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THE COORDINATION CHEMISTRY OF 2,2′:6′,2″-TERPYRIDINE AND HIGHER OLIGOPYRIDINES

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I. Introduction

A. HISTORICAL INTRODUCTION

The potentially terdentate ligand 2,2′:6′,2″-terpyridine (Fig. 1) was first isolated by Morgan and Burstall as one of the numerous products from the reaction of pyridine with iron(III) chloride (*323, 324, 326, 327*). The higher oligopyridines, 2,2′:6′,2″:6″,2‴-quaterpyridine (Fig. 2) and 2,2′:6′,2″:6″,2‴:6‴,2⁗-quinquepyridine (Fig. 3) were obtained in low yields from Ullmann reactions of bromopyridines (*93*). Improved methods for the synthesis of these interesting compounds are now available, and have been reviewed elsewhere (*285*). It was recognized from the first that these compounds should possess an interesting coordination chemistry. This review describes the coordination chemistry of these, and related, ligands.

Although a number of other reviews discussing general or specific aspects of the chemistry of these ligands have appeared, there has been none solely concerned with this class of compounds (*69, 130, 131, 178, 210, 211, 285, 286, 291, 314, 401, 406, 415*). There has been a considerable increase in the use of these ligands in recent years, prompted in part by the attractive photochemical and photophysical properties exhibited by complexes of the related ligands 2,2′-bipyridine (Fig. 4) and 1,10-phenanthroline (Fig. 5) (*491*). The availability of the ligands from facile, high-yielding syntheses suggests that their use will continue to increase (*129, 132–144, 285*).

It is also apparent that complexes of 2,2′:6′,2″-terpyridine differ in significant, and interesting, ways from those of 2,2′-bipyridine. Accordingly, a treatment of the coordination chemistry of 2,2′:6′,2″-terpyridine and the higher oligopyridines is felt to be justified and timely.

I have attempted to treat the subject as comprehensively as possible; errors and omissions will undoubtedly have occurred, and for these I proffer my

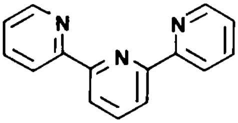

FIG. 1. 2,2′:6′,2″-Terpyridine.

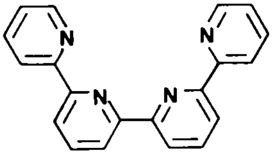

FIG. 2. 2,2′:6′,2″:6″,2‴-Quaterpyridine.

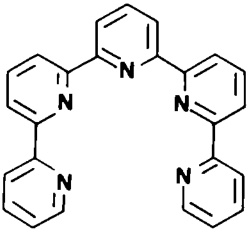

FIG. 3. 2,2′:6′,2″:6″,2‴:6‴,2⁗-Quinquepyridine.

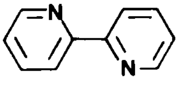

FIG. 4. 2,2′-Bipyridine.

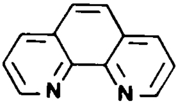

FIG. 5. 1,10-Phenanthroline.

apologies. Coverage of the primary journals is complete through November 1985, with *Chemical Abstracts* covered through Volume 103.

B. NOMENCLATURE

Nomenclature is always a vexing subject: the ligand (Fig. 1) has been known variously as 2,2′,2″-tripyridyl, 2,2′,2″-tripyridine, 2,6′-bis(2-pyridyl)-pyridine, and 2,2′:6′,2″-terpyridine. The latter is the systematic name (*262*) and will be used throughout this article. All other compounds will be named systematically, according to IUPAC recommendation A-54. In this article, the abbreviations terpy, quaterpy, quinquepy, bipy, and phen will be used for the ligands in Figs. 1–5, respectively. Substituted derivatives will not be similarly described; thus 4,4″-diethyl-4′-phenyl-2,2′:6′,2″-terpyridine (Fig. 6) will be denoted 4,4″-Et_2-4′-Phterpy.

C. STABILIZATION OF UNUSUAL COMPLEXES

The very concept of an "unusual" complex is suspect; what is uncommon or unusual to one person, or in one era, may be commonplace and unremarkable to another person or at another time. However, it is still a fact that the majority of transition metal complexes incorporate metal ions in the +2 or +3 oxidation state, in basically octahedral, tetrahedral, or square-planar geometries. The stabilization of other, higher or lower, oxidation states, and of other coordination numbers and geometries, is thus worthy of note. This class of ligands excels in all of these categories.

Low oxidation states are characterized by an excess of electron density at the metal atom; stabilization may be achieved by the use of ligands capable of reducing that electron density. One of the simplest ways to reduce the electron density is to design ligands with low-lying vacant orbitals of suitable symmetry for overlap with filled metal orbitals. This results in the transfer of electron density from the metal to the ligand (back-donation). In general, ligand nonbonding or π antibonding orbitals are of the correct symmetry for

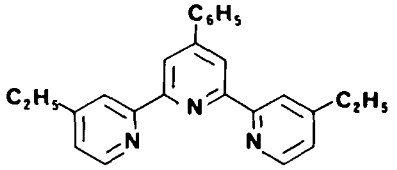

FIG. 6. 4,4″-Diethyl-4′-phenyl-2,2′:6′,2″-terpyridine.

such overlap. Similarly, metal ions in high oxidation states may be stabilized by powerful σ- or π-donor ligands.

The oligopyridines are ideally suited to such roles; they possess a filled highest occupied molecular orbital (HOMO) and a vacant lowest unoccupied molecular orbital (LUMO) of suitable energies for interaction with metal *d* orbitals (*283*). They are thus capable of stabilizing both high and low oxidation states of metal ions.

The geometries of complexes incorporating monodentate ligands are dominated by electronic, steric, and CFSE terms. In contrast, the geometries of complexes incorporating relatively inflexible polydentate ligands are predominantly determined by the configuration of the ligand; a planar pentadentate ligand *cannot* form octahedral complexes. This apparently facile observation has a number of far-reaching consequences. A compromise between the optimum geometry for the metal ion and that for the ligand must be reached. This may be expressed as a distorted geometry about the metal or as a distortion of the ligand. An extreme case of such a mismatch in the coordination requirements of the metal and the ligand will result in a polydentate ligand binding through only some of its potential sites; i.e., a bidentate terpy.

II. The Complexes—Types of Bonding

A. MONODENTATE, BIDENTATE, AND BRIDGING

In principle, terpy could act as a monodentate, bidentate, terdentate, or bridging ligand for a metal ion. Although monodentate and bidentate species have been widely assumed to be intermediates in the formation and dissociation of terpy complexes, there has been little evidence, until recently, that such species are isolable. On the basis of their vibrational spectra, the complexes $[M(CO)_3(terpy)X]$ (M = Mn, X = Br; M = Re, X = NO_3) were thought to contain bidentate terpy ligands (*4*, *205*). It was also suggested, on the basis of ESR studies, that the radical anion $terpy^{\cdot-}$ coordinates to group IA and group IIA ions in a bidentate manner (*79*, *349*). Solution NMR studies have indicated on–off terdentate–bidentate equilibria in $[Eu(terpy)_3]^{3+}$ (*110*). Conclusive proof of the bidentate bonding mode was provided by the X-ray structural analysis of the two (red and yellow) forms of $[Ru(terpy)(CO)_2Br_2]$, both of which contain a bidentate terpy ligand. The color differences arise from the orientation of the uncoordinated pyridine ring. In one case, a stacking interaction with the free pyridine ring of an adjacent molecule is observed in the solid state (*162*). No other examples of monodentate or bridging terpy ligands have yet been structurally characterized.

The higher oligopyridines are more likely to form complexes in which "dangling" pyridine rings are present (*vide infra*). There have been few structural studies of such complexes of the higher oligopyridines, but there is considerable evidence to suggest that they may act as bridging ligands. Lehn and co-workers demonstrated that the sterically demanding ligand 5,5′,3″,5‴-Me_4quaterpy forms a binuclear copper(I) complex, $[Cu_2L_2][ClO_4]_2$, in which the ligand acts as a bridging bis(bidentate) (*290*). A similar binuclear complex of quinquepy with copper has also been isolated (*136*).

B. TERDENTATE AND HIGHER POLYDENTATE

2,2′:6′,2″-Terpyridine commonly behaves as a chelating terdentate ligand, with the majority of complexes exhibiting 1:1 or 1:2 metal:ligand ratios. The 1:2 complexes are invariably based upon an octahedral geometry, and frequently exhibit D_{2d} local symmetry. These complexes are discussed at the appropriate points in the text.

Upon coordination to a metal center, the terpy ligand undergoes a number of significant changes. The most obvious results from the adoption of the cis,cis-configuration, in contrast to the trans,trans-equilibrium solution structure. It is also apparent that for terpy to act as an efficient terdentate, it is necessary to distort the ligand and reduce the interannular angle between the central and terminal pyridine rings (Fig. 7). It is regrettable that there appears to be no published crystallographic study of 2,2′:6′,2″-terpyridine itself. However, we have determined the crystal and molecular structure of 4′-Phterpy and the complex $[Ni(4'\text{-Phterpy})_2][PF_6]_2 \cdot 10H_2O$. The structure of the free ligand (Fig. 8a) displays slight differences in bond lengths from the coordinated ligand (Fig. 8b), but the major differences arise from distortion of the terminal rings. The dihedral angle between the terminal and central rings increases from 5.7 to 7.1° in the complex, while the C—C—N angles reduce from 116 in the free ligand to 114° in the complex. This is fully in accord with the prediction of increased strain in the complex (*129*).

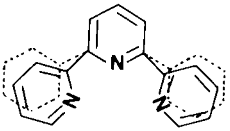

FIG. 7. The distortion experienced by a 2,2′:6′,2″-terpyridine ligand upon coordination to a metal ion in a planar terdentate mode.

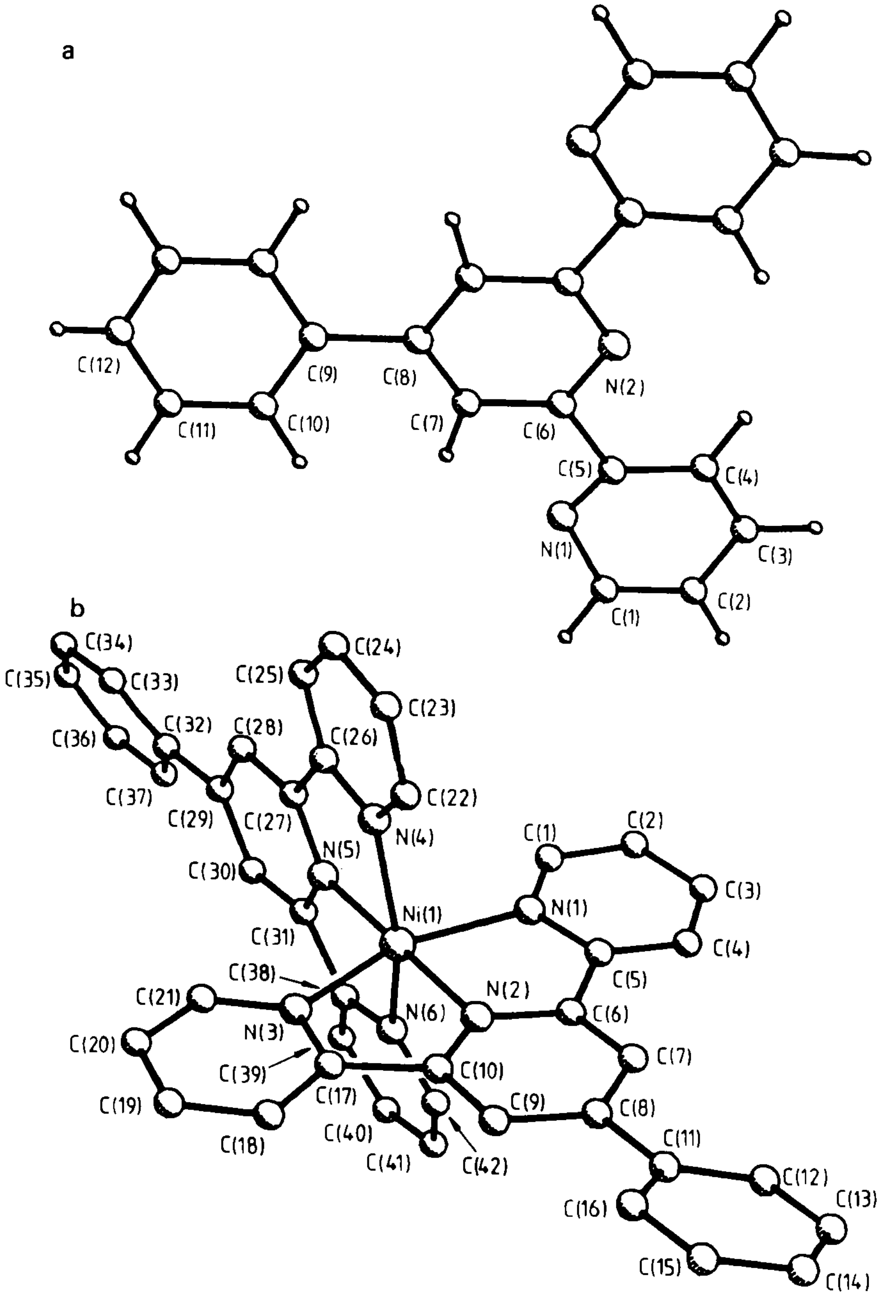

FIG. 8. The crystal and molecular structure of 4′-phenyl-2,2′:6′,2″-terpyridine (a) and its bis complex with nickel(II) (b) (*129*).

Numerous crystal structural analyses of complexes with the 1:1 metal: ligand stoichiometry have been reported. These are discussed in the appropriate sections. A wide variety of geometries are adopted, but it is clear that the essentially planar terdentate ligand imposes a steric requirement such that "uncommon" geometries are favored. In particular, the distorted trigonal-bipyramidal (Fig. 9a), square-pyramidal (Fig. 9b), and pentagonal-bipyramidal geometries (Fig. 9c) are commonly encountered.

The strain introduced into the ligand will be even higher in complexes of the higher oligopyridines, and it was at one time suggested that they could not exhibit their maximum denticity in monodentate complexes. It is now clear that quaterpyridine may act as a quaterdentate ligand, albeit with very unsymmetrical M—N distances.

