and entropy (eu) occurring in the stepwise formation of complexes are tabulated in Tables IV and V for bipyridyl and phenanthroline complexes. Some of the data from Atkinson and Bauman (*23*) have been criticized (*189*, *493*). As given, values are "overall" and not "stepwise." For the ferrous bipyridyl

TABLE III

STABILITY CONSTANTS FOR BIPYRIDYL AND PHENANTHROLINE COMPLEXES WITH DIVALENT METAL IONS[a]

	Bipyridyl			Phenanthroline				
M	Log K_1	Log K_2	Log K_3	Log K_1	Log K_2	Log K_3	T (°C)	Ref.
V[b]	4.9	4.7	3.9	—	—	—	25	(*178*)
Cr[b]	~4	~6.4	3.5	—	—	—	25	(*178*)
Mn	2.6	2	1	4	3.5	3	25	(*398*)
	2.6	—	—	4.1	3.5	2.7	20	(*17*)
	—	—	—	3.9	3.2	3.1	25	(*181*)
Fe	4.3	3.7	9.5	5.8	5.2	10.0	25	(*398*)
Co	5.7	5.6	4.8	7.0	6.7	6.2	25	(*398*)
	6.1	5.4	4.6	7.3	6.7	6.0	20	(*17*)
Ni	7.1	6.8	6.2	8.6	8.1	7.6	25	(*398*)
	7.1	6.9	6.5	8.8	8.3	7.7	20	(*17*)
Cu	8.1	5.5	3.4	9.0	6.7	5.0	25	(*398*)
	8.0	5.6	3.5	9.3	6.8	5.4	20	(*17*)
	—	—	—	—	6.4	4.6	25	(*181*)
Zn	5.2	4.4	3.8	6.4	5.6	5.0	25	(*398*)
	5.3	4.5	3.8	6.6	5.8	5.2	20	(*17*)
	—	—	—	6.8	5.2	4.9	25	(*181*)
Cd	4.3	3.5	2.6	6.0	5.1	4.2	25	(*398*)
	4.3	3.6	2.7	5.8	5.0	4.1	20	(*17*)
Hg	9.6	7.1	2.8	Log β_2 = 19.7		3.7	20	(*17*)

[a] At ionic strength of 0.1 *M*.
[b] At ionic strength of 0.3 *M*.

TABLE IV

ENTHALPY AND ENTROPY DATA FOR STABILITY CONSTANTS OF BIPYRIDYL COMPLEXES OF DIVALENT METAL IONS[a]

M	$-\Delta H_1$	$-\Delta H_2$	$-\Delta H_3$	ΔS_1	ΔS_2	ΔS_3	Ref.
Mn	3.5	—	—	0	—	—	(*18*)
	4.3	—	—	4.1	—	—	(*23*)
	5.7	6.1	6.2	−7.3	0	6.5	(*189*)
Fe	—	—	31.4	—	—	−27	(*18*)
	—	—	28.0	—	—	−13.8	(*189*)
Co	8.2	15.2	21.3	−0.4	0.4	1.4	(*18*)
	7.2	14.4	19.7	2.5	3.5	8.1	(*189*)
Ni	9.6	19.0	28.2	0	−0.7	− 2.1	(*18*)
	8.0	16.1	24.1	4.0	6.8	3.7	(*23*)
	8.9	17.8	26.7	2.5	4.4	4.1	(*189*)
Cu	11.9	17.3	23.8	−4.1	3.1	− 3.1	(*18*)
	8.3	16.7	25.0	3.8	2.5	—	(*23*)
	10.2	19.0	21.6	4.9	1.5	9.5	(*189*)
Zn	7.1	12.5	17.5	0	2.4	2.7	(*18*)
	5.3	10.5	15.9	4.7	8.0	9.6	(*23*)
	6.3	11.8	15.9	3.5	6.2	10.6	(*189*)
Cd	5.1	9.4	14.0	2.1	3.7	0.3	(*18*)

[a] At an ionic strength of 0.1 M.

TABLE V

ENTHALPY AND ENTROPY DATA FOR STABILITY CONSTANTS OF PHENANTHROLINE COMPLEXES OF DIVALENT METAL IONS[a]

M	$-\Delta H_1$	$-\Delta H_2$	$-\Delta H_3$	ΔS_1	ΔS_2	ΔS_3	Ref.
Mn	3.3	7.0	9.0	6.8	10.9	10.4	(*18*)
Fe	—	—	33.0	—	—	−15.4	(*18*)
	—	—	31.3	—	—	−11.3	(*469*)
Co	9.1	15.8	23.8	2.1	9.9	9.9	(*18*)
Ni	11.2	20.5	30.0	2.1	8.2	11.2	(*18*)
Cu	11.7	18.2	26.4	2.4	11.2	7.5	(*18*)
Zn	7.5	15.0	19.3	4.4	5.5	14.3	(*18*)
Cd	6.3	13.1	16.1	4.8	4.8	13.3	(*18*)

[a] At an ionic strength of 0.1 M.

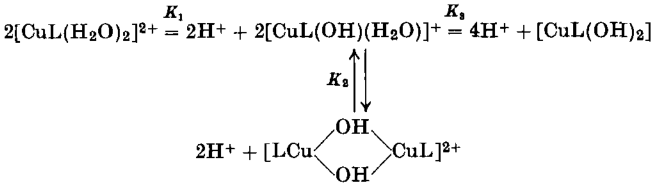
complexes Baxendale and George (*50*) obtained approximate values of 7.5, 14.5, and 24 kcal/mole for ΔH_{1-3}, respectively. From these tabulated data several points emerge clearly.

Comparison of stability constants for pyridine and bipyridyl complexes shows the expected chelate effect (*398*). The ratios of successive stability constants show that a steric factor operates when a second ligand is added to Cu(II) (*398*, *403*), *cis*-$CuL_2(H_2O)_2$ probably being formed (*82*), and that the addition of the third ligand molecule to Fe(II) is anomalous owing to the spin change occurring at this stage (*398*). The additional ligand field stabilization due to this change has been estimated to be 9 kcal/mole (*6*). The same authors also suggest that the lesser volume per formula weight of $Fe(phen)_3^{2+}$ as compared to the Co and Ni analogs, indicates the increased metal–ligand bond strength. For Cr(II) the spin change occurs on the addition of a second bipyridyl ligand, thus $K_2 > K_1 > K_3$ (*178*). The large value of K_2/K_3 for the Zn, Cd, and Hg complexes shows the relative difficulty of adding the third chelate ligand to these metal ions.

The differing results shown in Tables IV and V have been discussed (*189*); care should be taken in using these data until more consistency is obtained. Despite the poor agreement between measured values of entropy changes, inevitable for small values, unusual behavior is clearly shown for the formation of ferroin. The enthalpy data are much more consistent, and the agreement with the Irving–Williams order is clearly shown both by $\log K$ and ΔH. Finally it should be noted that $\log K$ and $-\Delta H$ are greater for phenanthroline than for bipyridyl complexes, and that for the bisoctahedral complexes, cis geometry is more stable than trans, as would be expected statistically, e.g., for Cr(III) (*393*).

Data are also available for substituted ligands (*95, 154, 403, 404, 470*). In the case of the 2-Me-phenanthroline complexes, the stability constants drop because of the steric effects of these large groups alpha to the metal–nitrogen bond. K_3 for Fe(II) is not anomalous and Cu(II) does not form a 1:3 complex. When the more sterically hindered 2,9-Me_2-phenanthroline ligand is used, stability constants become still smaller, and K_2/K_1 for Cu(II) is greater than unity (*399*). The change in behavior for K_3 in the Fe(II) cases corresponds to the absence of a spin change on adding the third ligand. A good correlation of data for FeL_3^{2+} and CuL_3^{2+} with the extended Hammett equation is found for several substituted phenanthroline ligands; thus the stability constants and pK_a values for these substituted ligands should and do vary regularly with each other. Because of the protonation tautomerism, however, the validity of attempting to correlate these functions, except for symmetrically disubstituted ligands, has been questioned (*152*).

There are few reports of work on more complicated systems. Schilt and Leman (*625*) report studies on the proton affinities of the cyanide groups in several complexes of the type $[\mathrm{Fe(phen)_2(CN)_2}]$, while Anderegg (*17*) reports data for the formation of the binuclear Fe(III)-phenanthroline complex. Studies on the system



$$\begin{tikzcd} 2[\mathrm{CuL(H_2O)_2}]^{2+} \arrow[r, phantom, "\overset{K_1}{=}"] & 2\mathrm{H}^+ + 2[\mathrm{CuL(OH)(H_2O)}]^+ \arrow[r, phantom, "\overset{K_3}{=}"] \arrow[d, shift right, "K_2"'] & 4\mathrm{H}^+ + [\mathrm{CuL(OH)_2}] \\ & 2\mathrm{H}^+ + [\mathrm{LCu(OH)_2CuL}]^{2+} \arrow[u, shift right] & \end{tikzcd}$$

have given values for K_1 (*304, 517*), K_1K_2 (*304, 582, 611*), and K_1K_3 (*304, 611*).

The formation constants of 1:1 bipyridyl complexes of $\mathrm{SnCl_4}$, n-$\mathrm{BuSnCl_3}$, and $\mathrm{R_2SnCl_2}$ (*523*), and $\mathrm{R_2Zn}$ (*281*) are also known. Values of log(K) at 25°C and with R = Et are, respectively, >7, >7, 3.5, and 3.5. The enthalpy and entropy data for the Sn complexes are also quoted.

C. OXIDATION–REDUCTION POTENTIALS

Although many water molecules are associated with ferroin cations on solvent extraction (*280, 526*), and the radii of $\mathrm{FeL_3^{2+}}$ ions in water, 11.8 Å for L = bipy and 13.0 Å for phen, show the presence of attached water molecules (*466*), the partial molar entropy changes for processes $\mathrm{ML_3^{3+}} \rightarrow \mathrm{ML_3^{2+}}$ are small (*278, 439*). The data for several substituted Fe(III) complexes in acetonitrile show little change in the entropy change on reduction, although the changes are marked in water, implying a specific interaction between substituent and solvent water (*439*).

Measured oxidation–reduction potentials also vary with changes of medium, e.g., with acidity (*214, 218*). Representative data for bipyridyl and phenanthroline complexes are given in Table VI. Available data usually refer to conditions of acidity between 1.0 and 0.1 *M*. Buckingham and Sargeson (*220*) have collected and discussed much of these data; to their tabulation should be added a more recent value of −1.023 volts for the $\mathrm{Fe(bipy)_3^{2+}/Fe(bipy)_3^{2+}}$ couple in 1 *M* $\mathrm{H_2SO_4}$ (*75*). For the three measured couples of first row transition metal ions with bipyridyl or phenanthroline ligands, the potentials may be discussed in terms of the appropriate aquo potentials and stability constants, when an effect over and above the replacement of water by a ligand higher in the spectrochemical series is found in all three cases. For the Fe couples the dominant effect is the spin change occurring in the ferrous complex. The

TABLE VI

OXIDATION–REDUCTION POTENTIALS IN ACID[a]

Reductant	$-E^0$ (volts)	Acid[a] (*M*)	Ref.	Reductant	$-E^0$ (volts)	Acid[a] (*M*)	Ref.
$\mathrm{Fe(bipy)_3^{2+}}$	1.10	0	*(219)*	$\mathrm{Fe(bipy)_3^{2+}}$	1.00	2.0(S)	*(617)*
$\mathrm{Ru(bipy)_3^{2+}}$	1.30	0	*(214)*	$\mathrm{Fe(bipy)_3^{2+}}$	0.8	10.0(S)	*(617)*
$\mathrm{Os(bipy)_3^{2+}}$	0.88	0	*(216)*	$\mathrm{Fe(bipy)_2(CN)_2}$	0.78	0.01(S)	*(617)*
$\mathrm{Co(bipy)_3^{2+}}$	0.37	0	*(570)*	$\mathrm{Fe(bipy)_2(CN)_2}$	0.79	2.0(S)	*(618)*
$\mathrm{Cu(bipy)_2^{+}}$	0.12	0	*(404)*	$\mathrm{Fe(bipy)_2(CN)_2}$	0.90	10.0(S)	*(618)*
$\mathrm{Fe(phen)_3^{2+}}$	1.10	0.1(N)	*(97)*	$\mathrm{Fe(5\text{-}Cl\text{-}phen)_3^{2+}}$	1.12	1.0(N)	*(95)*
$\mathrm{Fe(5,6\text{-}Me_2\text{-}phen)_3^{2+}}$	1.00	0.1(N)	*(97)*	$\mathrm{Fe(5\text{-}Me\text{-}phen)_3^{2+}}$	1.06	0.1(N)	*(97)*
$\mathrm{Fe(4,7\text{-}Me_2\text{-}phen)_3^{2+}}$	0.88	0.1(N)	*(97)*	$\mathrm{Fe(3,4,7,8\text{-}Me_4\text{-}phen)_3^{2+}}$	0.85	0.1(N)	*(97)*
$\mathrm{Fe(3\text{-}SO_3H\text{-}phen)_3^{2+}}$	1.23	1.0(S)	*(83)*	$\mathrm{Fe(5\text{-}SO_3H\text{-}phen)_3^{2+}}$	1.20	1.0(S)	*(83)*
$\mathrm{[Os(terpy)(bipy)(py)]^{2+}}$	0.87	0	*(111)*	$\mathrm{[Os(terpy)(bipy)Cl]^{+}}$	0.56	0	*(111)*
$\mathrm{[Os(terpy)(py)_3]^{2+}}$	0.80	0	*(111)*	$\mathrm{Os(terpy)_2^{2+}}$	0.99	0	*(218)*

[a] Either sulfuric (S) or nitric (N) acid was used.

estimated additional ligand field stabilization of 9 kcal/mole (*6*) is equivalent to this couple's being 0.4 volt more negative than the aquo couple, the observed difference being –0.35 volt. The Co couple is more positive than the equivalent aquo couple by 1.42 volts for phenanthroline, and here the Co(III) complex is diamagnetic, being more stabilized than the Fe(II) complex because of the greater ligand field splitting. As mentioned above, the addition of a second phenanthroline ligand to Cu(II) is accompanied by a change from 4- to 6-coordination, while the bis-Cu(I) complex may be 4- or 5-coordinate (see below); discussion of the value for the biscopper complex couples must therefore take a coordination change into account. The potential for the AgL_2^+/AgL_2^{2+} couple tabulated (*220*) should be suspected as the Ag(I) complex is oxidized by peroxydisulfate to the Ag(II) complex. Kinetic data suggest that the earlier and less negative values are more consistent (see Section IV, D).

Charton (*152*) has also applied the extended Hammett equation to the oxidation–reduction potentials of 5-substituted phenanthroline complexes of iron in various acidic media (*95, 97, 651*) and of bis-5- and 4,7-substituted phenanthroline complexes of copper in 50% dioxane (*404*). Thus, one should expect an overall similarity between the variations in pK_a, stability constant, and oxidation–reduction potential data for the various ligands. The variations in α and β values found for various substitution positions and the tautomerism in the LH^+ ions show that the correlation need not be good. A similar point may also be made about the comparison of data for the transoid bipyridylium ions and their cis complexes. Plots of E^0 versus pK_a for various systems (*95*, *404*) show a linear dependence to differing extents. As would be expected, the data for analogous complexes of iron (*28*), ruthenium (*214*, *217*, *531*), and osmium (*111*, *218*, *220*) show very good correlation. The assumption (*152*) that the effects of substituents are additive is borne out by these potential data, where the changes in potential on methyl substitution are additive (*97*).

While the effect on oxidation–reduction potentials of substituents on phenanthroline ligands is regular, studies of the oxidation of $[Os(bipy)(terpy)X]^{2+}$ species, where X is an alkyl-substituted pyridine molecule (*111*), do not show a linear dependence of E^0 on the pK_a of X. These results have been explained in terms of the Baker–Nathan effect. However, taken in conjunction with the entropy data of Kratochvil and Knoeck (*439*) for substituted iron complexes, an explanation involving changes in solvation with substituents seems preferable. The potentials of various Os(II)/Os(III) couples (*111*) and Ru(II)/Ru(III) couples (*220*) have been used to study the effect of the overall charge on the complex, of chelation, and of other ligands in mixed complexes. It is found that for similar complexes, decreasing the positive charge on the complex ions makes the oxidation–reduction potential less negative, suggesting that a change in charge affects the differences in the enthalpies of formation of the complex ions more than the differences in the enthalpies of solvation. For the oxidation of $[Os(terpy)(X)_3]^{2+}$ species the oxidation–reduction potential becomes less negative in the order $(X)_3$ = terpy, bipy + py, $(py)_3$—the order of decreasing polarizability. Data illustrating these points may be found in Table VI.

The most comprehensive studies of the effect of acidity on potentials are those of Schilt (*617*, *618*), where media up to 12 *M* in sulfuric acid were used. For M = Fe, Ru, or Os, the oxidation–reduction potential for $M(bipy)_3^{2+}/M(bipy)_3^{3+}$ becomes less negative as the medium becomes more acid, while the converse is true for $[M(bipy)_2(CN)_2]/[M(bipy)_2(CN)_2]^+$. These results are interpreted as showing the formation of stable ion-pairs derived from the tris complexes and acid anions: the CN groups in the mixed M(II) but not M(III) complexes may behave as bases yielding mono- and diprotonated species.

D. Polarographic Studies

Polarographic studies have been extensively used to investigate bipyridyl and phenanthroline complexes, in spite of the complications which arise in the use of this technique. In the reductions of Cr (*693*), Fe (*673*), and Co (*716*) bipyridyl complexes, distinct waves due to the 2-electron reduction of the ligand at the dropping mercury electrode are reported. The polarographic reduction of bipyridyl itself has also been studied (*240*, *640*) and shows two reduction waves. The first wave is caused by the reduction of ligand adsorbed on the mercury, giving an intermediate product assumed to be analogous to semiquinone. The nature of the final product is uncertain, probably being a dihydro or dimeric derivative. The prewave caused by the adsorption of the ligand may be removed by adding gelatin (*240*). The reduction catalyzes the evolution of hydrogen (*693*).

The polarographic reduction of chromium bipyridyl complexes has been investigated frequently (*25*, *420*, *693*, *694*, *707*). At 25°C and pH = 4, the initial processes involved in the reduction of $Cr(bipy)_3^{3+}$ are believed to be (*25*)

$$\begin{aligned}
CrL_3^{3+} + e^- &= CrL_3^{2+} && \text{reversible } E_{1/2} = -0.49 \text{ volt}\\
CrL_3^{2+} + 2H_2O &= CrL_2(H_2O)_2^{2+} + L && k_1 \text{ and } k_{-1}\\
CrL_2(H_2O)_2^{2+} + CrL_3^{3+} &= CrL_2(H_2O)_2^{3+} + CrL_3^{2+} && k_2 \text{ and } k_{-2}\\
CrL_2(H_2O)_2^{3+} + e^- &= CrL_2(H_2O)_2^{2+} && \text{reversible } E_{1/2} = -0.72 \text{ volt}
\end{aligned}$$

that is, the dissociation of Cr(bipy)$_3^{3+}$ is catalyzed by a Cr(II) complex. If k_{-2} is assumed to be negligible, and k_1 to be the rate-determining step, k_1 is calculated to be 0.38 sec^{-1} at 25°C with an activation energy of (22.6 ± 0.5) kcal/mole. These results are consistent with direct kinetic measurements. Tucker *et al.* (*694*) similarly suggest Cr(II)-catalyzed dissociation, and that the reactions of the mixed Cr(III) complex are

$$\begin{array}{rl} CrL_2Cl_2{}^+ + e^- = CrL_2Cl_2 & E_{1/2} = -0.78 \text{ volt} \\ 2CrL_2Cl_2 \rightarrow CrL_2Cl_2{}^+ + CrL_2Cl_2{}^- & \text{slow disproportionation} \\ CrL_2Cl_2{}^- + e^- = CrL_2Cl_2^{2-} & E_{1/2} = -1.26 \text{ volt} \end{array}$$

Oxidation by air or Ce(IV) of $CrL_2Cl_2{}^-$ and $CrL_2Cl_2^{2-}$ yields a stable complex $CrL_2Cl_2{}^+$ containing one labile bipyridyl ligand, so that chloroform extraction gives $[CrLCl_2]^+$ and L.

Dissociation catalyzed by a lower oxidation state is also found for freshly prepared blue Fe(bipy)$_3^{3+}$; on aging, however, the yellow dimeric ferric bipyridyl complex is formed which yields an irreversible polarogram (*580*). The reduction of Fe(bipy)$_3^{2+}$ shows three one-electron reduction waves finally giving Fe(bipy)$_3{}^-$, and two further waves due to the ligand itself, while the reduction of Fe(bipy)$_3^{3+}$ shows an additional wave due to the reduction to Fe(II) (*673*).

