CATENATED NITROGEN LIGANDS PART II.[1] TRANSITION METAL DERIVATIVES OF TRIAZOLES, TETRAZOLES, PENTAZOLES, AND HEXAZINE

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I. Introduction

This review, which complements an earlier one (Part I) dealing with transition metal complexes of triazenes, tetrazenes, tetraazadienes, and pentaazadienes, examines the coordination chemistry of related cyclic catenated nitrogen ligands. Six-membered rings containing three, four, or five adjacent nitrogen atoms—1,2,3-triazines, 1,2,3,4-tetrazines, and pentazines, respectively—are either unknown or are relatively unstable species whose coordination chemistry has yet to be explored.

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[1] Part I. Transition metal derivatives of triazenes, tetrazenes, tetrazadienes, and pentazadienes. *Adv. Inorg. Chem. Radiochem.* **30**, 1 (1986).

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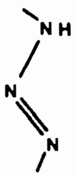
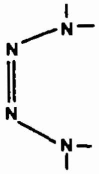
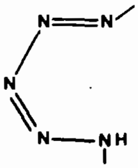


TRIAZENE

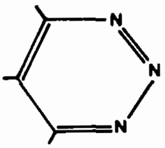


TETRAZENE

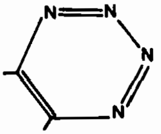
TETRAAZADIENE



PENTAAZADIENE



TRIAZINE



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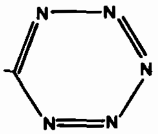

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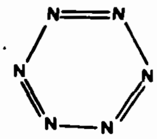
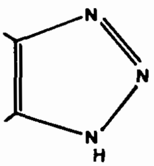
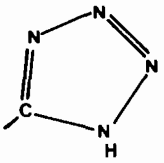


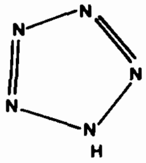
HEXAZINE



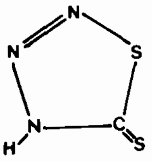
TRIAZOLE



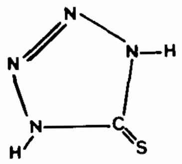
TETRAZOLE



PENTAZOLE



1,2,3,4-THIATRIAZOLINE -5-THIONE

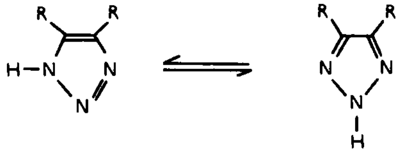


1,2,3,4-TETRAZOLINE -5-THIONE

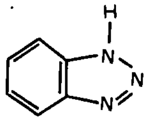
Consequently the area covered is essentially concerned with the chemistry of the more accessible five-membered 1,2,3-triazole and 1,2,3,4-tetrazole ring systems. Coverage of complexes containing related N,S heterocyclic ligands, notably 1,2,3,4-thiatriazoline-5-thione and 1,2,3,4-tetrazoline-5-thione, is selective since the coordination chemistry of these species has, in part, been reviewed elsewhere (*168*). Finally, prospects for the isolation of complexes containing higher nitrogen ligands, in particular the pentazolate anion (*cyclo*-N_5^-) and the hexazine molecule (*cyclo*-N_6), are briefly examined.

II. Triazole and Triazolate Complexes

This section covers ligands containing the 1,2,3-triazole ring system. These include, in addition to the parent triazole, various N- and/or C-substituted triazoles, benzotriazole, and a number of 8-azapurines. The coordination chemistry of 5-thio-1,2,3,4-thiatriazole is selectively reviewed. All of these molecules, with the exception of the N-substituted triazoles, are capable of coordinating in anionic as well as neutral form. 1,2,3-Triazole, first prepared by von Pechmann in 1888 (*215*), is a weak acid ($pK_a = 9.26$) (*88*) and exists as a mixture of the tautomeric forms (structures **1a** and **1b**). Benzotriazole (**2**), first correctly formulated by Ladenburg in 1876 (*120*), is also a weak acid ($pK_a = 8.38$) (*88*) and displays similar tautomerism. The use of 1,2,3-triazoles—notably benzotriazole and naphthotriazole—as corrosion inhibitors for copper (*99*) and as quantitative precipitating agents for copper (*46*) and the platinum group metals (*13*) has contributed substantially to the interest in the coordination chemistry of these ligands. The 1,2,3,4-thiatriazoline-5-thionate anion, formed by 1,3-cycloaddition of carbon disulfide to the azide anion, was formulated as the azidodithiocarbonate anion $N_3CS_2^-$ (*35*) before being correctly identified by Lieber and coworkers in 1957 (*127*). The parent acid is thought to be a tautomeric mixture of thione (**3a** and **3b**) and thiol forms (**3c**), with the latter being dominant (*45*). The 8-azapurines (aza analogs of the purine bases), several of which have attracted attention by virtue of their antitumor properties (*108*), include 8-azaadenine (**4**), 8-azaguanine (**5**), and 8-azahypoxanthine (**6**).



1a **1b**



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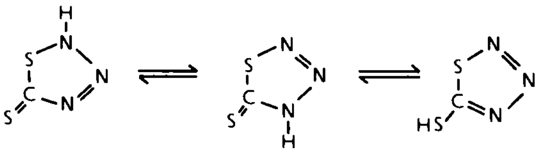
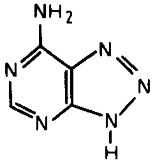


3a **3b** **3c**



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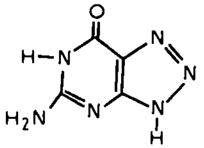

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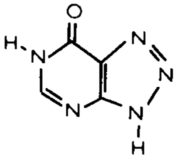

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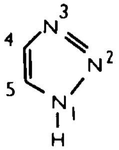
The generally accepted numbering schemes for 1,2,3-triazoles, thiatriazoline-5-thiones, and 8-azapurines, which are used throughout this section of the review, are given in (**7**), (**8**), and (**9**), respectively. Abbreviations used throughout this section to indicate neutral and anionic forms of the 1,2,3-triazole and benzotriazole ligands are taH/ta and btaH/bta, respectively.



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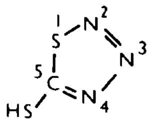

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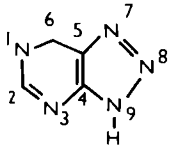

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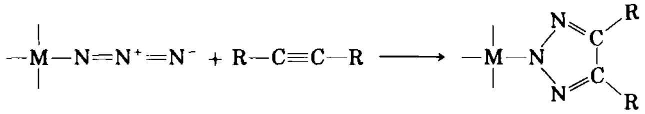
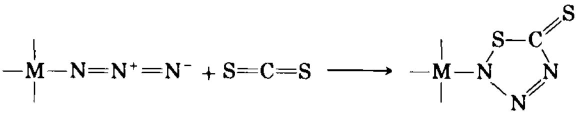
A. SYNTHESIS

Adducts of triazoles with transition metal salts are usually prepared by direct reactions between the two components involved and frequently precipitate or crystallize spontaneously from the reaction mixture (*55, 172, 194, 202*). Complexes containing triazolate anions can usually be obtained from the corresponding transition metal halide, carboxylate, nitrate, or perchlorate complex and an alkali metal (*146, 147, 172*) or thallium(I) triazolate salt (*33*). Other routes to triazolate complexes include the direct reactions of metal halides with triazoles in the presence of a base (*201*) and the treatment of triazole/metal halide adducts with base (*156, 194*). Direct reactions of triazoles with metal carboxylates have also been employed (*172*). 1,3-Dipolar cycloaddition of electron-deficient nonterminal acetylenes to coordinated azide anions [Eq. (1)] is a well-established route to complexes of 4,5-disubstituted triazolate anions (*37, 109, 114, 181*). A similar 1,3-dipolar addition of carbon disulfide [Eq. (2)] provides a useful route to derivatives of 1,2,3,4-thiatriazoline-5-thione (*17, 64, 121, 234, 235*).



(1)



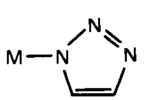
(2)

B. Structural Properties

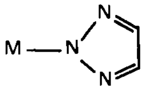
1,2,3-Triazoles and their conjugate bases, the triazolate anions, are potentially versatile ligands offering three adjacent donor sites. Although the generally preferred coordination positions appear to be N-3 for the parent triazoles and N-1 for the triazolate anions, all three N donor sites display considerable basicity and participate in metal–ligand bonding.

The neutral triazoles coordinate in monodentate fashion through N-3 (*197, 198, 202, 209*) or occasionally N-2 (*209*) donor sites and have also been found to act as N-2/N-3-bridging ligands (*1*). Coordination via N-1 has been established for the square-planar iridium(I) benzotriazolate complex $Ir(bta)(CO)(PPh_3)_2$ (*33*), but in certain octahedral cobalt(III) derivatives of 4,5-disubstituted triazoles kinetically determined N-1 isomers readily convert to the thermodynamically preferred N-2 isomers in response to steric influences (*109*). Iron(II) triazolate complexes, $Fe(triazolate)(C_5H_5)(CO)_2$, undergo irreversible thermal N-1 → N-2 or N-2 → N-1 isomerization, depending upon the nature of the substituents occupying the 4 and 5 positions on the triazole ring (*146*). Triazolate anions usually bridge through N-1 and N-2 sites in bi- or polynuclear structures containing single (*107*), double (*201, 208*), or triple (*1, 57, 133, 199*) triazolate linkages. However, examples of binuclear (*91*) and polynuclear (*198*) complexes containing single

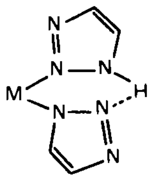
N-1/N-3 triazolate bridges are also known. There are in addition several X-shaped pentanuclear copper(I/II) or copper(II) benzotriazolate complexes in which the three nitrogen atoms of each triazolate anion are involved in bonding to three different metal atoms (*92, 113, 131*). A similar bonding arrangement has also been proposed for a tetranuclear rhodium benzotriazolate complex (*156*). By virtue of their cyclic nature, individual triazoles or triazolate anions are not capable of serving as chelate ligands. However H-bonded triazole–triazolate anion pairs have been shown to function as bidentate ligands, thereby generating six-membered chelate rings (*96*). Finally, since the triazolate anion is isoelectronic with the cyclopentadienide anion, there is the prospect, as yet unfulfilled, of η^3 or η^5 coordination of the triazolate ring to a metal center. Triazolate bonding modes are represented schematically in



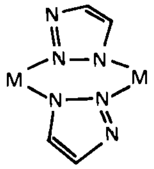
10a



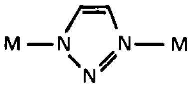
10b



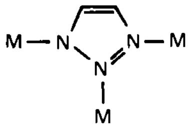
10c



10d



10e



10f

structures **10a**–**10f**. A list of crystallographically determined structures involving coordinated triazole moieties is given in Table I.