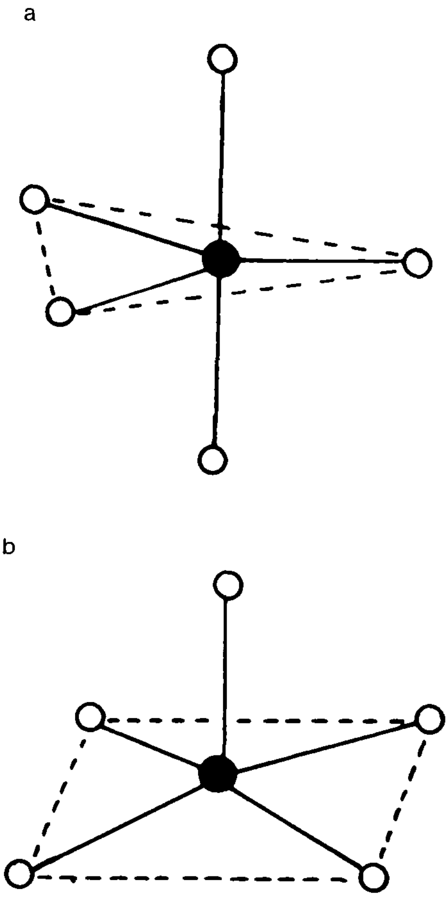

FIG. 9. The common five- (a,b) and seven-coordinate (c) geometries adopted in complexes of oligopyridines.

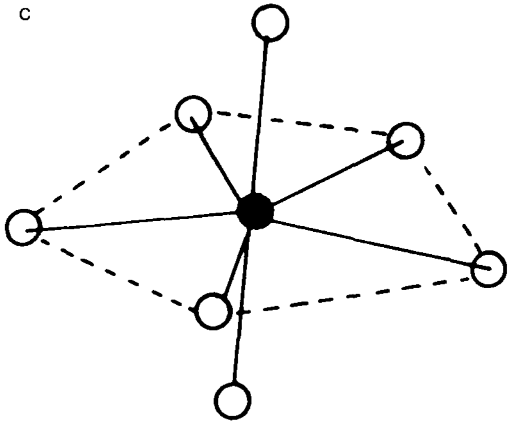

FIG. 9c. See legend on p. 75.

C. CYCLOMETALLATED

To date, the cyclometallated bonding mode has not been directly observed in complexes of terpy or higher oligopyridines. However, the unequivocal demonstration of a cyclometallated 2,2′-bipyridine moiety in iridium complexes suggests that such a possibility exists (*71*, *130*, *131*, *145*, *233*, *419*, *420*, *478*). There is ^{1}H NMR and kinetic evidence to suggest that cyclometallated intermediates are not involved in the deuteration of $[Ru(terpy)_2]^{2+}$ at the 3, 3′, 5′, and 5″ positions (*138*).

III. Coordination Compounds of 2,2′:6′,2″-Terpyridine

A. GROUP IA

It is not unreasonable to expect alkali metal ions to form complexes with the moderately hard nitrogen donor atoms of pyridine ligands, and it is now becoming apparent that a rich chemistry may exist in this area.

Vogtle *et al.* have demonstrated the formation of solid 1:1 adducts between terpy and MSCN (M = Li or Na); in contrast, $[NH_4][SCN]$ forms a 2:1 adduct with terpy. Although stability constants were not reported, it was shown by ^{23}Na NMR studies that terpy is superior to bipy, but inferior to phen, as a ligand for the sodium cation (*455*). Presumably, the metal–nitrogen interaction is predominantly ionic in character.

Reaction of alkali metals (Li, Na, or Rb) with terpy in inert solvents results in the formation of alkali metal complexes of the terpy radical anion (*349*).

B. GROUP IIA

The complexes $Mg(NO_3)_2 \cdot terpy \cdot 2H_2O$, $Ca(SCN)_2 \cdot 2terpy \cdot H_2O$, and $Ba(SCN)_2 \cdot terpy \cdot H_2O$ have been reported, but are of unknown structure (*455*). ESR studies of the terpy radical anion obtained from the reaction of terpy with alkaline earth metals (Mg, Ca, Sr, or Ba) have indicated that a significant interaction occurs between the anion and the cation (*79*). Spectrophotometric measurements have indicated that magnesium sulfate forms a 1:1 complex with terpy in water, with $K = 5.858 \pm 0.023\ mol^{-1}$ (*185*, *186*).

C. GROUP IIIB

Reaction of aluminum halides with acetonitrile solutions of terpy leads to the formation of $[Al(terpy)Cl_3]$ or $[Al(terpy)_2]X_3$ (X = Cl, Br, or I) (*48*). Spectroscopic and conductivity measurements suggest that these complexes are octahedral. Moore and co-workers have investigated the reaction of terpy with $[Al(DMSO)_6]^{3+}$ (DMSO, dimethylsulfoxide) by NMR methods; stepwise release of DMSO indicated sequential coordination of the pyridine rings, and it is noteworthy that the closure of the final ring is significantly slower than the other two, as predicted by our concepts of increasing strain in the chelated complex (*78*).

The complexes $[M(terpy)X_3]$ (M = Tl, X = Cl or Br; M = Ga or In, X = Cl, Br, or I) are all known, and may be prepared by the direct reaction of MX_3 with terpy (*52, 53, 458–462, 467*). The 2:1 complexes $[Tl(terpy)_2][TlX_4]$ (X = Cl, Br, or I) are also known. The $[M(terpy)Cl_3]$ compounds are isostructural, and a crystal structural analysis of $[Ga(terpy)Cl_3]$ revealed the expected distorted octahedral structure (*52, 53*).

The octahedral complexes $[In(terpy)_2]X_3$ (X = Cl, Br, I, ClO_4, or CNS) are readily prepared by the reaction of $InCl_3$ or indium perchlorate with terpy (*99*, *431*, *432*, *466*, *474*).

A number of organoindium complexes with terpy have been described, and include $[RIn(terpy)Cl_2]$ (R = Me or C_6F_5); it was proposed that these species incorporate a bidentate terpy ligand (*120*, *161*).

D. SILICON, GERMANIUM, TIN, AND LEAD

Silicon tetrachloride is reported not to react with carbon disulfide solutions of terpy; this is rather surprising in view of the facile reactions observed with the lower members of the group (*37, 470*). A number of

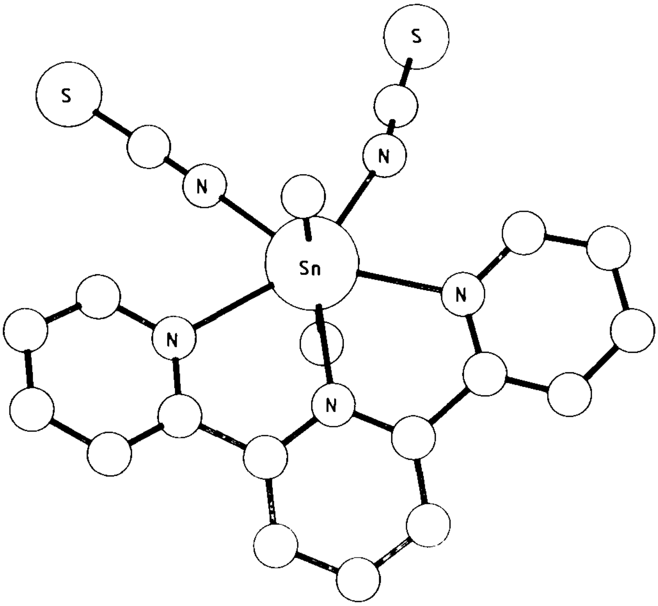

FIG. 10. The crystal and molecular structure of $[Me_2Sn(terpy)(NCS)_2]$ (*346*).

workers have investigated the interaction of terpy with $[R_2SnX_2]$ species, and have demonstrated the formation of 1:1 adducts (*468*, *469*). Crystal structural analyses of a number of these complexes have been reported. The 1:2 adduct with $[Me_2SnCl_2]$ should be formulated $[Me_2Sn(terpy)Cl][Me_2SnCl_3]$, with a highly distorted octahedral cation (*149*, *158*, *163*, *181–183*, *193*, *486*). Similar structures are expected for the 1:2 adducts with $[Ph_2SnCl_2]$ (*163*, *421*) and $[(\eta^1\text{-}C_5H_5)_2SnCl_2]$ (*448*). A structural analysis has revealed $[Me_2Sn(terpy)(NCS)_2]$ to possess a pentagonal-bipyramidal geometry, in which the methyl groups adopt the axial sites (Fig. 10) (*346*). This conclusion is also supported by ^{119}Sn NMR and Mössbauer spectroscopic studies (*310*, *357*). Mössbauer studies have also been reported for some vinyl, butyl, and phenyl derivatives (*310*, *347*), and for $[Sn(terpy)Cl_2]$, which is thought to be five-coordinate (*170*). The complex $SnCl_4 \cdot terpy \cdot 5H_2O$ is of unknown structure (*468*). The related lead complexes, $[Ph_2Pb(terpy)X_2]$ (X = Cl, Br, or I) and $[Ge(terpy)I_3]I$, have also been described (*193*).

Tetraphenyldihalostannoles (Fig. 11) react with terpy to form $[Ph_4C_4Sn(terpy)X][Ph_4C_4SnX_3]$ (*217*).

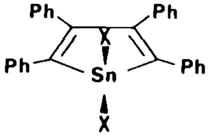

FIG. 11. Tetraphenyldihalostannole.

E. PHOSPHORUS, ARSENIC, ANTIMONY, AND BISMUTH

A number of complexes of the type $(EX_3)_n(\text{terpy})_m$ (E = As, X = Cl, $n = 2$, $m = 1$; X = Br, $n = 1$, $m = 1$; E = Sb, X = Cl, Br, or I, $n = 3$, $m = 2$; E = Bi, $n = m = 1$) have been described, and are formulated as containing five-coordinate $[EX_2(\text{terpy})]^+$ cations (*74*). The only other complex to have been reported is $[Bi(\text{terpy})(S_2CNEt_2)I_2]$, which has been structurally characterized, and shown to possess a pentagonal-bipyramidal structure with axial iodine atoms (Fig. 12) (*381*).

F. SULFUR, SELENIUM, AND TELLURIUM

The 1:1 adducts of terpy with $[ECl_4]$ (E = Se or Te) behave as 1:1 electrolytes, and are formulated $[M(\text{terpy})Cl_3]Cl$; the 1:2 adduct with $[TeCl_4]$ probably possesses the structure $[Te(\text{terpy})Cl_2][TeCl_6]$ (*151*).

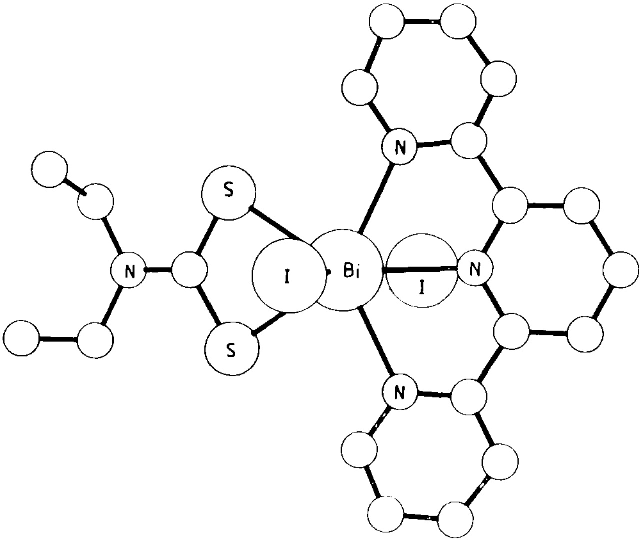

FIG. 12. The crystal and molecular structure of $[Bi(\text{terpy})(S_2CNEt_2)I_2]$ (*381*).

G. Transition Metals

1. Early Transition Metals

The complex [Sc(NO_3)$_3$(terpy)] has been structurally characterized; the metal is in a nine-coordinate environment (Fig. 13), in which each nitrate acts as a chelating bidentate ligand (*16*).

Although the tetrahalides of titanium, zirconium, and hafnium might be expected to react with terpy to give adducts, these reactions do not appear to have been investigated. It is claimed that titanium(III) chloride reacts with acetonitrile solutions of terpy to give a paramagnetic 1:1 adduct, although the adduct has not been fully characterized (*121*). The reaction of [(cp)$_2$Ti(CO)$_2$] (cp, cyclopentadienyl) with excess terpy gives the formally zero-valent compound [Ti(terpy)$_2$] (*43*).

The orange or brown compounds [M(terpy)X_5] (M = Nb, X = Cl or Br; M = Ta, X = Br) are readily prepared by the reaction of terpy with the

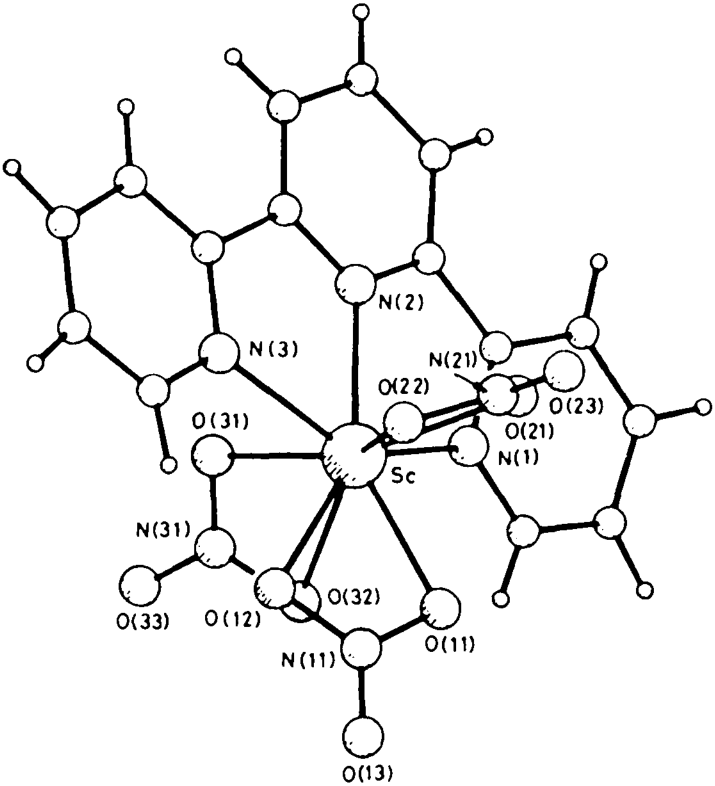

FIG. 13. The crystal and molecular structure of [Sc(NO_3)$_3$(terpy)] (*16*).

appropriate pentahalide in benzene. The only product isolated from the reaction with $TaCl_5$ was Ta_2Cl_{10}(terpy), which, like the previous compounds, is of unknown structure (*38*). The red vanadium(V) hydroxylamido complexes $[V(terpy)(H_2NO)(NO)X]$ ($X = CN$ or N_3) and $[V(terpy)(H_2NO)(NO)X]Y$ ($X = H_2O$ or NH_3; $Y = I$ or Br) have also been prepared (*481*).