The reduction of cobalt complexes of bipyridyl (*511*, *641*, *705*, *706*, *716*) and phenanthroline (*509*, *510*, *543*, *544*) is well documented. As in the case of chromium complexes, the effects of a labile, rapid reductant M(II) species are observed. Reduction to Co(I) occurs which probably then dissociates, ultimately giving Co(O) (*509*, *510*). It is suggested that at pH 7, Co(bipy)$_2$(H$_2$O)$_2^{2+}$ behaves as an oxygen carrier, being rapidly oxidized at higher pH (*580*). Several other polarographic studies have been reported. Ni(bipy)$_2^{2+}$ is reduced stepwise to Ni(bipy)^0 at a dropping mercury electrode (d.m.e.) (*704*). Mo(CO)$_4$bipy has been shown to be reversibly reduced (*194*), while both bipyridyl and phenanthroline catalyze the polarographic reduction of In(III) (*234*). Farver and Nord (*244*) have shown that the reduction of Tl(bipy)$_2^{3+}$ at a d.m.e. in 0.1 *M* KNO$_3$ proceeds via the process

$$TlL_2^{3+} = TlL_2^{2+} = TlL_2{}^+ = Tl/Hg$$

The half-wave potentials being 0.06, –0.125, and –0.45 volt, respectively.

Finally, some stability constants have been determined by this technique (*154*), the most recent being those for Cu(I) and Cu(II) bipyridyl complexes in 50% methanol (*579*).

IV. Kinetic Studies

A. FORMATION, DISSOCIATION, AND RACEMIZATION OF COMPLEXES

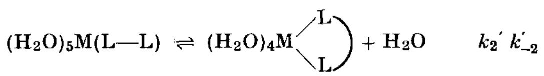
As a convenient subdivision we may consider complex formation, dissociation, and racemization as one distinct topic: i.e., the replacement of solvent as a ligand by bipyridyl, terpyridyl, or phenanthroline; the replacement of these ligands by a molecule of solvent or its conjugate acid or base; and the racemization of an optically active complex in a solvent, the solvent usually being water

The racemization of bipyridyl and phenanthroline complexes of iron (*100*, *186*, *187*, *630*) and nickel (*101*, *187*, *542*, *630*) has been extensively examined. The effect of pressure on the rate of racemization of the M(phen)$_3^{2+}$ complexes has been interpreted as showing a trigonal prismatic structure as that most likely for the activated complex (*630*). More frequently a comparison of the rates of racemization and dissociation is used to suggest a mechanism. Such a comparison also suggests an intramolecular mechanism for the Fe(II) and (III) complexes, as the racemization rate is markedly greater than the rate of dissociation. The mechanism for Ni(II) may vary from intra- to intermolecular on changing the solvent (*187*). For the group of complexes $[\mathrm{Ni(bipy)}_x(\mathrm{phen})_{3-x}]^{2+}$, rates of reaction vary markedly; both increasing x in an acidic medium and increasing the acidity of the medium increase the rates of racemization and dissociation (*101*). The increase in rate with increase in x is to be expected if rotation about the 2,2′-bond in bipyridyl allows protonation of the nonligated nitrogen (*449*) in a nonchelate intermediate. Such a mechanism also explains the variation with acidity and is consistent with the data discussed below, and with the behavior of Fe(bipy)$_3^{2+}$ in acid (*325*). A fuller discussion may be found elsewhere (*45*).

A detailed tabulation of data (*231*, *379*, *381*, *382*) and some isolated results (*43*, *76*, *394*, *580b*, *731*) for the kinetics of formation and dissociation of complexes of these ligands may be found in the literature. Representative data are presented in Table VII. Where a direct comparison is possible, stability constants measured kinetically agree with the values determined by other means. For a reaction scheme which may be represented by

$$\mathrm{(H_2O)_5M(H_2O) + L{-}L \rightleftharpoons (H_2O)_5M(H_2O)\cdot(L{-}L)} \qquad K_0$$

$$\mathrm{(H_2O)_5M(H_2O)\cdot(L{-}L) \rightleftharpoons (H_2O)_5M(L{-}L) + H_2O} \qquad k_1'\ k_{-1}'$$



$$\mathrm{(H_2O)_5M(L{-}L) \rightleftharpoons (H_2O)_4M\langle{}^{L}_{L}\rangle + H_2O} \qquad k_2'\ k_{-2}'$$

$k_f = K_0 k_1'$ if $k_2' \gg k_{-1}'$ The similarity in the formation data for pyridine, bipyridyl, and terpyridyl complexes suggests that the rate of loss of ligated water, i.e., k_1', primarily determines the rate of formation (*381*, *382*). This deduction is supported by the observation (*381*) that the variation of k_f with metal ion, namely, $d^3 < d^4 < d^5 \sim d^6 > d^7 > d^8 \ll d^9 > d^{10}$ and Zn < Cd < Hg, parallels the rates of water exchange for the same ions (*225*). As a necessary corollary of such a process, substituents on the ligand have little effect on k_f (*232*, *381*). When a phenanthroline ligand is already attached to Ni(II), the rate of formation of a subsequent mixed complex varies slightly with 5-substituents, in a manner consistent with the Hammett equation, an effect probably caused by the influence of the ligand on the remaining ligated water molecules (*660*). Two papers of relevance to this suggested mechanism have recently appeared (*79a*, *592a*).

If the assignment of k_f is correct, the rate of dissociation must be given by $k_d = k_{-1}' \; k_{-2}'/k_2'$. In this composite function the individual rate constants for the back reactions refer to the breaking of M–N bonds, and therefore k_d should vary markedly with substituents on the ligand (*232*); further, the variation of k_d with metal is $d^5 > d^6 > d^7 > d^8 < d^9 < d^{10}$, the order to be expected from ligand field considerations.

Available data for the addition of second and third bipyridyl and phenanthroline molecules are much more sparse. Where comparison is possible, successive formation constants vary little, whereas dissociation constants vary much more, e.g., $\log_{10}(k_3/k_1)_d$ for the Fe(II) and Ni(II) bipyridyl complexes are approximately –5 and 2, respectively (*382*). Again the effect of the spin change for the tris complex of Fe(II) is seen. These results are in marked contrast to the values of $\log(k_2/k_1$ for terpyridyl complexes (*382*). The respective values for Fe(II), Co(II), and Ni(II) are > 2, > 2 and 2.2 for formation, and –4.6, 0.8, and 1.8 for dissociation. While the formation data may be explained by a change in K_0, the evidence for 5-coordinate monoterpyridyl complexes in the solid state, discussed in Section II, suggests that k_f could be markedly different from the values for the other systems, for the addition of a second terpyridyl ligand, as the reaction might involve a 5-coordinate reagent or a very labile ligated water molecule. The dissociation of Fe(II) and Co(II) terpyridyl complexes at various pH values has recently been studied and reported (*241*).

As studies of formation and dissociation of complexes may be examined conveniently by taking the easily prepared tris complexes as initial reagents, and as such systems provide the simplest way of examining the effect of pH on these reaction rates, there is an extensive literature on the dissociation of such complexes, especially the low-spin Fe(II)

TABLE VII

KINETIC AND THERMODYNAMIC DATA FOR COMPLEX FORMATION AND DISSOCIATION[a]

Ion	Ligand	Log k_f	E_f	Log k_d	E_d	Log K_t	Log K_k	Ref.
V^{2+}	bipy	-0.5	~ 15	—	—	—	—	(*225*)
Cr^{2+}	bipy	~ 2.0	—	—	—	—	—	(*225*)
Mn^{2+}	phen	5.1^b	—	1.5^b	10.4	4.0	3.6^b	(*381*)
	terpy	5.0	6.6	0.6	12.3	—	4.4	(*382*)
Fe^{2+}	bipy	4.8	10.4	—	—	—	—	(*381*)
	terpy	4.9	10.0	-2.2	18.0	—	7.1	(*379*)
$Fe(terpy)^{2+}$	terpy	$\sim 7.0^c$	—	-6.8	28.7	—	~ 14	(*379*)
Co^{2+}	bipy	4.8	10.4	—	—	—	—	(*381*)
	phen	5.5	11.2	-1.8	19.4	7.2	7.3	(*231*)
	terpy	4.4	9.5	-4.0	20.2	—	8.4	(*382*)
Ni^{2+}	Py	~ 3.6	~ 12	1.6	16.0	—	~ 2	(*382*)
	bipy	3.2	13.8	-4.3	23.7	7.1	7.5	(*381*)
	terpy	3.1	14.7	-7.6	24.2	—	10.7	(*382*)
$Ni(terpy)^{2+}$	terpy	5.3	12.1	-5.8	20.8	—	11.1	(*382*)
Cu^{2+}	bipy	$\geqslant 7.0$	—	-0.7	14.1	8.0	$\geqslant 7.7$	(*381*)
Zn^{2+}	phen	~ 6.3	—	0.6	12.3	6.5	~ 5.7	(*381*)
Cd^{2+}	phen	~ 7.0	—	1.6	14.4	5.8	~ 5.4	(*381*)

[a] k_f in $mole^{-1}$ sec^{-1} and k_d in sec^{-1}. LogK_t taken from Section III and LogK_k that calculated from kinetic data. Activation energies (E) in kcal/mole.

[b] At 11°C.

[c] At 5°C.

complexes which react at conveniently slow rates. It is interesting that the slow decomposition of $Fe(phen)_3^{3+}$ in 95% sulfuric acid has been interpreted as showing that H_2O plays a definite part rather than merely assisting in the dissociation of these complexes (*599*).

The rate of exchange between aquo-ferrous ions and the tris bipyridyl and phenanthroline complexes of Fe(II) shows a first-order dependence on $[H^+]$ (*731*), but with the exception of 4,7-$(OH)_2$-phenanthroline the rate parameters for dissociation in dilute sulfuric acid vary little with ligand substituent for the Fe(II) complexes (*114*). For the tris-bipyridyl complexes at low acidities, the overall rate constants show both an acid-dependent and an independent term (*116*). In view of the dissociation rate constants for the monophenanthroline-Ni(II) complexes (*232*) this lack of discrimination between the complexes of the various substituted ligands is surprising, presumably being a function of the spin change associated with dissociation. The overall rate constant for the dissociation of the ferrous complexes in basic solution shows a more complicated dependence on $[OH^-]$ $k_{\text{overall}} = k_a + k_b[OH^-] + k_c[OH^-]^2$ with a third-power term being possible (*513*). The results of Burgess and Prince (*112*, *115*, *116*) have been obtained from the k_a and k_b terms. Within experimental error, k_a is the same in both acid and alkali. In basic solution also, ligand substitution usually has little effect on the rate parameters except in the case of 5-NO_2-, 3-SO_3H-, and 5-SO_3H-substituents. Although there is no evidence for the formation of $FeL_2(OH)_2$ in these reactions, dissociation in the presence of CN^- shows k_a and k_b terms in the rate constant and $FeL_2(CN)_2$ is the reaction product (*513*). For the dissociation of these Fe(II) complexes a modification of the scheme already proposed satisfies the information, e.g., to replace k'_{-1} by k_{-1} for reaction with water and k_x for reaction with a reagent x. When k'_{-2} and k'_1 terms are very slow and the steady state hypothesis holds for the nonchelate intermediate,

$$k_d = \frac{k'_{-2}\,(k_{-1} + k_x[x])}{k_2' + k_{-1} + k_x[x]}$$

which simplifies to the relationships found if $(k_2' + k_{-1})^2 \gg (k_x[x])^2$. Similar studies for $Ni(phen)_3^{2+}$ and $Fe(5\text{-}NO_2\text{-phen})_3^{2+}$ in a mixed solvent are also reported (*113*, *542*). Wolcott and Hunt (*737*) report experiments on the acid cleavage of $[(phen)_2Cr(OH)_2Cr(phen)_2]^{4+}$ which is believed to proceed via a single bridged intermediate. The thermal decomposition of some solid tris-bipyridyl complexes has also been examined (*198*)

B. Substitution Reactions of Complexes

Under this heading we collect together those reactions which do not involve substitution reactions between solvent molecules and bipyridyl, terpyridyl, or phenanthroline.

There has been recent interest in the substitution reactions of metal carbonyls. For a generalized reaction involving the replacement of Y in a complex CY by another ligand Z, the overall rate constant is frequently found to be described by

$$k_0 = k_1[CY] + k_2[CY][Z]$$

Vlček showed polarographically that the decomposition of $Co_2(CO)_8$ in ethanolic solution in the presence of ligand has, as the rate-determining step, the formation of $Co_2(CO)_7L$ (*703*). Where $C = Mo(CO)_4$, $Y = 1,5$-cyclooctadiene, and $Z =$ bipy or phen, the k_1 term is believed to correspond to bond fission as the rate-determining step (i.e., S_N1). Because of the value of the entropy of activation and the variation of k_2 with Z, an S_N2 process is postulated as being more likely to explain the k_2 term than a sequence of reactions (*744*). As a result of the substitution of phosphites (Z) into complexes of type $M(CO)_4Y$ where M = Cr, Mo, or W, and Y = bipy or phen (*19, 20, 297, 298*), three major products may be obtained: *cis*-$M(CO)_3YZ$, *trans*-$M(CO)_4Z_2$, and *cis*-$W(CO)_3Z_3$. Again either an S_N2 or a multistage S_N1 process is believed to explain the k_2 term. As such multistage processes satisfactorily explain those data discussed in Section IV, A, we feel that the postulation of an S_N2 process has not been proved at present, although 7-coordinate products such as $(bipy)(CO)_3ClMoSnCl_3$ have been made (*465*). The substitution reactions of metal carboxyl complexes have been reviewed by Angelici (*18a*).

The kinetics of substitution of bipy or phen into Co (*467*, *574*), Ni (*144*), and Pt (*697*) complexes have been reported. Several studies of the hydrolysis of complexes of form $[Co(III)(bipy)_2XY]$ may be found. For both cis and trans isomers where $X = Y = Cl^-$, hydrolysis is "instantaneous" (*581*), whereas for the cis isomer with X = acetate and Y = acetate or OH^-, reaction is very slow as a conjugate base mechanism cannot operate and the first-order reaction is therefore independent of $[OH^-]$ (*124*). One NO_2 group in *trans*-$[Co(bipy)_2(NO_2)_2]^+$ is labile and the rate is independent of $[OH^-]$ (*581*), reaction is however acid dependent and under acidic conditions is thought to proceed via protonation of one nitro group (*289, 472*). The interconversion of the cis and trans isomers, where $X = NO_2^-$ and $Y = H_2O$, has an overall rate constant equal to $k_a[H^+]^{-1} + k_b + k_c[H^+]$, implying reactions for both OH^- and NO_2H groups (*289*). The acid hydrolysis of $[FeL_2(CN)_2]$ also shows dependence on $[H^+]$, and shows that the protonated species react more slowly than the unprotonated form (*34*). Replacement reactions of $Pt(bipy)Cl_2$ (*145*), *cis*-$Ru(phen)_2(py)_2$ (*89*), and $[Ru(bipy)(terpy)X]^+$ (*188*) have also been examined.

C. Electron-Transfer and Oxidation–Reduction Reactions

There are few reported data for the rates of electron transfer between the large complexes of these ligands. The rates are very large, and for the iron group metals NMR studies only allow a lower limit of 10^7 l mole^{-1} sec^{-1} to be set (*200, 224, 473, 474*). The exchange between the tris complexes of Co(II) and Co(III) is found to catalyze ligand exchange for Co(III) (*230*); it has also been studied in nonaqueous media (*504*). Because of their convenient analytical properties, however, bipyridyl and phenanthroline complexes have been extensively examined in their oxidation reduction reactions.

1. Reduction of the Complexes

The rate of reduction of $Ru(bipy)_3^{3+}$ by Fe^{2+} is fast (*279*), as are the rates of all those relevant ferrous ion reductions so far studied. The rate constants for the reduction of several complexes in perchloric and sulfuric acid media have been measured (*294*) (see Table VIII). The log of the rate constant, or $\Delta G^{\ddagger}$, is observed to vary with the oxidation–reduction potential, or ΔG^0, of the complex ion, which is interpreted as showing that the Marcus theory may be applied. The Ag(II) data are also consistent if their oxidation–reduction potentials are of the order of −1.4 volts. A similar variation of kinetic with thermodynamic parameters is found for the ferrous ion reduction of various substituted Fe(III) complexes (*262*).

TABLE VIII

REDUCTION OF COMPLEXES BY Fe^{2+}[a]

Oxidant	ΔE^0 (volts)	$\log_{10} k$	Oxidant	ΔE^0 (volts)	$\log_{10} k$
$Ag(phen)_2^{2+}$	—	6.2	$Ag(bipy)_2^{2+}$	—	6.1
$Fe(bipy)_3^{3+}$	0.29	5.3	$Os(bipy)_3^{3+}$	0.15	4.1
$Fe(terpy)_2^{3+}$	0.25	5.9	$Fe(phen)_3^{3+}$	0.38	5.5
$Fe(5\text{-}Me\text{-}phen)_3^{3+}$	0.34	5.2	$Fe(5,6\text{-}Me_2\text{-}phen)_3^{3+}$	0.31	4.8
$Fe(5\text{-}Ph\text{-}phen)_3^{3+}$	0.40	5.5	$Fe(5\text{-}Cl\text{-}phen)_3^{3+}$	0.44	6.2

[a] In 0.5 *M* H_2SO_4 at 25°C; *k* in liters $mole^{-1}$ sec^{-1}. Data from Ford-Smith and Sutin (*262*) and Gordon *et al.* (*294*).

The reduction of ferriin by cyclohexanone (*484*), $Ag(bipy)_2^{2+}$ by water (*31*), and CrO_3 by aldehyde in the presence of ligand (*15*) have been reported, while the reduction of $Cu(phen)_2^{2+}$ by methanol catalyzed by $(t\text{-}Bu)_2NO$ is described as an example of a reaction with a memory (*91*). Several examples of electron transfer between two different complexes of these ligands are also known (*25*, *77*, *279*, *294*). The effect of changes of wavelength, concentrations, and pH on several photochemical reactions has been examined. These studies include the reduction of complexes of Fe(III) (*49*, *303*, *592*) and of $Ag(bipy)_2^{2+}$ (*135*), and the replacement of CN^- ligands on Fe(II) by bipy or phen (*32*, *33*).

2. Oxidation of Complexes

The $Cr(bipy)_3^{2+}$ ion has found frequent use as a reducing agent, yielding mainly the equivalent Cr(III) complex. This ion has been oxidized by various Pt(IV) species (*58*), Mn(III) and Fe(III) tetrapyridylporphines (*312*), and Co(III) complexes. The reactions with oxidants of type $[\mathrm{Co(III)(NH_3)_5X}]$ where $\mathrm{X = NH_3, NO_2^-, F^-, NCS^-, N_3^-, SO_4^{2-}}$, $\mathrm{OH_2}$, maleate, $\mathrm{Cl^-}$, or $\mathrm{Br^-}$ [ligands being listed in the order of increasing rate constant (*132*, *746*, *747*)], are thought to proceed via outer-sphere mechanisms. However, the rate of reaction when $\mathrm{X = NH_3}$ increases at low pH where mono- and bis-Cr(II) complexes may be formed (*746*); polarographic studies (*25*) suggest that the reaction may involve rapid electron transfer between Cr(II) and Cr(III) species, and when $\mathrm{X = PO_4^{3-}}$ the order and rate of reaction suggest that the rate-determining step involves dissociation of $\mathrm{Cr(bipy)_3^{2+}}$ (*132*). Thus, the mechanism does not necessarily involve a simple outer-sphere process. The slow oxidation of $\mathrm{V(bipy)_3^{2+}}$ by various reagents has been reported (*77*).