The tautomeric forms of the thiatriazoline-5-thionate anion offer three possible coordination sites, N-1, N-3, and S, and scope for N/S chelate or bridging structures. Spectroscopic evidence for N-1- and N-3-bonded isomers has been reported for the silver(I) complex

TABLE I

X-RAY DIFFRACTION STUDIES ON TRIAZOLE AND TRIAZOLATE COMPLEXES

Complex	Triazole- and Triazolate-bonding mode	Reference
Benzotriazole Derivatives		
$Mo_2(btaH)_3(CO)_6$	Bridging/N-2/N-3	*1*
$\{MnCl_2(btaH)_2\}_n$	Monodentate/N-3	*202*
$Fe(1\text{-}CH_2{=}CH{-}CH_2\text{-}bta)(CO)_3$	Chelate/N-2, $—CH{=}CH_2$	*143*
$OsH(bta)(btaH)(CO)(PPh_3)_2$	Chelate/bta-H···bta/N-1/N-2	*96*
$CoCl_2(btaH)_2$	Monodentate/N-3	*191*
$CoCl_2(1\text{-}CH_2{=}CH\text{-}bta)_2$	Monodentate/N-3	*196*
$[btaH_2]_2[CoCl_4]$	$btaH_2^+$ cations	*198*
$[Rh(bta)(C_8H_{12})]_2$	Bridging/N-1/N-2	*208*
$Ir(bta)(CO)(PPh_3)_2$	Monodentate/N-1	*33*
$NiCl_2(btaH)_2$	Monodentate/N-3	*191*
$Ni_3(bta)_6(NH_3)_6\cdot 2Me_2CO\cdot 2H_2O$	Bridging/N-1/N-2	*199*
$Ni_3(bta)_6(NH_2\cdot CH_2\cdot CH{=}CH_2)_6(Ph_3PO)_2$	Bridging/N-1/N-2	*133*
$\{CuCl_2(btaH)_2\}_2\cdot H_2O$	Monodentate/N-3	*197*
$CuSO_4(btaH)_3(H_2O)\cdot btaH$	Mondentate/N-3	*97*
$\{Cu(bta)_2(H_2O)\}_n$	Bridging/N-1/N-2	*201*
$Cu_5(bta)_6(Bu^tNC)_4$	Bridging/N-1/N-2/N-3	*92*
$Cu_2(bta)(tmbma)_2(NO_3)_3$[a]	Bridging/N-1/N-3	*91*
$Ag(NO_3)(btaH)_2$	Monodentate/N-3; bridging/N-2/N-3	*200*
$ZnCl_2(btaH)_2$	Monodentate/N-3	*198*
$\{Zn_2(bta)_4\}_n$	Bridging/N-1/N-3	*198*
$\{CdCl_2(btaH)_2\}_n$	Monodentate/N-3	*202*
$\{HgMe(bta)\}_2$	Bridging/N-1/N-2	*203*
Miscellaneous Triazole Derivatives		
$[Fe(taH)(C_5H_5)(CO)_2][HSO_4]$	Monodentate/N-3	*5*
$Co(4,5\text{-}R_2\text{-}ta)(dmg)_2(PPh_3)$ $[R = C(O)OMe]$	Monodentate/N-2	*142*
$Rh_2(\mu\text{-}N_3)(\mu\text{-}4,5\text{-}R_2\text{-}ta)(4,5\text{-}R_2\text{-}ta)_2(C_5Me_5)_2$ $(R = CF_3)$	Monodentate/N-2; bridging/N-1/N-2	*178*
$Cu(4,5\text{-}R,R'\text{-}ta)_2(H_2O)_2\cdot 2H_2O$ $(R = CO_2, R' = CO_2H)$	Chelate/N-3, $—CO_2^-$	*155*
$Cu(4,5\text{-}R,R'\text{-}taH)_2Cl_4$ $[R = NH_2, R' = C(NH_2){=}NH_2^+]$	Monodentate/N-2	*167*
8-Azapurine Derivatives[b]		
Cu(3-methyl-8-azaxanthinato)$_2$(NH$_3$)$_2$	Monodentate/N-8	*168a*
ZnCl$_3$(8-azaadeninium)	Monodentate/N-3	*166*
Cd(8-azahypoxanthinato)$_2$(H$_2$O)$_4$	Monodentate/N-7	*165*
HgCl$_2$(8-azaadenine)$_2$	Monodentate/N-3	*85*
[HgMe(8-azaadenine)]NO$_3$	Monodentate/N-9	*192*
HgMe(8-azaadeninato)·4H$_2$O	Monodentate/N-9	*192*
[(HgMe)$_2$(8-azaadeninato)]NO$_3$·H$_2$O	Bidentate/N-3/N-9	*192*
[(HgMe)$_3$(8-azaadenine-H$_2$)]NO$_3$	Tridentate/N-1/N-6/N-9	*192*
Hg(8-azahypoxanthinato)$_2$·4H$_2$O	Monodentate/N-9	*85*

[a] tmbma, tris(*N*-Methylbenzimidazol-2-ylmethyl)amine.

[b] Note: Nitrogen numbering scheme different from that employed for simple triazoles (see p. 174).

$Ag(CN_3S_2)(PPh_3)$ (*235*), and N/S-bridging thiatriazoline-5-thionate ligands have been proposed for some binuclear palladium(II) complexes (*37*).

C. SPECTROSCOPIC STUDIES

This section highlights some of the more important spectroscopic results obtained for triazole and triazolate complexes.

1. *Vibrational Spectra*

Infrared data have been tabulated for benzotriazole and a wide range of its transition metal complexes or adducts (*172*). Far infrared spectra have been recorded for copper(II) benzotriazole adducts and bands at ~270–320 cm^{-1} have been assigned to Cu–N vibrations (*172*). Infrared absorptions at approximately 825, 800, and 775 cm^{-1} in the spectra of cobalt(III)/4,5-disubstituted triazolate complexes have been attributed to triazolate ring vibrations (*109*). Infrared data have been reported and assignments made for palladium and platinum thiatriazoline-5-thionate complexes (*37*) and for the parent thione (*127*). Vibrational spectroscopy has been employed in an attempt to determine coordination sites for a range of 8-azapurine complexes (*108*).

2. *Electronic Spectra*

Relatively little has been reported on the electronic spectra of triazole and triazolate complexes. Copper(II) benzotriazolate adducts and benzotriazolate complexes show ligand-field maxima in the range 12.5–15.9 kK, in agreement with the proposed octahedral coordination geometry (*172*). Electronic spectra have also been reported for rhodium(I) and iridium(I) benzotriazolate complexes (*33*).

3. *Nuclear Magnetic Resonance Spectra*

Proton and ^{13}C NMR spectra have been used to distinguish between symmetrically (N-2) and asymmetrically (N-1) coordinated benzotriazole (*209*) or 4,5-disubstituted triazolate (*109, 146*) ligands, and to measure equilibrium constants for the N-1/N-2-coordinated benzotriazole system $[Fe(CN)_5(btaH)]^{3-}$ (*209*). Hydrogen bond formation and proton transfer reactions in $[Fe(taH)(C_5H_5)(CO)_2][HSO_4]$ have been followed by variable-temperature ^1H and ^{13}C NMR (*5, 146*).

4. *Electron Paramagnetic Resonance Spectra*

EPR data have been reported for iron triazole complexes (*101*) and a particularly wide range of copper(II) benzotriazole derivatives (*172*). The EPR spectra of the copper(II) complexes all show either isotropic g values or indications of axial or rhombic splittings; in no case were copper hyperfine splittings observed (*172*). A more detailed examination of $[CuCl_2(btaH)_2]_2 \cdot H_2O$ gave a g value of 2.045 ± 0.003 and produced evidence of a weak paramagnetic interaction indicative of a triplet ground state lying $1.8 \pm 0.2\ cm^{-1}$ below the singlet excited state (*93*). The EPR spectrum (9, 24, and 54 GHz) of the copper(I/II) complex $Cu_5(bta)_6(Bu^tNC)_4$ has been recorded at temperatures ranging from that of liquid nitrogen to room temperature. The appearance of Cu(II) hyperfine structure in almost all the spectra confirmed the expectation that the large Cu(II)–Cu(II) separation (12.858 Å) would be sufficient to ensure that the effects of exchange interactions are virtually nonexistent and that electronic dipolar broadening is small. At low temperatures the EPR spectra are quite normal and consistent with a $d_{x^2-y^2}$ type of ground state. Above 128 K a "reversed spectrum" is observed and is interpreted in terms of a two-dimensional dynamical Jahn–Teller effect (*113*). A later study of the Jahn–Teller effect in $Cu_5(bta)_6(Bu^tNC)_4$ places emphasis on the temperature-dependent quantitative dynamical changes which occur as the critical temperature is approached from above and suggests a possible transformation of localized molecular vibration into lattice phonons (*10*). For the closely related copper(II) complex $Cu_5(bta)_6(acac)_4$ the much closer approach of adjacent copper(II) centers (~3.5–4.0 Å) leads to dipolar and electron-exchange interactions which are substantially larger than the Cu(II) hyperfine interactions, hence a broad structureless resonance is observed at $g \approx 2$. An additional weak resonance at $g = 4$ confirms the presence of spin-coupled pairs (*131*). Q-Band and X-band EPR spectra show typical $S = 1$ signals for $[Cu_2(tmbma)_2(bta)][NO_3]_3 \cdot 4H_2O$ [tmbma = tris(N-methylbenzimidazol-2-ylmethyl)amine] and variable-temperature magnetic susceptibility measurements indicate antiferromagnetic interactions with J values of -10 to $-12\ cm^{-1}$ (*91*). A more recent single-crystal EPR study has established that even with a Cu(II)–Cu(II) distance of 5.536 Å an exchange contribution to the zero-field splitting is operative and that ferromagnetic exchange interactions can be propagated through triazolate bridges connecting ions separated by that distance (*21*).

D. Group Survey

To date no triazole complexes appear to have been reported for the scandium, yttrium, and lanthanum group of metals.

1. Titanium, Zirconium, and Hafnium

A trans structure with N-3-coordinated benzotriazole ligands has been proposed for the air- and moisture-sensitive orange adduct $TiCl_4(btaH)_2$ obtained by addition of the free ligand to a solution of $TiCl_4$ in dry dichloromethane (*172*).

2. Vanadium, Niobium, and Tantalum

The green-brown paramagnetic complex $VO(bta)_2 \cdot H_2O$ obtained when vanadyl sulfate reacts with benzotriazole in aqueous solution at pH 7–8 (*58*) probably has a polymeric structure with N-1/N-2-bridging bta ligands. The reaction of TaF_5 with benzotriazole in CH_2Cl_2/CH_3CN solution affords the salt *trans*-$[TaF_4(btaH)_2][TaF_6]$, which has been characterized by ^{19}F NMR (*98*).

3. Chromium, Molybdenum, and Tungsten

The red complex, $Mo_2(btaH)_3(CO)_6 2 \cdot 5THF$, obtained by treatment of $Mo(CH_3CN)_3(CO)_3$ with benzotriazole in tetrahydrofuran (THF) has been shown by X-ray diffraction methods to contain binuclear btaH-bridged units (Fig. 1) linked by H-bonded THF molecules. *N*-1-Methylbenzotriazole affords an analogous product. Deprotonation of $Mo_2(btaH)_3(CO)_6$ with NaH generates the yellow-green salt $Na_3[Mo_2(bta)_3(CO)_6]2 \cdot 5THF$ (*1*). A purple substitution product, $MoCl(C_5H_5)(btaH)(CO)_2$, has been obtained from $MoCl(C_5H_5)(CO)_3$ and benzotriazole in hexane (*111*).