The adducts MCl_4(terpy) and M_2Cl_8(terpy) (M = Nb or Ta) have been described. The structures are not known with any certainty, although the mononuclear complexes are nonelectrolytes, whereas the bromo compounds are 1:1 electrolytes with extensive magnetic interactions between the paramagnetic centers (*38*).

The compound $[VCl_3(terpy)]$ is a paramagnetic, octahedral complex formed in the reaction of VCl_3 (*100*) or $[VCl_3({}^tBuNC)_3]$ (*408*) with terpy. A bis(terpy)vanadium(III) complex is presumably the product of oxidation of $[V(terpy)_2]^{2+}$ (*49*). A red polynuclear complex is formed from the reaction of aqueous vanadium(III) solutions with one equivalent of terpy (*49*).

The complex $[V(terpy)_2]I_2$ may be isolated as a green air-sensitive solid from aqueous ethanolic solution (*238*). Taube and co-workers have investigated the electron-transfer reactions of $[V(terpy)_2]^{2+}$, prepared by the direct interaction of terpy with aqueous vanadium(II) solutions (*49*).

The reduction of $[V(terpy)_2]I_2$ by magnesium or $Li[AlH_4]$ leads to the formation of $[V(terpy)_2]$ (*239*), which may also be prepared by the reaction of terpy with $[V(CO)_4(dppe)]$, $[V(CO)_2(dppe)_2]$, $[V(cp)_2]$, or $[V(cp)(CO)_4]$ (*40*). The solid is black ($\mu_{eff} = 1.73$ BM) and is thought to possess considerable ligand radical character, similar to the analogous bipy and phen complexes.

2. *Chromium, Molybdenum, and Tungsten*

The majority of studies of group VIA polypyridyl complexes has been concerned with the photophysical and electrochemical properties of the $[Cr(terpy)_2]^{3+}$ cation. However, a number of other complexes have been described.

2,2′:6′,2″-Terpyridine has been investigated as a reagent for the colorimetric detection of molybdenum(VI) (*232*). The molybdenum(IV) complex cation $[Mo(terpy)(H_2NO)(NO)(H_2O)]^{2+}$ is prepared by the reaction of terpy with $[MoO_4]^{2-}$ and $[H_3NOH]Cl$ in water (*484*). The compound is diamagnetic, and reacts with cyanide to give $[Mo(terpy)(NO)(CN)(NHO)]$ (*483*). This cyano complex has been structurally characterized, and shown to adopt a distorted pentagonal-bipyramidal geometry, with axial nitrosyl and cyanide ligands, and a bidentate N,O-bonded hydroxylamido ligand (*482*). The unusual complex cation $[Mo(terpy)(H_2NO)(H_2NOH)(NO)]^{2+}$ is formed from the reaction of

$[Mo(terpy)(H_2NO)(NO)(H_2O)]^{2+}$ with excess hydroxyammonium chloride (*483*).

The complex $[Cr(terpy)_2]^{3+}$ was first prepared by reaction of $CrCl_3$ with excess terpy in the presence of a reducing agent (*62, 328*), but is more readily obtained from the reaction of a chromium(II) source with terpy, followed by oxidation (*80, 189, 252–258, 406, 479, 480*). The photophysical properties of this yellow cation have excited considerable interest, and play an integral role in a number of potential solar energy conversion schemes. There is still some controversy over the precise photoexcited states involved in the photoaquation and other reactions of $[Cr(terpy)_2]^{3+}$ and related polypyridylchromium(III) cations, but the major species of importance appears to be the low-lying ^2E_g state, reached by intersystem crossing from the $^4T_{1g}$ or $^4T_{2g}$ states (ground state = $^4A_{2g}$) (*10, 80, 405*). The ^2E_g state is remarkably short-lived, and has $\tau = 0.05$ μsec [cf. $[Cr(bipy)_3]^{2+}$, $\tau = 63$ μsec], an observation which has been ascribed to an intimate association with solvent molecules approaching close to the metal in "interligand pockets." This is of obvious relevance to the photoaquation of the complexes, which has also been ascribed to direct nucleophilic attack of water upon the coordinated ligands. To some extent these differences have been settled by an X-ray crystal structure of the salt $[Cr(terpy)_2](ClO_4)_3 \cdot H_2O$ (Fig. 14) (*479, 480*). Although there was no evidence for the *water* molecule occupying a site close to the metal, perchlorate ions were found to have oxygen atoms within the proposed pockets (Cr—O, ~4.5 Å), reminiscent of the outer-sphere complexes proposed for a number of transition metal α,α′-diimine complexes with more or less innocent anions. These observations provide strong support for the photoaquation reactions proceeding via attack at the metal to form a seven-coordinate intermediate, rather than at the ligand. The electron-

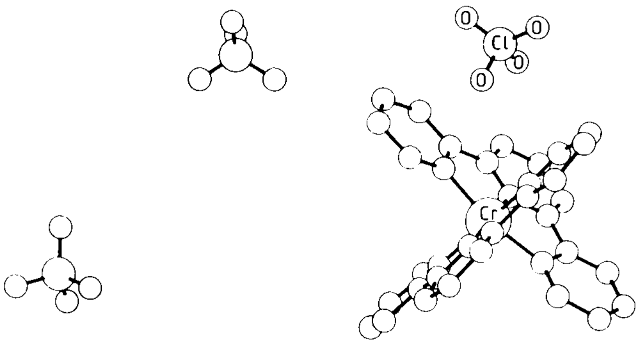

FIG. 14. The crystal and molecular structure of $[Cr(terpy)_2][ClO_4]_3 \cdot H_2O$ (*479, 480*).

transfer reaction between $[Cr(bipy)_3]^{2+}$ and $[Cr(terpy)_2]^{3+}$ was found to be too fast to follow ($k \geq 3 \times 10^6\ M^{-1}\ sec^{-1}$) (*189*).

Related to the above studies are a number of investigations into the electrochemical properties of $[Cr(terpy)_2]^{3+}$ and some substituted derivatives (*61, 252–258*). The parent complex exhibits at least six reductions, the first four of which are fully reversible. It is suggested that the first three reductions are metal-centered, whereas the last is ligand-centered. In the absence of ESR evidence, these conclusions must be regarded as tentative. The complexes of 4′-Phterpy and 4,4″-Ph_2terpy have also been investigated. The complex $[Cr(terpy)Cl_3]$ has been described (*77*).

The chromium(II) cation $[Cr(terpy)_2]^{2+}$ is conveniently prepared by the interaction of aqueous chromium(II) solutions with excess terpy, and may be isolated as its perchlorate or iodide salt (*239, 255, 299*). The magnetic properties of $[Cr(terpy)_2][ClO_4]_2$ have been recorded over the temperature range 20–300 K; the complex is low spin its μ_{eff} exhibits a nearly linear temperature dependence over this range (*299*). The complex may be reduced electrochemically (*255*) or chemically (*239*). Herzog and Aul have isolated the various $[Cr(terpy)_2]^{n+}$ complexes that may be obtained by chemical reduction; $[Cr(terpy)_2]I_2$ (red-brown, $\mu_{eff} = 2.80$ BM), $[Cr(terpy)_2]I$ (wine-red, $\mu_{eff} = 1.85$ BM), and $[Cr(terpy)_2]$ (green, $\mu_{eff} = 0.63$ BM) (*239*).

The molybdenum(II) chloroclusters $[Mo_6Cl_8]X_4$ (X = Cl or I) react with terpy in tetrahydrofuran (THF) to give $[Mo_6Cl_8(terpy)X_3]X$, which are of unknown structure (*191, 219*). The compounds behave as 1:1 electrolytes (*191*); the X-ray photoelectron spectrum (PES) of $[Mo_6Cl_8(terpy)Cl_3]Cl$ has been reported (*219*).

The complex $[(C_3F_7)CrCl_2(py)_3]$ reacts with terpy to form $[(C_3F_7)Cr(terpy)Cl_2]$ (*305*).

The very air-sensitive compounds $[Mo(terpy)_2]$ (purple) and $[W(terpy)_2]$ (green) have been described by a number of workers (*44, 174*). The chromium compound may be prepared by the reaction of $[Cr(CO)_6]$ (*44*), $[Cr(CN)_6]^{6-}$ (*42, 47*), $[Cr(CO)_3(C_6H_6)]$ (*47*), or $[Cr(bipy)_3]$ (*44*) with two equivalents of terpy. The molybdenum (*44, 174*) and tungsten (*44*) compounds have been prepared from $[M(CO)_6]$ in a similar manner. Electrochemical studies on $[Mo(terpy)_2]$ indicate three one-electron oxidations (*8*). Photosubstitution reactions of $[M(CO)_6]$ in the presence of limited amounts of terpy lead to the formation of $[M(CO)_4(terpy)]$ (M = Cr, Mo, or W) (*205*). It is unlikely that these compounds are seven-coordinate, and they may well provide examples of a bidentate terpy. $[Mo(CO)_3(terpy)]$ may be prepared by the reaction of terpy with $[Mo(CO)_3(mesitylene)]$, but attempts to prepare the other group VI complexes of this stoichiometry lead to the formation of $[M(CO)_4(terpy)]$ (*205*).

3. *Manganese, Technetium, and Rhenium*

Although no terpy complexes of manganese(VII) have been described, the perrhenate, [terpyH][ReO_4], has been reported by Morgan and Davies (*329*). These authors also described the rhenium(IV) salt [$terpyH_2$][$ReCl_6$]. The complex [Mn(terpy)Cl_3] may be isolated; magnetic measurements indicate that the compound possesses a simple octahedral structure (*214*). In contrast to the mononuclear manganese(III) complex, a number of trirhenium(III) clusters have been described. The purple complexes [$Re_3Cl_9(terpy)_n$] (n = 1, 2, or 1.33) result from the reaction of terpy with [Re_3Cl_9]. Conductivity measurements indicate that the first two compounds should be formulated [Re_3Cl_8(terpy)]Cl and [Re_3Cl_6(terpy)]Cl_3, respectively; the terpy is thought to bind to one rhenium atom as a planar terdentate, perpendicular to the plane of the trirhenium triangle (*192*).

Manganese halides react with terpy to form well-characterized 1:1 complexes of the type [Mn(terpy)X_2] (X = Cl, Br, or I), which have been shown to be isomorphous with the corresponding zinc complexes. They are thus thought to possess a five-coordinate trigonal-bypyramidal environment (*225*, *271*). The magnetic moments of these complexes are close to the expected spin-only value (*271*). There have been a number of investigations of the formation of the 1:1 complexes in water (*245*), methanol, or DMSO solution (*50*, *51*, *83*, *84*). In water, the Eigen-Wilkins mechanism, in which the rate of formation of the complex is controlled by the rate of exchange of coordinated water with the bulk solvent, appears to operate (*243*, *245*). In methanolic solution, the system is not so simple, and there is a suggestion that the formation of the second metal-to-nitrogen bond (i.e., formation of a chelate ring) may be the rate-determining step (*50*, *51*). The reaction in DMSO is complex; $[Mn(DMSO)_6]^{2+}$ reacts with terpy in a fast step to form $[(DMSO)_4Mn(terpy)]^{2+}$ (bidentate terpy), which reacts rapidly with excess $[Mn(DMSO)_6]^{2+}$ to give a binuclear species $[(DMSO)_4Mn(terpy)Mn(DMSO)_5]^{4+}$ (bridging-terdentate terpy). The rate-determining step in the reaction is formation of the final chelate ring to give $[Mn(DMSO)_3(terpy)]^{2+}$ (*83*, *84*). The complexes [Mn(terpy)X_2] dissociate rapidly in aqueous solution to give the $[Mn(terpy)_2]^{2+}$ cation (*243*). Studies show that the activation parameters for the reaction of manganese(II) with terpy in aqueous solution indicate an associative mechanism, in common with a number of other reactions of early transition metal compounds (*322*).

A number of workers have investigated the electrochemical behavior of the $[Mn(terpy)_2]^{2+}$ cation (*6*, *61*, *256*, *330*, *377*). In acetonitrile solution, there is a well-defined oxidation to the manganese(III) state at +1.28 V relative to the standard calomel electrode; this species is stable, in contrast to the tris(bipy) and tris(phen) analogues, which are converted to binuclear dimanganese(III,IV) species (*256, 330, 377*). The complex also shows at least five reduction waves (*6, 61, 256, 377*). The final reductions are probably due to free terpy, liberated in dissociative processes.

The complex $[Mn(CO)_3(terpy)Br]$ has been isolated, and is thought to contain a bidentate terpy ligand, on the basis of the similarity of its infrared spectrum to that of $[Mn(CO)_3(bipy)Br]$ (*205*). The reaction of $[Re(CO)_5(NO_3)]$ with terpy leads to the formation of $[Re(CO)_3(terpy)(NO_3)]$; this complex is a nonelectrolyte in nitromethane, and is also thought to contain a bidentate terpy ligand (*4*).

4. *Iron, Ruthenium, and Osmium*

2,2′:6′,2″-Terpyridine and its derivatives have been widely proposed as analytical reagents for the detection of iron in biological and other materials (*146, 164, 199, 218, 293, 331, 333, 358, 400–404, 416, 422, 450, 451, 485, 496–498*). These applications have been reviewed elsewhere, and will not be considered further (*69, 285, 291, 314, 401*).