The oxidation of Fe(II) and Ru(II) complexes by the Ce(IV) ion has been extensively examined (*130*, *206*, *530*, *532*). As might be expected for reactions where the net effect is to transfer an electron from a large substitution-inert ion to another large ion, these reactions are fast and appear to proceed by an outer-sphere mechanism. There is no evidence that substituents on the reductant ligands change the mechanism by allowing the ligand to act as an electron mediator. Typical data are given in Table IX. Plots of $\Delta G^\ddagger$ against ΔG^0 for the unmixed complexes show a gradient of 0.5, agreeing well with the Marcus theory. For a given value of ΔE^0, the ruthenium complexes are oxidized more rapidly than the ferrous complexes (*532*), while the effect of replacing phenanthroline by

TABLE IX

OXIDATION OF COMPLEXES BY Ce(IV)[a]

Reductant	ΔE^0 (volts)	$\log_{10} k$	Reductant	ΔE^0 (volts)	$\log_{10} k$
$\mathrm{Fe(phen)_3^{2+}}$	0.36	5.1	$\mathrm{Ru(phen)_3^{2+}}$	0.14	3.8
$\mathrm{Fe(5\text{-}Me\text{-}phen)_3^{2+}}$	0.40	5.3	$\mathrm{Ru(5\text{-}Me\text{-}phen)_3^{2+}}$	0.16	4.1
$\mathrm{Fe(5,6\text{-}Me_2\text{-}phen)_3^{2+}}$	0.45	5.6	$\mathrm{Ru(5,6\text{-}Me_2\text{-}phen)_3^{2+}}$	0.20	4.2
$\mathrm{Fe(5\text{-}Cl\text{-}phen)_3^{2+}}$	0.30	4.4	$\mathrm{Ru(bipy)_3^{2+}}$	0.15	3.9
$\mathrm{Fe(5\text{-}NO_2\text{-}phen)_3^{2+}}$	0.18	3.6	$\mathrm{Ru(terpy)_2^{2+}}$	0.16	3.8
$\mathrm{Fe(3\text{-}SO_3H\text{-}phen)_3^{2+}}$	0.21	3.8	$\mathrm{Fe(phen)_2(CN)_2}$	0.63	6.9
$\mathrm{Fe(5\text{-}SO_3H\text{-}phen)_3^{2+}}$	0.24	4.1	$\mathrm{Fe(phen)(CN)_4^{2-}}$	0.79	6.9
$\mathrm{Fe^{2+}}$	0.76	6.1	$\mathrm{Fe(CN)_6^{4-}}$	0.75	6.3

[a] In 0.5 *M* $\mathrm{H_2SO_4}$ at 25°C; *k* in liters $\mathrm{mole^{-1}\,sec^{-1}}$. Data from Sutin *et al.* (*130*, *206*) and Miller and Prince (*530*, *532*).

cyanide ligands is rationalized in terms of the Marcus theory and the slower rates of electron transfer for the cyanide complexes (*130*). The oxidation of several Fe(II) species by Cl_2 (*634a*), Co(III) (*130*), Mn(III), and Mn(III) pyrophosphate (*199*) has been examined. Again linear plots of ΔG^0 versus $\Delta G^\ddagger$ are obtained; in the case of Co(III) the gradient is only 0.27 and the rate constants markedly less than would be expected from a study of data for other systems. This phenomenon has been discussed, but the cause is uncertain.

Oxidation by Tl(III) is slow, proceeding through two one-electron steps involving Tl(II) as the intermediate (*531*). At low $[H^+]$, both Tl^{3+} and $Tl(OH)^{2+}$ behave as oxidants, giving rate constants for the oxidation of $Os(bipy)_3^{2+}$ of $3.6 \times 10^6 \exp(-6900/RT)$ and $3.6 \times 10^9 \exp(-11500/RT)$ l mole^{-1} sec^{-1}, respectively (*395*). In 4.75 *M* $HClO_4$, the hydroxy complex does not occur to any appreciable extent, and the oxidation of various Ru(II) complexes by the Tl^{3+} ion has been examined (*531*). No data for ΔG^0 under these conditions are available to allow the results to be compared with the Marcus theory. A linear relationship is found between $\Delta H^\ddagger$ and $\Delta S^\ddagger$; this is ascribed to variations in the solvation of the reductant with substitution in the ligand, as discussed in Section III, C. Such an effect will give a linear enthalpy/entropy relationship if alterations in the entropy changes are much more marked than those in the free energy changes. The data for the oxidation of Fe(II) complexes by Tl(III) agree with the Marcus theory (*113a*).

A similar phenomenon is found in the oxidation of the tris-Fe(II) complexes by peroxydisulfate (*112*, *117*, *397*, *592b*). For the $Ag(bipy)_2^+$ reductant ion in 50% acetone, the overall stoichiometry and rate equation suggest that each $S_2O_8^{2-}$ ion oxidizes two reductant ions, the second rapidly by SO_4^- (*528*). For the iron group complexes, the rate constants given in Table X are calculated for the early part of reaction where the results may be fitted to a pseudo first-order rate equation. Again a dependence of $\Delta G^\ddagger$ on ΔG^0 is seen. The rate constant for the Ag complex, which corresponds to catalysis by uncomplexed Ag^+, is most reasonably explained by postulating an inner-sphere mechanism for this reaction, while the others are outer-sphere, thus allowing rapid charge transfer within the complex intermediate formed. The other anomalous result for these reactions is the rate constant for the 3-SO_3H-substituted ferroin; the absence of data for other 3-substituted complexes unfortunately makes interpretation of this result impossible.

Crystals containing $Fe(bipy)_3^{2+}$ and $IrCl_6^{2-}$ show neither charge-transfer bands nor conductivity, and therefore the reaction in solution between these ions must proceed either via the solvent or a special stereochemical relationship (*483*). In solution the oxidation of the tris-Fe(II) complexes

TABLE X

OXIDATION OF COMPLEXES BY $S_2O_8^{2-}$ [a]

Reductant	ΔE^0 (volts)	$\text{Log}_{10}k$	E_a (kcal/mole)
$Ag(bipy)_2^+$ [b]	<0.6	+0.7	9.5 ± 1.0
$Os(bipy)_3^{2+}$	1.13	+1.7	9.4
$Ru(bipy)_3^{2+}$	0.71	−2.0	14.6
$Fe(bipy)_3^{2+}$	0.91	−0.4	10.3 ± 0.3
$Fe(phen)_3^{2+}$	0.89	−1.0	13.5 ± 0.5
$Fe(5\text{-Me-phen})_3^{2+}$	0.95	−1.1	11.9 ± 0.4
$Fe(5\text{-Cl-phen})_3^{2+}$	0.89	−1.4	20.7 ± 0.5
$Fe(5\text{-}SO_3H\text{-phen})_3^{2+}$	0.81	−1.5	25.4
$Fe(3\text{-}SO_3H\text{-phen})_3^{2+}$	0.78	−0.5	24.0
$Fe(4,7\text{-}Me_2\text{-phen})_3^{2+}$	1.13	+0.3	6.9 ± 0.3

[a] At 25°C; k in liters $mole^{-1}$ sec^{-1}. Data from Burgess (*112*), Burgess and Prince (*117*), Irvine (*396, 397*), and Miller (*528*).

[b] In 50% acetone.

by $IrCl_6^{2-}$ and $IrBr_6^{2-}$ is very fast, being measured by the temperature-jump method (*311*, *391*). Data for the reaction between $Ru(phen)_3^{2+}$ and $RhCl_6^{2-}$ are also reported, but the extinction coefficient used for the Ru complex is incorrect (*391*). Both forward and back reactions for these systems are of the order of 10^9 liters $mole^{-1}$ sec^{-1}. Similarly the reaction of $Os(bipy)_3^{2+}$ with the large $Mo(CN)_8^{3-}$ ion is rapid (*131*). The complex $Co(bipy)_3^+$ is found to oxidize CCl_4 "instantaneously," probably giving CCl_3 radicals (*328*).

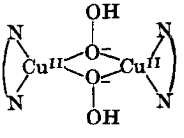
D. CATALYSIS

Little is known of the effect of coordination on the reactions of these ligands themselves. The hydrogenation of bipyridyl over PtO_2 in acetic acid has been studied and the reaction is found to be first order in hydrogen and zero order in bipyridyl (*554*). Both Ni^{2+} and Cu^{2+} catalyze the hydrolysis of 2-CN-phenanthroline, the rates increasing by 10^7 and 10^9, respectively. The catalysis is attributed to changes in the entropy of activation, thus for Ni^{2+} catalysis, $\Delta H^\ddagger = (15.7 \pm 0.2)$ kcal/mole and $\Delta S^\ddagger = (14 \pm 1)$ eu, while the equivalent data for OH^- catalysis are (15.1 ± 1.2) and (-20 ± 4). It is suggested that the Lewis acid Ni^{2+} interacts with the cyanide nitrogen atom facilitating hydroxide attack on carbon (*98*). The nitration of phenanthroline at position 5 is also facilitated by complex formation with either Co(III) or Fe(III) (*600*), while the acidity of ethylenediamine (en) is found to be greater in $[Pt(bipy)(en)]I_2$ than in $[Pt(en)_2]I_2$ (*698*).

The effect of the ligands on metal ion-catalyzed reactions has been more extensively examined. A wide range of behavior is observed; the ligands may merely reduce the concentration of metal ion catalyst (*24*, *567*) or form truly catalytic complexes.

$[Co(bipy)_2(H_2O)_2]^{2+}$ behaves as an oxygen carrier at pH 7 (*641*), whereas other phenanthroline and bipyridyl complexes catalyze autoxidation. Thus bipyridyl accelerates both homogeneous and heterogeneous copper-catalyzed autoxidation (*202*) and phenanthroline the autoxidation of unsaturated carbonyl-containing molecules (*710*). The kinetics of reaction between ferriin and cyclohexane vary when carried out under N_2 and O_2 (*484*). Under nitrogen, $\Delta H^\ddagger = 12$ kcal/mole, $\Delta S^\ddagger = -21$ eu and $k_h/k_d = 2.2$; while under oxygen the corresponding figures are 16.5, −2.1, and 6.3. This catalyzed autoxidation probably involves cyclohexanone radicals.

Studies of the oxidation of FeL_3^{2+} species by H_2O_2 show that the rate-determining step is the dissociation of the first ligand molecule (*116*). This is in accord with the observation that the species $Fe(bipy)_x^{2+}$, where $x = 1$ or 2, react rapidly with H_2O_2, reaction being accompanied by extensive oxidation of ligand (*39*); mono- and bisphenanthroline-iron(III) complexes are poorer catalysts than the aquo ion even though the activation energy is much lower (*714*). Zell and Sigel (*743*) show that the catalysis by $Ni(bipy)_2^{2+}$ proceeds via a complex $[NiL_2(O_2H)]^+$, for whose formation they calculate an equilibrium constant. A similar intermediate (**6**) is suggested for the catalysis by Cu(II) and bipyridyl (*99*). The reaction between $Cu(I)(bipy)_2{}^+$, and both O_2 and H_2O_2, has been examined (*581a*).



(**6**)

[Reproduced after (*99*).]

The most interesting catalytic data available are those of Rund *et al.* (*608*, *609*) on the catalyzed decarboxylation of dimethyloxalacetic acid. Phenanthroline enhances Mn(II) and Ni(II), but not Zn(II) and Mg(II) catalysis, while ligand substituents appear to alter the rate-determining step. The catalytic process suggested is

$$L_xM + S \xrightarrow[k_1]{} L_xMS \xrightarrow[k_2]{} L_xMP + CO_2 \xrightarrow[k_3]{} L_xM + P$$

where L = ligand, M = metal ion, S = substrate, and P = product. When M = Mn(II) and L = 2,9-Me_2-phen, k_1 is slow; for 5-NO_2-phen, k_2 is slow; and for 4,7-MeO_2-phen, k_3 is rate determining. The catalytic effect varies with x in the order $2 > 1 > 0$, while the Ni(II)/phen catalysts appear to undergo an aging effect

Bipyridyl and phenanthroline are also known to catalyze the oxidation of alcohols by chromic acid (*701*) and to enhance the Cu(II)- and Co(II)-catalyzed hydrolysis of 1,3-dicarboxyphenyl-2-phosphate (*550*). Reductions catalyzed by Co(I) complexes are discussed in Section VIII.

V. Spectroscopic Studies

A. INFRARED SPECTRA OF COMPLEXES OF 2,2′-BIPYRIDINE AND 1,10-PHENANTHROLINE

In the absence of normal coordinate calculations for the free bases all investigations of the infrared spectra of bipyridyl and phenanthroline complexes have necessarily been empirical.

4000–600 cm^{-1}. The infrared spectra in the "rock-salt" region of a comprehensive range of complexes have been tabulated (*392, 520, 556, 626, 644*). The spectra are very similar with the exception of those of the spin-paired iron(II) complexes (*392*). The spectra of iron(II) complexes with bipyridyl, phenanthroline, and related α-diimine ligands have been discussed by Busch and Bailar (*122*).

Schilt and Taylor have attempted a partial analysis of the spectrum by indicating the regions in which predominantly hydrogen (C–H) and predominantly ring (C–C; C–N) modes occur (*626*). For the case of bipyridyl complexes it was demonstrated (*520*) that the spectra agreed closely with those of 2-substituted pyridines in general as reviewed by Katritzky (*413*). Popov *et al.* (*589*) have attempted more detailed assignments of some major bands by comparison with the spectrum of pyridine. Little or no Raman data are available for the ligands and their complexes, although Gondo and Kanda do report some peak positions for CCl_4 and CS_2 solutions of bipyridyl (*291*).

The spectra of the free ligands undergo slight modification on coordination to a metal ion; in particular, the ring frequencies (1600–1000 cm^{-1}) tend to undergo small but observable shifts to higher wave number. Slight perturbations of the C–H in-plane deformation modes (β-CH) are also seen. Bands which have been suggested to be most usefully diagnostic of coordination of bipyridyl to a metal ion are those at 995 and 759 cm^{-1} (free ligand). The former peak shifts to 1010 cm^{-1} in the complex spectra (*644*) and the strong band at 759 cm^{-1} (γ-CH) frequently shifts 10–20 cm^{-1} to higher frequency; also a satellite of this band at 741 cm^{-1} (free ligand) gains intensity and is strongly split away from the parent peak (*520*, *644*).

It has been suggested that *cis*-bis(2,2′-bipyridyl) complexes show greater complexity in the region 700–800 cm^{-1} than do *trans*-bis(2,2′-bipyridyl) complexes (*500*). One complex, $[Rh(III)(bipy)_2Cl_2]^+$, which is now known to be definitely cis and which gives a rich spectrum between 700 and 800 cm^{-1}, has also been said to be the trans isomer (*287*, *452*). Since the complex spectra are generally recorded for the solid state, it is clear that spectra–structure correlations of the above type must be used with caution.

The infrared spectra of substituted bipyridyls have been studied (*155*); it was concluded that the overtone region of 1600–2000 cm^{-1} was diagnostic of the substitution pattern. At least one study of the protonated base has appeared (*173*), but N–H modes were primarily discussed.

600–200 cm^{-1}. The far-infrared region of the spectrum is of great potential interest and importance since fundamental modes which involve a considerable contribution from vibrations of the metal-to-ligand bond are expected in this low frequency region.

The far-infrared spectra of free phenanthroline (*253*, *392*) and bipyridyl (*78*, *253*, *291*, *392*, *453*, *544*) have been examined. In the solid state the spectrum of bipyridyl consists of bands at 625, 430, 405, 164, and 92 cm^{-1}; in chloroform solution (660–222 cm^{-1}) this is modified to 616, 401, and 385(sh) cm^{-1}. Attempts have been made to offer assignments on an empirical basis; thus it is reasonably certain that the bands at 625 $[\alpha(CCC)\text{-}\nu_{6a}]$ and 405 cm^{-1} $[\phi(CC)\text{-}\nu_{16a}]$ are ring-deformation modes.

Inskeep (*392*) studied the spectra of the tris-chelate complexes of Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} and observed broad bands between 300 and 288 cm^{-1} (phenanthroline complexes) and 297 and 264 cm^{-1} (bipyridyl complexes) which were not characteristic of the ligands or any anions present. The bands were assigned as "metal–nitrogen stretching" frequencies. The spectra of $Fe(II)(bipy)_3^{2+}$ and $Fe(II)(phen)_3^{2+}$ differed considerably from the other complexes and Inskeep suggested assignments of $\nu(FeN)$ at 530 (phen) (see also Duncan and Molz, *207*) and 423 cm^{-1} (bipy). These assignments have been criticized by Clark and Williams (*160*, *162*) who reasonably point out that the force constant for the metal-to-ligand bond in the iron(II) complexes is not likely to be modified sufficiently to bring the frequencies into the region associated with the stretching of metal–ammine bonds. Also it may be noted that for $Fe(II)(bipy)_3^{2+}$ the band at 423 cm^{-1} is very close to the free ligand band reported in the Raman spectrum at 428 cm^{-1} (*291*). It seems extremely unlikely that any single mode will correspond even approximately to a relatively pure iron–nitrogen stretch in these highly conjugated systems.

Inskeep's assignments of metal–nitrogen modes in other complexes have also been questioned (*162*). Thus contrary to simple mass considerations the band positions reported by Inskeep are at considerably higher frequency than bands assigned with some certainty as ν(MN) in complexes of pyridine (*161*). However, at least one study of a closely related series of complexes of 2-substituted pyridines suggests that simple mass arguments cannot be taken too far for this class of ligand (*503*). It is also known that other bipyridyl complexes of tri- or tetrapositive metal ions do not necessarily exhibit the band in question above 200 cm^{-1}, whereas it is anticipated that ν(MN) will increase as the oxidation state of M increases. $TiCl_4$(bipy) is one example for which no such bands appear above 200 cm^{-1}, yet it is debatable what the relative effective positive charges on the metal atom in this complex and in, say Ni(bipy)_3^{2+}, really are. A much more closely related series is required; the isoelectronic pair V(bipy)_3^{2+} and Cr(bipy)_3^{3+} might serve as an example.

The important problem of metal–nitrogen frequencies is unlikely to be resolved without at least a vibrational analysis of the ligands (no easy task); more extensive Raman data would also help. It has, in fact, been suggested that the bands discussed above are possibly ligand modes excited on complex formation (*162*), although it is not clear why this should occur so randomly. Tentative assignments of ν(MN) above 200 cm^{-1} have been made for a number of bipyridyl and phenanthroline complexes (e.g., *253*, *254*, *452*, *502*).

Mixed Ligand Complexes. Infrared measurements have been applied with some success to the problem of structure determination for a number of mixed ligand complexes. The complex $\text{Cu(bipy)SO}_4 \cdot 2\text{H}_2\text{O}$ is probably polymeric containing bridging sulfato groups (*501*); the complexes $\text{M(2,9-Me}_2\text{-phen)SO}_4$ (M = Fe, Co, or Ni) are similar, whereas the corresponding complexes of copper and zinc are believed to contain chelating sulfato groups (*308*). Pd(phen)SO_4 is also formulated with chelating sulfato group (*237*), and sulfito-palladium complexes are also known (*238*).

A number of dimeric complexes have been investigated, e.g., $[\text{L}_y\text{M(OH)}_2\text{ML}_y]^{n+}$ (*254*, *393*, *502*) and $[(\text{bipy})_2\text{ClOs} \cdot \text{NH} \cdot \text{OsCl(bipy)}_2]^{2+}$ (*371*).

Metal–halogen stretching frequencies are often a quite reliable guide to stereochemistry and a large number of mixed halogenobipyridyl (or phenanthroline) complexes have been studied. These include complexes of the following which will not be mentioned subsequently: zinc(II)

(*161*), titanium(IV) (*57*), zirconium(IV) and hafnium(IV) (*57*, *595*), germanium(IV), and tin(IV) (*55*, *733*), palladium(II) and platinum(II) (*208*, *209*, *717*), and molybdenum(IV) (*57*). The α- and β-forms of $Co(II)(bipy)Cl_2$ contain cobalt(II) ions in octahedral and tetrahedral environments, respectively (*162*).

Finally Kraihanzel and Cotton's analysis of the infrared spectrum of $(bipy)M(CO)_4$ (M = Cr, Mo, or W) has revealed evidence of π bonding between bipyridyl and the central metal atom (see Section VIII).

B. ELECTRONIC SPECTRA

1. *Ultraviolet Spectra*

The ultraviolet spectra of the free bases consist of absorption maxima at 35,700 (band I) and 42,550 cm^{-1} (band II) (bipyridyl) and at 34,480, 37,740, and 44,250 cm^{-1} (phenanthroline). The bands correspond essentially to $\pi \rightarrow \pi^*$ transitions (*245*, *282*, *421*). Kiss and Császár consider the $n \rightarrow \pi^*$ transitions to lie under the long wavelength tail of the bipyridyl spectrum (*421*).