4. Manganese, Technetium, and Rhenium

A mononuclear structure with N-1 benzotriazolate ligands is proposed for the yellow complex, $Mn(bta)(CO)_5$, obtained from Li(bta) and $MnBr(CO)_5$ in dry THF solution (*172*). High-spin ($\mu_{eff} = 5.92–6.05$ BM) manganese(II) complexes $MnCl_2(btaH)$, $MnX_2(btaH)_2 \cdot nH_2O$ ($X =$ Cl, Br, I, NCS, or NO_3; $n = 0–2.5$), and $Mn(O_2CCH_3)(bta)$ deposit as creamy white precipitates when the appropriate manganese salts are treated with benzotriazole in hot alcohol solution. Neutralization of the acetate reaction mixture to pH 7–8 with alcoholic ammonia af-

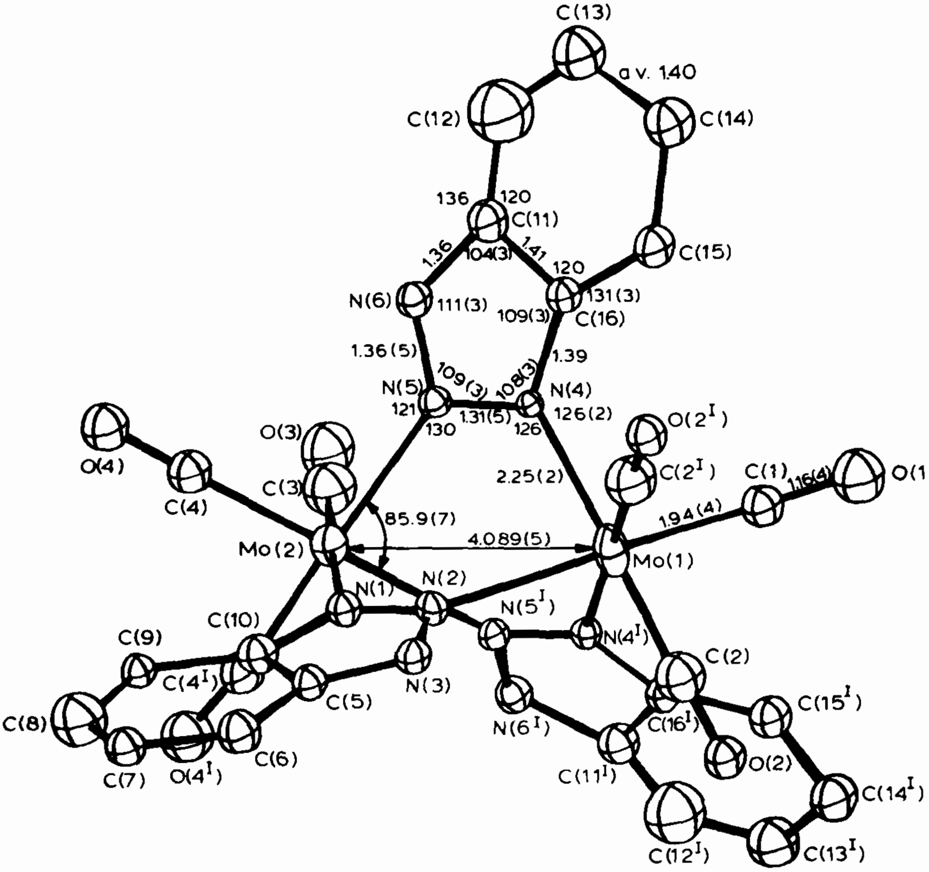


FIG. 1. Molecular structure of $Mo_2(btaH)_3(CO)_6$.

fords $Mn(bta)_2 \cdot 2.5H_2O$. All the hydrates lose water at ~120°C (*183*). More recently, crystals of $MnCl_2(btaH)_2$ (*191*), obtained by mixing $MnCl_2 \cdot 4H_2O$ and benzotriazole in methanol, have been described as rose colored and have been shown to possess a chloride-bridged ribbon structure with octahedral coordination about each manganese center completed by a trans pair of N-3-bound btaH ligands (Fig. 2) (*202*).

5. Iron, Ruthenium, and Osmium

Thermogravimetric analysis of the yellow salt $(btaH)_2H_2[Fe(CN)_6]$, deposited from $K_4[Fe(CN)_6]$/btaH solutions on acidification with HCl, reveals *o*-aminobenzonitrile to be the major organic product (*226*).

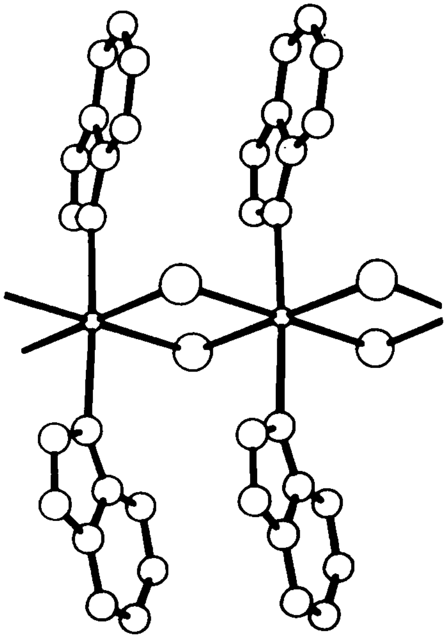
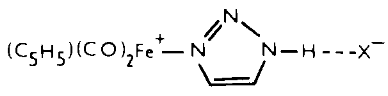


FIG. 2. Coordination about the metal atoms in $[MCl_2(btaH)_2]_2$ (M = Mn or Cd).

Benzotriazole reacts with the complex anion $[Fe(CN)_5(H_2O)]^{3-}$ to afford a mixture of N-2- and N-3-coordinated isomers $[Fe(CN)_5(btaH)]^{3-}$; characterization by ^1H and ^{13}C NMR spectroscopy yielded an equilibrium constant $K = 1.9 \pm 0.3$ favoring the less symmetric N-3 isomer (*209*). Relaxation times obtained from cyclic voltammetry data indicate an intramolecular mechanism for the (N-2)$\rightleftharpoons$(N-3) isomerization process (*210*). The N-2-coordinated triazolate complex Fe(ta)-$(C_5H_5)(CO)_2$, obtained from $FeX(C_5H_5)(CO)_2$ (X = Cl, Br, or I) and Na(ta) in THF at 25°C, undergoes irreversible thermal isomerization in neutral or acidic media to afford the N-1 isomer (*144, 146*). Treatment of the N-1-bonded isomer with acids affords H-bonded products (**11**). Dibasic acids (H_2SO_4 and $H_2C_2O_4$) form insoluble adducts (*145, 146*), one of which $[Fe(taH)(C_5H_5)(CO)_2][HSO_4]$ has been



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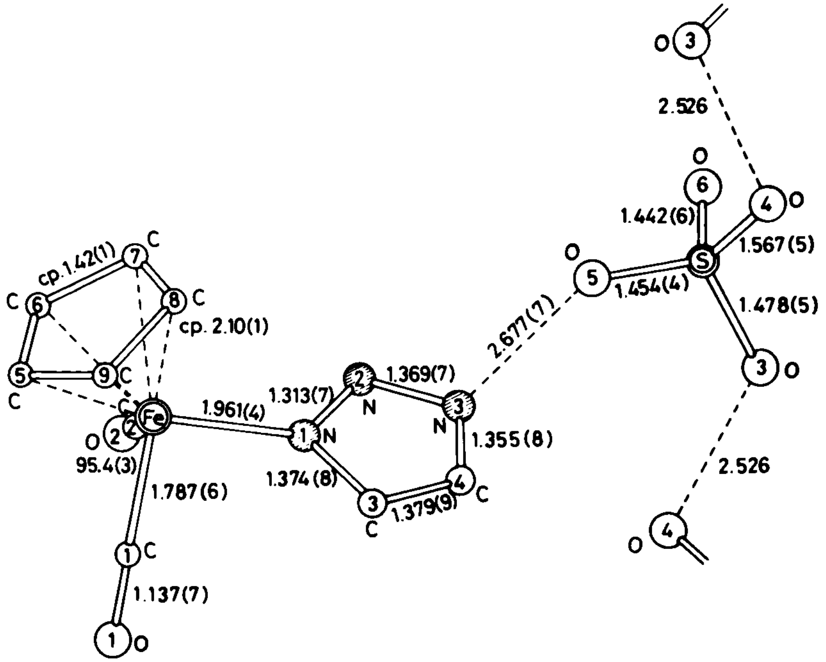
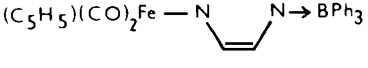


FIG. 3. The structure of 1-*N*-(1,2,3-triazole)(cyclopentadienyl)dicarbonyliron bisulfate.

characterized by diffraction methods (Fig. 3) (*5*). With aqueous $NaBPh_4$ the solvate initially formed decays to liberate triphenylboron, which in turn acts as a Lewis acid to generate the adduct (**12**) (*145*). Benzotriazole displays a similar behavior pattern but 4-phenyl-1,2,3-triazole (4-Ph-taH) initially forms an N-1-bonded complex (**13a**) which subsequently transforms to the N-2 isomer (**13b**). This difference in



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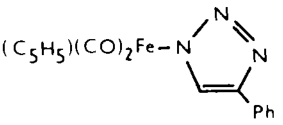
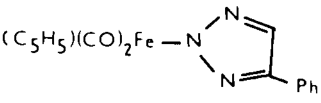
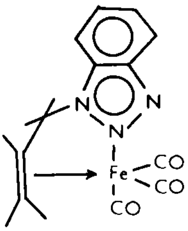


13a



13b

behavior is attributed to a kinetically controlled initial step involving primary attack at the N atom with highest electron density (N-2 for btaH and taH; N-1 for 4-Ph-taH) followed by thermal isomerization to the thermodynamically preferred isomers (N-1 for btaH and taH; N-2 for 4-Ph-taH) (*146*). The N-2 to N-1 isomerization observed for Fe(4-Ph-ta)(C_5H_5)$(CO)_2$ under acid conditions (H_2SO_4/THF) is attributed to stabilization of the N-1 isomer by H bonding to the sulfuric acid (*146*). Hydrogen bond formation and proton transfer reactions have been investigated by variable-temperature ^1H NMR and mass spectra have been recorded (*146*). On the basis of the X-ray crystal structure determined for [Fe(taH)(C_5H_5)$(CO)_2$][HSO_4] (Fig. 3) and variable-temperature ^{13}C NMR data for this and related complexes, a bifunctional concerted mechanism is proposed for proton exchange in these systems (*5*). α-Ferrocenyl alkylation of the benzotriazolate anion has been achieved (*112*) by the reaction of the salts [Fe(C_5H_5)(C_5H_4CHR)]$^+BF_4^-$ with Na(bta). Diiron nonacarbonyl reacts with 1- and 2-allylbenzotriazoles to give isomeric species (**14**) and (**15**), respectively (*20, 143*). The former product is also obtained when FeI(C_3H_5)$(CO)_3$ is treated with Na(bta) (*20*), and has been characterized by X-ray diffraction methods (*143*). In marked contrast, $Fe_2(CO)_9$ reacts with 4-benzoyl- and 4-butyryl-1,2,3-triazole in THF to afford air- and moisture-sensitive rose-violet crystals of stoichiometry Fe(4-RCO-ta)$_2$ (R = Ph or C_3H_7). Structures involving delocalized π or localized Fe–N σ bonds have been considered; the most probable structure appears to be one analogous to that reported for bis(1,4-diazobutadiene)iron. These triazolate complexes are attacked by air or moisture to give brown products similar to those previously obtained from ferrous chloride and the sodium salts of the corresponding triazoles. The latter products, which analyze for Fe(4-RCO-ta)$_2$$nH_2$O ($n$ = 1 or 2, R = Ph or C_3H_7), are insoluble in



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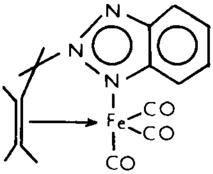

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noncoordinating organic solvents and presumably possess polymeric triazole bridged structures (*147*). Addition of dimethyl acetylenedicarboxylate to the azide $Fe(N_3)(C_5H_5)(CO)_2$ yields the corresponding N-1-coordinated triazole dicarboxylate derivative $Fe(4,5\text{-}R_2\text{-ta})(C_5H_5)(CO)_2$ (R = COOMe) (*181*). EPR data have been recorded for an iron nitrosyl/1,2,3-triazole complex of indeterminate stoichiometry (*101*).