With the exception of salts of the $[Fe(terpy)_2]^{3+}$ cation (*vide infra*), iron(III) complexes of terpy are remarkably sparse. The complexes $[Fe(terpy)Cl_3]$ and $[(terpy)FeOFe(terpy)][NO_3]_4 \cdot H_2O$ are prepared by addition of chloride or nitrate ions to solutions containing $[Fe(terpy)_2]^{3+}$ (*383, 384*). Mössbauer, magnetic, and other spectroscopic properties of the oxy-bridged complexes are consistent with a sextet ($S = \frac{5}{2}$) ground state.

The complexes of stoichiometry $[Fe(terpy)X_2]$ (X = Br, I, or NCS) are probably five-coordinate trigonal-bipyramidal species (*385*), whereas "$[Fe(terpy)Cl_2]$," which was originally thought to possess a similar structure (*75, 76, 243, 271, 388, 389*), has been shown to be $[Fe(terpy)_2][FeCl_4]$ (*385*).

The purple complex cation $[Fe(terpy)_2]^{2+}$ and its blue oxidation product $[Fe(terpy)_2]^{3+}$ have been known since the first description of terpy by Morgan and Burstall (*93, 176, 282, 286, 323, 326, 418*). The crystal structural analysis of $[Fe(terpy)_2][ClO_4]_2 \cdot H_2O$ reveals the cation to possess the expected distorted octahedral geometry (*22*). The lattice water and the perchlorate anions are oriented toward the interligand pockets, reminiscent of the structure of $[Cr(terpy)_2][ClO_4]_3 \cdot H_2O$. The stability constants for the iron(II) complexes are high ($\lg\beta_2 = 18$–21) (*70, 85, 306*). The stability constants and rates of formation and dissociation of the complexes are both pH and water dependent, an observation which has been interpreted in terms of covalent hydration of the ligand or of more conventional effects involving protonation of dissociated pyridines (*85–87, 89, 190, 200, 243, 245, 457*). There have been a number of studies involving the use of $[Fe(terpy)_2]^{3+}$ as an oxidizing agent. There is evidence that the oxidation of $[Fe(H_2O)_6]^{2+}$ and organotin compounds by $[Fe(terpy)_2]^{3+}$ follows a non-Marcus pathway in addition to the expected outer-sphere electron transfer (*152, 360*). Peroxodisulfate, peroxodiphosphate, or peroxide oxidation of $[Fe(terpy)_2]^{2+}$ may proceed by parallel Marcus and non-Marcus pathways; the latter *may* involve the oxidant approaching an interligand pocket (*35, 88, 106*). As with the ruthenium and osmium analogues, the luminescent properties of the bis complexes have suggested applications as potential photocatalysts (*115, 116, 153, 198, 352, 363*). A novel application of these complexes is seen in the extraction of long-chain alkyl surfactants by $[Fe(terpy)_2]^{2+}$ and derivatives (*440, 441*).

The $[Fe(terpy)_2]^{2+}$ cation is low-spin, as demonstrated by Mössbauer, electronic, ^1H NMR, and resonance Raman spectroscopy and magnetic measurements (*20, 184, 187, 228, 266*). Similarly, spectroscopic studies of the iron(III) cation have indicated a low-spin (^2B) ground term (*382*). There have been numerous electrochemical studies of the bis complexes (*177, 200, 256, 298, 332, 344, 373, 378, 379, 397, 398*). Ligand-centered reductions to formal oxidation states of iron(I), iron(0), and iron(−1) and oxidations to iron(III) are observed. The complex $[Fe(terpy)L][ClO_4]_2$ [L = tris(2′-pyridyl)1,3,5-triazine (Fig. 15)] has been prepared (*399, 442*).

The iron(0) complex $[Fe(terpy)(CO)_2]$ is readily prepared by the reaction of terpy with $[Fe(cot)(CO)_3]$ (cot, cyclooctatetraene) (*41, 46*); in contrast, $[Fe(terpy)_2]$ may be obtained as an air-sensitive, paramagnetic solid from the reduction of $[Fe(terpy)_2]I_2$ with lithium benzophenone ketyl (*240*).

Until recently there has been surprisingly little interest in high oxidation state complexes of terpy. Meyer and co-workers have demonstrated that the ruthenium(IV) complex $[Ru(terpy)(bipy)O]^{2+}$ is an effective active catalyst for the electrocatalytic oxidation of alcohols, aromatic hydrocarbons, or olefins (*335, 443, 445, 446*). The redox chemistry of the $[M(terpy)(bipy)O]^{2+}$ (M = Ru or Os) systems has been studied in some detail, and related to the electrocatalytic activity (*437, 445, 446*). The complexes are prepared by oxidation of $[M(terpy)(bipy)(OH_2)]^{2+}$. The related osmium(VI) complex $[Os(terpy)(O)_2(OH)]^+$ exhibits a three-electron reduction to $[Os(terpy)(OH_2)_3]^{3+}$ (*365, 366*). The complex $[Ru(terpy)(bipy)(H_2NCHMe_2)]^{2+}$ undergoes two sequential two-electron

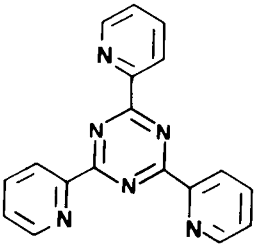

FIG. 15. Tris(2′-pyridyl)-1,3,5-triazine.
]

oxidations to produce $[Ru(terpy)(bipy)(HN{=}CMe_2)]^{2+}$ and $[Ru(terpy)(bipy)(NCMe_2)]^{3+}$; this corresponds to the net oxidation of coordinated isopropylamine (*3*). In contrast, $[Ru(terpy)(bipy)(NH_3)]^{2+}$ undergoes a clean *chemical* oxidation to the corresponding Ru(III) compound (*64, 345, 387, 495*), but *electrochemical* oxidation results in the oxidation of coordinated ammonia to nitrate via coordinated imine, hydroxylamine, nitrosyl, and nitrite (*444*). The reverse reaction, the net six-electron reduction of $[Ru(terpy)(bipy)(NO)]^{3+}$ to $[Ru(terpy)(bipy)(NH_3)]^{2+}$ has also been effected electrochemically (*339*). The nitrite complex $[Os(terpy)(bipy)(NO_2)]^{2+}$ disproportionates to yield $[Os(terpy)(bipy)(NO_2)]^{+}$, $[Os(terpy)(bipy)(NO)]^{3+}$, and $[Os(terpy)(bipy)(ONO_2)]^{2+}$ (*365*). Electrochemical studies of the behavior of $[Ru(terpy)(bipy)(OH_2)]^{3+}$ at Nafion-coated electrodes have been reported (*312*). Reductive cleavage of diphenylacetylene occurs upon heating aqueous solutions with $[Ru(terpy)(PPh_3)(H_2O)_2]^{2+}$ to yield $[Ru(terpy)(PPh_3)(CO)(CH_2Ph)]^{+}$ and toluene (*428*).

The complex $[Ru(terpy)Cl_3]$ is obtained as a red solid from the reaction of terpy with ethanolic "$RuCl_3{\cdot}3H_2O$" (*429*); in dimethylformamide (DMF), carbonyl abstraction occurs, and $[Ru(terpy)Cl_2(CO)]$ is obtained (*117*). It is, perhaps, surprising that $[Os(terpy)Cl_3]$ is reported as the product of the reaction of terpy with $K_2[OsCl_6]$ in DMF (*81*). The complexes $[Ru(terpy)(NO)Cl_2]_2[RuCl_5(NO)]$ and $[Ru(terpy)(NO)Cl_2]Cl{\cdot}3.5H_2O$ result from the reaction of terpy with $K_2[RuCl_5(NO)]$ (*325, 327–329*).

Intense room temperature charge-transfer emission was detected in terpy complexes for the first time in the complexes $[Os(terpy)LL']^{n+}$ ($L = Ph_2PCH{=}CHPPh_2$, $L' = Cl$, $n = 1$; $L' =$ py, MeCN, or CO, $n = 2$; $L = Ph_2PCH_2PPh_2$, $L' = Cl$, $n = 1$) (*7*). Phosphines react with $[Ru(terpy)Cl_3]$ in $CHCl_3$ in the presence of Et_3N to give *trans*-$[Ru(terpy)Cl_2L]$, which undergoes a thermal rearrangement to the *cis* complex (also available by the reaction of terpy with $[RuL_3Cl_2]$) (*429*). The reaction of $[Ru(bipy)_2(CO)_2]Cl_2$ with terpy in the presence of amine oxide results in the formation of the $[Ru(terpy)(bipy)Cl]^{+}$ cation (*56*). Substitution reactions of $[Ru(terpy)(bipy)(H_2O)]^{2+}$ with a range of nucleophiles have been reported (*159*).

Both *cis*- and *trans*-$[Ru(terpy)(CO)Cl_2]$ have been structurally characterized (*162*); the *cis* complex is obtained by reaction of $[Ru(terpy)(CO)_2Cl_2]$ with Me_3NO, and the *trans* by reaction of terpy with "$RuCl_3{\cdot}3H_2O$" in DMF (*117, 162, 429*). The two (red and yellow) forms of $[Ru(CO)_2Br_2(terpy)]$ have also been structurally characterized (Fig. 16); each contains a *bidentate* terpy ligand. The color differences arise from differences in intermolecular ligand contacts (*162*).

The complexes $[M(terpy)(bipy)L]^{n+}$ (M = Ru or Os; $L = NH_3$, NO, NO_2, H_2O, H_2NCHMe_2, phenothiazine, Cl, Br, I, *N*-methylphenothiazine,

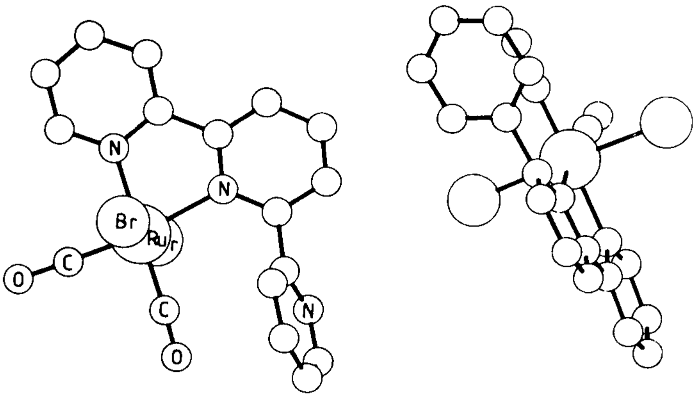

FIG. 16. The crystal and molecular structures of the two crystal forms of $[Ru(terpy)(CO)_2Br_2]$ (*162*).

thianthrene, OH, py, thiourea, N_3, SCN, 4-vinylpyridine, or substituted pyridines) are readily prepared by the reaction of [M(terpy)(bipy)Cl] with L in a variety of solvents and conditions (*3*, *64*, *81*, *82*, *95*, *160*, *179*, *216*, *261*, *312*, *335*, *345*, *365*, *366*, *387*, *395*, *428*, *437*, *444–446*, *495*). Numerous studies of the photophysical, photochemical, electrochemical, and kinetic properties of these complexes have been reported. A number of complexes of the type $[Ru(terpy)(bipy)L]^{2+}$ (L = sulfur, selenium, or tellurium donor) have been prepared; the peroxide oxidation of $[Ru(terpy)(bipy)(SMe_2)]^{2+}$ gives $[Ru(terpy)(bipy)(S(O)Me_2)]^{2+}$ by nucleophilic attack of the coordinated sulfur upon the oxygen—oxygen bond (*394*).

Red $[Ru(terpy)_2]Cl_2$ and green $[Os(terpy)_2]Cl_2$ were first prepared by the reaction of terpy with mixtures of metal chloride and metal at elevated temperatures (*328*). More convenient procedures involve the reaction of terpy with $K_2[RuCl_5(H_2O)]$ in the presence of H_2PO_2 (*118*, *292*), the reaction of "$RuCl_3 \cdot 3H_2O$" with excess terpy in DMF (*63*) or ethanol (*418*), or the reaction of terpy with "ruthenium blue solutions" (*424*). Numerous electrochemical studies of these systems have been reported (*24*, *63*, *107*, *118*, *177*, *319*, *320*, *332*, *398*, *447*). The ruthenium(II) complex exhibits a reversible oxidation and four reduction waves; ESR studies indicate that the first three reductions are ligand centered, whereas the last is associated with an ECE process (*332*). The photophysical properties have also attracted some interest; the ruthenium(II) complex is very weakly luminescent in liquid aqueous or ethanolic solution, although flash photolysis in the presence of a quencher indicates electron transfer from an excited state followed by a back reaction. The lifetime of the excited state is short (1.2 nsec $< \tau_0 <$ 5.0 nsec) (*63*, *153*, *197*, *292*, *318*, *320*, *494*). A negative enthalpy of activation for the quenching of $[Ru(terpy)_2]^{2+*}$ by $[Fe(H_2O)_6]^{3+}$ indicates a non-Marcus electron-transfer process. At lower temperatures in frozen glasses, efficient photoluminescence occurs, with charge-transfer emission from at least three strongly spin-orbit coupled excited states (*5, 165, 166, 197, 280, 424*). The absorption spectra of $[Ru(terpy)_2]^{n+}$ are pH dependent in the range pH 0–6, and the ruthenium(II) complex exhibits an apparent pK_a of 2.9; these observations are clearly related to the anomalous pH dependence of ligand dissociation from $[Fe(terpy)_2]^{n+}$ (*118, 275*). Ruthenium complexes of substituted terpy ligands and $[Os(terpy)_2]^{2+}$ exhibit similar photophysical properties (*172, 173, 231, 359*). The FD mass spectrum of $[Os(terpy)_2][PF_6]_2$ exhibits weak peaks due to the monocation (*105*). The ^1H NMR spectra of $[M(terpy)_2]^{2+}$ (M = Ru or Os) salts have been reported; DMSO-d_6 solutions of the ruthenium complex undergo a specific base-catalyzed deuterium-exchange reaction at the 3, 3′, 5′, and 3″ positions (*138, 300*). Salts of $[Ru(terpy)_2]^{2+}$ exhibit potent bacteriostatic properties, and inhibit the action of acetylcholinesterase; effects similar to those exhibited by *d*-tubocurarine are observed (*180, 281, 282*). The bifunctional osmium complexes $[(bipy)ClOsLOs(bipy)Cl]^{2+}$ and $[(bipy)(py)OsLOs(bipy)(py)]^{4+}$ (L = Fig. 17) also exhibit potent curariform activity (*439*).