Coordination of the bases to metal ions results in a red shift of the spectrum (*245*, *400*, *421*, *519*, *520*, *652*). In the case of bipyridyl, where the charge on the metal ion is +2 or greater, band I is often split. The constancy of the splitting (~1000 cm^{-1}) suggests it to be vibrational in origin (*652*). In some cases the spectra are complicated by the shift of charge-transfer ($t_{2g} \rightarrow \pi^*$) bands into this region, e.g., $Ir(III)(bipy)_3^{3+}$ (*410*, *519*). Schläfer (*627*) has interpreted the complex spectra in terms of an electrostatic model in which the field due to the positive ion perturbs the term system of the ligand; if the cationic charge is held constant the spectra are very similar, e.g., those of $Fe(bipy)_3^{2+}$ and $Zn(bipy)_3^{2+}$ are alike. The internal ligand transitions have yielded little information about bond type, but a reasonable correlation between the position of band I in bipyridyl complexes and the charge on the metal ion has been observed (Table XI).

TABLE XI

CORRELATION BETWEEN BAND POSITION AND CHARGE

Charge on metal ion	Band I (cm^{-1})
+1	35,100–35,330
+2	32,260–34,015 33,330–34,970 } (split)
+3	31,550–31,750 32,470–32,790 } (split)

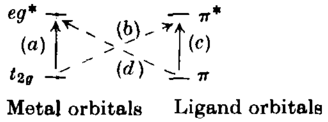
The spectrum of monoprotonated bipyridyl consists of bands I and II at 33,000 and 41,150 cm^{-1}, respectively, and that of the diprotonated base of a single band at 34,480 cm^{-1}. The corresponding data for phen H^+ are 36,230 and 45,050 cm^{-1}. Beattie and Webster (*56*) have examined the spectra of the solids bipy•2HCl and bipy•HCl•$2H_2O$ in KCl discs. The position of band I is similar for the two compounds and suggests that the former is correctly formulated as $bipyH^+$ HCl_2^- in the solid state.

The structure of the monoprotonated base was at one time considered to be cis (*553*), but recent NMR work now suggests a transoid conformation (*143*; see Section V, C). This would appear to invalidate the suggestion (*553*) that complexes in which bipyridine is chelating and necessarily cis can be differentiated from those in which it is catenating by considering the position of band I.

The helical disposition of the aromatic ligands in the tris complexes confers optical rotatory strength on the ligand transitions (*372*, *495*). This fact may be used to arrive at the absolute configuration of the complex, e.g., $(+)Ru(phen)_3^{2+}$ has been shown to exist as a left-handed helix (*495*). The optical rotatory dispersion of phenanthroline complexes of zinc, cadmium, and mercury has also been studied (*419*).

2. *Charge-Transfer and Ligand Field Spectra*

The intense red-colored diamagnetic tris-bipyridyl and tris-phenanthroline iron(II) complex cations are perhaps the most widely studied compounds of these ligands. It is now accepted that the absorption responsible for their characteristic deep color results from a Laporte-allowed transition of the $t_{2g} \rightarrow \pi^*$ type (7). This is supported by the fact that the intensity increases in cooling (*578*) and by measurement of the circular dichroism of the complexes (*372*). The corresponding complexes of ruthenium(II) (*578*) and osmium(II) (*252*) have very similar charge transfer spectra.



(7)

Transitions for spin-paired d^6 complex of the type ML_3^{2+} (schematic).

Fergusson and Harris (*252*) have reported the spectra of a wide variety of complexes of the type $M(bipy)_2X_2$ where M = Fe(II), Fe(III), Ru(II), Ru(III), Os(II), and Os(III) and X = halogen. The study also included the tris complexes. The bivalent metal complexes show four distinct regions of absorption (*i*) ~42,000 cm^{-1}, (*ii*) ~33,000 cm^{-1}, (*iii*) ~28,000 cm^{-1}, and (*iv*) ~19,000 cm^{-1}. The trivalent metal complexes also give bands (*i*) and (*ii*) [internal ligand transition, **7** (*c*)], together with another band at ~25,000 cm^{-1} which is assigned as halogen $\rightarrow e_g^*$. Bands (*iii*) and (*iv*) of the divalent complexes are assigned as $\pi \rightarrow e_g^*$ and $t_{2g} \rightarrow \pi^*$, respectively [**7** (*d*) and (*b*)].

Day and Sanders (*190*) have published a theoretical treatment of the tris complexes of iron(II) and iron(III) with phenanthroline and substituted phenanthrolines together with the corresponding bis complexes of copper(I). The results suggest that for the iron(II) and copper(I) complexes electron transfer occurs between the metal *d* orbitals and molecular orbital (MO)9 in a Hückel molecular orbital scheme for phenanthroline. In the case of iron(III) the metal reduction band arises from MO 8 → Fe(III). Substitution of the ring with methyl groups causes additive shifts in band positions; it is considered that both the energies of the π-MO (hyperconjugative effect) and of the metal *d* orbitals (σ inductive effect) are perturbed. The main source of intensity is believed to be the transition moment resulting from the charge transfer itself. The somewhat complex structure of the band for Fe(II) $(\text{phen})_3^{2+}$ is attributed to vibrational coupling (*190*). Other authors have considered the electronic spectra of $\text{Fe(II)(L)}_2\text{X}_2$ (*506, 655*) and the spin-paired iron(III) complexes (*728*). An important paper giving a theoretical treatment of $\text{Fe(II)(bipy)}_3^{2+}$ has recently appeared; the ground state of the complex is stabilized to the extent of 0.86 eV by the charge transfer interaction (*313a*).

Many complexes of bipyridyl and phenanthroline in which the metal atom is in a formally low oxidation state are intensely colored solids (Section VIII). Experimental methods for examining the diffuse reflectance spectra of these oxygen-sensitive solids have been discussed (*433*). The absorption responsible for the intense colors are also presumably or the $t_{2g} \rightarrow \pi^*$ type. Pappalardo (*580a*) has recently published a paper in which the spectra of Li_2bipy, Ti(bipy)_3, V(bipy)_3, and Cr(bipy)_3 are discussed.

It is now recognized that in particular for the case of iron(II), even α-diimine complexes give spectra similar to the $\text{Fe(II)(bipy)}_3^{2+}$ cation. Also systems with the grouping $\text{—Fe(II)} \leftarrow \text{N=C—C=N—C—C—N—}$ give very similar spectra to that observed for Fe(II) $(\text{terpy})_2^{2+}$ (*450*).

The addition of Lewis acids such as BX_3 (X = F, Cl, Br, Me, or H) to $\text{Fe(II)(phen)}_2\text{(CN)}_2$ affords complexes $\text{Fe(II)(phen)}_2(\text{CN}\cdot\text{BX}_3)_2$ for which a linear relationship between E^0 and the position of the charge-transfer band is observed (*639*). CNBX_3^- is considered to be a poorer

σ donor but a better π acceptor than CN^- in the order $X = Br > Cl > F > Me > H$. The spectra of protonated dicyanobisbipyridine iron(II) complexes are also known (*278*)

Another charge-transfer phenomenon has been observed for the series $[Cr(bipy)_2Cl_2]X \cdot nH_2O$ (*29*), and for $[Ir(phen)_3]X_3 \cdot nH_2O$ (*156*). The color of the complex is a function of X. As the reducing power of X increases, the absorption band undergoes a red shift. The phenomenon is attributed to a redox process of the variety $M(III)X^- \leftrightarrow M(II)X$.

a. Ligand Field Spectra. The study of $d \leftrightarrow d$ transitions within bipyridyl and phenanthroline complexes is often complicated by the presence of the more intense charge transfer bands. In Table XII we tabulate some values of the ligand field splitting parameter Δ. The data for bipyridyl are more extensive than those for phenanthroline.

TABLE XII

SPLITTING PARAMETER FOR LIGAND FIELD

Complex	Δ (Estimated value; cm^{-1})	Ref.
$VCl_4(bipy)$	19,350	(*157*)
$VCl_4(phen)$	19,850	(*157*)
$K[Cr(bipy)(NCS)_4]$	18,700	(*79*)
$[Fe(bipy)_3]SO_4 \cdot 7H_2O$	$16{,}500 < \Delta < 19{,}000$	(*578*)
$[Co(bipy)_3]SO_4 \cdot 7H_2O$	12,670	(*578*)
$[Ni(bipy)_3]SO_4 \cdot 7H_2O$	12,790	(*578*)
$[Cu(bipy)_3]SO_4 \cdot 7H_2O$	~11,700	(*578*)
$Ru(bipy)_3^{2+}$	19,000	(*179*)
$Ru(phen)_3^{2+}$	19,450	(*179*)
$Cr(phen)_3^{3+}$	23,500	(*477*)
$Co(phen)_3^{3+}$	21,270	(*477*)
$[Co(bipy)_3](ClO_4)_3 \cdot 3H_2O$	22,300	(*519*)
$Ni(terpy)_2^{2+}$	12,750	(*379*)

Some useful tabulations of data are available (*408*, *421*) and in addition a number of important new contributions have recently appeared. Robinson *et al.* (*604*) have now resolved the problem of the assignment of the $^3A_{2g} \rightarrow {}^3T_{2g}\,(F)$ transition for NiL_3^{2+}. The lowest frequency bands in the spectra of these complexes do, in fact, correspond to the spin forbidden $^3A_{2g} \rightarrow {}^1E(D)$ transitions. This is confirmed by work with single crystals containing the tris cations (*578*). Values of the Racah parameter B in the complexes are ~710 cm^{-1}, approximately a 30% reduction of the free ion value.

The $3d^3$ complex V(II)(bipy)$_3^{2+}$ has been treated theoretically, and the longest wavelength absorption (${}^4A_{2g} \rightarrow {}^4T_{2g}$) is said not to correspond exactly to Δ (*614*). Crosby *et al.* have analyzed the luminescence spectrum of Ru(II)(bipy)$_3^{2+}$ and Ru(II)(phen)$_3^{2+}$ to obtain values of Δ, B, and C (*179*) (see also Hercules and Lytle, *329*).

Furlani and Piovesana (*272*) reported spectroscopic data for "LH$^+$ MoLCl$_4^-$" but Walton *et al.* isolated $\mathrm{MoL_2X_2 \cdot MoLX_4}$ (X = halogen) from the same preparation (*718*). Assignment of the spectrum is rendered difficult by the presence of Mo(III) in two forms. Both groups of workers do however agree that a method reported by Steele to give Mo(III)(bipy)$_3$Cl$_3$ does not, in fact, afford that complex.

An important paper by Palmer and Piper (*578*), which also includes a valuable literature survey, reported the single crystal spectra of M(II)(bipy)$_3^{2+}$ (M = Fe, Ru, Co, Ni, and Cu). The most interesting case is that of copper(II). The rigidity of bipyridine and phenanthroline are such that only small tetragonal distortions should be possible in the tris complexes (*429*). ESR data for both Cu(II)(phen)$_3^{2+}$ and Cu(II)(bipy)$_3^{2+}$ (Section V, D) indicate tetragonal symmetry; yet Palmer and Piper obtain a more satisfactory interpretation of the spectral data by assumption of trigonal (D_3) symmetry, although this requires the choice of a very high value (–2600 cm^{-1}) for K the trigonal splitting parameter. It is apparent that the optical and magnetic axes in these complexes do not coincide (*422*). The single crystal electronic and ESR spectra of the complex [Cu(bipy)$_2$(NO$_2$)](NO$_3$) have been determined by Hathaway *et al.* (*590a*). The compound is known to be cis octahedral and the order of the d orbitals was established as $d_{z^2} > d_{xy} > d_{x^2-y^2} > d_{xz} \sim d_{yz}$. Thus it is dangerous to assume that copper(II) complexes of the type CuL$_2$X$^+$ (X = uninegative ligand) are necessarily five coordinate.

There has been some discussion of the spin-forbidden bands seen on the long wavelength tail of the $t_{2g} \rightarrow \pi^*$ band of FeL$_3^{2+}$ (*506*, *628*, *637*). Palmer and Piper are able to see one such band at 11,500 cm^{-1} and assign it as ${}^1A_1 \rightarrow {}^3T_1$ (*578*).

b. f-Block Elements. Few spectroscopic data are available for bipyridine and phenanthroline complexes of the actinides, although the spectrum of UCl$_4$·phen has been reported (*275*, *276*).

The search for new laser materials has inspired a considerable preparative effort in the lanthanide bipyridyl/phenanthroline/terpyridyl field. The terms arising from the $4f^n$ configuration of a lanthanide undergo small shifts of energy on complex formation. Sinha (*645*) has proposed a measure of the relative covalency of the lanthanide-to-ligand bond based on the ratio ν (aquo complex)/ν (nitrogen base complex) since the bands of the aquo ion undergo a slight red shift when the nitrogen base is added. This gave the result: terpy < bipy < 4,4′-Me_2-bipy. A study of the reflectance spectra of some complexes of bipyridyl and of the 4,4′-dimethyl-substituted base also indicated the greater nephelauxetic effect of the latter ligand (*642*). The photoluminescence of a series of terpyridyl complexes has been investigated (*646*) as has the fluorescence of a number of bipyridine complexes (*643*, *648*). A supposedly pure specimen of the gadolinium complex, $Gd(bipy)_2Cl_3 \cdot 2H_2O$, showed the characteristic fluorescence of terbium(III) and europium(III) on irradiation with ultraviolet light. The energy absorbed by the aromatic ligands was transferred to the metal ions (*643*). The ligand field splitting in $[Eu(phen)_2(NO_3)_3]$ has been investigated (*123*).

C. NUCLEAR MAGNETIC RESONANCE SPECTRA

Several studies of bipyridyl, phenanthroline, and their complexes in solution have been reported. There is good experimental agreement between workers. The spectrum of bipyridyl itself in various solvents (*143*, *283*, *438*, *551*, *659*) is known. Castellano *et al.* (*143*) studied this ligand in a range of solvents, and from their results assign differing conformations to bipyridyl in inert and proton donor solvents. In inert solvents the molecule is trans planar (interplanar angle = 0°), while in proton donor solvents mono- and diprotonated species exist in transoid skew conformations with interplanar angles of the order of 25°–30° and 55°–72°, respectively. Spotswood and Tanzer (*659*), however, suggest that there is no change from trans conformation with solvent. The changes in electron density relative to pyridine for the various ring positions have been reported (*557*). For phenanthroline (*85*, *138*, *203*, *533*, *534*, *606*) the molecule is, of course, rigid. The spectrum of the ligand has been shown to be consistent with the calculated net charges at the various ring positions (*533*), while the effect of methyl substituents has been examined (*138*).

When these ligands are coordinated onto metal ions, small changes occur in the proton chemical shifts (*143*, *533*, *534*, *606*) with the exception of those protons alpha to the donor atom, i.e., 2 and 9 for phenanthroline, 6 and 6′ for bipyridyl, which shift to high field by approximately one part per million. This shift is directly related to the M–N bond length (*533*, *534*). If this shift is caused by the magnetic anisotropy of a neighboring ligand, the Fe–N bond length in $Fe(bipy)_3^{2+}$ may be calculated to be 2 Å, a reasonable value (*143*). When complexes of type *cis*-$[Co(III)(phen)_2X_2]$ are examined the two halves of the ligand are no longer magnetically and chemically equivalent, and the chemical shifts for the two halves differ markedly, for example, one of the 2,9-protons is still found to high field of the free ligand while the other is shifted to low field. This technique therefore provides an absolute method of determining the geometry of bis complexes (*535*). Spin densities around the ligand for tris-phenanthroline iron(III) complexes have been determined by contact shifts (*473*), but because of the 2,9 high field shift, the meaning of the result for these positions is uncertain. Other studies include the spectra of $[ML_2(NO_3)_3]$ for a rare earth element (M) and L = 4,4′-dibutylbipyridyl, where rapid exchange between two nonequivalent ligands is postulated to account for the single spectrum obtained (*390*), ^{59}Co magnetic resonance of $Co(bipy)_3^{3+}$ (*197*), the spectra of some bridged biquaternary bipyridyl systems (*127*, *658*), and proton spin relaxation in solutions containing Cu(II) and bipyridyl (*541*). Spin delocalization mechanisms in $Ni(II)(bipy)_3^{2+}$ have been discussed (*731a*).

D. ELECTRON SPIN RESONANCE SPECTRA

Various attempts (*233*, *327*, *434*, *613*, *742*) have been made to study the ESR spectrum of the bipyridyl anion ($bipy^-$) in the presence of alkali metal ions, but there is considerable doubt about the existence of the free ion. Dos Santos-Veiga *et al.* (*613*) find that splitting due to the metal ion is seen for all metals in the group Li–Rb. Henning (*327*) reports the spectrum of potassium bipyridide in tetrahydrofuran (THF) at –50°C as being essentially due to the free ion, and obtains fair agreement between the observed proton splitting constants and the theoretical spin densities for the free ion. This spectrum differs markedly from that of the sodium salt in DME (1,2-dimethoxyethane) as solvent (*742*) which is probably the spectrum of the Na • bipy complex. There is some evidence (*107*) for biradical dimers in frozen concentrated solutions of potassium reduction products, which show zero field splittings similar to those found for the alkaline earth chelates. The rate of exchange between bipyridyl and potassium bipyridide has been measured in DME (*598*), and values of 10 kcal/mole and 5 eu were found for the enthalpy and entropy of activation. From these data, Reynolds suggests that the reaction may proceed via an activated complex involving a K^+ bridge.

Spectra have also been reported for alkaline earth complexes of bipyridyl, terpyridyl, and substituted bipyridyls and phenanthrolines (*106*, *107*) of the type $M^{2+}(L^-)_2$. For Be, Mg, Ca, and Sr the spectra show the presence of a ground, or very low excited, triplet state consistent with a divalent metal cation in a tetrahedral environment with one electron on each chelate ligand. The similarity in splittings for Be and Mg is thought to show that interligand interactions prevent the achievement of the small Be^{2+} ionic radius. Treatment of bipyridyl with zinc amalgam does not give a paramagnetic product, although substituted bipyridyl and phenanthroline molecules do so and exhibit splittings larger than those of typical metals (*106*). Some spectra for boron-containing species are discussed in Section VI.

The ESR spectra of the tris-bipyridyl complexes of Cr(I), V(0), and Ti(–I) have been reported (*183*, *233*, *427*). Isotropic g values and hyperfine coupling constants are given in Table XIII. König (*427*) shows that

TABLE XIII

DATA FOR Ti, V, AND Cr

Metal	g	A_M (gauss)	$A_{^{14}\mathrm{N}}$ (gauss)	Ref.
Ti	2.007	—	—	(*427*)
^{51}V	1.983	84 ± 0.5	—	(*183*)
^{51}V	1.983	83.5 ± 1.0	2.3 ± 0.1	(*427*)
^{53}Cr	1.997	21.8 ± 0.5	3.05 ± 0.05	(*427*)

there is a strong σ interaction between the metal $4s$ orbitals and the ligand $\sum_0^+$ orbitals increasing in the order Ti(–I) < V(0) < Cr(I), while Davidson *et al.* (*183*) deduce the unpaired electrons to be strongly localized on the ligand. Orgel (*568*) suggests that extensive delocalization of metal electrons in a very low oxidation state will cause the energy of the e orbitals to be below a, hence causing Ti(bipy)$_3$ to be diamagnetic, perhaps involving bipy$^-$.

ESR and spectroscopic studies have been reported for VO(bipy)$_2^{2+}$ where $g_{\parallel} = 1.950$ and $g_{\perp} = 1.987$ (*738*); and ESR and magnetic studies of Fe(III)/phenanthroline species, where evidence of a monocomplex containing high-spin Fe(III) in an asymmetric field is presented (*547*). The majority of ESR results available refer to copper(II) complexes. At high temperatures CuL$_3^{2+}$ exhibits a single absorption (*10*), explained by Hudson (*388*) in terms of a dynamic model. At lower temperatures (*10*, *687*) several absorptions are observed. The data for liquid nitrogen temperatures are given in Table XIV. Both reports mention hyperfine structure due to ligand N. Using ^{63}Cu, nine such components were observed, indicating the interaction of four ligand nitrogen atoms with the unpaired electron. More recent work which examined the ESR spectra of copper-doped crystals of Zn(phen)$_3$(NO$_3$)$_2$·2H$_2$O suggested that the data were best interpreted by a dynamic model assuming two equivalent distortions rather than the three required by Hudson's theory (see also Section V, B, 2) (*422*). The spectrum of Cu(bipy)$_2^{2+}$ is also known (*559*, *656*) and is consistent with a square planar structure (however, see Section VII). In the case of compounds [Cu(bipy)$_2$X]Y $g_\parallel$ (i.e., g_3) < $g_\perp$ (i.e., g_1) which is interpreted as showing a compressed trigonal bipyramidal structure (*229*). The complexes of silver(II), first studied by ESR in the early 1950s (*90*, *301*), have been examined in detail by McMillan and Smaller (*497*) whose results at 77°K are given in Table XIV. In this table quoted values of $g_\parallel$ and $g_\perp$ have been listed under g_3 and g_1, respectively, for Allen *et al.* (*10*) and Elliot *et al.* (*229*).