In a series of articles published between 1956 and 1967, R. F. Wilson and co-workers described numerous benzotriazole derivatives of the platinum group metals. Spectroscopic studies on ruthenium/benzotriazole solutions established the formation of reddish-orange (1:4) and green (1:2) complexes in solution (*221*). Treatment of $RuCl_3 \cdot 3H_2O$ with benzotriazole in aqueous alcohol solution followed by addition of alkali or alkaline earth metal salts afforded insoluble purple compounds which were formulated as oxyruthenium(III) species $M^I[Ru(O)_2(btaH)_2]$ (M^I = Li, Na, or K) or $M^{II}[Ru(O)_2(btaH)_2]_2$ (M^{II} = Mg, Sr, or Pb). When warmed in acetic acid in a steam bath the purple sodium salt converted to an isomeric green product. Treatment with acids HX in aqueous solution afforded purple (X = Cl or Br) or dark green crystalline products of stoichiometry $RuX(O)(btaH)_2$ (*227*). Since oxy complexes of ruthenium are usually confined to higher oxidation states it seems probable that the oxy–ruthenium(III) formulations originally proposed are incorrect, and that the complexes are really polymeric species containing octahedral ruthenium(III) centers linked by bridging bta, oxide, and/or halide ligands. The feasibility of such structures has been demonstrated by the results of X-ray diffraction studies on several other transition metal/benzotriazole derivatives (see p. 196). More recently Kukushkin *et al.* have demonstrated that solid-phase dehydrohalogenation (Anderson rearrangement) of the complexes $[btaH_2]_2[RuCl_6]$ and $[btaH_2]_2[Ru(NO)Cl_5]$ leads to formation of the benzotriazole complexes $RuCl_4(btaH)_2$, $RuCl_3(NO)(btaH)_2$, and $[btaH_2][RuCl_4(NO)(btaH)]$ (*117*). Complex formation between benzotriazole and ruthenium(IV) perchlorate in solution has been reported (*38*).

A spectrometric study of the OsO_4/btaH/NaOH system in aqueous solution has established the formation of red and green osmium benzotriazole complexes with metal/ligand ratios of 1:4 and 1:2, respectively (*224*). Addition of benzotriazole to OsO_4 in ethanol affords a red stock solution which on acidification precipitates a yellow product of stoichiometry "$Os(OH)_3(btaH)_3$." This in turn converts to the green (X = Cl) or purple (X = Br) halides "$OsX_3(btaH)_3$" on heating in NaX/HX solution at 100°C. Treatment of the same stock solutions with metal salts leads to precipitation of bright red or yellow complex salts "$M_3[Os(O)_3(btaH)_4(H_2O)_2]$" (M = Na, $\frac{1}{2}$Ba, or $\frac{1}{2}$Ca), "$M_3[Os(O)_3(btaH)_4]$" (M = K or $\frac{1}{2}$Pb), or "$M_2[Os(O)_2(OH)(btaH)_3]$" (M = Ag or $\frac{1}{2}$Zn) (*222*). In the absence of magnetic and spectroscopic data it is not possible to establish the true nature of these products, although probably polymeric benzotriazolate-, oxide-, or halide-bridged structures are involved, similar to those postulated above for the related ruthenium complexes. Thermogravimetric studies reveal that the hydrated complexes lose water between 130 and 150°C and decompose completely in the range 380–560°C (*223*). The use of $Os(OH)_3(btaH)_3$ as a precipitate for the gravimetric determination of osmium has been described (*225*). More recently the complex $OsH(bta)(btaH)(CO)(PPh_3)_2$, isolated from the reaction of $OsH_2(CO)(PPh_3)_3$ with benzotriazole, has been shown to contain an H-bonded chelate bta-H···bta ligand (Fig. 4) (*96*).

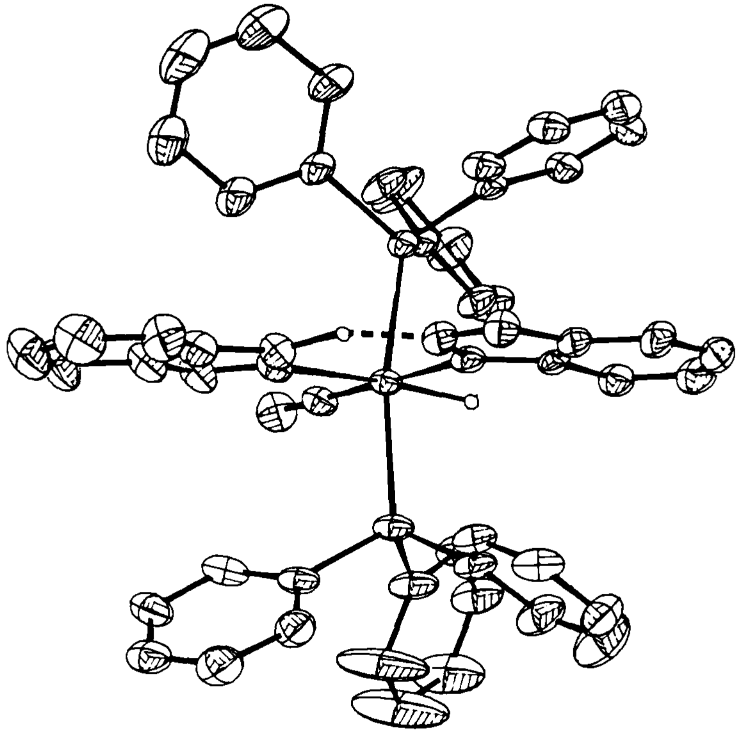
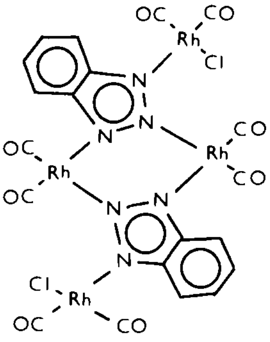


FIG. 4. Molecular structure of $OsH)(bta\text{-}H\cdots bta)(CO)(PPh_3)_2$.

6. *Cobalt, Rhodium, and Iridium*

The blue crystalline salt $[btaH_2]_2[CoCl_4]$ obtained by addition of benzotriazole to $CoCl_2 \cdot 6H_2O$ in 2 *M* HCl solution has been shown by X-ray diffraction methods to contain planar $btaH_2^+$ cations (protons at N-1 and N-3) and almost regular tetrahedral $CoCl_4^{2-}$ anions (*198*). The synthesis and X-ray diffraction study of the adduct $CoCl_2(btaH)_2$ have been reported (*191*). Reaction of cobalt(III) salts with benzotriazole are reported by Cambi *et al.* to involve reduction to cobalt(II) (*41*); complexes isolated include $Co(bta)_2 \cdot H_2O$ (*40, 42*) and $Co_3(bta)_8$ (*40*). Cobalt(III) ammine and ethylenediamine complexes afford $[Co(bta)(NO_2)(NH_3)_4]Cl$, $Co(NO_2)_3(btaH)(NH_3)_2$ (*40*), $Co(bta)(NO_2)_2(NH_3)_3$, and $[Co(bta)Cl(en)_2]Cl$ (*137*). Magnetic data have been reported for some of these products (*39*). Other cobalt(III) benzotriazole derivatives include the species $Co(nqo)_2(NO_2)(btaH)$ (nqoH = 2-nitro-1-naphthol or 1-nitro-2-naphthol) (*43*). Sodium salts of 4-butyroyl- and 4-benzoyl-1,2,3-triazole react with cobalt(II) halides to afford $Co(4\text{-}RCO\text{-}ta)_2$ ($R = C_3H_7$ or Ph) (*147*). Absorption of oxygen by solutions of $CoCl_2(PPh_3)_2$ in allylamine in the presence of benzotriazole leads to formation of the novel trinuclear complex $Co_3(bta)_6(CH_2{=}CH{-}CH_2NH_2)_6(Ph_3PO)_2$, which has a linear chain structure analogous to that determined for the corresponding nickel(II) complex (see page 191) (*57*). 1-Vinylbenzotriazole ligands are coordinated through N-3 to a slightly distorted tetrahedral cobalt(II) center in $CoCl_2(1\text{-}CH_2{=}CH\text{-}bta)_2$ (*196*). An extensive range of cobalt(III) triazolate complexes have been prepared by 1,3-dipolar cycloaddition of the electron-poor acetylene $CH_3O_2CC{\equiv}CCO_2CH_3$ to cobalt(III) azides $CoN_3(chel)_2L$ (chel = dmg or acac; $chel_2$ = salphen or salen; L = P or N donor ligand). Initial products are thought to be kinetically controlled N-1 isomers which rapidly rearrange to thermodynamically preferred N-2 isomers (*109*). The crystal structure of one such product, $Co(4,5\text{-}R_2\text{-}ta)(dmg)_2(PPh_3)$ (R = MeOCO), confirms the trans stereochemistry of the complex and the N-2 coordination of the triazolate ligand (*142*). Reactions of alkenes with cobalt(III) azides afford Δ^2-triazoline derivatives which are too unstable to isolate (*109*). Addition of carbon disulfide to $[AsPh_4]_2[Co(N_3)_4]$ affords a transient thiatriazoline-5-thionato complex $[AsPh_4]_2[Co(N_3CS_2)_4]$ which rapidly decomposes to the isothiocyanate $[AsPh_4]_2[Co(NCS)_4]$ (*64*). The orange complex $CoCl_2$(8-azahypoxanthine)$_2$, obtained by treatment of $CoCl_2 \cdot 6H_2O$ with the free ligand in aqueous solution, is thought to possess a polymeric structure with bridging 8-azahypoxanthine ligands (*108*). Rose-colored precipitates of stoichiometry $Rh(bta)_3(H_2O)_3$ have been obtained from reactions between $RhCl_3 \cdot 3H_2O$ (*229*), Na_3RhCl_6 (*129*), or $Rh(NO_3)_3$ (*232*) and benzotriazole. Under similar conditions rhodium sulfate and rhodium halides afford $Rh(OH)(bta)_2(H_2O)_3$ and $RhX_2(bta)(btaH)_n$ ($X = Br$, $n = 2$; $X = I$, $n = 1$), respectively (*232*). The low solubility of these products suggests the presence of polymeric structures with bridging halide and bta^- or btaH ligands. Osmometric molecular weight data imply a hexameric formulation for the yellow complex $[Rh(bta)(CO)(PPh_3)_2]_n$ obtained from $RhCl(CO)(PPh_3)_2$ and Tl(bta) (*83*). The benzotriazole adduct $RhCl(btaH)(C_8H_{12})$ carbonylates to give $RhCl(btaH)(CO)_2$ and reacts with base (NEt_3) to form $[Rh(\mu\text{-bta})(C_8H_{12})]_2$ (*156*). Carbonylation of the latter product affords $[Rh(\mu\text{-bta})(CO)_2]_2$, which in turn reacts with triphenylphosphine to generate $[Rh(\mu\text{-bta})(CO)(PPh_3)]_2$ (*156*). The N-1/N-2-bridging benzotriazolate ligands are proposed for the binuclear complexes (*156*) and this arrangement has been confirmed for $[Rh(\mu\text{-bta})(C_8H_{12})]_2$ by an X-ray diffraction study (*208*). $[Rh(bta)(\eta\text{-}C_3H_5)_2]_3$ has been assigned a trinuclear benzotriazolato-bridged structure on the basis of X-ray data for related trinuclear azolate complexes (*156a*). A novel tetranuclear structure (**16**) involving benzotriazolate ligands coordinated



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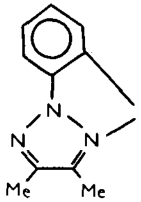
through all three nitrogen atoms has been proposed for the complex $Rh_4Cl_2(bta)_2(CO)_8$ obtained by mixing solutions of $RhCl(btaH)(CO)_2$ and $Rh(acac)(CO)_2$ (*156*). Related tetranuclear complexes form when $[RhCl(C_8H_{12})]_2$ is added to $[Rh(\mu\text{-bta})(C_8H_{12})]_2$ and when Rh(acac)-(C_8H_{12}) is added to $RhCl(btaH)(C_8H_{12})$ (*156*). The complex RhCl(btaH)-$(CO)_2$ has also been obtained from $RhCl(benzothiadiazole)(CO)_2$ and benzotriazole (*116*). 2-Aryl-4,5-dimethyl-1,2,3-triazoles react with $RhCl_3 \cdot 3H_2O$ in boiling 2-methoxyethanol to afford the cyclometallated products $[RhCl(C{-}N)_2]_2$ ($C{-}N = $ **17**), which are cleaved by