The Strasbourg group extended their studies to highly hindered derivatives of terpy. The ligand 6,6″-Ph_2terpy is very hindered, but forms a bis complex with ruthenium(II); the NMR and photophysical properties of this complex have been reported (*168, 279*). The steric requirements of the ligand are expressed in dissociative photoanation reactions.

5. *Cobalt, Rhodium, and Iridium*

The majority of interest in cobalt(III) complexes of terpy has centered on the $[Co(terpy)_2]^{3+}$ cation, although a few 1:1 complexes have been reported. A crystal structural analysis of the complex $[Co(terpy)(CO_3)(OH)]\cdot 4H_2O$, obtained by the reaction of $[Co(terpy)_2]^{2+}$ with aqueous carbonate, has revealed the expected distorted octahedral geometry about the metal ion, with a bidentate chelating carbonate and *meridional* terpy ligands (*287*). The

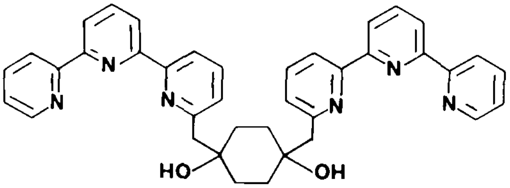

FIG. 17. A bridging bis-2,2′:6′,2″-terpyridine ligand (*439*).

complexes $[Co(terpy)L(H_2O)]^{2+}$ [L = phen, bipy, or bis(2-pyridyl)ketone] react readily and reversibly with dioxygen to form adducts $[(terpy)LCo(O_2)CoL(terpy)]^{4+}$, which may be oxidized to the superoxo species $[(terpy)LCo(O_2)CoL(terpy)]^{5+}$ (*223, 250, 251, 321, 356*). If the mononuclear complex is stabilized in an inert zeolite Y matrix, the superoxide adduct $[Co(bipy)(terpy)O_2]^{2+}$ may be characterized (*321*).

Complexes of the lower members of the group with terpy have attracted little attention. A number of salts of the $[Rh(terpy)_2]^{3+}$ cation have been characterized, as have the complexes $[Rh(terpy)X_3]$ (X = Cl, Br, or I) (*55, 224, 328*). In each case, the compounds are thought to possess a distorted octahedral geometry. The luminescent 1:1 chelate formed between iridium(III) and terpy has been studied, and may be of some application in the determination of iridium (*197, 198, 328*).

The complex cation $[Co(terpy)_2]^{3+}$ is readily prepared by the oxidation of the cobalt(II) complex (*304, 328*), and has been widely used as an oxidizing agent. Reduction by superoxide (*65, 313*), dithionite (*65, 315*), titanium(III) (*21*), ascorbate (*487*), metallophthallocyanines (*353, 355*), galactose oxidase (*267*), methylene blue (*355*), or deoxyhemerythrin (*220*) has been investigated, and the results are generally in accord with a Marcus outer-sphere mechanism. Pulse radiolysis of $[Co(terpy)_2]^{3+}$ produces a transient ligand-centered radical, which collapses to "normal" $[Co(terpy)_2]^{2+}$ (*36*). The structure of $[Co(terpy)_2]Cl_3 \cdot 11H_2O$ has only recently been determined; it possesses the expected distorted octahedral structure (*194–196*).

Salts of $[Co(terpy)_2]^{2+}$ are obtained by the reaction of cobalt(II) salts with excess terpy. Structural analyses of $[Co(terpy)_2]X_2 \cdot nH_2O$ ($X = ClO_4$, $n = 1.3$; $X = I$, $n = 2$; $X = ClO_4$, $n = 0.5$; $X = Br$, $n = 3$; $X = SCN$, $n = 2$) have been reported; this apparent overkill is explained by the spin-crossover properties of the salts (*195, 196, 235, 307, 380*). It is clear that the spin-state crossover between high- and low-spin forms of these cobalt(II) complexes is dictated by lattice forces. The perchlorate is close to the high-spin limit, but the temperature dependence of the moment is critically dependent upon the degree of hydration (*196, 235*). The complex $[Co(terpy)_2][SCN]_2 \cdot 2H_2O$ undergoes an X-ray-induced phase transition, apparently linked with a crossover phenomenon (*380*). The spin-crossover properties of these salts have been investigated by magnetic, ESR, and Mössbauer methods (*169, 221, 269, 284, 302, 303, 402, 425*). The cobalt(II) complexes are moderately stable, but are acid-labile (*190, 243, 245, 278, 372*). Oxidation to the cobalt(III) complexes is facile and has been studied intensively (*12, 155, 189, 208, 276, 311, 374, 423, 493*). The redox properties of the $[Co(terpy)_2]^{2+/3+}$ system have been scrutinized by the solar energy fraternity (*116*). Electrochemical studies indicate that reduction to formal oxidation states of cobalt(I) and cobalt(0) is possible (*6, 256, 301, 373, 377, 378, 398*). A colorimetric method utilizing terpy has been proposed for the determination of cobalt (*334*).

Numerous 1:1 complexes [Co(terpy)X_2] (X = SCN, SeCN, Cl, Br, I, CN, NO_2, or F) have been described (*157, 212, 225, 268, 270, 272, 277*). It has long been suspected that these complexes are five-coordinate, and structural analyses of [Co(terpy)$(NCO)_2$] (*277*) and [Co(terpy)Cl_2] (*21*) have confirmed this formulation. The isocyanato complex is of interest in exhibiting a weak hydrogen-bonding interaction between an isocyanate oxygen atom and H-3,3′ of the terpy (*277*). The displacement of terpy from the complexes [Co(terpy)L_3]$^{2+}$ (L = H_2O or hmpa) has been studied; in the acid-catalyzed dissociation of [Co(terpy)$(H_2O)_3$]$^{2+}$ there is some evidence for a monodentate intermediate [Co(terpyH_2)$(H_2O)_n$]$^{4+}$ (*1, 2, 249*).

The cobalt(I) complex [Co(terpy)(BH_4)] has been shown to possess a five-coordinate structure in which the borohydride acts as a chelating bidentate ligand (Fig. 18) (*148*). The bridging hydride atoms were located in a neutron-diffraction study of the compound. Although the solid is weakly paramagnetic, solutions are essentially diamagnetic, and ^1H NMR studies indicate a high barrier to the interconversion of the bridging and terminal hydridic sites (*488*).

The complex [Co$(terpy)_2$][Co$(CO)_4$] has also been reported (*45*).

6. *Nickel, Palladium, and Platinum*

Although there have been numerous reports of nickel(II), palladium(II), and platinum(II) complexes of 2,2′:6′,2″-terpyridine, complexes in higher oxidation states are all but unknown. Morgan and Burstall described the

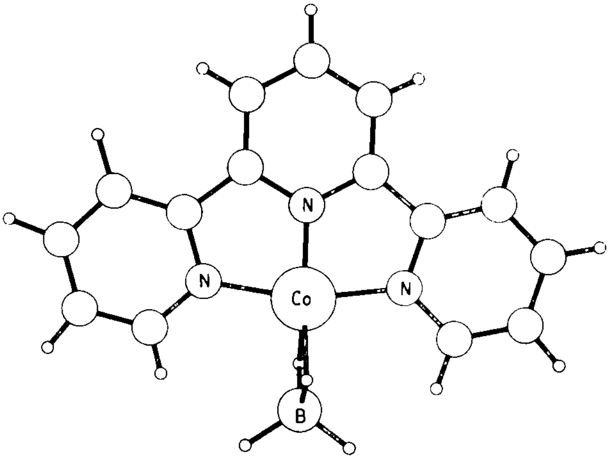

FIG. 18. The crystal and molecular structure of [Co(terpy)(BH_4)] (*148*).

platinum(IV) complex [Pt(terpy)Cl_3]Cl·3H_2O as the product from the chlorine oxidation of [Pt(terpy)Cl]Cl (*324*); although the compound has not been investigated since, there seems to be little doubt that it is an octahedral platinum(IV) species with a terdentate 2,2′:6′,2″-terpyridine ligand. The dimethylplatinum(IV) complex [PtMe_2(terpy)(PMe_2Ph)$_2$][PF_6]$_2$ has also been described; the structure is not known, but a bidentate 2,2′:6′,2″-terpyridine seems to be more likely than a seven-coordinate platinum(IV) center (*119*). Electrochemical oxidation of [Ni(terpy)$_2$]$^{2+}$ leads to the formation of [Ni(terpy)$_2$]$^{3+}$, which may be isolated as its tris(perchlorate) salt (*373*).

There are a number of distinct types of complexes with the stoichiometry M(terpy)X_2. Nickel(II) complexes with a 1:1 stoichiometry may be prepared by addition of terpy to solutions of nickel(II) halides; the hydrated forms appear to be typical octahedral nickel(II) compounds (*294*). Magnetic measurements and spectroscopic studies have indicated that these 1:1 complexes obtained from solution, usually hydrated, are best formulated as the cation–anion species [Ni(terpy)$_2$][NiX_4] (*222*). These complexes may be prepared by addition of terpy to acetone solutions containing the appropriate tetrahalonickel(II) (*222*). The complexes Ni(terpy)X_2 (X = CN, N_3, or CNS) have also been reported. The cyano and azido compounds are best described as [Ni(terpy)$_2$][NiX_4], on the basis of their spectroscopic and magnetic properties (*222*). In contrast, the complex Ni(terpy)(NCS)$_2$ is polymeric, with bridging thiocyanates and a ferromagnetic interaction between the nickel atoms (*222*). The anhydrous complexes Ni(terpy)X_2 (X = Cl, Br, or I) are prepared by pyrolysis of the [Ni(terpy)$_2$]X_2 species, and are of rather more interest (*243, 268–271, 294*). The spectral and magnetic properties of these complexes are not compatible with octahedral or square-planar structures, and give a best fit with five-coordinate trigonal-bipyramidal or square-based pyramidal schemes (*294*). This formulation is supported from a study of the X-ray powder photographs obtained from the complexes: [Ni(terpy)Cl_2] is isomorphous with [Zn(terpy)Cl_2] (form II); [Ni(terpy)Br_2] and [Ni(terpy)I_2] are isomorphous with the appropriate zinc halide (forms II and I, respectively). The solution chemistry of these nickel(II) complexes is deferred until later in this section.

The reactions of [MCl_4]$^{2-}$ (M = Pd or Pt) with terpy are complex, the major products being [M(terpy)Cl]$_2$[MCl_4] and [M(terpy)Cl]Cl (*324, 328*). These complexes are diamagnetic, square-planar compounds, in contrast to the five-coordinate anhydrous nickel(II) complexes. The crystal structures of [Pd(terpy)Cl]$_2$[PdCl_4] (*259*) and [Pd(terpy)Cl]Cl·2H_2O (*260*) have been reported. The terpy ligand does not have an entirely suitable bite for square-planar coordination, and some distortion of the interring bonds and of the square plane results. In each case the bond to the central ring is shorter than

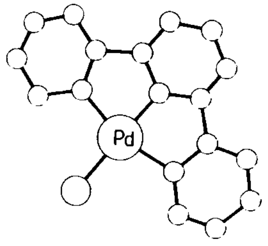

FIG. 19. The crystal and molecular structure of [Pd(terpy)Cl]Cl (*260*).

those to the terminal pyridines (Fig. 19), as observed in the majority of terpy complexes. It is of interest that, in each case, there is a stacking interaction, in which the planar cations are at an average separation of 3.4 Å. This observation is of relevance to the properties of the related $[Pt(terpy)X]^+$ complexes, which have not been structurally characterized. Morgan and Burstall described a number of other related complexes (*324*).

Burmeister and colleagues have described the related pseudohalogen derivatives $M(terpy)X_2$ (X = SCN or SeCN) (*90–92*). The platinum compound exhibits the two thiocyanate stretching frequencies expected for a square-planar complex, and is formulated [Pt(terpy)(NCS)][NCS]. However, the palladium complexes are less easily formulated, exhibiting absorptions due to coordinated ECN (E = S or Se) only. These observations were interpreted in terms of a square-planar structure, with a bidentate terpy ligand; in view of the known ability for palladium and platinum diimine complexes to form five-coordinate species, this formulation must also be considered. In the absence of definitive structural evidence, the formulation as five-coordinate species must be regarded as speculative.

The substitution reactions of square-planar complexes of the type $[M(terpy)X]^+$:

$$[\mathrm{M(terpy)X}]^+ + \mathrm{Y} \rightleftharpoons [\mathrm{M(terpy)Y}]^+ + \mathrm{X}$$

obey the expected rate law:

$$\text{rate} = k_{\text{obs}}[\mathrm{M(terpy)X}^+]$$

where

$$k_{\text{obs}} = k_1 + k_2[\mathrm{Y}]$$

However, the rates of substitution by pyridine are considerably faster than might be expected on comparison with other terdentate complexes. Specifically, rate enhancements of three to four orders of magnitude are observed upon comparison with complexes of 1,5-diamino-3-azapentane (diethylenetriamine, dien) (*34*, *156*, *337*, *338*). There is some disagreement over the dependence of the k_1 term on the nature of the incoming nucleophile, although all workers agree on the rate enhancement. Explanations of this rate enhancement have invoked attack by the incoming nucleophile at the coordinated 2,2′:6′,2″-terpyridine ligand, or an extensive interaction between π-bonding nucleophiles and the planar 2,2′:6′,2″-terpyridine. A π-bonding or stacking interaction, as postulated in reactions of $[Ni(terpy)L_3]^{2+}$ complexes, would seem to be most likely; in particular, there is now *no* evidence for attack by nucleophiles at the ligand in platinum(II) complexes of 2,2′-bipyridine, 1,10-phenanthroline, or 2,2′:6′,2″-terpyridine.