TABLE XIV

DATA FOR COPPER AND SILVER COMPLEXES

Compound	g_1	g_2	g_3	A_1 (cm^{-1})	A_3 (cm^{-1})	Ref.
[Cu(bipy)$_2$]SO$_4$	2.065	2.078	2.189	—	—	(*656*)
[Cu(bipy)$_2$Cl]ClO$_4$	2.19	—	2.01	—	—	(*229*)
[Cu(bipy)$_2$Br]ClO$_4$	2.18	—	2.02	—	—	(*229*)
[Cu(bipy)$_2$I]ClO$_4$	2.17	—	2.03	—	—	(*229*)
[Cu(bipy)$_3$](NO$_3$)$_2$	2.046	—	2.268	Small	164×10^{-4}	(*10*)
[Cu(phen)$_3$](NO$_3$)$_2$	2.062	—	2.273	36×10^{-4}	161×10^{-4}	(*10*)
[Ag(py)$_4$]S$_2$O$_8$	2.049	2.098	2.148	—	—	(*497*)
[Ag(phen)$_2$]S$_2$O$_8$	2.046	2.046	2.168	—	—	(*497*)
[Ag(bipy)$_2$]S$_2$O$_8$	2.032	2.032	2.164	—	—	(*497*)
[Ag$_2$(bipy)$_5$]S$_2$O$_8$	2.040	2.056	2.176	—	—	(*497*)
[Ag(bipy)$_3$](NO$_3$)$_2$	2.037	2.047	2.168	—	—	(*497*)

E. MÖSSBAUER SPECTRA

1. *Iron Complexes*

A small, but resolvable splitting of the resonance line for the tris-chelate complexes of iron(II) is observed (*235*, *261*). In the case of Fe(II)(bipy)$_3$Cl$_2$ ΔE_Q (0.34 mm sec^{-1}) has been shown to be independent of temperature (*298*°–145°K) to within experimental error, although for the series Fe(II)(phen)$_3$X$_2$ ΔE_Q was shown to vary slightly with the anion X (*207*). The small quadrupole splitting presumably reflects the D_3 symmetry of the cations (*261*). Epstein (*235*) has compared the spectra of Fe(bipy)$_3^{2+}$, Fe(phen)$_3^{2+}$, and Fe(phen-R)$_3^{2+}$ where R = 5-nitro, 5-chloro, 5,6-dimethyl, or 3,4,7,8-tetramethyl. Since in such a closely related series the *d*-electron shielding effects should be similar, it was considered that the isomer shift (δ) should be a measure of covalent bond strength. The values of δ varied over a range of 0.03 mm sec^{-1} which was too small to permit firm conclusions to be drawn. However, $Fe(bipy)_3^{2+}$ gave the smallest value, implying a greater degree of covalency than for the phenanthroline complexes.

Attempts have been made to use the technique to identify geometric isomers of $Fe(II)L_2X_2$. Thus it is now known that the two forms of $Fe(II)(phen)_2(CN)_2$, said by Schilt (*619*) to be cis and trans isomers on the basis of infrared spectroscopy, give identical Mössbauer spectra and cannot be geometrical isomers (*80*).

Duncan and Mok (*207*) have not accepted a dimeric formulation for the series $Fe(II)(phen)_2X_2$, and suggest the complexes to be cis on the basis of Mössbauer and UV–visible spectroscopy. Also it was noted that δ and ΔE_Q were approximately constant for the series ($X = Cl$, Br, I, N_3, or SCN); the greater sensitivity of ΔE_Q than μ_{eff} to small deviations from octahedral symmetry has been demonstrated for these compounds together with several others of the $Fe(II)(pyridine)_4X_2$ variety (*288*).

Reports of Mössbauer parameters for various iron-bipyridyl and phenanthroline complexes have appeared (*93*, *672*). In some cases details of preparation and characterization are not given and, for example, the compound "$[(phen)_2Fe(OH)_2Fe(phen)_2]Cl_4$" is almost certainly incorrectly formulated (*672*). For one series $Fe(CN)_6^{4-}$, $Fe(CN)_4(bipy)^{2-}$, and $Fe(CN)_2(bipy)_2$, the values of δ are identical but, since the quadrupole splitting is different for the three cases, this does not imply identical ligand field strengths for CN^- and bipy (*93*).

It is well known that for the series $F(II)(phen)_2X_2$ ($X = Cl$, Br, I, N_3, SCN, SeCN, or CN) the magnetic behavior is a function of X. Thus the ground state of $Fe(II)(phen)_2Cl_2$ is $^5T_{2g}$, whereas that of $Fe(II)(phen)_2(CN)_2$ is $^1A_{1g}$ (*506*). Also the magnetic susceptibilities of $Fe(II)(phen)_2(NCS)_2$ and $Fe(II)(phen)_2(NCSe)_2$ show anomalous temperature dependence, the moments decreasing on cooling (*27*). The original suggestion that these two compounds were dimers (*27*) is not supported by a more detailed magnetic and spectroscopic study (*429*); also, one report that the Mössbauer spectra were insensitive to temperature (*167*) is now admitted to be in error (*429*). In fact the large quadrupole splitting at room temperature observed for the isothiocyanato and isoselenocyanato complexes is characteristic of the $^5T_{2g}$ ground state, whereas at liquid nitrogen temperatures the splitting is small and compatible with the $^1A_{1g}$ ground state (*196*, *428*, *429*). The value of $\nu(CN)$ also alters on cooling (*28*). Table XV presents some Mössbauer data and calculated values of Δ and β for the complexes $FeL_2(NCS)_2$. The magnetic properties of $^5T_2$ terms have been discussed (*430*). Although the radius of iron(II) will alter as the change of spin state occurs (*6*), $Fe(phen)_2(NCS)_2$ and

TABLE XV

SOME SPECTROSCOPIC DATA FOR THE COMPOUNDS $Fe(phen)_2(NCS)_2$ AND $Fe(bipy)_2(NCS)_2$

Complex		Δ (cm^{-1})	β	δ (mm sec^{-1})	(E_Q (mm sec^{-1})
$Fe(phen)_2(NCS)_2$	$^5T_2$	11,900	0.61	0.98 ± 0.03	2.67 ± 0.03
	$^1A_1$	16,300	0.55	0.34 ± 0.05	0.34 ± 0.06
$Fe(bipy)_2(NCS)_2$	$^5T_2$	11,200	0.57	—	—
(*i*)[a]	$^5T_2$	—	—	1.06 ± 0.04	2.18 ± 0.03
	$^1A_1$	—	—	0.36 ± 0.04	0.50 ± 0.03
(*ii*)[a]	$^5T_2$	—	—	1.06 ± 0.05	2.31 ± 0.03[b]
	$^1A_1$	—	—	0.36 ± 0.04	0.47 ± 0.02
(*iii*)[a]	$^5T_2$	—	—	1.06 ± 0.04	2.13 ± 0.03
	$^1A_1$	—	—	0.34 ± 0.04	0.50 ± 0.03

[a] Polymorphs (see text).

[b] Small amount of the 77°K ($^1A_1$) spectrum present.

$Fe(phen)_2(NCSe)_2$ have been said, on the basis of X-ray powder data, not to undergo a phase change on cooling. However, by holding the temperature of a specimen of $Fe(phen)_2(NCS)_2$ constant at 173°K, it was shown that the change in magnetic properties occurred slowly, but discontinuously, at this temperature (*142*). The change of susceptibility with time followed a first-order rate law and the slow nature of the change implied an activation energy compatible with a crystallographic phase change (dissimilar phases may sometimes give similar powder patterns) (*113*). Dézsi *et al.* have measured Mössbauer spectra in the region of the critical temperature and they find a four-peak spectrum consistent with the presence of both high and low spin species (*196*).

A recent study of the related bipyridyl complex has revealed further complications. This complex may be prepared as three distinct polymorphs: (*i*) rhombic crystals, (*ii*) diamond-shaped thick plates, and (*iii*) hexagonal prisms. Initially μ_{eff} for (*i*) and (*iii*) increase, but there is a sudden decrease at 216°K (*i*) and 210°K (*iii*) after which the moments approach 0.94 (*i*) and 1.61 (*iii*) at 77°K. The behavior of polymorph (*ii*) is more complex; initially μ_{eff} decreases ($5.21 \rightarrow 3.60$) between 293° and 220°K, at 220°K there is a sharp drop over 12° to 2.42 B.M.* and a value of 1.39 B.M. is approached at 77°K (*432*). The sharp change is believed to coincide with a change of molecular dimensions; infrared analysis indicates stronger Fe–N bonds, but weaker Fe–NCS bonds, at

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* B. M., Bohr magneton.

liquid nitrogen temperatures. The different detailed magnetic behavior of specimens of $Fe(phen)_2(NCS)_2$ prepared by different routes (*27*, *429*) may arise from the failure to recognize the possible existence of polymorphs of the compound (*432*).

The magnetic properties of tris(2-Me-phen) iron(II) salts (I^-, ClO_4^-, BF_4^-, and PF_6^-) were recently examined (*293*). The Curie–Weiss law is obeyed over a limited temperature range, but the detailed behavior is a function of the anion present. The system is also considered to exhibit a change of spin state on cooling and attempts have been made to calculate values of the equilibrium constant defined as $K = [\text{spin free}]/[\text{spin paired}]$ Plots of $\log K$ vs T^{-1} are curved implying that ΔH is a function of temperature, possibly due to changes in other factors, e.g., lattice parameters, on cooling (*293*).

$^{57}Co(bipy)_3(ClO_4)_3 \cdot 3H_2O$ has been used as a source of 14.4 keV gamma radiation and it has been shown that the daughter iron nucleus is stabilized as $Fe(III)(bipy)_3(ClO_4)_3$ within 10^{-7} seconds after electron capture (*587*).

2. *Tin Complexes*

The Mössbauer spectra of a number of bipyridine and phenanthroline complexes of tin(IV) have been reported, although in many cases the presence of these bases has been incidental (*236*). It has been noted that whereas zero quadrupole splitting is seen for SnX_4(bipy) (X = Cl, Br, or I) diorganotin halide complexes of bipyridyl exhibit large quadrupole splitting (*299*, *549*). Greenwood and Ruddick suggest, on the basis of their observations on a large number of six-coordinate tin(IV) derivatives, that ΔE_Q will be zero if all six ligand atoms (L) in SnL_6 have nonbonding p_π electrons (*299*).

It has been demonstrated that the tin(IV) complexes R_2SnX_4 exhibit quadrupole splittings of 2 mm sec^{-1} when the organic groups are cis and of 4 mm sec^{-1} when they are trans. On this basis complexes R_2SnCl_2L (R = Me, *n*-Bu) have been shown to have trans organic groups (*260*).

VI. Complexes of Nonmetals

In this section we will discuss the complexes of Be, B, C, Si, Ge, P, As, Sb, Bi, and S; the complexes of H^+, mentioned in Section III, A, have frequently been used as large cationic species but will not be further discussed here.

The complexes of bipyridyl and phenanthroline with nonmetals may be considered to arise through the formation of adducts between Lewis acids and bases; the formation of complexes of the negatively charged ligands; or some stage between these extremes. ESR spectra (Section V, D) suggest the second possibility for the electropositive elements of groups I and II and perhaps also for B, whereas groups IV and V form ligand-containing cations where the charge may reside within the chelate grouping (*176*), thus suggesting that these species are best regarded as direct analogs of pyridylium species, i.e., the first possibility. These complexes are frequently colored owing to charge transfer to antibonding ligand molecular orbitals (*166*).

The reaction of $BeCl_2$ and Li(bipy) in ether gives $Be(bipy)_2$ (*166*), whose ESR spectrum has been discussed in Section V, D. Compounds of type $X_2Be(bipy)$ have been prepared where X = Cl, Br, I, Ph, Me, and Et, and λ_{max} varies with the electronegativity of X, this absorption being ascribed to charge transfer from Be–X to an antibonding bipyridyl molecular orbital (*165*, *166*). The weakly paramagnetic $Li[Be(bipy)_2]$ may be prepared by the action of excess Li on $Be(bipy)_2$. The brick red $[R(Ph_2N)Be(bipy)]$, where R = Me or Et, has been prepared by the addition of bipyridyl to the parent compound; this adduct decomposes (but not quantitatively) by disproportionation giving some $Me_2Be(bipy)$ (*164*).

When $AgClO_4$ is added to Ph_2BCl in nitromethane, and bipyridyl then added, the ion $[Ph_2B(bipy)]^+$ is formed. This group remains cationic with a variety of anions and is sufficiently resistant to hydrolysis for metathetical reactions to be carried out in water (*37*, *184*, *185*). Other cationic species of type $[X_2BL]^+$, where $X_2 = (RO)_2$, $(PhO)_2$, (o-$C_6H_4O_2$), $(Me_2N)_2$ (*37*), $(C_6H_4OC_6H_4)$ (*185*), or (p-biphenyl (*383*), have been prepared. By reacting chloroboranes with Li(bipy) or $Li_2(bipy)$, Kruck and Urry (*442*) were able to prepare the diamagnetic $[(Me_2N)B(bipy)]$ and the paramagnetic species $B(bipy)_2$, $[(Me_2N)_2B(bipy)]$, and [(2,2-biphenylene)B(bipy)] whose ESR spectra were measured. For $B(bipy)_2$ equal splittings due to the central boron and the ligand nitrogen atoms are observed and the compound may therefore contain $bipy^-$ ligands. These authors also suggested that $[(Me_2N)_2B(bipy)]$ abstracts hydrogen from such solvents as THF giving a diamagnetic nonchelate compound $[(Me_2N)_2B(bipyH)]$.

The irradiation of bipyridyl and CH_2I_2 in acetonitrile produces the chelate ion $[bipyCH]^+$, which is protonated in 70% sulfuric acid to $[bipyCH_2]^{2+}$, and also attacked by nucleophiles at the bridgehead carbon (*125*, *126*). The nitrogen atoms of bipyridyl may also be linked by $(CH_2)_n$ groups where $n = 2$, 3, or 4 to yield dications. As n increases the longest wavelength UV bands move to shorter wavelength, while the oxidation–reduction potentials become more positive: thus $Na_2S_2O_4$ in aqueous solution reduces only that cation having $n = 2$ (*384*). Bipyridyl and phenanthroline, but not terpyridyl, form stable 1:1 adducts, which are fairly resistant to hydrolysis, with silicon tetrahalides. They are believed to contain a chelate grouping, and perhaps Si in an octahedral environment (*51*, *52*, *305*, *722*; *723*). The reduction of $SiCl_4$(bipy) by Li_2(bipy) yields black paramagnetic (1.37 B.M.) crystals of Si$(bipy)_3$ (*350*). More recently NaSi$(bipy)_3 \cdot 7$THF, Na_2Si$(bipy)_3 \cdot 7$THF, and related Li derivatives (*369*) have been reported. There is some evidence that $SiCl_4$ and bipyridyl form a 1:3 adduct without recourse to reducing agents (*675*); 1:1 adducts have also been prepared by the action of bipyridyl on R_3SiX where R is an alkyl or phenyl group and X a halogen. In CH_2Cl_2 these adducts give conducting solutions in which dissociation to $[R_3Si(bipy)]^+X^-$ is believed to occur (*176*, *675*, *729*). Similarly $SiCl_4$(bipy) and SiI_4(bipy) give conducting solutions in acetonitrile where 4-coordinate Si has been tentatively suggested (*631*). Mixtures of Me_2SiCl_2 and bipyridyl (1:2) appear to yield a uni-bivalent electrolyte (*675*). X-Ray analysis of $[Ph_3Si(bipy)]I$ shows that the ionic formulation is maintained in the solid state, the Si–I distance being 6 Å (*729*). Adducts similar to those of silicon may be obtained with germanium halides (*476*, *675*); however, GeI_4 yields $[GeI_2(bipy)_2]2I$, and the Ge and Sn tetraiodides form stable 1:1 ionic adducts with terpyridyl, while undissociated 1:1 adducts of terpyridyl with Ph_2PbX_2 may be prepared (*250*).

Adducts (1:1) of bipyridyl and MX_3 are known, where M = As, Sb, or Bi, and X is a halogen (*605*, *629*, *647*). In nitrobenzene these adducts ionize to $[MX_2(bipy)]^+X^-$, ionization decreasing as M is changed from As to Bi, and increasing as X goes from Cl to I (*605*). In contrast to this report, however, Sutton (*667*) stated that bipyridyl or phenanthroline did not coordinate to BiX_3, but merely formed $[LH_3O]^+[BiX_4]^-$. The reaction of chlorine with a solution of $AsCl_3$ and ligand in CCl_4 yields orange or yellow solids which readily evolve chlorine giving $AsCl_3L$. The initial product may contain As(V) (*629*). The cations $[MCl_4(phen)]^+$ where M = P or Sb, and probably also that where M = As, have been prepared and characterized by infrared (*53*), conductivity (*195*), and analytical techniques. Finally, SCl_2 and bipyridyl yield SCl_2(bipy) which is readily hydrolyzed (*724*).

VII. Complexes of Metals in "Normal" Oxidation States

We arbitrarily define the majority of metal ions in oxidation states II and III as being in "normal" oxidation states, but we do not adhere rigorously to this classification.

A. REPRESENTATIVE ELEMENTS

1. *Group II*

An infrared spectroscopic investigation suggests the phenanthroline molecules to be coordinated in $M(phen)_4(ClO_4)_2$ ($M = Ca$, Sr, or Ba) (*626*). Treatment of calcium metal in liquid ammonia with the ligands at −70°C produces the solids $Ca_2(bipy)(NH_3)_{1.29}$ (violet) and $Ca(phen)(NH_3)_{0.74}$ (purple) which become hot and turn yellow in air (*699*). They are probably best regarded as containing the ligand anions.

A common use of these ligands is to stabilize organometallic species which would be readily hydrolyzed. In this way a number of organozinc (*561, 562, 679, 682, 683, 685, 686*), organocadmium (*680*), and organomercury (*133, 151, 171*) compounds have been obtained as relatively stable monomers. The zinc dialkyl complexes are often highly colored. This is attributed to a $\pi^* \leftarrow d$ transition (*562*); the charge-transfer band shifts into the ultraviolet as the electronegativity of the organic group increases; thus, $Et_2Zn(bipy)$ is orange, $Ph_2Zn(bipy)$ is yellow, and $(F_5C_6)_2Zn(bipy)$ is colorless. The order of stability for the dialkyl zinc complexes is t-Bu > i-Pr > Et > Me, i.e., the order of expected ease of d_π–p_π bond formation. With *N,N,N′,N′*-tetramethylethylenediamine, the order is reversed (*561*). It is peculiar that the complex of dialkylzinc with bipyridyl (m.p. 94°C) is stable at room temperature, whereas the corresponding phenanthroline complex decomposes spontaneously at 0°C (*682*).

It is said that alkyl- and arylmercurials do not form bipyridyl and phenanthroline complexes (*151*); however, perfluoroalkylmercurials are known to do so (*133, 151, 172*). A convenient preparation of such compounds has been described (*170*). Sutton (*668*) has reported the preparations of the compounds HgX_2L, HgYL, and HgL_2^{2+} ($X =$ halogen, $Y =$ oxalato or sulfato).

2. *Group III*

The anhydrous tris-chelate complexes of aluminum perchlorate are stable beyond 300°C (*669*). Trialkylaluminums form colored complexes with bipyridyl and phenanthroline (*109*) which are five-coordinate monomers (*681*).

Few complexes of gallium are known (*560*) although GaL_3X_3 [$X = Cl^-$, Br^-, or I^- (*137*), $X = ClO_4^-$ (*669*)] have been reported. The reaction of bipyridyl with "GaX_2" affords $[Ga(bipy)_2]^+[GaX_4]^-$ ($X = Cl$ or Br) (*7*).

Simple preparations of $InL_3(ClO_4)_3$ and $In(terpy)_2(ClO_4)_3$ are known (*140, 669*). All three are normal six-coordinate complexes of indium(III). The compounds $In(bipy)_3X_3$ ($X = Cl$, Br, or I) have also been obtained

(*670*). A product of the composition $In(bipy)_{1.5}Cl_3$ is also known (*141*, *406*) which is $[In(bipy)_2Cl_2][In(bipy)Cl_4]$ (*719*), although the molar conductivity is rather low (*141*). Conductivity data can, in fact, be misleading for these systems since the Onsagar law is not always obeyed (*141*, *719*). Other known indium(III) complexes include $[InL_2(NO_3)_2]NO_3$, $[In(phen)_3](NO_3)_3$ (*141*), and $[In(2,9\text{-}Me_2\text{-}phen)_2Cl_2]Cl$ (*406*). The latter, if correctly formulated, is presumably a cis complex.