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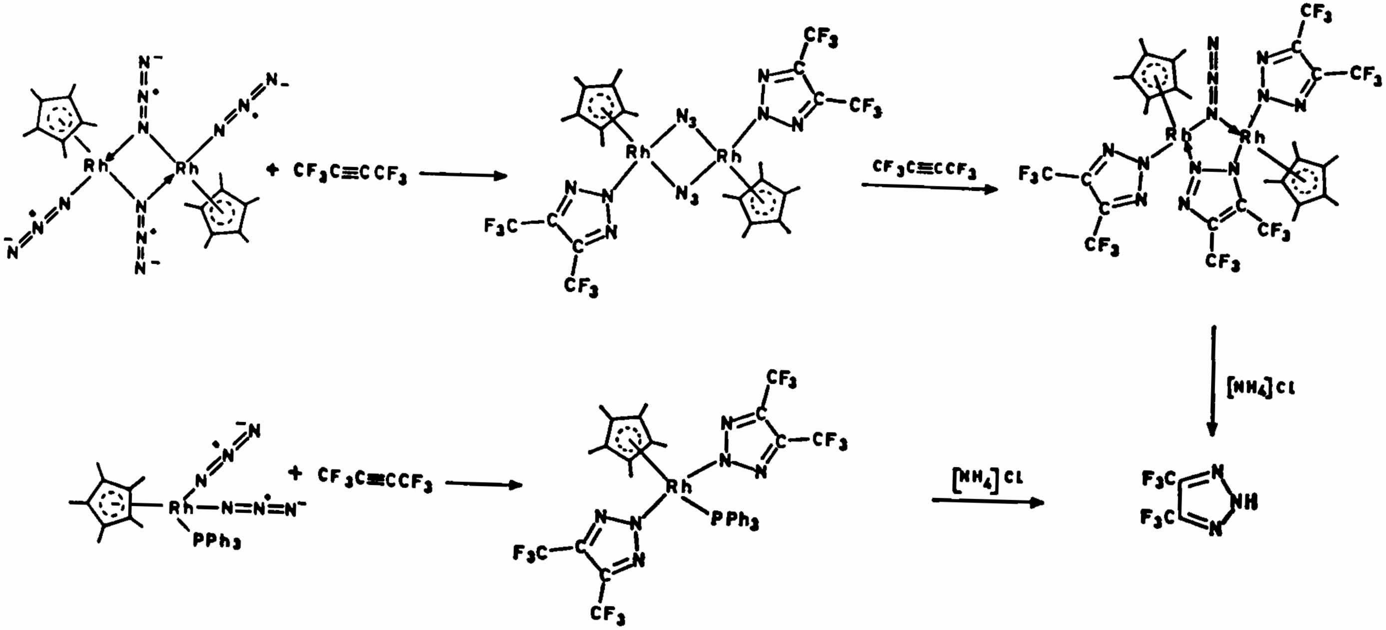
pyridine and tributylphosphine to form $RhCl(C{-}N)_2py$ and $RhCl(C{-}N)_2(PBu_3)$, respectively (*152*). Rhodium(III) azides react with hexafluorobut-2-yne to yield products containing N-2-coordinated and/or N-1/N-2-bridging bis(trifluoromethyl)triazolate ligands (Scheme 1) (*178*). An X-ray diffraction study on the complex $Rh_2(\mu\text{-}N_3)\{\mu\text{-}4,5\text{-}(CF_3)_2\text{-ta}\}\{4,5\text{-}(CF_3)_2\text{-ta}\}_2(C_5Me_5)_2$ has confirmed the proposed structure (*178*). An unstable 1,2,3,4-thiatriazole-5-thiolate complex of rhodium formed from $Rh(C_5Me_5)(N_3)_2(PPh_3)$ and CS_2 easily breaks down to form $Rh_2(C_5Me_5)_2(SCN)_4$ (*178*).

Reactions of Na_3IrCl_6 with benzotriazole afford $Ir(bta)_3 \cdot 3H_2O$ and $Ir(bta)_3(btaH)$; "bromobenzotriazole" gives analogous products (*129*). Thallium benzotriazolate reacts with $[Ir(CO)(Me_2CO)(PPh_3)_2][PF_6]$ and $IrCl(CO)(PPh_3)_2$ to yield tetrameric $[Ir(bta)(CO)(PPh_3)]_4$ and bimetallic $Ir(bta)_2(CO)(PPh_3)Tl \cdot C_6H_6$, respectively. The latter product breaks down in methanol to form *trans*-$Ir(bta)(CO)(PPh_3)_2$, which has been shown by diffraction methods to contain N-1-coordinated benzotriazolate ligands bound to square-planar iridium(I) (*33*). *mer*-$IrH_3(PPh_3)_3$ reacts with benzotriazole to form $IrH_2(bta{-}H\cdots bta)(PPh_3)_2$, an octahedral iridium(III) complex with an H-bonded bta–H···bta chelate ligand (*96*). The cyclometallated iridium(III) complex $[IrCl(C{-}N)_2]_2$ (C—N = **17**) has been obtained from iridium(IV) chloride and 2-*p*-tolyl-4,5-dimethyl-1,2,3-triazole (*152*).

7. *Nickel, Palladium, and Platinum*

Benzotriazole, 1-ethylbenzotriazole, and 1-vinylbenzotriazole form 1:1 or 2:1 adducts with nickel(II) chloride (*55*). X-Ray crystallographic data have been recorded for $NiCl_2(btaH)_2$ (*191*). Benzotriazole reacts with nickel acetate to form $Ni(bta)_2 \cdot H_2O$; 1,2,3-triazole gives a product of uncertain nature (*42*). 4-Butyroyl- and 4-benzoyl-1,2,3-triazolate complexes of nickel (II), $Ni(4\text{-}RCO\text{-ta})_2 \cdot nH_2O$ ($R = C_3H_7$, $n = 1$; R = Ph, $n = 2$), have been obtained as lilac precipitates by treatment of $NiCl_2 \cdot 6H_2O$ with the sodium salts of the triazoles (*147*). A light brown product, $[Ni(bta)(btaH)][BF_4]$, of unknown structure forms



SCHEME 1. Reactions between $CF_3C{\equiv}CCF_3$ and some rhodium azides.

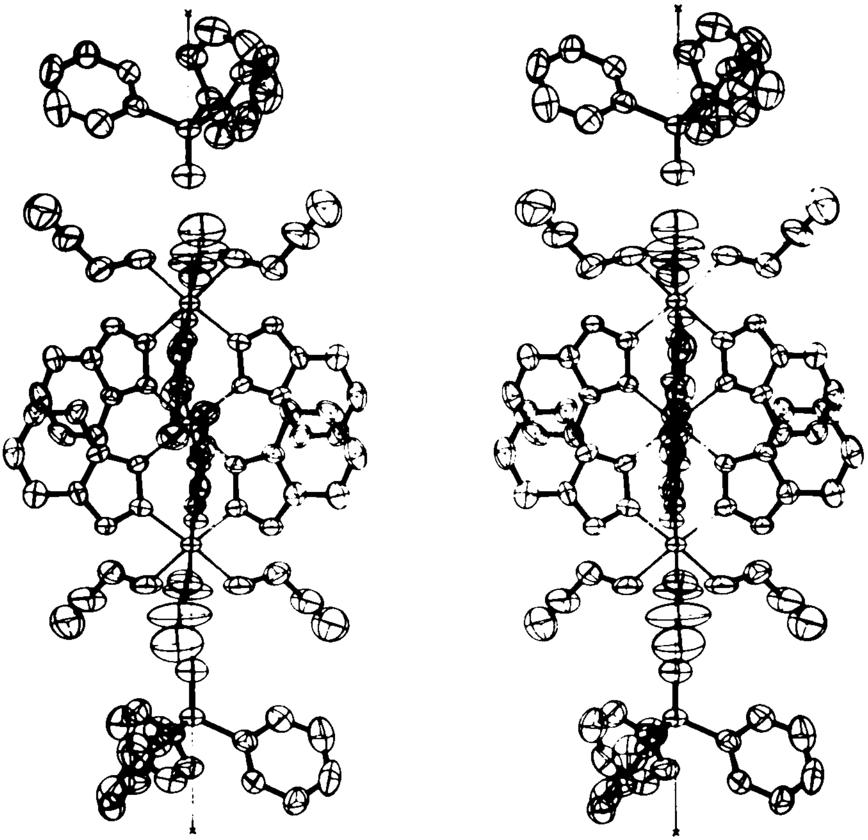


FIG. 5. Stereoscopic view of the structure of $Ni_3(bta)_6(CH_2$ CH -CH_2– $NH_2)_6$-$(OPPh_3)_2$.

when benzotriazole and triethylamine is added to a suspension of $[Ni(C_5H_5)(C_7H_8)][BF_4]$ in THF (*172*). Mixtures of $NiI_2(PPh_3)_2$ and benzotriazole in neat allylamine react under nitrogen to form blue crystals of the trinuclear complex $Ni_3(bta)_6(CH_2$ CH $CH_2NH_2)_6$-$(PPh_3)_2$, which are oxidized by air to yield the closely related phosphine oxide adduct $Ni_3(bta)_6(CH_2$ CH -$CH_2NH_2)_6(OPPh_3)_2$ (*57*). The latter product has been shown by X-ray diffraction methods to possess a novel linear trinuclear structure (Fig. 5) and to be isostructural with the corresponding cobalt(II) derivative (*57*, *133*). A rather similar linear trinuclear structure (Fig. 6) has been reported for the pale purple complex $Ni_3(bta)_6(NH_3)_6 \cdot 2Me_2CO \cdot 2H_2O$ obtained by mixing solutions of $NiCl_2 \cdot 6H_2O$ in 7 *M* ammonia and benzotriazole in

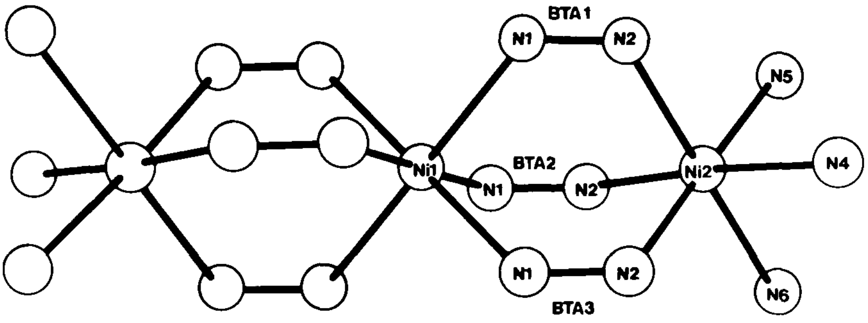
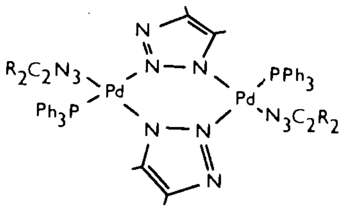


FIG. 6. Coordination about the nickel atoms in $Ni_3(bta)_6(NH_3)_6{\cdot}2Me_2CO{\cdot}2H_2O$.

acetone (*199*). An N-bonded thiatriazoline-5-thionato complex of nickel(II), $Ni(CS_2N_3)(C_5H_5)(PBu^n{}_3)$, obtained by addition of carbon disulfide to $[Ni(C_5H_5)(PBu^n{}_3)_2][N_3]$ pyrolyzes to form the corresponding isothiocyanate $Ni(C_5H_5)(NCS)(PBu^n{}_3)$ (*184*).

Benzotriazole adducts with palladium(II) salts include $PdCl_2(btaH)$ (*230*), $PdCl_2(btaH)_2$ (*95, 172, 219, 230*), $PdI_2(btaH)_2$ (*95*), $Pd(NO_3)_2(btaH)_2$ (*95*), $PdCl_2(1\text{-}Bz{-}btaH)_2$, and $PdCl_2(1\text{-}CH_2{=}CH{-}btaH)_2$ (*216, 219*). Far infrared data [ν(Pd–Cl) 370 and 320 cm^{-1}] indicate a cis configuration for $PdCl_2(btaH)_2$; the solvate $PdCl_2(btaH)_2(DMSO)_2$ is thought to contain dimethyl sulfoxide (DMSO) hydrogen bonded to the btaH ligands (*172*). Quantitative estimation of palladium by precipitation as $PdCl_2(btaH)_2$ (*229*) or $PdCl_2(5\text{-}Br{-}btaH)_2$ (*130*) and by amperometric titration of $PdCl_2$ with btaH (*229*) has been described.