Removal of chloride from $[Pt(terpy)Cl]^+$ may be achieved with silver(I) compounds, although the aqua or hydroxo compounds produced are relatively unstable (*337*, *338*). Mureinik and Bidani reported the formation of $[Pt(bipy)(SCN)_2]$ in the reaction of [Pt(terpy)Cl]Cl with silver(I) followed by excess thiocyanate (*337*); this remarkable observation might indicate attack by hydroxide (free or coordinated) on the coordinated terpy, although the reaction certainly deserves reinvestigation. Much of the recent interest in complexes of platinum(II) and palladium(II) with terpy has stemmed from the discovery that they show specific interactions with nucleic acids. Planar aromatic compounds may show "stacking" interactions, in which configurations with the rings parallel, and interactions between the π systems, represent minima on the potential energy surface. Square-planar complexes with aromatic ligands may also show such interactions, which are almost certainly of more general occurrence than hitherto recognized. Such stacking interactions are of importance in the solid-state structures adopted by complexes, and are invoked to explain the observed crystal structures for $[Pd(terpy)Cl]_2[PdCl_4]$ and $[Pd(terpy)Cl]Cl \cdot 2H_2O$. It is also apparent that stacking interactions are important solution phenomena, and have been invoked to explain the reaction rates of terpy and related complexes. Nucleic acids are characterized by sequences of planar heterocyclic bases arranged in a mutually parallel fashion, and a number of planar aromatic drugs (e.g., acridines, phenanthridines) have been shown to insert between them in a stacking fashion. This process is known as intercalation, and may provide a mechanism for the action of such compounds. Planar transition metal complexes are also expected to show intercalation behavior with nucleic acids.

Initial studies on $[Pt(terpy)Cl]^+$ revealed that the complex showed specific interactions with calf thymus DNA, as shown by inhibition of the fluorescence of the ethidium bromide–DNA intercalate (*247*). The complex contains a labile halide, however, and shows covalent interactions with the bases in addition to the expected intercalation. These covalent interactions are probably responsible for the observed chain scission of PM-2 DNA (*247*). The palladium complex shows the same behavior (*247*). These covalent interactions may be utilized in introducing heavy metal atoms onto nucleic acids as an aid to imaging in electron microscopy. Thus, $[Pt(terpy)X]^+$ ($X = Cl$ or H_2O) binds covalently to the sulfur atoms of adenosine monophosphorothioate and uridine monophosphorothioate, and those of the polynucleotides poly($_{\overline{s}}$A–U) (*426*). Binding of modified polynucleotides to sulfur atoms is also of importance with yeast tRNA^{Phe} modified at the C_s–C_s–A terminus, which binds 2 mol$[Pt(terpy)Cl]Cl$ (*433*). The 2:2 intercalation product of $[Pt(terpy)Cl]Cl$ with adenosine 5′-monophosphate has been structurally characterized (*490*). The intercalate exhibits an unusual head-to-head stacking interaction. It is of interest that $[Pt(terpy)Cl]Cl$ stacks with itself in solution, with a dimerization constant of $4 \pm 2 \times 10^3$ (*264*). This may explain the observed concentration dependence of the ^1H NMR spectra of D_2O solutions (*264*).

In order to avoid the ambiguities resulting from competing intercalation and covalent interactions, a number of $[Pt(terpy)X]^{n+}$ complexes with nonlabile ligands have been investigated. The most widely studied complex ion is $[Pt(terpy)(SCH_2CH_2OH)]^+$, which has been shown to intercalate with calf thymus DNA (*265*). The platinum atoms are separated by 10.2 Å in the calf thymus DNA intercalate, which is thought to undergo unwinding of $22 \pm 6°$ per intercalator (*57*). In the absence of covalent interactions, $[Pt(terpy)(SCH_2CH_2OH]^+$ does not produce chain scission with PM-2 DNA (*242*, *247*). Similar interactions occur with salmon sperm DNA (*203*), and are possibly responsible for the observed inhibition of genetic recombination in pneumococci (*407*). Intercalation also occurs with polynucleotides, and the duplex structure of polyA·polyU is stabilized by the platinum intercalate (*32*). Although useful ^{31}P NMR spectra are not obtained from normal nucleic acid samples, such spectra may be obtained from the short ($\sim$200 base pairs) double-helical sequences obtained from prolonged sonication (*489*). The ^{31}P NMR spectra of $[Pt(terpy)(SCH_2CH_2OH)]^+$ intercalates of such DNA samples are compatible with an unwinding angle of $18 \pm 2°$ (*489*).

Crystal structures of $[Pt(terpy)(SCH_2CH_2OH)][NO_3]$ (*264*) and its intercalates with deoxymethoxy-pTpA and deoxy-CpG (*463*, *464*) have been described. The parent compound shows two types of stacking interactions in the solid, with the planes separated by 3.4 Å (*264*). The intercalate with deoxymethoxy-pTpA contains the novel trinuclear cation $[Pt(H_2NCH_2CH_2SPt(terpy))_2]^{4+}$, which has been prepared independently by Lippard and co-workers (*167*). A structural investigation of the tetrafluoroborate salt (Fig. 20) revealed the two Pt(terpy) units to be parallel and stacked. Since the sulfur atoms are sp^3 hybridized, the molecules are chiral.

A number of other 1:1 complexes with 2,2′:6′,2″-terpyridine have also been reported. Complexes with monothiodiketonates, $[NiL_2(terpy)]$, have been

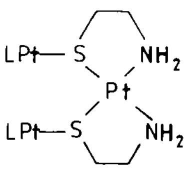

FIG. 20. The molecular structure of the cation $[Pt(H_2NCH_2CH_2SPt(terpy)_2]^{4+}$ (*167*).

described for a range of substituted ligands (*111*, *241*, *296*). The electronic spectra of these complexes indicate that they adopt an octahedral geometry, and the infrared spectra are compatible with a formulation containing a tridentate 2,2′:6′,2″-terpyridine ligand, and one monodentate S-bonded and one bidentate O,S-bonded thiodiketone. Related trinuclear species have also been described. Other ternary complexes incorporating 2,2′:6′,2″-terpyridine include $[NiL_2(terpy)]$ $[HL = (RO)_2P(S)SH]$, in which only one sulfur is coordinated to the (octahedral) metal (*297*), and [NiL(terpy)] (H_2L = 2,6-pyridinedicarboxylic acid) (*246*).

The solution properties of the 1:1 complexes of nickel(II) with 2,2′:6′,2″-terpyridine are poorly characterized; this is particularly unfortunate, since the nickel(II)-2,2′:6′,2″-terpyridine system has been widely studied in investigations into the binding of 2,2′:6′,2″-terpyridine to metal ions. The rate of the reaction:

$$\mathrm{Ni(terpy)^{2+} + terpy} \rightleftharpoons \mathrm{[Ni(terpy)_2]^{2+}}$$

is apparently faster than a simple water loss (Eigen-Wilkins) mechanism would predict, and numerous studies in water and mixed solvent systems have been described (*101*, *103*, *112–114*, *125–128*, *236*, *243*, *245*, *317*, *375*, *386*, *434–436*). It is particularly relevant that the rate is affected by added halide ion. It is apparent that a number of 1:1 species may be formed in aqueous (and nonaqueous) solutions. Freshly prepared solutions of the five-coordinate complex $[Ni(terpy)Cl_2]$ in water possess absorption spectra different from those of aged samples and 1:1 mixtures containing 2,2′:6′,2″-terpyridine and nickel(II). Similar observations are obtained with DMSO solutions, in which equilibria of the type:

$$\mathrm{[Ni(terpy)Cl_2(DMSO)]} \rightleftharpoons \mathrm{[Ni(terpy)Cl(DMSO)_2]^{+}}$$

$$\mathrm{[Ni(terpy)Cl(DMSO)_2]^{+}} \rightleftharpoons \mathrm{[Ni(terpy)(DMSO)_3]^{2+}}$$

are postulated.

The crystal structure of $[Ni(terpy)_2][PF_6]_2$ has been described (*17*). Several authors have reported the spectroscopic and magnetic properties of $[Ni(terpy)_2]^{2+}$ species (*236*, *243*, *269*, *278*, *328*). The electrochemical reduction of these complexes has also been investigated (*6*, *373*). To date, only two

2,2′:6′,2″-terpyridine complexes of nickel(0) have been described: $[Ni(terpy)(PPh_3)_2]$ (*452*) and $[Ni(terpy)_2]$ (*39*). The latter complex is prepared by reaction of nickelocene with terpy, and may well be a ligand-radical complex of nickel(I) or nickel(II).

7. *Copper, Silver, and Gold*

Although Morgan and Burstall had difficulties in isolating 1:2 complexes of terpy with copper(II), salts of $[Cu(terpy)_2]^{2+}$ are readily prepared with excess terpy (*8*, *18*, *236*, *243*, *309*). Crystal structural analyses of $[Cu(terpy)_2]X_2$ ($X = NO_3$ or PF_6) have been reported (*8*, *18*, *309*); the cation is Jahn–Teller distorted. As a result of the initial D_{2d} local symmetry, the two terpy ligands become nonequivalent upon Jahn–Teller distortion. ESR studies indicate the presence of a static Jahn–Teller distortion (*8*, *62*, *236*).

The 1:1 complexes $[Cu(terpy)X_2]$ (X = F, Cl, Br, I, or NCS) have all been reported (*209*, *225*, *227*, *243*). These complexes possess a distorted trigonal-bipyramidal geometry, as indicated by ESR studies (*23*, *213*, *234*) and structural determinations of $[Cu(terpy)X_2]$ (X = Cl, Br, or I) (*147*, *225*, *234*, *393*, *396*). Gagné *et al.* reported the PES spectra of $[Cu(terpy)Cl_2]$ (*204*). One of the few coordination compounds of copper(II) fluoride is $[Cu(terpy)F_2]\cdot 2H_2O$, which is assumed to be five-coordinate (*209*). The Jahn–Teller distortion of these compounds has stimulated numerous structural studies, and has also resulted in a certain ambiguity in describing the structures as trigonal-bipyramidal, tetragonal-pyramidal, or square-pyramidal. Treatment of solutions of $[Cu(terpy)Cl_2]$, which is five-coordinate in the solid state, with hexafluorophosphate results in the formation of $[Cu(terpy)Cl][PF_6]$. Anomalies in the ESR and magnetic properties led to the formulation of the cation as a dimeric chloro-bridged species $[(terpy)CuCl_2Cu(terpy)]^{2+}$ (Fig. 21) (*392*). The related complexes $[Cu(terpy)CN][NO_3]\cdot H_2O$ and $[Cu(terpy)CN][ClO_4]$ also exhibited anomalous magnetic properties (*289*). A structural analysis of the nitrate revealed a distorted five-coordinate geometry about the metal, with the fifth contact provided by the nitrogen atom of the cyanide of an adjacent cation (*11*).

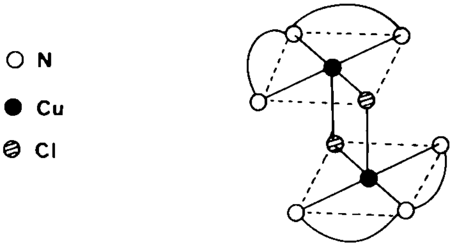

FIG. 21. The proposed structure of the cation $[(terpy)CuCl_2Cu(terpy)]^{2+}$ (*392*).

Similar magnetic anomalies are associated with another chain compound $[Cu(terpy)L][ClO_4]_2$ (L = pyrazine), incorporating bridging pyrazine groups; once again a five-coordinate structure is proposed (*150*). The five-coordinate square-pyramidal geometry is also observed in the structurally characterized complex $[Cu(terpy)(ONO)(H_2O)][NO_2]\cdot H_2O$ (*9*).

It seems likely that the complex cation $[Cu(terpy)(bipy)]^{2+}$ is also five-coordinate (*15*, *227*). Structural studies of $[Cu(terpy)(O_2CCH_2ECH_2CO_2)]\cdot nH_2O$ (E = NH, O, S, or Se) have been reported, and the two compounds exhibit interesting differences. The oxy diacetate complex consists of mononuclear octahedral metal centers, linked by water molecules (*73*); in contrast, the thio diacetate thioether sulfur is a weaker donor to copper(II) than an ether oxygen, and is noncoordinated. The metal is in a distorted trigonal-bipyramidal arrangement with bridging thio diacetate groups (Fig. 22) (*60*). Numerous mixed-ligand complexes with other polydentate species have been described (*13*, *14*, *58–60*, *72*, *73*, *102*, *215*, *246*, *288*, *343*, *492*).

The formation of copper(II) complexes with terpy has been investigated fairly intensively. The interaction is pH dependent, and numerous hydroxy, aqua, and polynuclear species are present in aqueous solution (*94*, *245*, *278*). In general, an Eigen–Wilkins mechanism appears to be operative, although the kinetics are complicated by ligand-protonation equilibria (*263*, *390*, *391*). In acidic solution, 1:1 complexes predominate (*361*). A number of substituted terpyridine ligands have been evaluated as potential colorimetric reagents for copper (*400*). The adsorption behavior of copper(II)–terpy complexes at silica surfaces has been studied (*499*). Such complexes are reasonably active as catalysts for the hydrolysis of fluorophosphate esters (*456*).

2,2′:6′,2″-Terpyridine is reported to form a 1:1 complex with copper(I) in aqueous solution (*362*), and [Cu(terpy)Cl] has been isolated (*336*). These complexes have been found to be surprisingly effective oxygen-transfer

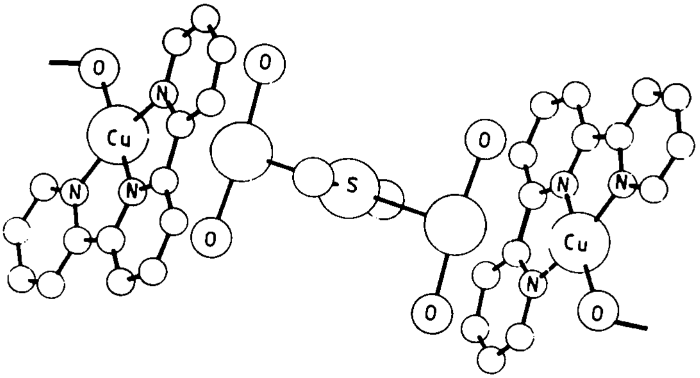

FIG. 22. The crystal and molecular structure of $[Cu(terpy)(O_2CCH_2SCH_2CO_2)]$ (*60*).

catalysts for the oxidation of thiosulfate to sulfate (*108*, *109*). The complex [Cu(terpy)Cl] only displays weak oxidase activity for the oxidation of ethanol to acetaldehyde (*336*). In aqueous acetonitrile, $[Cu(terpy)_2]^+$ undergoes a two-electron oxidation by dioxygen to yield $[Cu(terpy)_2]^{2+}$ and hydrogen peroxide (*154*). It was suggested that both terpy ligands are bidentate in $[Cu(terpy)_2]^+$.