Sutton (*666*) and Kul'ba (*458–460*) have prepared a number of bipyridyl and phenanthroline complexes of various thallium(III) salts; those with nitrate and perchlorate are generally bis-chelate compounds, whereas the halides give compounds of stoichiometry TlX_3L. Stability constants have been reported for some of the complexes (*457*). Other mixed ligand species containing ethylenediamine (*461*) and oxalate (*456*) and salts containing both bipyridyl and phenanthroline coordinated to the same thallium(III) ion (*456*) are also claimed.

$Tl(bipy)_2(ClO_4)_3$ and $Tl(bipy)_2(NO_3)_3$ contain both coordinated and ionic oxy anions (*243*). $Tl(bipy)_3(ClO_4)_3$ possibly loses one molecule of ligand in nitrobenzene to give $Tl(bipy)_2ClO_4^{2+}$ and $2ClO_4^-$ (*243*).

A convenient method of preparing thallium(III) halide complexes involves the use of methyl cyanide as a solvent (*405*, *406*). Infrared spectra in the $\nu(TlCl)$ region indicate that crystals of the complexes $TlCl_3L$ do not contain the $TlCl_4^-$ ion (*406*, *499*). It is improbable that a cationic species containing thallium-to-chlorine bonds is present in the solid state. The position and multiplicity of the thallium–chlorine stretching frequencies for $TlCl_3L$ (*499*) are compatible with the formulation $Tl(bipy)_3^{3+}Tl_2Cl_9^{3-}$. The solution conductivity data, which are difficult to interpret (*405*, *406*), may then arise from the following dissociation:

$$2[Tl(bipy)_3][Tl_2Cl_9] \rightleftharpoons 3Tl(bipy)_2Cl_2^+ + 3TlCl_4^-$$

This interpretation is consistent with the known solution behavior of $Tl(bipy)_3^{3+}$ and $Tl_2Cl_9^{3-}$.

Walton (*720*) however, in a recent paper favors the presence of a neutral specie in the crystals of TlX_3L on the basis of a combined conductivity and infrared investigation. The work again stresses the need to determine conductivities over a concentration range. New compounds including $R_4N[TlX_4L]$, $TlI_3 \cdot L$ (possibly five-coordinate), $TlCl_3(terpy)$, and $(TlCl_3)_2$ terpy (possibly $[Tl(terpy)Cl_2][TlCl_4]$) were also reported. Bis-chelate compounds of thallium(I) are known although no structural data are available (*460*); the cations $Tl(I)L_2^+$ are possibly distorted tetrahedra.

Organothallium compounds afford complexes with bipyridyl and phenanthroline (*636*). Most work has involved perfluoroarylthallium(III) compounds of the variety $(C_6F_5)_2TlX \cdot L$ (X = Cl, Br, NO_3, or CF_3COO) which are considered to contain five-coordinate thallium (*192*, *193*). A preparative distinction between the two chelate ligands is found when $(RCOO)Tl(C_6F_5)_2$ is the acceptor molecule; the phenanthroline complex is formed between stoichiometric amounts of reactants whereas an excess of bipyridyl must be used (*191*).

3. *The Lanthanides*

The possibility of efficiently transferring energy to lanthanide ions via a strongly absorbing organic ligand and the consequent importance of such systems in laser technology has motivated much recent research in this field. Kononenko and Polnektov (*435*) were the first to demonstrate complex formation between phenanthroline and the rare earths; subsequently many complexes of bipyridyl, phenanthroline, and terpyridyl with lanthanide halides (*47*, *136*, *644*, *646*), nitrates, and sulfates (*417*, *489*, *646*, *649*, *650*) have been prepared. Also numerous examples of mixed ligand complexes based on acetylacetone (acac) and substituted acetylacetones have been reported, e.g., $M(acac)_3(phen)$ (*47*); these compounds generally contain eight-coordinate lanthanide ions (*435*, *524*, *525*). The use of the lanthanide perchlorates affords complexes of high coordination number with respect to phenanthroline, e.g., $M(phen)_4(ClO_4)_3$; the perchlorate groups are not coordinated (*441*).

Hart and Laming have carried out the most complete comparative surveys (all lanthanides except promethium) of the compounds: $ML_3(SCN)_3$, $M(phen)_2Cl_3$, $M(phen)_2Cl_3H_2O$ (*322*), $M(acetate)_3 \cdot L$, $M(bipy)_2Cl_3 \cdot nEtOH$ ($n = 1$ or 2, the ethanol is readily lost), and $ML_2(NO_3)_3$ (all nitrate groups are coordinated; the bipyridyl compounds have greater thermal stabilities than the corresponding phenanthroline complexes) (*323*, *324*). It seems probable that in all cases the lanthanide ions are more than six-coordinate. It was noted that $\nu(CN)$ for the thiocyanate ion is not reliable criterion for the detection of the coordinated group in the presence of weakly polarizing metal ions (*324*). The spectroscopic properties of many of these compounds have been studied in detail by Sinha (*644*, *646*; see also Section V, B).

Little work with scandium has been reported (*401*) and the actinide elements have been surprisingly neglected as far as bipyridyl and phenanthroline complexes are concerned (*688*).

B. TRANSITION ELEMENTS

1. *Titanium, Zirconium, and Hafnium*

The tetrahalides of titanium and zirconium generally afford six-coordinate adducts with bipyridyl and phenanthroline (*157*, *158*, *266*), although the complex $ZrF_4(bipy)_2$ has an infrared spectrum in agreement with an eight-coordinate structure (*158*). Zirconium and hafnium tetrachlorides form sparingly soluble materials of stoichiometry $MCl_4 \cdot 1.5$(bipy) which are possibly $M(bipy)_3Cl_2{}^+MCl_6{}^-$ (*158*).

Titanium(III) chloride gives three types of compound with bipyridyl: $TiCl_3$(bipy), $TiCl_3$(bipy)MeCN, and $TiCl_3 \cdot 1.5$(bipy) (*264*). All, according to their electronic spectra and magnetism, contain octahedrally coordinated titanium(III) ions. An original suggestion that $TiCl_3 \cdot 1.5$(bipy) contains a bridging bipyridyl group (*264*) has now been discounted in favor of the alternative formulation $[Ti(bipy)_2Cl_2][Ti(bipy)Cl_4]$ (*263*). Reactions of $TiBr_3$ have been studied (*267*) and the compounds $[Ti(bipy)_2I_2][Ti(bipy)I_4]$ and $[Ti(phen)_2I_2]$ are known (*265*). A colorless compound said to be $[Ti(bipy)_2Cl_2]Cl$ has been claimed (*676*). This formulation should be substantiated by further physical measurements.

Considerable stabilization of $(CH_3)_4Ti$ is obtained by complexing with bipyridyl or phenanthroline to give $(CH_3)_4Ti \cdot L$ (*684*).

2. *Vanadium, Niobium, and Tantalum*

The coordination chemistry of the intermediate oxidation states of niobium and tantalum is an unexplored field with respect to bipyridyl and phenanthroline.

A range of vanadyl(IV) complexes have been studied, e.g., VOL_2^{2+} (*632*) as well as mixed ligand complexes $VOLL'^{2+}$, e.g., where L′ = oxalate (*210*, *213*, *471*, *632*). $VOLX_2$ (X = Cl, Br) is less tetragonal than $VO(H_2O)_5^{2+}$ from the ligand field point of view (*157*), i.e., there is less double-bond character in the VO bond when L is present. Quite marked splitting (3700 cm^{-1}) of the first excited state ($^2E_g \rightarrow {}^2A_1 + {}^2B_1$) is found for VCl_4L (*157*).

Vanadium(III) complexes have been studied by Fowles and Greene (*263*). The compounds are of the type $V(bipy)_2X_3$ (X = Cl, Br, or SCN) and contain octahedral $V(bipy)_2X_2{}^+$ cations. In addition, the compounds $[VCl_3(bipy)]_2$, $[VCl_3 \cdot bipy \cdot MeCN]$, and $[V(bipy)_2Cl_2][V(bipy)Cl_4]$ are known. The complex anion of the latter compounds has been studied by Clark *et al.*, who prepared quaternary ammonium salts and estimated Δ to be 14,300 cm^{-1} (*159*).

3. *Chromium, Molybdenum, and Tungsten*

$CrLCl_3 \cdot DMF$ have normal magnetic moments (*103*) and are probably monomeric. The purple diol complex $[(phen)_2Cr(OH)_2Cr(phen)_2]^{4+}$ as the iodide has been the subject of a magnetochemical investigation (*221*). The same cationic specie as the nitrate may be hydrolyzed to the orange *cis*-diaquobis(phenanthroline) chromium(III) ion (*393*). The tris-chelate chromium(II) complexes $CrL_3X_2 \cdot nH_2O$ (X = Cl, Br, or I; n = 0, 2, or 4) have virtually constant magnetic moments over the range 77°–300°K, whereas the Kotani theory would predict a maximum at 140°K. There is also less orbital contribution than expected; this could be explained either by means of the Jahn–Teller effect, or by invoking delocalization of the t_{2g} electrons on the ligands (*222*). Mixed ligand complexes of chromium(III) have been prepared (*212*), and two peculiar paramagnetic compounds (benzene)Cr(bipy)$_2$I and $Ph_2Cr(bipy)_2I$ have been synthesized via a Grignard method (*692*). Phenanthroline replaces two tetrahydrofuran ligands from $Ph_3Cr(THF)_3$ (*548*).

The reaction between $MoCl_3$ and bipyridine or phenanthroline is complex. Apart from $[Mo(bipy)_2Cl_2][Mo(bipy)Cl_4]$ (Section V) other products isolated include $Mo_2O_3(bipy)_2Cl_4$ and for the phenanthroline system (phen H^+) $[Mo(phen)Cl_4]^-$, $Mo_2O_4Cl_2(phen) \cdot H_2O$, and K^+(phen $H^+)_2$ $[MoCl_6]^{3-}$ (*521*). The molybdenum(IV) complexes, $MoCl_4L$, are considered to be monomeric (*9*). The interaction of bipyridine, phenanthroline, or terpyridyl with the metal cluster compound "$MoCl_2$" has been studied. The products retain the basic Mo_6 cluster structure, e.g., $[(Mo_6Cl_8)X_2L_2]X_2$ (X = Cl or I) and $[(Mo_6Cl_8)X_3(terpy)]X$. When $[(Mo_6Cl_8)I_2(bipy)_2]I_2$ is treated with silver nitrate six halogens (4I + 2Cl) are labilized; the structures have been discussed in rather general terms (*251*). Simple preparations of yellow seven-coordinate molybdenum(II) complexes which are unstable to light and air result from the interaction of the carbonyl dihalides with either bipyridine or phenanthroline (*169*).

$$Mo(CO)_4Br_2 + bipy \rightarrow Mo(CO)_3(bipy)Br_2 + CO$$

Also some six-coordinate derivatives of molybdenum dinitrosyl dihalides have been reported, e.g., $Mo(NO)_2(phen)Br_2$ (*134*).

4. *Manganese, Technetium, and Rhenium*

Labile red-brown compounds $Mn(III)(L)Cl_3 \cdot H_2O$ have been reported (*269*, *292*). On heating to 200°C they afford yellow compounds $MnLCl_2$, whereas treatment with iodide ion gives $Mn(II)L_3(I_3)_2$. $MnLCl_4$ has been isolated as black crystals; on heating to 150°C $MnLCl_3$ is produced. The latter compound is probably dimeric as indicated by a rather low magnetic moment (3.9 B.M.).

A number of manganese(I) derivatives are known, e.g., $Mn(CO)_3 \cdot LX$ whereX = NO_3^- (*2*), NCS (*735*), and Cl^-, Br^-, or I^- (*377*). The nitrate species undergoes substitution reactions with one or two moles of triphenylphosphine with the loss of one carbon monoxide ligand; it may be oxidized to a pair of isomeric manganese(II) complexes $[Mn(bipy)_2(NO_3)_2]$. These have been designated cis and trans isomers on the basis of their infrared spectra between 700 and 800 cm^{-1} (*4*). Other known mixed ligand complexes of manganese(II) include Mn(acac)$_2$(phen), which dissociates in benzene solution (*296*), MnLCl$_2$ (*21*), and MnLBr$_2$ (*671*).

The rhenium(IV) complexes Re(bipy)X$_4$ (X = Cl or Br) are known; the magnetic moments are 3.41 B.M. (*149*, *690*). The cation Re(bipy)$_3^{3+}$ has been reported (*150*); Re(phen)$_3$Cl$_3$ is also known (*463*), but other derivatives of rhenium(III) are more complex. Thus the compound originally formulated [Re$_2$LCl$_4$]$_n$ (*168*) appears to contain trinuclear Re$_3$ units (*602*). The chemistry of a well-defined bipyridyltetracyanorhenate(II) species has been discussed (*462*, *464*). Prolonged reaction of the sodium salt with excess bipyridyl is said to yield Re(bipy)$_2$(CN)$_2$; reaction of this violet material with mercury(II) iodide and iodomethane in a sealed tube then gives the isonitrile complex [(bipy)$_2$Re(CNMe)$_2$]HgI$_4$ (*462*). A binuclear structure involving both rhenium(I) and rhenium(III) has been suggested for the black diamagnetic compound Re(bipy)I$_2$ (*271*, *272*).

The red rhenium(I) complex [Re(CO)$_4$(phen)]Co(CO)$_4$(compound A) on warming to 90°C affords the compound (phen)(CO)$_3$Re–Co(CO)$_4$ which contains a rhenium to cobalt bond. The irradiation of a THF solution of the latter material gives the yellow binuclear compound [Re(CO)$_3$(phen)]$_2$ (*443*, *444*). Compound A (above) undergoes the following reversible reaction with various alkoxide species RO$^-$ (*446*):

$$[\mathrm{Re(CO)_4(phen)}]^+ + \mathrm{RO}^- \rightleftharpoons [\mathrm{Re(CO)_3(phen)(CO_2R)}]$$

5. *Iron, Ruthenium, and Osmium*

The temperature dependence of the magnetic moments of FeL$_3$(ClO$_4$)$_3$ has been discussed by Figgis (*256*); the results suggest an extremely small degree of delocalization of the t_{2g} electrons onto the ligands. The treatment has been extended to dicyano complexes, FeL$_2$(CN)$_2$·X (X = ClO$_4^-$, or NO$_3^-$) and also to (bipy H$^+$) [Ru(bipy)Cl$_4$]$^-$·H$_2$O where again only a very small degree of t_{2g} electron delocalization need be invoked (*258*).

The reaction between phenanthroline and ferric chloride in glacial acetic acid gives the yellow complex Fe(phen)Cl$_3$, which has been formulated to contain six-coordinate iron(III), possibly Fe$_2$(phen)$_2$Cl$_6$. The direct reaction between aquo-ferric ions and phenanthroline gives a brown material containing two iron atoms per molecule, whereas oxidation of the deep red tris(phenanthroline)iron(II) ion affords the pale blue Fe(III)(phen)$_3^{3+}$ ion (*96*). The brown dimer and related species have been the subject of many investigations (*16*, *96*, *205*, *222*, *416*). They were originally formulated with a diol bridge (*96*), but it is now accepted that a single oxo bridge is present (*16*, *222*, *416*), although one recent paper continues to use the diol formulation (*205*); the stretching frequency for the FeOFe unit has been assigned close to 840 cm^{-1} (*16*, *416*). The magnetic properties of the complex derived from ferric chloride have been interpreted in terms of the interaction of two Fe(III) species ($S = \frac{1}{2}$) via the oxo bridge in an unsymmetrical structure (*222*). More recent work has led to the preference for the symmetrical structure $[\mathrm{Cl(phen)_2Fe \cdot O \cdot Fe(phen)_2Cl}]^{2+}$ and it is now considered that the interacting magnetic centers have, individually, $S > \frac{1}{2}$ (*416*). The chloride may be replaced completely by sulfate or partially by perchlorate; bipyridyl gives a similar complex $[\mathrm{Cl(bipy)_2FeOFe(bipy)_2Cl}](\mathrm{ClO_4})_2 \cdot 7\mathrm{H_2O}$.

There has been interest in monophenanthroline and bipyridyl complexes of iron(II). Heating $\mathrm{Fe(bipy)_2Cl_2}$ to 156°C *in vacuo* gives $\mathrm{Fe(bipy)Cl_2}$ (*44*), which has a magnetic moment of 5.72 B.M. (*103*); the phenanthroline complex is similar. The terpyridyl complex $\mathrm{Fe(terpy)Cl_2}$ ($\mu_{\mathrm{eff}} = 4.60$ B.M.) may be five-coordinate (Section II). The polymeric compound $[\mathrm{Fe(phen)F_2}]_n$ may be prepared from $\mathrm{Fe(py)_4F_2}$ (*507*).

Schilt has prepared an extensive series of cyano complexes of iron(II), the major species being $\mathrm{Fe(phen)_2(CN)_2}$ and $\mathrm{Fe(phen)(CN)_4^{2-}}$; some iron(III) complexes have also been formed by oxidation of the iron(II) compounds (*620–622*). It was recognized that the complexes have considerable affinity for protons (*621*) and the work of Hamer and Orgel has shown protonation (and methylation) to occur on the cyano ligand (*313*). The charge-transfer band of $\mathrm{Fe(phen)_2(CN)_2}$ undergoes a large shift on protonation corresponding to 14 kcal per proton. The complex $\mathrm{Fe(phen)_2(CN)_2}$ is, in fact, a general Lewis base forming complexes with a wide variety of Lewis acids, e.g., $\mathrm{Fe(phen)_2(CN \cdot BF_3)_2}$ (*638*) and $\mathrm{Fe(phen)_2(CN)_2 \cdot MX_4}$ (M = Si, Ge, or Sn; X = F or Cl) (*610*). The corresponding diisothiocyanato (*624*) and difulminato complexes (*59*, *60*) have similar properties. The cyano complexes have found use as indicators in analytical chemistry (*618*, *623*).

The organometallic derivative $\mathrm{Et_2(bipy)_2Fe(II)}$ catalyzes the oligomerization of butadiene and acetylene (*740*); $\mathrm{Et_2(bipy)Ni(II)}$ behaves similarly (*741*). The iron–perfluoroalkyl bond in $\mathrm{C_3F_7 \cdot Fe(CO)_4I}$ decreases in stability as two CO ligands are replaced by ligands having a poorer π-acceptor capacity, e.g., $\mathrm{C_3F_7Fe(CO)_2(bipy)I}$ (*588*). The complexes $\mathrm{Fe(O)(CO)_2L[Hg(I)Cl]_2}$ contain metal-to-metal bonds and possibly have *cis*-carbonyl groups (*481*).

The absolute configuration of $(-)\mathrm{Fe(phen)_3^{2+}}$ (Λ) has been determined by X-ray methods (*677*) and that of $(-)\mathrm{Ru(phen)_2(py)_2^{2+}}$ (Δ) by consideration of the rotatory power of the ligand transitions (*88*).

New preparative methods are now available for ruthenium(II) and osmium(II) complexes (*110*, *215*, *215a*, *487*), including an asymmetric synthesis of $M(II)(bipy)_3^{2+}$ (M = Ru or Os) in the presence of *d*-tartrate ions (*486*). A series of tetrahaloosmates has been prepared *viz.* $OsLX_4$, $OsLX_4^-$, and $OsLX_4^{2-}$ (*215*); a similar ruthenium series is known (*215a*), the halogen atoms here being labile. The bis complexes of ruthenium(II) and osmium(II) have cis stereochemistry, the trans isomers being unknown (*213*, *215a*). Pflaum and Brandt have made a spectroscopic study of the ruthenium–L system (*586*). A weakly paramagnetic complex $[RuI_2NO(bipy)]_x$ has been reported. The infrared spectrum suggests the nitrosyl ligand to be NO^+ and the compound is possibly dimeric (*399a*).