Buffered solutions of $Pd(NO_3)_2$ and $Pd(SO_4)$ react with benzotriazole to form gray, beige, or yellow insoluble complexes $Pd(NO_3)(bta)$ (*231*), $Pd(NO_3)(bta)(btaH)$ (*95, 231*), $Pd_2(SO_4)(bta)_2$, and $[Pd(bta)(btaH)]_2SO_4$ (*231*). Possible structures for these complexes and their platinum(II) analogs are described below. Cleavage of $[PdCl(\eta^3\text{-}C_3H_5)]_2$ with benzotriazole affords $PdCl(\eta^3\text{-}C_3H_5)(btaH)$, which in dimethyl sulfoxide solution converts to the fluxional η^1-allyl $PdCl(\eta^1\text{-}C_3H_5)(btaH)(DMSO)$, similar behavior is reported for 1-benzyl- and 1-vinylbenzotriazoles (*219*). 2-Aryl-1,2,3-triazoles undergo cyclometallation reactions with palladium and platinum chlorides to form binuclear complexes $[MCl(C{-}N)]_2$ ($C{-}N = \mathbf{17}$) (*3, 152*); chlorination of the palladium products yields 2-(*o*-chloroaryl)-1,2,3-triazoles (*3*). 1,3-Dipolar cycloaddition of $RC{\equiv}CR$ ($R = CO_2Me$) (*114*) and CS_2 (*17, 64*) to $Pd(N_3)_2(PPh_3)_2$ generates products with structures **18** and **19**, respectively. The latter complex has also been obtained from $Pd(NO_3)_2$, $Na(CN_3S_2)$, and triphenylphosphine (*17, 64*). Crystallization



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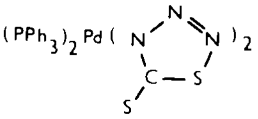

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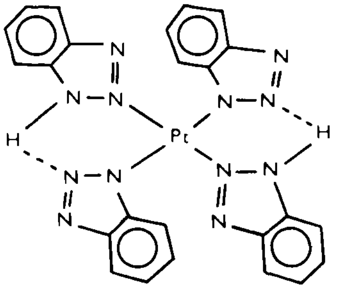
of **18** in the presence of free triphenylphosphine affords monomeric $Pd(R_2C_2N_3)_2(PPh_3)_2$ (*114*). Azido-bridged complexes of palladium(II) and platinum(II), $[M(N_3)(diene\text{-}OMe)]_2$ and $[Pd(N_3)(\eta^3\text{-allyl})]_2$, undergo 1,3-cycloaddition reactions with CS_2 to form thiatriazolate-bridged species, $[M(CN_3S_2)(diene\text{-}OMe)]_2$ and $[Pd(CN_3S_2)(\eta^3\text{-allyl})]_2$, respectively (*37*). Reactions between platinum(II) or platinum(IV) halides and benzotriazole under pH-controlled conditions have afforded a wide variety of insoluble precipitates (see Table II). The rather intractable nature of these products has prevented collection of evidence concerning their structures (*228*). However, given the strong preference of platinum(II) and platinum(IV) for four and six coordination, respectively, it is possible to speculate, on the basis of stoichiometry alone, that these complexes contain bridging bta and/or chelating bta–H···bta ligands. Thus products 1 and 8 in Table II can be tentatively assigned structures **20** and **21**, respectively. Similar structures can be advanced for the related palladium complexes mentioned above. The 8-azapurine adducts $PdCl_2$(8-azaguanine) and $PtCl_2$(8-azaadenine) have been synthesized and their infrared spectra reported (*108*).

TABLE II

PLATINUM–BENZOTRIAZOLE COMPLEXES

Reagents	pH	Product	Color
1 $[PtCl_4]^{2-}$/btaH	6.5	$Pt(bta)_2(btaH)_2$	White
2 $[PtCl_4]^{2-}$/btaH	1	$PtCl(bta)(btaH)_3$	Greenish white
3 $[PtI_6]^{2-}$/btaH	1	$PtI(bta)(btaH)H_2O$	Beige
4 $[PtI_6]^{2-}$/btaH	6	$Pt(bta)_2(H_2O)_2$	Gray
5 $[PtBr_6]^{2-}$/btaH	6	$Pt(bta)_4Pt(bta)_2(btaH)_2$	Beige
6 $[PtCl_6]^{2-}$/btaH	—	$PtCl(bta)_3(btaH)_2$	Yellow
7 $[PtCl_6]^{2-}$/btaH	6.7	$Pt(bta)_4(btaH)_2H_2O$	Gray-white
8 $[PtCl_6]^{2-}$/btaH	1	$PtCl_2(bta)_2(btaH)_2$	Yellow
9 $[PtBr_6]^{2-}$/btaH	1	$PtBr(bta)_3$	Orange



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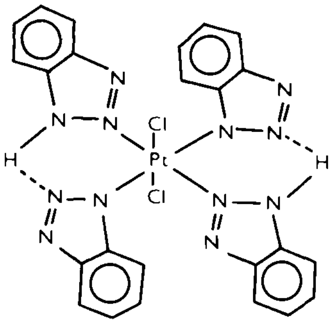

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8. *Copper, Silver, and Gold*

The technological importance of triazoles in general and benzotriazole in particular as anticorrosion agents for copper and its alloys (*99*) has generated much interest in copper triazole complexes. The protective action of benzotriazole is thought to involve attack on surface oxide or hydroxide, leading to formation of an impenetrable layer of copper(I) [or possibly copper(II)] benzotriazolate salts, which serve as a barrier to further reaction (*2, 182, 233*). For a full discussion of the technological aspects of this field interested readers are referred to recent papers (*2, 171, 172, 182, 217*) and references therein. Many copper(I) and/or copper(II) benzotriazole complexes have been reported and several of these have been found to display novel structural features. The yellow tetrameric copper(I) adduct $[CuCl(btaH)]_4$, obtained from CuCl and benzotriazole in dichloromethane solution, is converted by triethylamine to the insoluble polymeric copper(I) complex $\{Cu(bta)\}_n$. The copper(I) chloride adduct displays intense yellow luminescence ($\lambda_{max}^{excit} = 381$ nm, $\lambda_{max}^{emiss} = 563$ nm); for a series of copper(I) halide adducts λ_{max}^{emiss} displays a bathochromic shift $I < Br < Cl < CN$, indicating emission from an excited state produced by a metal → ligand charge transfer process (*194*). Benzotriazole attacks copper surfaces to give a yellow surface layer with the characteristics of $\{Cu(bta)\}_n$ (*193, 194*). Acid solutions of CuX/KX (X = Cl, Br, or I) and Cu_2SO_4 react with benzotriazole to deposit insoluble, diamagnetic pale yellow to orange precipitates of the adducts $Cu_2X_2(btaH)$ and $Cu_2(SO_4)(btaH)$, respectively (*106*).

Benzotriazole adducts of copper(II) halides include $CuCl_2(btaH)$ (*172*), $CuCl_2(btaH)_2$ (*191*), $CuCl_2(btaH)_2 \cdot 0.5H_2O$, $CuCl_2(btaH)_3$, $CuCl_2(btaH)_3 \cdot H_2O$, $CuBr_2(btaH)$, and $CuBr_2(btaH) \cdot 0.25H_2O$ (*172*). Similar

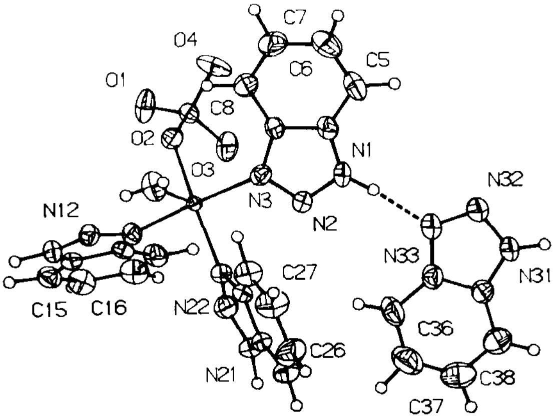


FIG. 7. Structure of $Cu(SO_4)(btaH)_3(H_2O)\cdot btaH$.

adducts have been reported for 1-methyl- and 5-nitrobenzotriazole (*172*). Green crystals of $CuCl_2(btaH)_2\cdot 0.5H_2O$ have been shown to contain binuclear chloride-bridged units. The geometry around each copper atom is approximately trigonal–bipyramidal with equatorial chlorine atoms and axial N-3-coordinated benzotriazole ligands (*197*). The complex exhibits a weakly ferromagnetic interaction indicative of a triplet ground state lying $1.8 \pm 0.2\ cm^{-1}$ below the singlet excited state (*93*). A copper sulfate adduct, "$CuSO_4(btaH)_4\cdot 2H_2O$," prepared from the components in aqueous sulfuric acid at pH 1 (*105*), has been reformulated as a monohydrate and shown to adopt a structure (Fig. 7) comprising tetragonal–pyramidal $Cu(SO_4)(btaH)_3H_2O$ units and noncoordinated btaH groups linked in a three-dimensional array by H bonds (*97*). On attempted dissolution in water the complex converts to an insoluble green product of stoichiometry "$[Cu(btaH)_2(OH)(H_2O)]OH$" (*105*).

Green polymeric $Cu(bta)_2$, obtained from copper(II) carboxylates and benzotriazole in anhydrous toluene, is insoluble in dimethyl formamide and dimethyl sulfoxide but forms a yellow solution in pyridine (*172*). It has been reported that copper can be quantitatively separated and gravimetrically estimated as $Cu(bta)_2$ (*46*). The monohydrate $Cu(bta)_2H_2O$, obtained as blue crystals from $CuCl_2\cdot 2H_2O$ and benzotriazole in 7 *M* ammonia solution, has been shown to possess a polymeric structure (Fig. 8) with tetragonal–bipyramidal copper(II) centers linked by bridging benzotriazole and water ligands (*201*). A dihydrate $Cu(bta)_2\cdot 2H_2O$ has also been described (*42*). The adduct

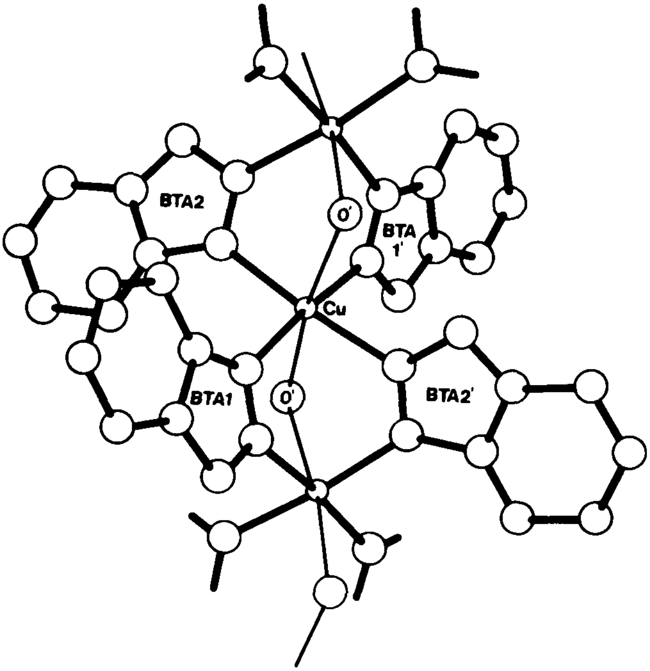
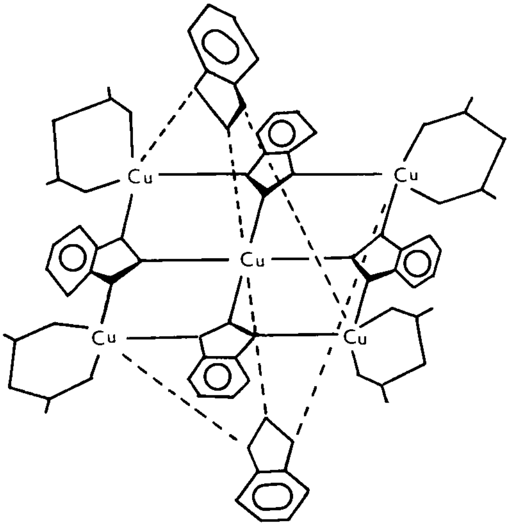


FIG. 8. Coordination about copper atoms in $[Cu(bta)_2(H_2O)]_n$.