Morgan and Burstall described the silver(I) complexes [Ag(terpy)X] ($X = NO_3$ or ClO_4), and the silver(II) species $Ag(terpy)X_2$ ($X = NO_3, ClO_4, \frac{1}{2}S_2O_6$, or $\frac{1}{2}S_2O_8$) of unknown structure (*328*). The complexes are unstable in aqueous solution and give the corresponding silver(I) complexes (*226*). More recently, $[Ag(terpy)_2][S_2O_8]$ has been prepared; PES spectra of this and other octahedral $[Ag(terpy)L]^{2+}$ species have been reported (*340–342*). Salts of $[Ag(terpy)_2]^{2+}$ are obtained by electrochemical oxidation of silver(I) in the presence of terpy (*453*, *501*).

The only gold complexes of terpy to have been reported are $[Au(terpy)Cl]Cl_2 \cdot 3H_2O$ and the mixed-valence compound $[Au(terpy)Cl]_2[AuCl_2]_3[AuCl_4]$, both of which have been structurally characterized (*244*). The complex $[Au(terpy)Cl]Cl_2 \cdot 3H_2O$ possesses the expected distorted square-planar cation, whereas the mixed-valence compound exhibits a chainlike structure with three spiral $[AuCl_2]$ units bridging the two [Au(terpy)Cl] centers, with tetrachloroaurate(III) chlorine atoms occupying the remaining axial sites of the now octahedral gold(III) sites (Fig. 23) (*244*).

8. *Zinc, Cadmium, and Mercury*

Zinc or cadmium halides react readily with terpy to form a series of compounds $[M(terpy)X_2]$. The complex $[Zn(terpy)Cl_2]$ has been most intensively investigated, and exists in two crystal modifications (*147*). Similar modifications are observed for the majority of $[M(terpy)X_2]$ complexes. It was initially proposed that the compounds were four-coordinate and of the type [M(terpy)Cl]Cl (*328*), although it later became apparent that this formulation was not entirely satisfactory. The complexes $[M(terpy)X_2]$ (M = Zn or Cd; X = Cl, Br, or I) behave as nonelectrolytes in nitrobenzene(*171*). A crystal structural analysis revealed $[Zn(terpy)Cl_2]$ (form II) to be a distorted trigonal-bipyramidal five-coordinate species (*147*). A later refinement of this structure has been reported; there is considerable variation in the Zn—N distances, with appreciable shortening of the bond to the central pyridine ring (*182*). The Zn—Cl distances are similar, and there is some distortion of the ligand, resulting in a nonplanar configuration. The crystal structure of form I has also been described; this is also a distorted trigonal-bipyramidal species (*454*). Gerloch suggested that the structure is better described in terms of a distorted square-based pyramid, with a basal

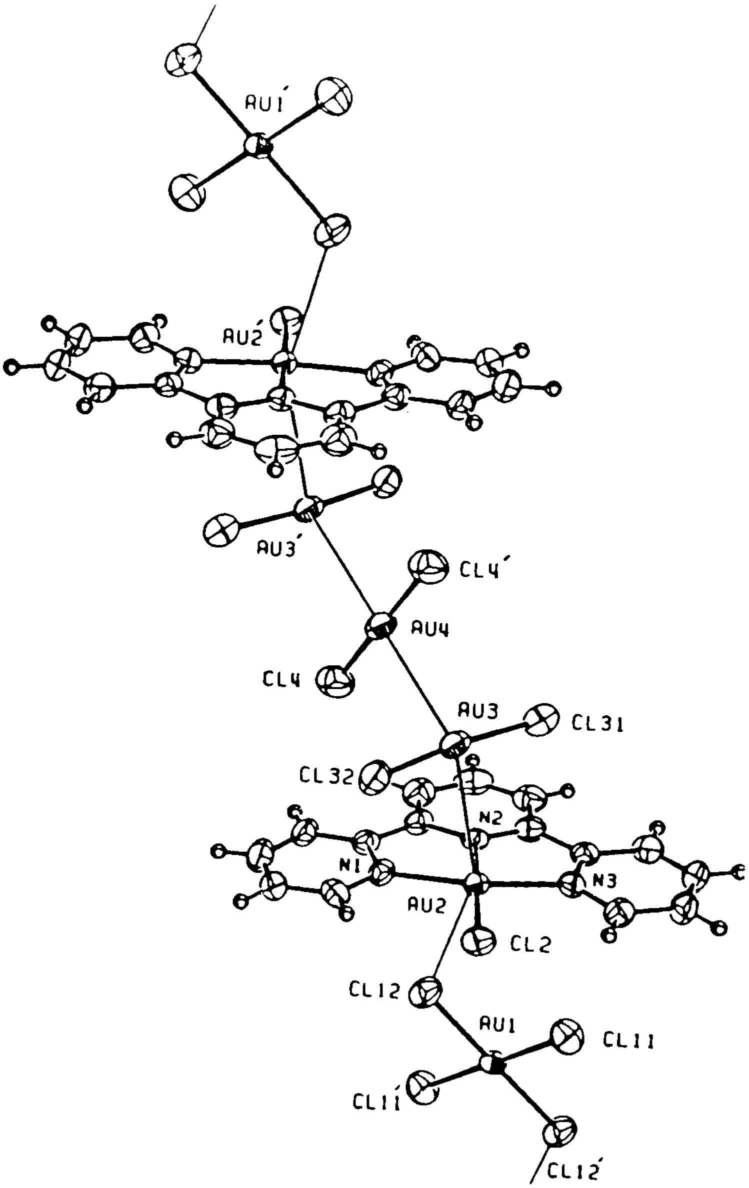

FIG. 23. The crystal and molecular structure of $[Au(terpy)Cl]_2[AuCl_2]_3[AuCl_4]$ (*244*).

N_3Cl plane (*207*). The other halids and the cadmium complexes are isomorphous with the appropriate forms, and undoubtedly possess related five-coordinate structures. A number of studies of the vibrational spectra of the $[M(terpy)X_2]$ species have been described, all of which support the formulation as isomorphous five-coordinate complexes (*124*, *171*, *225*, *371*). The copper(II) complexes $[Cu(terpy)Cl_2]$ are isostructural, and a number of studies of the paramagnetic species doped into a host matrix of $[Zn(terpy)Cl_2]$ have been reported (*23*, *213*). The zinc complex $[Zn(terpy)Cl_2]$ exhibits absorption maxima at 22,650 and 18,000 cm^{-1} (*23*, *348*). The mercury(II) halide adducts are not so well characterized, but may be prepared by the direct reaction or HgX_2 with terpy (*171*) or by transmetallation of $[Ph_2Sn(terpy)Cl_2]$ with $HgCl_2$ (*471*). They are thought to possess similar, five-coordinate structures. The structures of the 1:1 adducts of the nitrates $M(NO_3)_2\cdot$terpy are not known with any certainty (*171*, *328*). A ^{113}Cd NMR study of $Cd(NO_3)_2\cdot$terpy has been reported (*430*).

A related trigonal-bipyramidal structure is observed in the heterotrinuclear complexes $[(terpy)Cd(Mn(CO)_5)_2]$, which are readily prepared by the reaction of $[Cd(Mn(CO)_5)_2]$ with 2,2′:6′,2″-terpyridine (*122*, *123*, *248*). The five-coordinate trigonal-bipyramidal structure is encountered in $[Hg(terpy)(CF_3)_2]$, which has been structurally characterized (*274*).

A number of alkylmercury(II) and arylmercury(II) complexes of terpy have been described, and appear to have a pronounced tendency for the ligand to adopt a bidentate, rather than terdentate, mode. The reaction of [MeHgOH] with terpy has been studied by T-jump techniques; the complex shows a very high reaction rate with hydroxide, and it is proposed that a bidentate intermediate is involved (*206*). The complexes $[MeHg(terpy)][NO_3]$ and $[MeHg(4,4',4''\text{-}Et_3terpy)][NO_3]$ are also thought to possess bidentate terpy ligands in solution; specifically, the values of $^2J(Hg—H)$ are compatible only with a bidentate N_2 donor (*97*, *98*). In the solid state, the 4,4′,4″-Et_3terpy complex, and presumably that with terpy also, is terdentate; a crystal structural analysis has established unequivocally that the metal is in an approximately planar four-coordinate environment, with a weak interaction between the metal and the nitrate group (*97*, *98*). The structure of $[(C_6F_5)_2Hg(terpy)]$ is not known, but it is proposed that the ligand acts in a bidentate or bridging bidentate mode (*96*). It is of interest that the complex $[ZnL_2(terpy)]$ [HL = 4,4′,4″-trifluoro-3-oxo-1-(2-thienyl)butane-1-thione] is six-coordinate, with the 2,2′:6′,2″-terpyridine acting as a terdentate, and one of the other ligands adopting a monodentate S-bonded mode (*241*)

The complex $[(terpy)CdFe(CO)_4]$, prepared by the reaction of terpy with $[\{CdFe(CO)_4\}_4]$, is probably monomeric, although the structure is not known with any certainty (*188*).

Formation of the 1:1 complexes with zinc and cadmium has been studied in aqueous solution, and the complexes are more stable than the corresponding 1:1 adducts with bipy (*245*). Ternary mercury(II)-hydroxo-terpy complexes are active catalysts for hydrolysis of esters and amides (*477*).

The 1:2 complexes $[M(terpy)_2]^{2+}$ are known, and are presumably octahedral (*243*).

The reaction of terpy with zinc amalgam in 2-methyltetrahydrofuran results in the formation of the ligand radical complex $[Zn(terpy)_2]$, which has been characterized by ESR spectroscopy (*79*).

H. LANTHANIDES AND ACTINIDES

The lanthanides form a range of complexes with terpy, with stoichiometries of 1:1, 1:2, and 1:3, although the 1:1 compounds are the most widely investigated. A number of workers have reported difficulties in the preparation of the 1:2 complexes, particularly with the lighter lanthanides, and it seems to be essential that only weakly coordinating counterions are present.

The only complexes of lanthanum or cerium to be described are $[La(terpy)_3][ClO_4]_3$ (*175*) and $Ce(terpy)Cl_3 \cdot H_2O$ (*411*). The lanthanum compound is a 1:3 electrolyte in MeCN or $MeNO_2$, and is almost certainly a nine-coordinate mononuclear species; the structure of the cerium compound is not known with any certainty. A number of workers have reported hydrated 1:1 complexes of terpy with praseodymium chloride (*376*, *411*, *438*), and the complex $PrCl_3(terpy) \cdot 8H_2O$ has been structurally characterized (*376*). The metal is in nine-coordinate monocapped square-antiprismatic $[Pr(terpy)Cl(H_2O)_5]^{2+}$ cations (Fig. 24). Complexes with a 1:1 stoichiometry have also been described for neodymium (*33*, *409*, *411*, *413*, *417*), samarium (*33*, *411*, *412*), europium (*33*, *316*, *411*, *414*, *417*), gadolinium (*33*, *411*), terbium (*316*, *410*, *414*), dysprosium (*33*, *410*, *412*), holmium (*33*, *410*), erbium (*33*, *410*, *417*), thulium (*410*, *412*), and ytterbium (*410*). The 1:2 stoichiometry has only been observed with the later lanthanides, europium (*33*, *411*, *414*), gadolinium, dysprosium, and erbium (*33*).

Hart and co-workers have demonstrated that the nine-coordinate cations $[M(terpy)_3]^{3+}$ may be prepared in the absence of coordinating counterions in the cases of europium, samarium, lanthanum, and lutetium (*175*, *201*, *202*). The most widely investigated compound in this series is $[Eu(terpy)_3][ClO_4]_3$, which has been structurally characterized. The metal is in a nine-coordinate tricapped trigonal-prismatic arrangement (Fig. 25) (*201*). The distortion from D_3 symmetry to C_2 is explained by the nonplanarity of the terpy ligands, and is predicted from spectroscopic observations. It is not clear how the above observations may be correlated with a report that

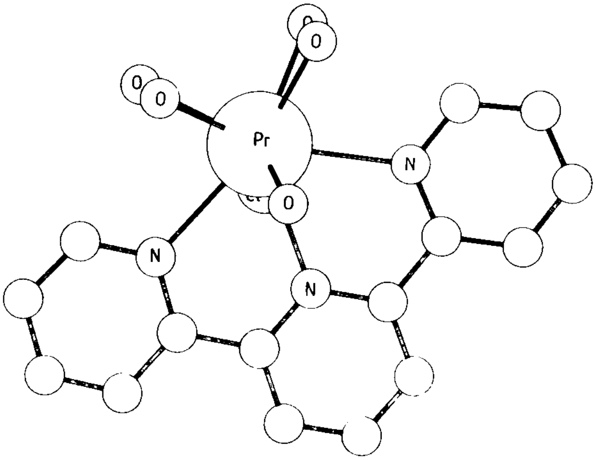

FIG. 24. The crystal and molecular structure of [Pr(terpy)Cl(H_2O)$_5$]Cl_2·3H_2O (*376*).