6. *Cobalt, Rhodium, and Iridium*

The resolution of $Co(phen)_3^{3+}$ has been achieved. This has enabled a comparison of empirical (sign of the Cotton effect of the longest wavelength $d \leftrightarrow d$ band, ${}^1A_g \leftrightarrow {}^1T_{1g}$) and nonempirical methods of assignment of absolute configuration to be made. The results of the two methods were identical, and as a consequence it is now known that the absolute configurations of the following ions are all Λ = $(+)Co(phen)_3^{3+}$, $(+)Ni(phen)_3^{2+}$, $(-)Fe(phen)_3^{2+}$, $(-)Ru(phen)_3^{2+}$, $(-)Ru(phen)_3^{3+}$, $(+)Os(phen)_3^{2+}$, and $(+)Os(phen)_3^{3+}$ (*522*). Important and definitive papers dealing with nonempirical methods for the determination of absolute configuration have recently been published (*495a*, *522a*). Ferguson *et al.* consider the different methods available for the determination of absolute configuration of bipyridyl and phenanthroline complexes (*249a*) and Bosnich (*88a*) has deduced the absolute configuration of $(+)Ru(phen)_2(bipy)^{2+}$ to be Λ.

The preparation of bis(bipyridyl) (*702*) and bis(phenanthroline) cobalt(III) complexes (*576*) has been the subject of a number of papers. Interest centers on the possibility of cis–trans isomerism in these complexes, since it would seem that the close approach of the 6,6′-(bipyridyl) and 2,9-(phenanthroline) protons in the trans complex would make this stereochemistry unattractive for central ions such as cobalt(III), rhodium(III), or iridium(III). Cis complexes are well established, but a violet compound claimed to be *trans*-$[Co(bipy)_2Cl_2]Cl \cdot 7H_2O$ (*654*) is now suggested to be $[Co(bipy)_2(CO_3)]Cl$ (*575*). The oxidation of cobalt(II) chloride (one part) and phenanthroline (or bipyridyl) (two parts) gives mixtures of products which certainly include $Co(phen)_3^{3+}$ as well as anionic cobalt(II) species (*21*, *573*, *591*).

A large number of mixed ligand complexes of cobalt(III) are known in which one ligand is either bipyridyl or phenanthroline and the other ligands are, for example, dimethyl glyoxime (*569*), 8-hydroxyquinoline

(*480*), β-diketones (*22*), cyanide (*128, 129, 569*), ethylenediamine or ammonia (*577*), and biguanide (*211*).

Ionic derivatives of π-cyclopentadienylcobalt(III) include $[(\pi\text{–}cp)\text{Co(bipy)X}]^+\text{Y}^-$ where $\text{X} = \text{C}_3\text{F}_7$ and $\text{Y}^- = \text{ClO}_4^-$ (*689*) and $\text{X} = \text{I}$, $\text{Y} = \text{I}^-$ or PF_6^- (*418*). Terpyridyl gives only insoluble mixtures of which $[(\pi\text{–}cp)\text{Co(terpy)}]\text{I}_2$ is probably a major component.

Russian workers have reported some terpyridyl complexes of cobalt(III) (*35*), and the bis(terpyridyl) cobalt(II) ion is now known. The magnetic properties of Co(terpy)_2^{2+} depend critically on the anion present in the crystal; thus, at 20°C the magnetic moments are 4.3 (perchlorate), 2.7 (bromide dihydrate), 2.1 (chloride monohydrate), and 2.2 B. M. (aqueous solution). A study of the temperature dependence of the moment for $\text{Co(terpy)}_2\text{Br}_2\cdot 2\text{H}_2\text{O}$ indicated that no simple explanation was possible (*379*). The subject has been considered more recently by Judge and Baker (*412a*). Some peculiar bipyridyl derivatives of cobalt(II) cyanide were reported some years ago (*571*); these could warrant further investigation. The UV spectra of Co(II) and Co(III) complexes have also been measured.

A new preparation of $\text{Rh(bipy)}_3(\text{ClO}_4)_3$ has been reported (*519*), the compound is colorless when pure. Compounds containing the $\text{Rh(bipy)}_2\text{Cl}_2^+$ cation have been known for many years. An improved method of preparation is now available (*285*) in which reducing agents such as ethanol or hydrazine hydrochloride are present in the reaction mixture. The cation was at one time thought to be cis (infrared spectrum 700–800 cm^{-1}) (*520*), but the isolation of adducts with hydrochloric (*287*) and nitric acids (*284*) which contain the H_5O_2^+ and hydrogen dinitrate ions, respectively, was taken to indicate trans stereochemistry. The recent work of Rund (*607*) indicates that the reducing agents present in rhodium(III) preparations generate catalytic quantities of rhodium(I) which can undergo a rapid substitution reaction with a ligand such as pyridine and then revert to rhodium(III) via a chloride-bridge mechanism; this would require the product to have trans stereochemistry. Since bipyridyl and phenanthroline stabilize rhodium(I) (Section VIII), it is unlikely that a similar mechanism would operate for preparations involving these ligands. There is, in fact, generally sufficient reducing agent present to reduce all the rhodium to rhodium(I); Rund suggests this to occur and also suggests that the resulting rhodium(I) bipyridine or phenanthroline complex is then oxidized to rhodium(III). Some support for this view is provided by the fact that rhodium perchlorate will react with bipyridyl or phenanthroline in aqueous ethanol to give, directly, rhodium(I) complexes; in the presence of chloride ion rhodium(III) products result (*529*). There would appear to be no mechanistic reason for the products being trans, and indeed both from steric and statistical reasoning a cis complex would be expected; studies including the nuclear magnetic resonance spectrum of the recently reported [Rh(phen)$_2$X$_2$]X (X = Cl or Br) (*285*, *452*, *529*) conclusively prove that the cations are cis complexes (*529*), despite the fact that the rhodium–halogen stretching frequencies are not resolved (*452*). Evidence is also available to confirm the cis stereochemistry of Rh(bipy)$_2$Cl$_2$$^+$ (*564*).

Preparations of tris-bipyridyl (*156*, *519*) and tris-phenanthroline indium(III) complexes have been described. The $d \leftrightarrow d$ bands fall in the region of the ligand $\pi \leftrightarrow \pi^*$ transitions. The luminescence spectra of the cations are considered to arise from $\pi^* \leftrightarrow d$ transitions (*739*). *Cis*-[Ir(phen)$_2$Cl$_2$]Cl is known (*156*) and has been resolved (*104*). However, the complex originally claimed as *trans*-[Ir(phen)$_2$Cl$_2$]Cl·3H$_2$O (*156*) and shown to react with hydrochloric acid (*452*) is, in fact, (phen H$^+$)[Ir(phen)Cl$_4$]$^-$ (*104*). The compounds [Ir(phen)$_2$X$_2$]$^+$·[Ir(phen)X$_4$]$^-$ are known (X = Cl, Br, or I) and the cations probably have cis configurations.

Two new preparative methods for iridium(III) complexes were recently reported. One involves the use of a mixture of hexachloroiridates(III) and (IV) as the source of iridium (*287a*); the other involves the addition of hypophosphorous acid (*47a*). Gillard and Heaton (*287b*) have now demonstrated that all compounds IrL$_2$X$_2$$^+$ are cis; also, they present additional evidence to confirm the cis stereochemistry of the rhodium analogs, although it would appear that the compound they identify as *cis*-Rh(phen)$_2$Br$_2$·Br·2H$_2$O is probably [phen H] [Rh(phen)-Br$_4$] (cf. *529*).

7. *Nickel, Palladium, and Platinum*

A simple resolution of Ni(phen)$_3^{2+}$ using potassium antimonyl tartrate has been published (*415*). Also the resolution of the mixed chelate complexes Ni(phen)$_2$(bipy)$^{2+}$ and Ni(bipy)$_2$(phen)$^{2+}$ has been achieved (*102*). The spectra of these two cations are similar, but that of the bisbipyridyl complex changes rapidly in acid solution (red → blue).

The complex Ni(phen)$_2$(ClO$_4$)$_2$·3H$_2$O may be dehydrated with no change in color or magnetic properties, whereas similar treatment of the bisethylenediamine complex gives a diamagnetic product (*319*). Conductance data for the phenanthroline complex indicate the possibility of coordinated perchlorate groups. A large variety of bis-phenanthroline and bipyridyl nickel(II) complexes may be prepared using nonaqueous solvents (*319*, *320*).

New complexes have been prepared by the thermal decomposition of tris(2,2′-bipyridyl)nickel(II) and cobalt(II) chlorides, i.e., M(bipy)$_2$Cl$_2$,

$M_3(bipy)_4Cl_6$, $Ni(bipy)Cl_2$, α- and β-$Co(bipy)Cl_2$ (see also Section V, A), $Co(bipy)_{0.80}Cl_2$, and $M(bipy)_{0.5}Cl_2$. All the cobalt–nickel pairs are isomorphous with the exception of $M(bipy)_2Cl_2$ (*478*). Other mixed ligand complexes include the green high-spin species derived from the reaction of bipyridyl or phenanthroline with the purple low spin $Ni[S_2P(OEt)_2]_2$ (*411*), some thio acid derivatives (*440*), and some paramagnetic phenanthroline derivatives of some nickel(II) salicylaldimine complexes (*315*). Nickel(II) is also considered in an extensive study of complexes of substituted bases (*309*).

Routes to dialkyl (*732*) and diperfluoroarylnickel(II) compounds (*587*) stabilized by bipyridyl have been reported. The addition of phenanthroline to solutions of nickel carbonyl induces disproportionation to Ni(II) and Ni(−1), e.g., $[Ni(phen)_3][Ni_2(CO)_6]$ is a typical product (*373*).

Bis(phenanthroline)palladium(II) perchlorate readily loses one mole of ligand in the presence of halide ions to give $Pd(phen)X_2$ (X = halide) (*488*). Rund has given preliminary data for the crystal structure of $Pd(phen)_2(ClO_4)_2$ from which it appears that the phenanthroline ligands are trans, but bent about their C_2 axes (*607*). The corresponding complex of the larger platinum(II) has less tendency to lose ligand and compounds such as $Pt(phen)_2I \cdot ClO_4 \cdot 2H_2O$ have been prepared. The compound $Pt(bipy)_2I_2 \cdot 2H_2O$ originally prepared in 1934 is, in fact, $[Pt(bipy)_2I(H_2O)]I \cdot H_2O$ (*488*).

The linkage isomers $Pd(bipy)(NCS)_2$ and $Pd(bipy)(SCN)_2$ have been isolated (*120*), but $Pd(phen)(SCN)_2$ exists only in the dithiocyanato form (*612*), whereas $Pd(bipy)(NCO)_2$ occurs only as the diisocyanato isomer (*563*). Substitution of the phenanthroline with electron-withdrawing substituents (e.g., 5-NO_2) can induce the formation of the isothiocyanato isomers (*612a*). These facts have been explained in terms of the relative π-acceptor capacities of the chelate ligands and the thiocyanato group, but the arguments provide a less satisfactory explanation of linkage isomerism for the selenocyanato group (*121*). Moreover, recent work with phosphine complexes of platinum has cast doubt on the assumption that π bonding need be important to any extent in this class of complex (*700*). However, the phenomenon of π bonding continues to be much invoked, e.g., to explain some anomalously fast substitution reactions of dichloro(bipyridyl)platinum(II) (*306*).

Sulfato(bipyridyl)platinum(II) is yellow, unlike $(pyridine)_2PtSO_4$ which is reported to be black (*286*). It is not possible to introduce *N*,*N*,*N′*,*N′*-tetramethylethylenediamine directly into a platinum(II) complex. An indirect route involving the *in situ* synthesis of the ligand is available; bipyridyl is present in the molecule (*725–727*). Other mixed ligand complexes that have been reported include one in which paludrine is present in the molecule (*653*) and a glycinato complex of platinum(IV) in which two phenanthroline molecules are present, but not in the inner coordination sphere (*302*). Cationic π-allyl complexes of the type $[(\pi\text{-}C_3H_5)Pd(bipy)]X$ ($X = Cl^-$ or PF_6^-) have been isolated as colorless solids which dissociate as uni-univalent electrolytes in water. Also $[(\pi\text{-}C_3H_5)Pd(bipy)]^+ [(\pi\text{-}C_3H_5)PdCl_2]^-$ is known (*572*).

8. Copper, Silver, and Gold

Jørgensen indicated that the absorption spectra of aqueous ethanolic solutions of cupric ion containing bipyridyl or phenanthroline (ratio 1:2) were compatible with the presence either of a *cis*-diaquobischelate cation or with a trigonal bipyramidal monoaquo species (*409*). The weak electrolyte behavior in nitrobenzene or nitromethane of deep blue $Cu(bipy)_2(ClO_4)_2$ has been attributed to the following equilibrium:

$$Cu(bipy)_2ClO_4^+ + \text{solvent} \rightleftharpoons Cu(bipy)_2(\text{solvent})^{2+} + ClO_4^-$$

Furthermore, $[Cu(bipy)_2ClO_4]PF_6$ has been prepared and the spectrum of the compound in anhydrous nitrobenzene is altered on the addition of perchlorate ions. The solid state spectra of $[Cu(bipy)_2ClO_4]PF_6$ and $Cu(bipy)_2(ClO_4)_2$ are identical between 25,000 and 12,500 cm^{-1}, but differ from the spectrum of $Cu(bipy)_2(PF_6)_2$ (*26*).

The reaction of $CuL_2(ClO_4)_2$ with a number of unidentate ligands in acetone affords the complexes $[CuL_2X]\cdot ClO_4$ ($X = Cl^-$, Br^-, I^-, SCN^-, NO_2^-, or RCO_2^-) or $CuL_2Y(ClO_4)_2$ ($Y = py$, NH_3, or H_2O) (*318*). The compounds $[CuL_2X]X$ are also known; in particular the crystal structure of $[Cu(bipy)_2I]^+I^-$ has been determined and the copper(II) cation is situated within a pseudotrigonal bipyramidal CuN_4I environment (*42*). Faye has examined the spectra of copper(II)-phenanthroline solutions and has concluded that $Cu(phen)(solvent)_4^{2+}$ is distorted octahedral, $Cu(phen)_2(solvent)^{2+}$ is trigonal bipyramidal, and $Cu(phen)_3^{2+}$ is trigonal. A simple crystal field treatment was also given (*247*). Bisbiquinolinylcopper(II) cations are also trigonal bipyramidal (*248*). The magnetic properties of many of the above complexes have been investigated and shown to obey the Curie law between 80° and 300°K (*257*). A thermodynamic study of copper(II) phenanthroline solutions has also been published (*92*).

Substituted bipyridines and phenanthrolines have been used as ligands for copper(II) ions. 4,4′:6,6′-Tetramethyl-2,2′-bipyridyl(L) gives monomeric $CuL(NO_3)_2$, two sulfato complexes, and a series $[CuL_2X]^+ClO_4^-$, as well as forming copper(I) complexes readily (*309*). 2,9-Dimethyl-1,10-phenanthroline affords 1:1 complexes with cupric halides which give nonconducting solutions in nitrobenzene, and the series $[CuL_2X]ClO_4$ (*310*). The complexes are very readily reduced to the intensely colored copper(I) compounds (*310*). Terpyridyl gives a 1:1 complex with copper(II) at pH 4 (*585*).

Bipyridyl and phenanthroline give polymeric 1:1 complexes with copper(II) chloride (*597*). The existence of the dimeric ion $[(bipy)Cu(OH)_2Cu(bipy)]^{2+}$ in solution has been established (*177*, *566*) and it has been isolated as the lilac perchlorate (*498*). The species $(bipy)Cu^{2+}$ has surprisingly large affinity for ligands other than OH^- (*370*). The di-μ-hydroxo cation considered above has now been prepared with a variety of counter ions; the corresponding phenanthroline salts are also known. There is no evidence of antiferromagnetic interaction between the copper(II) ions even at 80°K (*321*). When the counter ion is iodide or thiocyanate there is evidence for metal ion–counter ion interaction.

A variety of mixed ligand complexes of copper(II) are known which contain bipyridine and phenanthroline. Examples of the other ligands are β-diketones (*479*), salicylaldehyde and salicylaldimines (*552*), and nitrate (*721*). The use of some mixed ligand copper(II) phenanthroline complexes as absorbents for gas chromatography has been considered (*14*).

Reduction of copper(II) solutions containing bipyridyl or phenanthroline with reductants such as hydroxylamine gives intense orange-brown solutions of $Cu(bipy)_2^+$. The stoichiometry has been verified by Job's method (*585*). Syntheses of iodo(bipyridyl)tri-*n*-butylphosphinecopper(I) (*414*) and chloro(phenanthroline)triphenylphosphinecopper(I) (*137*) have been reported. Both these complexes are presumably tetrahedral. The compounds CuL(CN) are polymeric and stable to oxidation (*174*). There are few new data for silver(I) and gold(I) complexes of the two bases, although with 4,4′:6,6′-tetramethyl-2,2′-bipyridyl(L), silver(I) gives two types of complex: $Ag(L)_2X$ ($X = NO_3^-$ or ClO_4^-) and the insoluble AgLY (Y = halide) (*309*).

Bisbipyridylsilver(II) perchlorate has been examined spectroscopically and a square planar structure was postulated (*36*); it is possible however that a structure of lower symmetry may be the correct one. It is apparently very difficult to prepare bisbipyridyl or phenanthroline complexes of gold(III). The compounds $[AuLX_2]X$ and $[AuLX_2]ClO_4$ have been prepared (X = Cl or Br). In nonaqueous solvents the compounds $AuLX_3$ have low conductivities; this is attributed to the rapid establishment of the following equilibrium:

$$2AuLX_3 \rightleftharpoons [AuLX_2]^+ + [AuX_4]^- + L$$

The complex $[Au(bipy)Cl_2]ClO_4$ is hydrolyzed by water and $[Au(bipy)Cl(OH)]ClO_4$ has been isolated (*314*, *316*).

VIII. Complexes of Metals in "Low" Oxidation States

The mechanism of valence-state stabilization cannot be deduced from available thermodynamic data, but it is generally accepted that molecules such as bipyridyl or phenanthroline stabilize low oxidation states by functioning as electron acceptors as well as electron donors. Complexes containing metals in low oxidation states are often highly colored; the origin of the intense color is attributed to symmetry allowed transitions of the $\pi^* \leftarrow t_{2g}$ type (Section V, C). Complexes of metals in formally negative oxidation states and complexes of representative elements in a formally zero oxidation state [e.g., $Be(bipy)_2$] are, with some exceptions, probably best regarded as complexes of the ligand anion (Section V, D).

There is little or no experimental information which enables the relative importance of the σ and π components of the metal-to-ligand bond to be assessed for the compounds considered here. Attempts have been made to place various ligands in a "π-bonding" spectrochemical series by using infrared spectroscopy to assess competition of a ligand (L) with CO for available π electrons in the complex $M(CO)_4L_2$ (M = Cr, Mo, or W). Combining the results of studies by Stiddard (*662*) and Kraihanzel and Cotton (*437*) we obtain the following order of π-acceptor capacity: diphosphine > diarsine > 2,2′-bipyridyl > pyridine. This applies to $M(CO)_4L_2$ *only*, and although such results may be interpreted as evidence to support the concept that π bonding can occur, the situation in the complex $M(bipy)_3^{n+}$ may well be very different. Thus the degree of π bonding will certainly be a function of n and also bipyridyl may well be a stronger π acceptor in $M(O)(bipy)_3$ than in $M(O)(CO)_4(bipy)$.

The preparation of many complexes of bipyridyl-containing metals in low oxidation states have been achieved by Herzog and his co-workers (e.g., *367*). These and other compounds of interest are cited in Table XVI together with magnetic moments measured at ambient temperature (the most widely determined property). Although most work has been carried out with bipyridyl, it is apparent that phenanthroline and terpyridyl will afford similar complexes. There is a general paucity of physical data for the compounds listed in Table XVI. The determination of magnetic susceptibilities as a function of temperature would be worthwhile in many cases and the two iron compounds are obvious candidates for a Mössbauer study.