$Cu(bta)_2$(*o*-phen)$_2$ has been obtained as green nodules by adding triethylamine to a blue solution of [Cu(*o*-phen)$_2$][BF_4]$_2$ and benzotriazole in methyl cyanide (*172*). Mixtures of $CuX_2 \cdot 2H_2O$ (X = Cl or Br) and benzotriazole in ethanol deposit green precipitates of stoichiometry CuX(bta) (*100, 172, 194*); an acetate, $Cu(O_2CMe)(bta)$, has also been reported (*42*). Under similar conditions $Cu(NO_3)_2 \cdot 3H_2O$, $Cu(BF_4)_2$, and $Cu(SO_4) \cdot 5H_2O$ afforded green $Cu_2(NO_3)_2(bta)_2(btaH)$, turquoise $Cu_2(bta)_3(BF_4)$, and dull green $Cu_2(SO_4)(bta)_2(btaH)$, respectively (*172*). A remarkable pentanuclear structure (**22**) has been proposed for the dark green copper(II) complex $Cu_5(bta)_6(acac)_4$ obtained from equimolar amounts of $Cu(NO_3)_2 \cdot 3H_2O$, acetylacetone, and benzotriazole in ammoniacal methanol or from $Cu(acac)_2$ and benzotriazole in dichloromethane solution (*131*). A closely related pentanuclear structure (Fig. 9) has been established by X-ray diffraction methods for the copper(I/II) complex $Cu_5(bta)_6(CNBu^t)_4$; the central copper(II) is octahedrally coordinated whereas the peripheral copper(I) ions are in an approximately tetrahedral environment (*92, 113*). The form of the



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copper(II) hyperfine structure in the EPR spectrum is consistent with the conclusion that the large Cu(II)–Cu(II) distance (12.858 Å) is sufficient to ensure that the effects of exchange interactions are virtually nonexistent and that electronic dipolar broadening is small

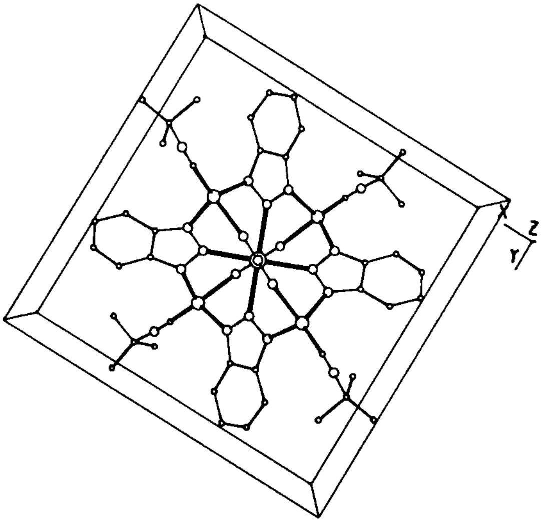


FIG. 9. Structure of $Cu_5(bta)_6(CNBu^t)_4$ viewed down a crystallographic $\bar{4}$ axis.

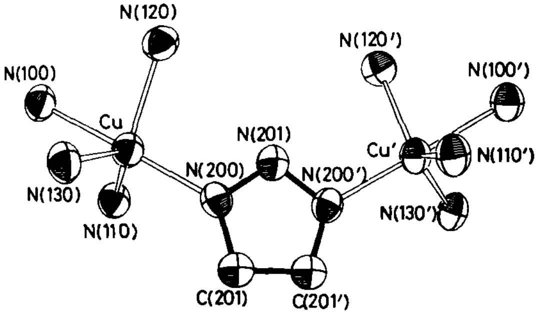


FIG. 10. Coordination geometry of the copper atoms in $[Cu_2(tmbma)_2(bta)][NO_3]_3$.

(*113*). Related complexes $Cu_5(bta)_6(RNC)_4$ ($R = c\text{-}C_6H_{11}$, Pr^i, and Ph) have also been studied by EPR methods (*10, 113*). Studies on models for superoxide dismutase have afforded a green binuclear copper complex $[Cu_2(\mu\text{-bta})(tmbma)_2][NO_3]_3$ [tmbma = tris(N^1-methylbenzimidazol-2-ylmethyl)amine] in which the copper centers [Cu···Cu = 5.536(2) Å] are linked by an N-1/N-3-bridging benzotriazolate ligand (Fig. 10) (*91*). Variable-temperature magnetic susceptibility measurements indicate antiferromagnetic interactions with J values of approximately -12 cm^{-1}. Q- and X-band EPR spectra show typical $S = 1$ signals (*91*). A more detailed single-crystal EPR study has established that even with a Cu···Cu distance of 5.536 Å an exchange contribution to the zero-field splitting is operative (*21*). An N,O-chelate structure (Fig. 11) has been

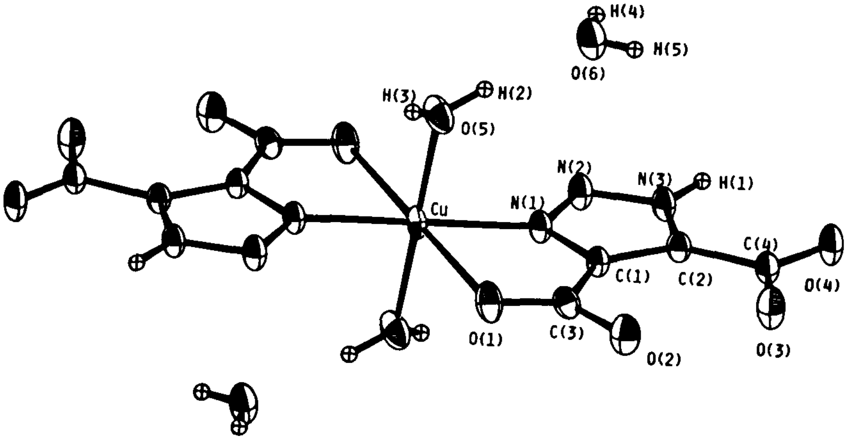
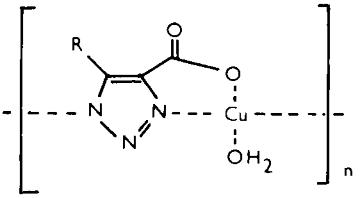


FIG. 11. ORTEP view of diaquabis(1,2,3-triazole-4,5-dicarboxylato)copper(II)dihydrate.



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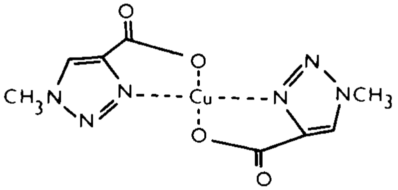

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found for the copper(II) derivative of 1,2,3-triazole-4,5-dicarboxylic acid; related structures **23** and **24** are proposed for complexes of 1,2,3-triazole-4-carboxylic acid and 1-methyl-1,2,3-triazole-4-carboxylic acid (*155*). A polymeric structure with the 8-azaguanine bridging by coordination through any two of the nitrogen atoms, N-3, N-7, or N-8, is proposed for Cu(8-azaguanine)$(OH)_2 \cdot 5H_2O$ (*108*). The reaction of 8-azaadenine with $CuCl_2$ in 0.36 *M* HCl is accompanied by ring opening at C-2, leading to formation of tetrachlorobis-2-[(5-amino-4-carboxamidinium)-1,2,3-triazole]copper(II) monohydrate, which has been shown to possess a tetragonally distorted structure (Fig. 12) with axial Cu–Cl (2.967 Å) and equatorial Cu–Cl and Cu–N distances of 2.258 and 2.049 Å, respectively (*167*). Copper(I) azides $Cu(N_3)(PPh_3)_2$ (*234*), $Cu_2(N_3)_2(dppe)_3$ (*234, 235*), and $Cu(N_3)$(*o*-phen)(PPh_3) (*121*) react with carbon disulfide to form N- or N,S-coordinated 5-thio-1,2,3,4-thiatriazolato complexes $Cu(CN_3S_2)(PPh_3)$, $Cu_2(CN_3S_2)_2(dppe)_3$, and $Cu(CN_3S_2)$(*o*-phen)(PPh_3), respectively, which undergo thermal or photolytic decomposition to the corresponding N thiocyanates.

Silver(I) salts of 1,2,3-triazole (*9*) and various substituted triazoles

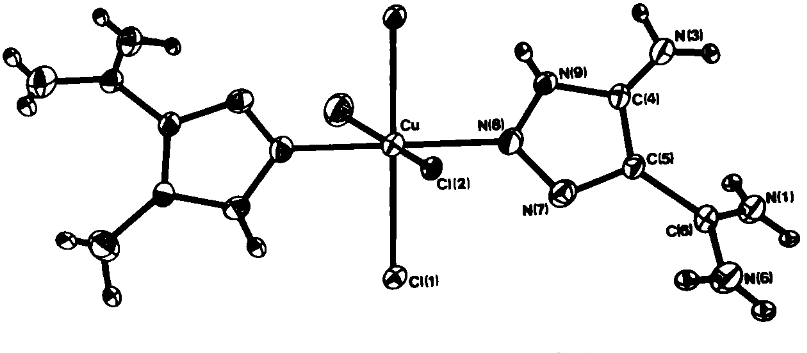
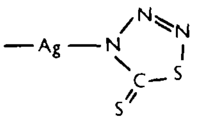


FIG. 12. View of tetrachlorobis-2-[(5-amino-4-carboxamidinium)[1,2,3]triazole]copper-(II) molecule.

(*8, 26, 82, 86, 207*) were reported by von Pechmann and others soon after the discovery of the parent compounds. Silver(I) benzotriazole derivatives include the salt Ag(bta) (*59, 206*) and the complex nitrate $[Ag(btaH)_2][NO_3]$ (*200*). A structure composed of alternate layers of two-coordinate $[Ag(btaH)_2]^+$ cations and NO_3^- anions has been established for the latter product (*200*). Benzotriazole (*44, 173, 206*) and 5-bromobenzotriazole (*206*) have been proposed as precipitants for silver(I). Silver(I) 5-thio-1,2,3,4-thiatriazolate has been isolated as a white, slightly photosensitive solid (*126*). 1,3-Dipolar addition of carbon disulfide to silver(I) azides $Ag(N_3)(PAr_3)_2$ affords 5-thio-1,2,3,4-thiatriazolate complexes $Ag(CN_3S_2)(PAr_3)_2$, which are thought to exist in two isomeric forms, structures **25** and **26** (*235*). A related gold(I) monophosphine derivative $Au(CN_3S_2)(PPh_3)$ has been similarly prepared (*235*). By comparison with the simple salts $M(CN_3S_2)$ ($M = Cu$, Ag, or Au) (*195*), these phosphine-containing complexes are relatively stable. The gold(I) complexes $AuCl(PPh_3)$ and $AuCl(SMe_2)$ react with benzotriazole in alcoholic KOH solution to yield $Au(bta)(PPh_3)$ and $\{Au(bta)\}_3$, respectively (*28, 135*). ^{197}Gold Mössbauer spectra for the latter product consist of a single doublet, indicating that the three gold atoms in each molecule are equivalent and thus favoring a symmetrical nine-membered ring structure with N-1/N-2-bridging benzotriazolate ligands (*107*). The azaguanine derivative $Au(azaguaninate)(PPh_3)$ has been similarly prepared (*29*). 8-Azahypoxanthine and 8-azaguanine adducts of gold(I) and gold(II) chlorides $AuCl(8\text{-azahypoxanthine})\text{-}H_2O$, $AuCl_3(8\text{-azahypoxanthine})$, and $AuCl_3(8\text{-azaguanine})$ have been synthesized and their infrared spectra reported (*108*).