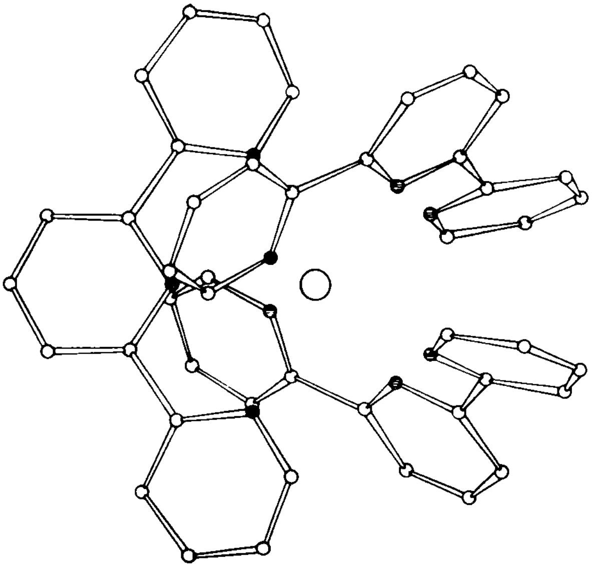

FIG. 25. The crystal and molecular structure of [Eu(terpy)$_3$][ClO_4]$_3$ (*201*).

acetonitrile solutions of $[Eu(terpy)_3]^{3+}$ exhibit on-off equilibria of the pyridine rings, giving a predominantly eight-coordinate solution structure (*110*). An interesting ligand-transfer reaction occurs when $[Eu(terpy)_3]^{3+}$ reacts with Tb^{3+}; the products are $Eu(terpy)_2{}^{3+}$ and $Tb(terpy)^{3+}$, formed after rate-determining loss of terpy from the tris complex (*202*).

All of the complexes are intensely fluorescent, and have been subjects of numerous spectroscopic investigations (*33*, *175*, *202*, *273*, *316*, *409–414*, *427*, *438*, *500*). 2,2′:6′,2″-Terpyridine has been investigated as a colorimetric reagent for the determination of cerium(IV), praseodymium(III), and gadolinium(III) (*19*).

A single example of a europium(II) complex has been described by Hart and Zhu, who obtained $[Eu(terpy)Cl_2]$ from the reaction of $EuCl_2$ with terpy in MeCN (*229*, *230*). It seems unlikely that the compound is monomeric.

A number of adducts of terpy with thorium(IV) nitrate or chloride (*472*, *476*) or uranium (*434*, *465*) have been reported. No structural details are available for these poorly characterized species.

IV. Coordination Compounds of Higher Oligopyridines

A. 2,2′:6′,2″:6″,2‴-QUATERPYRIDINE

The majority of complexes of the higher oligopyridines have been reported for 2,2′:6′,2″:6″,2‴-quaterpyridine (Fig. 2). In their pioneering studies of the coordination chemistry of this group of ligands, Morgan and Burstall investigated the complexes of 2,2′:6′,2″:6″,2‴-quaterpyridine (*327*). In these studies, they reported the complexes with silver(I), iron(II), cobalt(II), cobalt(III), nickel(II), copper(II), zinc(II), cadmium(II), iridium(III), and platinum(II). Although these authors speculated upon the structure of these complexes, they presented no unambiguous evidence. In a later paper, they reported the compounds $[Ru(NO)Cl(quaterpy)]Cl_2 \cdot 5H_2O$ and $[Ru(NO)Cl(quaterpy)][RuCl_5(NO)]$ (*325*). Brandt (*69*) questioned the ability of quaterpy to act as a planar quaterdentate, on the basis of a study of molecular models. This is indeed true, and it is necessary to introduce considerable strain in the ligand *or* to have a very distorted coordination. After these initial reports, there was very little interest in the ligand until 1964, when the interaction of quaterpy with iron(II) and iron(III) was reinvestigated (*54*). It was shown that 1:1 and 1:2 complexes were formed with iron(II) and a 1:1 complex with iron(III). Presumably, the 1:2 complex contains a quaterpy acting in a terdentate or bidentate mode. Lip and Plowman (*295*) reinvestigated the properties of $[Pt(quaterpy)]X_2$ (X = I,

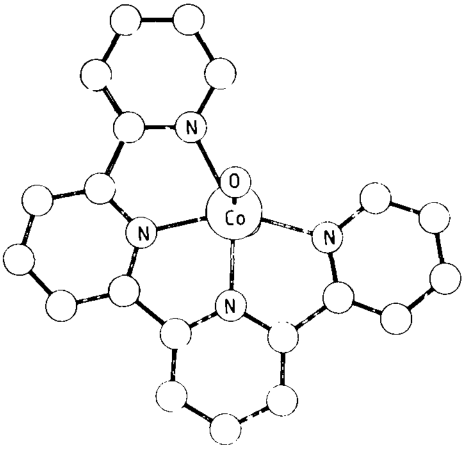

FIG. 26. The crystal and molecular structure of $[Co(quaterpy)(H_2O)_2][NO_3]_2$ (*237*).

ClO_4, BPh_4, or NO_3), and suggested, on the basis of conductivity measurements, that quaterpy was acting as a tetradentate ligand. The first unequivocal evidence that quaterpy could act as a tetradentate came from the structural analysis of $[Co(quaterpy)(OH_2)(SO_3)][NO_3]\cdot H_2O$, which revealed the quaterpy to be acting as a planar tetradentate ligand (*308*). The bonds to the terminal pyridine rings were longer than those to the central ones. Crystal structural analyses have also been reported for the complexes $[Cu(quaterpy)(H_2O)(NO_3)][NO_3]\cdot H_2O$ and $[Co(quaterpy)(H_2O)_2][NO_3]_2$ (Fig. 26) (*237*). Once again, the quaterpy was shown to act as an asymmetric planar tetradentate.

There have been numerous reports concerning the properties of iron complexes of quaterpy by an Italian group. Treatment of iron(II) sulfate with quaterpy in air led to the formation of the oxy-bridged complex $[(quaterpy)FeOFe(quaterpy)][SO_4]_2\cdot 7H_2O$ (*66*, *104*). The complex ions $[Fe(quaterpy)X_2]^{n+}$ have been shown to exhibit specific interactions with a wide range of biological substrates. Poly(L-glutamate) forms a helical structure upon reaction with $[Fe(quaterpy)(OH)_2]^+$ (*67*, *68*). Once the [Fe(quaterpy)] unit has been bound to the poly(L-glutamate) it is found to be an active catalyst for the hydrogen peroxide oxidation of L-adrenaline (*367*, *368*, *370*) or ascorbate (*27–29*, *367*). The polymer-bound complex is also active as a catalyst for the decomposition of hydrogen peroxide (*25*, *26*, *30*, *31*, *369*).

The Strasbourg group has investigated the coordination chemistry of 5,5',3'',5'''-Me_4-quaterpy, and reported a crystal structural analysis of the complex $[Cu_2L_2][ClO_4]_2\cdot H_2O$ (Fig. 27) (*290*). The methyl groups prevent the ligand from acting as a planar tetradentate, and a twist about the central

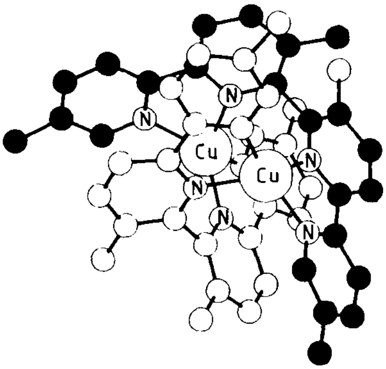

FIG. 27. The crystal and molecular structure of $[Cu_2(5,5',3'',5'''\text{-}Me_4quaterpy)_2][ClO_4]_2 \cdot H_2O$ (*290*).

C—C bond enables it to act as a bis bidentate. Each copper(I) is bound to two bidentate quaterpyridine moieties.

B. HIGHER OLIGOPYRIDINES

There have been very few reports concerning the coordination chemistry of the higher oligopyridines. Oepen amd Vogtle reported the formation of a 1:1 adduct of quinquepy with $Li[ClO_4]$ (*351*). This observation indicates that there may well be a hitherto to unsuspected coordination chemistry of alkali metal cations with pyridine derivatives. It is worthy of note that cyclosexipyridines and other planar sexidentate nitrogen-donor ligands form very stable alkali metal complexes. Complexes of $4',4'''\text{-}Ph_2$-quinquepy with cobalt(II), nickel(II), and cadmium(II) have been reported (*135*). The structures of these compounds are not known in any detail, although it is tempting to propose a planar quinquedentate donor set. A combination of electrochemical and ESR studies has indicated that metal-centered nickel(I) or cobalt(I) compounds are obtained upon one-electron reduction. A brown mixed oxidation state complex of the type $[Cu_2(quinquepy)(O_2)][PF_6]_2$ has also been described (*132*).

V. Coordination Compounds of Macrocyclic Derivatives

The archetypal macrocyclic oligopyridine is cyclosexipyridine (Fig. 28). The synthesis of this molecule was achieved by Newkome and co-workers (*350*). The elegant synthesis reported appears to be low-yield, and, as yet, no coordination chemistry has been reported. However, 4,4'''-diaryl derivatives

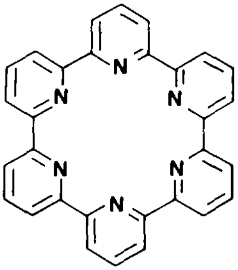

FIG. 28. Cyclosexipyridine.

have been prepared in a moderately high-yield (42 %) two-step reaction (*449*), and the development of the coordination chemistry of cyclosexipyridine is due. It is interesting that the 4,4‴-diaryl derivatives were isolated as sodium complexes; no sodium was present in the reaction mixtures, and one is led to speculate upon the possibility of the ligands leaching alkali metal ions from the glassware.

The Cambridge group has recently developed the chemistry of macrocyclic ligands based upon 2,2′:6′,2″-terpyridine (*133*, *135*, *136*, *139–143*). The macrocycles (Figs. 29 and 30) are prepared by template condensations of

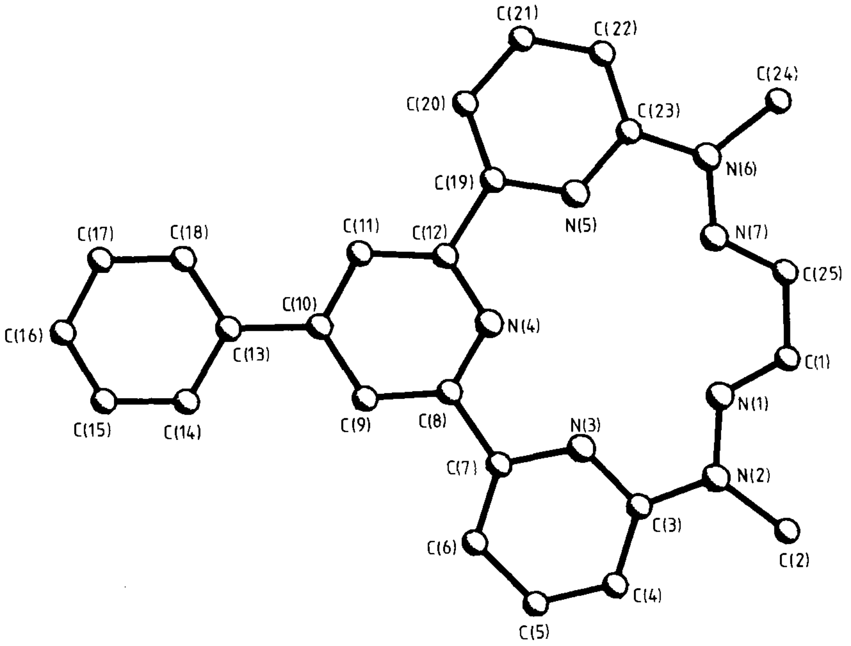

FIG. 29. A pentadentate macrocycle based upon 2,2′:6′,2″-terpyridine.

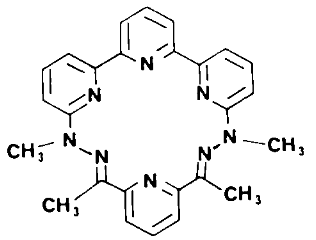

FIG. 30. A sexidentate macrocycle based upon 2,2′:6′,2″-terpyridine.

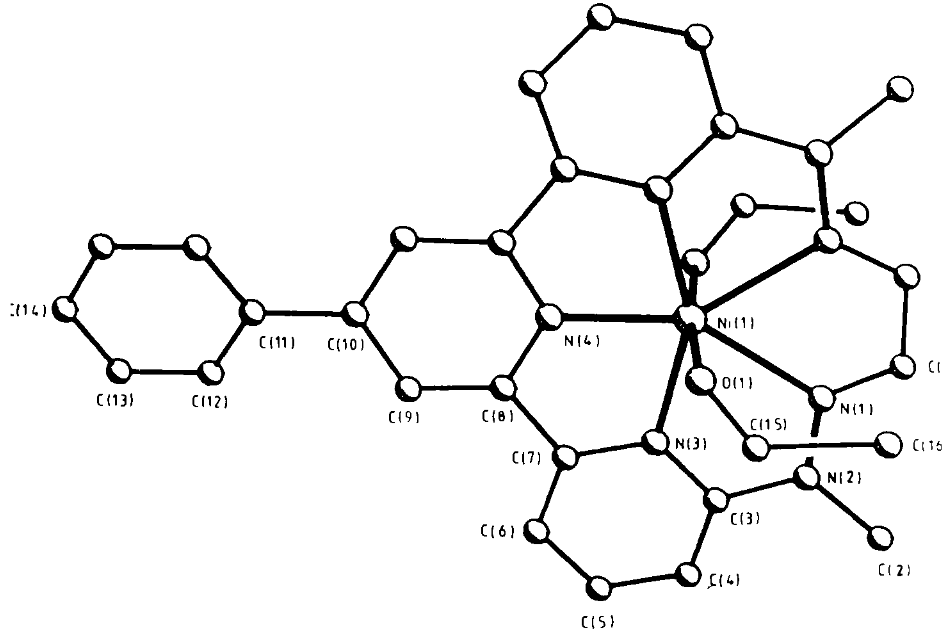

FIG. 31. The crystal and molecular structure of a pentagonal-bipyramidal nickel(II) complex of the ligand shown in Fig. 29.

6,6″-bis(hydrazino)-2,2′:6′,2″-terpyridines with appropriate dicarbonyls. In general, pentagonal-bipyramidal complexes are formed (Fig. 31), in which the axial sites are occupied by solvent molecules. The electrochemistry of these compounds is of interest, and metal-centered reductions are observed. Some novel template effects, by which free ligands are obtained, have been observed in these systems.

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