TABLE XVI

MAGNETIC MOMENTS

Compound	μ_{eff} (B.M.)	Ref.	Compound	μ_{eff} (B.M.)	Ref.
$Al(bipy)_3$	2.32	(*339*)	$Li[Cr(bipy)_3]\cdot 4THF$	1.83	(*343*)
$Sc(bipy)_3$	1.99	(*338*)	$Na_2[Cr(bipy)_3]\cdot 7THF$	2.79–2.91	(*343*)
$Y(bipy)_3$	1.84	(*344, 345*)	$Na_3[Cr(bipy)_3]\cdot 7THF$	3.80–3.89	(*343*)
$Li(bipy)Y(bipy)\cdot 3THF$[b]	2.76	(*345*)	$Ca_3[Cr(bipy)_3]\cdot 7NH_3$	2.43–2.49	(*343*)
$La(bipy)_4$	1.82–1.78	(*346*)	$Cr(phen)_3I_2\cdot 2H_2O$	—	(*331*)
$Ba(bipy)_4$	2.31–2.33	(*337*)	$Cr(phen)_3$	Diamagnetic	(*70, 335, 347*)
$U(bipy)_4$	2.52–2.81	(*352*)	$Cr(terpy)_2$	Diamagnetic	(*70, 71*)
$Li[U(bipy)_4]\cdot 3.5THF$	3.51	(*368*)	$Mo(bipy)_3$	Diamagnetic	(*363*)
$Na_4[U(bipy)_4]\cdot 8THF$[a]	2.7 –2.8	(*368*)	$W(bipy)_3$	1.03	(*351*)
$Ti(bipy)_3$	Diamagnetic	(*366*)	$Mn(bipy)_3$	4.10	(*362*)
$Ti(phen)_3$	Diamagnetic	(*63*)	$Li[Mn(bipy)_3]$	3.71	(*361*)
$Li[Ti(bipy)_3]\cdot 3.7THF$	1.74	(*366*)	$[Re(bipy)_3]CN\cdot HCN$	Diamagnetic	(*182*)
$Ti(terpy)_2$	Diamagnetic	(*63*)	$Fe(bipy)_3$	Paramagnetic	(*307, 356, 358*)
$Zr(bipy)_3$	Diamagnetic	(*745*)	$Na[Fe(bipy)_3]$	Paramagnetic	(*508*)
$Li[Zr(bipy)_3]\cdot 4THF$	—	(*366*)	$Co(bipy)_3ClO_4$	3.2 –3.4	(*705, 708, 716*)
$V(bipy)_3I_2$	3.67	(*330, 333, 334, 583*)	$Co(bipy)_2ClO_4$	2.89	(*518, 520*)
$V(bipy)_3$	1.68–1.93	(*330, 332, 333, 583*)	$Co(bipy)_3$	2.23	(*348*)
$Li[V(bipy)_3]\cdot 4THF$	Diamagnetic	(*583*)	$Co(phen)_3ClO_4$	No data reported	(*512*)
$V(terpy)_2$	1.84	(*64, 335*)	$Rh(bipy)_2ClO_4\cdot 3H_2O$	Diamagnetic	(*518, 520*)
$V(phen)_3$	—	(*340, 347*)	$Rh(bipy)_2Cl\cdot ClO_4\cdot 2H_2O$	Diamagnetic	(*518, 520*)
$Li[V(phen)_3]\cdot 3.5THF$	Diamagnetic	(*341*)	$Ni(bipy)_2$	Diamagnetic	(*71*)
$Nb(bipy)_3$	1.75	(*365*)	$Ni(phen)_2$	Diamagnetic	(*71*)
$Cr(bipy)_3I_2$	2.9	(*333*)	$Zn(bipy)_3\cdot 2NH_3$	2.01	(*340a*)
$Cr(bipy)_3I, ClO_4$	2.07	(*71, 333, 583*)			
$Cr(bipy)_3$	Diamagnetic	(*70, 71, 359, 360, 364*)			

[a] Other similar compounds include $Na_3M(bipy)_3\cdot n$THF (M = Al, V, or Y), $Na_4Th(bipy)\cdot 8THF$, and $Na_4Mn(bipy)_3\cdot 5$dioxane·3THF (*342*).

[b] THF, tetrahydrofuran.

Earlier preparative studies used conventional reducing agents, e.g., magnesium metal (*332*, *334*), but the usual method now is to use the lithium salt of the bipyridyl anion, $Li_2(bipy)$ (diamagnetic). For example,

$$MX_y + yLi_2(bipy) + n(bipy) \xrightarrow{THF} M(bipy)_n + yLiX + yLi(bipy) \quad (S = \tfrac{1}{2})$$
$$(X = \text{halide})$$

Tetrahydrofuran (THF) is the most commonly used solvent, although other ethers may be used. The sodium salts of bipyridyl or benzophenone may also be used as the reducing agent.

An early claim (*332*, *334*) to have prepared $V(bipy)_3^+$ has been revised (*431*); the compound $V(bipy)_3I$ is considered to be a mixture of $V(bipy)_3$ and $V(bipy)_3I_2$. The reaction of $V(bipy)_3^{2+}$ or of $Cr(bipy)_3^{2+}$ with aluminum hydride gives the neutral tris-bipyridyl complexes, but with other dipositive metals $Al(bipy)_3$ is the major product (*357*). Attempts to prepare bipyridyl and phenanthroline derivatives of hexacarbonylvanadium led to the disproportionation of vanadium(0) (*376*).

A convenient preparation of $Cr(bipy)_3(ClO_4)_2$ has been published (*380*) and methods of examining spectra of low valent compounds in general have been discussed (*349*). In contrast to the iron(II) system, spin pairing occurs on the chromium(II) cation on addition of the second molecule of bipyridyl, thus $[Cr(bipy)_2(H_2O)_2](ClO_4)_2$ is low spin (*178*).

A recent magnetochemical study of $Cr(bipy)_3^{2+}$ in several crystals suggests the ion to be trigonally distorted, trigonally shortened in $Cr(bipy)_3I_2$, but trigonally elongated in $Cr(bipy)_3Br_2$; $Cr(phen)_3Br_2 \cdot 2H_2O$ is also considered to contain trigonally elongated cations (*696*). Kotani theory cannot fit the observed magnetic data for $Cr(bipy)_3^{2+}$, but a theory due to Figgis does give a reasonable fit (see Section VII, under iron) (*678*).

The low valence complexes of chromium show a strong tendency to disproportionate. For example, Herzog and Aul (*335*) have shown the following reaction to occur in nonaqueous media:

$$Cr(phen)_3 + Cr(phen)_3^{2+} \rightleftharpoons 2Cr(phen)_3^+$$

Also the light sensitivity of the following equilibrium has been demonstrated (*277*):

$$Cr(bipy)_3 + Cr(bipy)_3^{2+} \underset{dark}{\overset{light}{\rightleftharpoons}} 2Cr(bipy)_3^+$$

The reaction between chromium(II) acetate and bipyridyl has been extensively studied. If a metal-to-ligand ratio of 2:3 is employed, disproportionation occurs and $Cr(bipy)_3$ is the product (*359*). A 1:2 ratio of reactants affords the neutral monomeric complex $Cr(bipy)_2(OAc)_2$

[$\mu_{\text{eff}} = 3.01$ B.M., cf. $Cr(bipy)_2Cl_2$, $\mu_{\text{eff}} = 2.95$ B.M.] (*354*). The complex loses one molecule of bipyridyl in solution (in solvents other than water or methanol), and compounds such as $Cr(bipy)(i\text{-}PrNH_2)_2(OAc)_2$ may be prepared; this is also, surprisingly, a low spin complex ($\mu_{\text{eff}} = 2.83$ B.M.) (*353*). The reaction of copper(II) acetate with bipyridyl has also been investigated (*355*). Phenylisonitrile will displace bipyridyl from the neutral complexes of chromium, molybdenum, and tungsten (the reverse reaction does not occur), but attempts to substitute $Li[M(bipy)_3]$ (M = Ti or V) led to reduction of the isonitrile (*347*).

The hexacarbonyls of chromium, molybdenum, and tungsten readily undergo substitution reactions with bipyridyl and phenanthroline to give $M(CO)_4 \cdot L$ (*491*, *662*); an alternative route to the compounds is to react $M(CO)_5X$ (X = I or CN) (*68*, *69*) or $[M_3(CO)_{14}]^{3-}$ (*65*, *73*) with L. More vigorous reaction conditions will give the dicarbonyl compounds $M(CO)_2L_2$ (*66*, *72*); tricarbonyl derivatives $M(CO)_3L \cdot X$ (X = unidentate ligand) are also well known (*67*, *385*, *386*, *663*). Under appropriate experimental conditions complete replacement of the carbonyl groups may occur, in this way a number of terpyridyl derivatives have been prepared (*61*). The cyano complexes $Cr(CN)_6^{6-}$ and $Ni(CN)_4^{4-}$ as potassium salts in liquid ammonia also provide an easy route to the neutral complexes of bipyridyl, phenanthroline, and terpyridyl (*71*); $Cr(benzene)_2$ and $Cr(benzene)(CO)_3$ may also be used as the source of Cr(0) (*70*). As would be anticipated on entropy grounds, terpyridyl will replace bipyridyl from $Cr(bipy)_3$ (*61*).

Oxidation of the bipyridyl tetracarbonyl derivatives of molybdenum and tungsten affords seven-coordinate derivatives of the dipositive metals (*662*), e.g., the compound $W(CO)_3(bipy)(HgCl)_2$ contains tungsten-to-mercury bonds (*273*). Compounds containing bidentate terpyridyl have been obtained from $Cr(CO)_6$ and $Mo(CO)_6$ by reaction with terpyridyl in isopentane solution under the influence of UV light. Pentacarbonylmanganese bromide affords the compound $Mn(CO)_3(terpy)Br$ (*274*) which has an infrared spectrum identical with that of $Mn(CO)_3(bipy)Br$ (*1*, *78*, *242*, *377*).

The cationic manganese carbonyl derivative $Mn(CO)_4(phen)^+$ has been isolated as the $Co(CO)_4^-$ and $Mn(CO)_5^-$ salts (*445*) and the technetium derivatives $Tc(CO)_3(phen)X$ are also known. The color is a function of the halogen X, changing from colorless (X = Cl), through bright brown (X = Br), to brown (X = I) (*374*). The reaction of bipyridyl with pentacarbonyliron induces disproportionation (*375*); this can also occur when bis(1,3-cyclohexadiene)tetracarbonyldicobalt is the reactant. However, $[L_2(CO)_4Co_2]$ has been prepared (*62*).

Tris(bipyridyl)iron(0) does not dissociate into ions despite the fact that the absorption spectrum of the complex is similar to that of

Na^+bipy^- (*307*). The ESR spectrum supports a formulation based on iron(0), whereas in the case of the $Fe(bipy)_3^-$ anion the ESR results suggest that unpaired electrons are localized on the ligands (*508*).

An early report (*518*) following the discovery of bipyridyl complexes of cobalt(I) (*705*, *716*; and Section III, D), that diamagnetic solids were obtained by reduction of the tris(bipyridyl)cobalt(III or II) cations with sodium borohydride or sodium amalgam has not been substantiated (*520*, *708*). The tris(bipyridyl)cobalt(I) cation has a magnetic moment of 3.2–3.4 B.M. which is independent of temperature between 70° and 340°K (*708*). The cation is formed when the corresponding cobalt(III or II) complexes are reduced homogeneously with borohydride. The heterogeneous reduction of the higher valent complexes with sodium amalgam gives the paramagnetic bis(bipyridyl)cobalt(I) perchlorate (*520*) which possibly contains coordinated perchlorate groups. The brown-black $[Co(phen)_3ClO_4]$ is known (*512*), and $Co(bipy)_3$ was recently reported (*348*); being isoelectronic with $Cu(bipy)_3^{2+}$, the latter complex is of some interest.

The $Co(bipy)_3^+$ ion is a useful catalyst for a number of borohydride reductions, e.g., organic nitro compounds are reduced smoothly to amines at pH 6.5–7; the true reducing agent is $Co(bipy)_3^+$. The oxidation–reduction potential for Co(I)/Co(II) is 0.91 volt (vs. standard calomel electrode in 50% aqueous ethanol) and this should fall between the potentials of the other reactants (*709*). Catalytic reductions of organic halogen compounds may be achieved (*436*), and the system is reactive to small molecules such as N_2O (*38*).

The rhodium(I) compound $Rh(bipy)_2ClO_4 \cdot 3H_2O$ is diamagnetic, as are the complexes $[Rh(bipy)_2Cl \cdot X \cdot 2H_2O]_n$ ($X = ClO_4$ or NO_3) (*520*). All three compounds are obtained by sodium amalgam reduction of rhodium(III) compounds. If $[Rh(bipy)_2Cl \cdot X \cdot 2H_2O]_n$ actually contains rhodium(II), the structure is possibly a dimer involving chlorine bridges and with antiferromagnetic interaction between the paramagnetic centers. However, all three compounds give the same rhodium(I) species in solution, so either $[Rh(bipy)_2Cl \cdot X \cdot 2H_2O]_n$ disproportionates or it is actually a mixture of rhodium(I) and rhodium(III) (*520*). There is no evidence to support the alternative formulation of these compounds as hydrides of rhodium(III). The red complex bipyridyl(cycloocta-1,3,5,7-tetraene)rhodium(I) perchlorate has been prepared (*153*), and the reaction of di-μ-chlorotetracarbonyldirhodium with bipyridyl affords $[(CO)_2RhCl]_2(bipy)$ which, according to molecular weight determinations, contains a bridging bipyridyl molecule (*661*).

The borohydride reduction of neutral or strongly alkaline suspensions of *cis*-dichlorobis(bipyridyl)rhodium(III) salts gives paramagnetic products. The stoichiometrically best defined compound is $Rh(bipy)_2NO_3 \cdot 3H_2O$ ($\mu_{eff} = 1.86$ B.M.) (*520*). No evidence for hydrido-complex formation was found, in contrast to the reaction of BH_4^- with the dichlorobis(di-2-pyridylamine)rhodium(III) cation in the presence of perchlorate ions which gives the paramagnetic hydrido complex $Rh(dipyam)H_n \cdot ClO_4$ ($n = 1$ or 2, $\mu_{eff} = 1.78$ B.M.) (*451*).

Complexes of phenanthroline and palladium(II) chloride react with carbon monoxide in aqueous solution to give the stable violet compound $[(phen)Pd(CO)_2Pd(phen)] \cdot 4H_2O$; bipyridyl gives an unstable product (*119*). The formation of the compound has been suggested as the basis of an analytical method for the determination of carbon monoxide (*118*).

IX. Complexes of Metals in "High" Oxidation States

For a metal in a high oxidation state, the stability of its complexes with neutral ligands will be determined by the ability of the ligand to donate an electron pair, and by the chelate effect rather than the ability to accept electrons back-donated from the metal. With the reservations already made in Section III, B, one should therefore expect the pK_a of the ligand to provide a reasonable measure of its ability to complex metal ions in high oxidation states. From that data tabulated in the *Chemical Society Special Publication on Stability Constants*, a suggested order for this ability would be en $>$ NH_3 $>$ Py $>$ phen $>$ bipy. Thus, from a comparison of the chemistry of these ligands, one might expect bipyridyl and phenanthroline to be found in complexes where the overall charge is not large, e.g., coordinated to such groups as Ag^{2+}, VO_2^{2+}, or $MnCl_4$, but not in complexes of high overall charge, e.g., $M(bipy)_3^{4+}$.

Adducts (1:1) of bipyridyl and phenanthroline with both Sn(IV) (*55*) and Pb(IV) (*163*) are known. The stability constants for the adducts of bipyridyl and $SnCl_4$, n-$BuSnCl_3$, and R_2SnCl_2, where R is an alkyl group, have been determined in acetonitrile and at high $SnCl_4$ concentrations; it is suggested that two tin atoms may be bridged by a nonchelating bipyridyl molecule, and that the tin atoms become 6-coordinate by picking up a solvent molecule (*423*, *523*). A similar structure has been suggested for $(Ph_2Sn(NCO)_2)_2 \cdot (bipy)$ (*545*, *546*). For the formation of $[Me_2Sn(phen)_2]^{2+}$ the average value of $\log_{10}(K)$ is 4.2 (*741*). Stable 1:1 adducts with R_2SnX_2 and R_2PbX_2 species (*11*, *12*, *54*, *84*, *295*, *378*, *387*, *546*, *674*, *715*) and the weak acceptor Me_3SnCl (*160*) are also known. Terpyridyl forms a stable undissociated 1:1 adduct with Ph_2PbI_2 and an ionic 1:1 adduct with SnI_4 (*250*). X-Ray analysis of the solid adduct with Me_2SnCl_2 shows a structure $[Me_2SnCl(terpy)][Me_2SnCl_3]$ (*226*). Tris and tetrakis complexes of Pb(II) have been reported (*300*, *424*, *426*) as well as an 8-coordinate Th(IV) complex, $ThCl_4(phen)_2$ (*259*).

Many complexes of high oxidation state transition metals have been reported; these vary from simple species such as the stable [$VOCl_3$(bipy)] (*270*) and [$NbCl_4$(bipy)] (which ionizes in acetonitrile to [$NbCl_3$(MeCN)-(bipy)]Cl (*8*)) to complexes of uncertain nature such as the oxochloroalkoxybipyridyl complexes of Nb and Ta (*201*), and the complex formulated as Na_2[Cr$(Ph)_5$$(bipy)_2$] (*326*). Other V(IV) and Ti(IV) complexes are included in Section VII for convenience of comparison. An X-ray analysis of $CrO(O_2)_2$(phen) shows a 7-coordinate structure (*635*). From a solution of [$M(CO)_4$(bipy)] in CH_2Cl_2 (where M = Mo or W) Hull and Stiddard (*389*) have prepared [MCl_4(bipy)], [$MOCl_3$(bipy)], and [MO_2Br_2(bipy)], all being nonelectrolytes or weak electrolytes. The weak conductance of the solution of [$MoCl_4$(bipy)] in CH_3NO_2 may be caused by some dissociation to [$MoCl_3(CH_3NO_2)$(bipy)]Cl. The parent compound obeys the Curie–Weiss law and μ_{eff} (which is virtually temperature independent) is appreciably less than the spin only value (*139*). The compounds [WCl_5L] (*87*) and [WCl_4(bipy)] (*105*), [(bipy)·H_2MoO_4] (*74*) and [MoO(OH)Cl_2(phen)] (*537*) are also known, the latter two probably contain the organic molecule as a protonated cation rather than as a chelate ligand. MoO_2Cl(bipy) and $Mo_2O_3Cl_4(bipy)_2$ are considered to be polymeric, but $MoOCl_3L$ is monomeric (*223*, *536*, *657*).

Mn(IV) complexes are easily converted to Mn(III). Thus, on heating [$MnCl_4$(bipy)] a μ-dichloro-Mn(III) dimer is formed (*292*), while the species $[Mn(bipy)_2O]_2(S_2O_8)_{1.5}\cdot 3H_2O$ and $[Mn(bipy)_2O](ClO_4)_3\cdot 2H_2O$ are found to have an oxidation number of 3.4 and $\mu_{eff} = 1.7$ B.M. at 25°C. They are postulated to be μ-dioxo species of mean oxidation number 3.5 (*565*). The rhenium complexes [$ReBr_4$(bipy)], [$ReOBr_3$(bipy)] (*148*), [(bipy)Cl_2OReOReOCl_2(bipy)] (*407*), and [$ReOCl_3$(bipy)] (*147*) have been reported. However, as the complex [$ReOCl_3$(4,4′-bipyridyl)] is also stable, the formulation of the simple oxyhalides may be incorrect. The complexes [$OsO_2(OH)_2$(bipy)], [OsO_2Cl(bipy)], and [OsO_2(biguanide)(bipy)]Cl have been prepared (*593*, *594*) and shown by IR spectroscopy to contain the trans O–Os–O grouping.

Of the high oxidation state complexes, those of Ag(II) are the most thoroughly investigated. Magnetic (*540*, *665*) and ESR studies (*497*) have been discussed in Section V, D, and some kinetic studies have been reviewed in Section IV, C. The paramagnetic techniques include studies of the complexes $[Ag(bipy)_3]^{2+}$ and $[Ag_2(bipy)_5](S_2O_8)_2$, this latter being of unknown structure, although a bridging bipyridyl group is conceivable. The ions $[Ag(phen)_2]^{2+}$, $[Ag(bipy)_2]^{2+}$, and $[Ag(terpy)]^{2+}$ are known (*40*, *538*, *633*). They may be prepared from AgO or by the oxidation of the Ag(I) complexes by $S_2O_8^{2-}$, O_3, or electrolytically. In the case of ozone oxidation, nonaqueous protonic solvents may be used (*633*). The stereochemistry of the product is obviously critical as the bidentate ligands usually give bis complexes, the terdentate a monocomplex, while there is no reaction between $K_2S_2O_8$ and the Ag(I) complex of 6,6′-di-2″-pyridyl-2,2′-bipyridyl (*539*). The visible and UV spectra of these Ag(II) complexes are recorded (*36*, *146*, *712*).

For UO_2^{2+} the order of complexing ability for ligands DMSO > py > phen > bipy (*30*) is consistent with that suggested above. Because of their low complexing ability with this group, bipyridyl and phenanthroline yield only protonated cations in acidic solutions containing UO_2^{2+} (*514*, *516*); but in aqueous or alcoholic solution, chelate complexes may be formed in which the uranium atom can exhibit a coordination number of either 6 or 7 (*496*, *514–516*, *601*, *635*).

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