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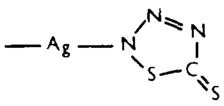

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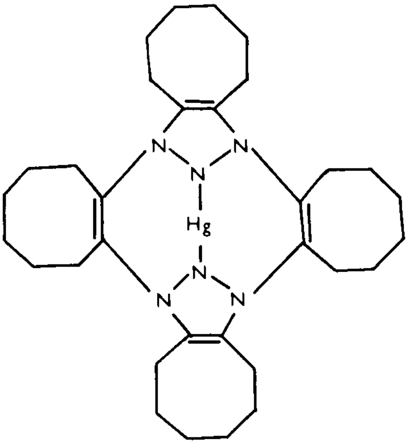
9. *Zinc, Cadmium, and Mercury*

The white crystalline adduct $ZnCl_2(btaH)_2$ (*191*) obtained by mixing the components in ethanol (*172*) or in aqueous HCl/NH_3 solution (*198*) has been shown to possess the expected tetrahedral structure with N-3-coordinated benzotriazole ligands (*198*). The same components react together in 7 *M* ammonia solution to afford colorless, polymeric

$[Zn_2(bta)_4]_n$ in which tetrahedral Zn^{II} centers are linked by N-1/N-3 benzotriazolate bridges (*198*). The salt $[btaH_2]_2[ZnCl_4]$, obtained from $ZnCl_2$ and benzotriazole in 2 *M* HCl solution, is isostructural with the corresponding cobalt salt (see p. 187) (*198*). Complex formation between 5-thio-1,2,3,4-thiatriazolate anions and Zn(II) or Cd(II) has been studied by potentiometric (*149*) and polarographic (*148*) methods.

Cadmium dichloride is reported to form a 1:1 adduct with benzotriazole in aqueous ethanol (*172*). However, a colorless 1:2 adduct $[CdCl_2(btaH)_2]_n$ has recently been obtained by a similar procedure and shown to possess an infinite $>CdCl_2CdCl_2Cd<$ ribbon structure, with octahedral coordination about each cadmium completed by N-3-coordinated benzotriazole ligands (see Mn^{II} analog, p. 181) (*198*). Under their original formulation as salts of azidodithiocarbonic acid (HS_2CN_3), 5-thio-1,2,3,4-thiatriazolate derivatives of cadmium $Cd(CN_3S_2)_2 \cdot 2H_2O$, mercury(I) $Hg(CN_3S_2)$, and mercury(II) $Hg(CN_3S_2)_2$ have been synthesized and found to be shock sensitive (*195*).

A chloride-bridged structure has been proposed for the 1:1 adduct, $[HgCl_2(btaH)]_2$ (*172*). Mercury(II) benzotriazolate, $Hg(bta)_2$, has been obtained from mercury(II) perchlorate, benzotriazole, and triethylamine in ethanol (*172*), and from mercuric oxide and benzotriazole (*158*). Mercuric acetate and chloride react with benzotriazole to form mixed mercury(II) salts, HgX(bta) (X = $MeCO_2$ or Cl) (*139*). A dimeric structure (Fig. 13) with T-shaped coordination at mercury has been determined by X-ray diffraction methods (*203*) for the methyl derivative Hg(Me)(bta) (*172*). Cyclooctane-1,2-dione dihydrazide reacts with HgO



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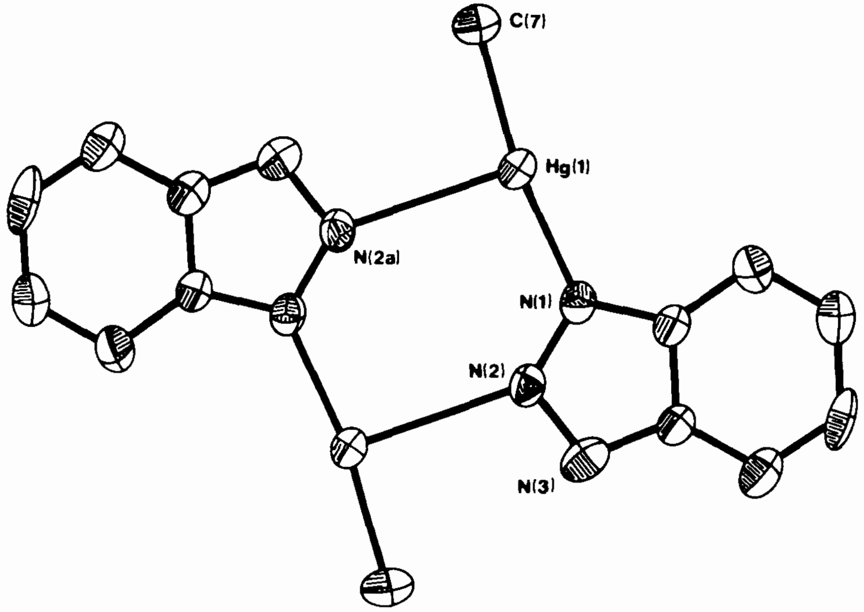
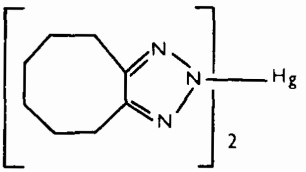


FIG. 13. ORTEP view of centrosymmetric $[HgMe(bta)]_2$ dimer.

to form the product, **27**, which is converted by aqueous HCl into the N-2-coordinated cyclooctane triazolate complexes, **28** and **29** (*139*).



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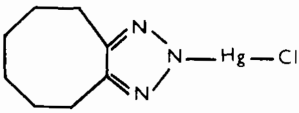

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A series of papers by Hodgson and co-workers describe the synthesis and structural characterization of zinc, cadmium, and mercury derivatives of the 8-azapurines—8-azaadenine and 8-azahypoxanthine. Coordination through N-3 occurs in the 8-azaadenine complexes $ZnCl_3$(8-azaadeninium) (Fig. 14) (*166*) and $HgCl_2$(8-azaadenine)$_2$ (Fig. 15) (*85*), but through N-7 and N-9 in Cd(8-azahypoxanthinato)$_2$(H_2O)$_4$ (Fig. 16) (*165*) and Hg(8-azahypoxanthinato)$_2$(H_2O)$_4$ (Fig. 17) (*85*), respectively. An 8-azaadenine adduct of zinc chloride, $ZnCl_2$(8-azaadenine)·$2H_2O$, has also been reported (*108*). X-Ray diffraction

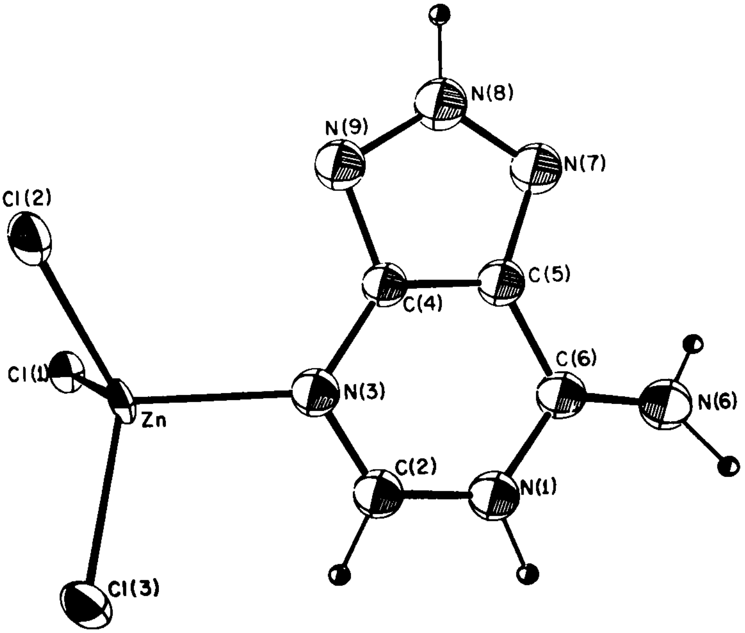


FIG. 14. View of a single molecule of trichloro(8-azaadeninium)zinc(II).

studies on four complexes isolated from the reaction of methylmercury(II) hydroxide with 8-azaadenine (Scheme 2) reveal MeHg groups bound at N-1, N-3, and N-9 as well as at the primary (N-6) metal coordination site (*192*).

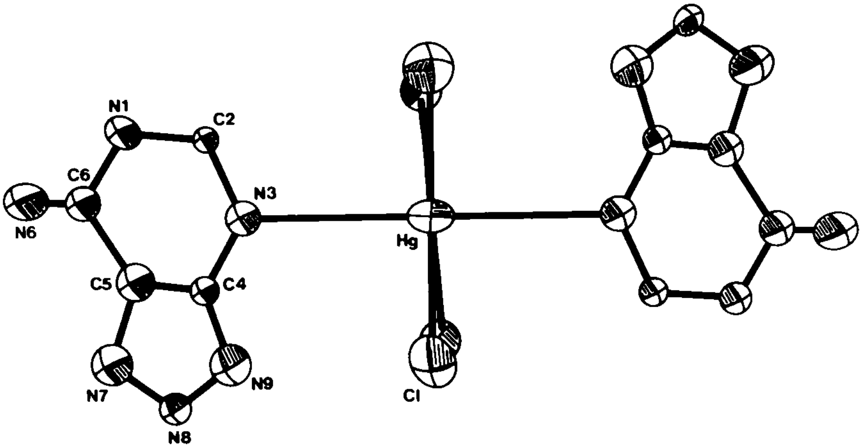


FIG. 15. View of coordination about mercury in dichlorobis(8-azaadenine)mercury(II).

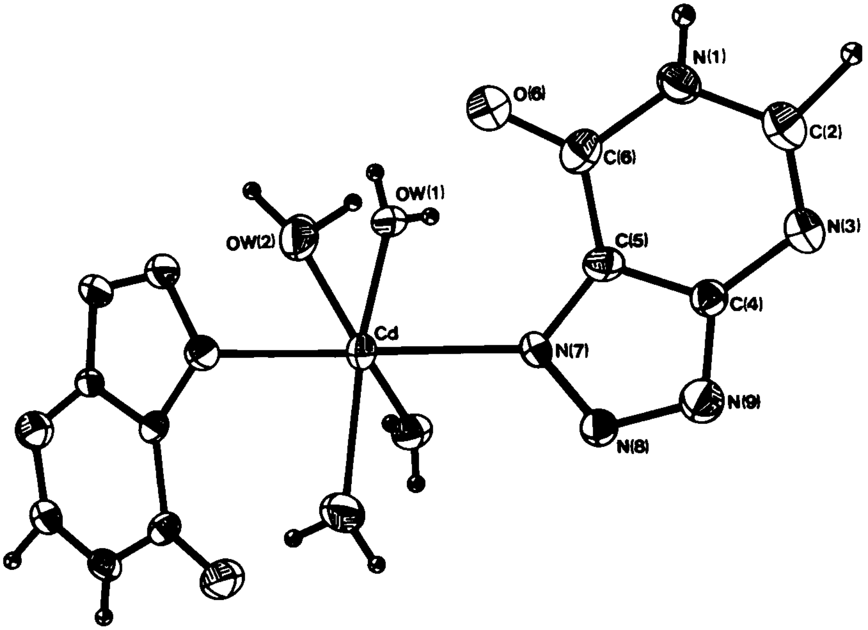


FIG. 16. View of the coordination about cadmium in tetraaquabis(8-azahypoxanthinato)cadmium(II).

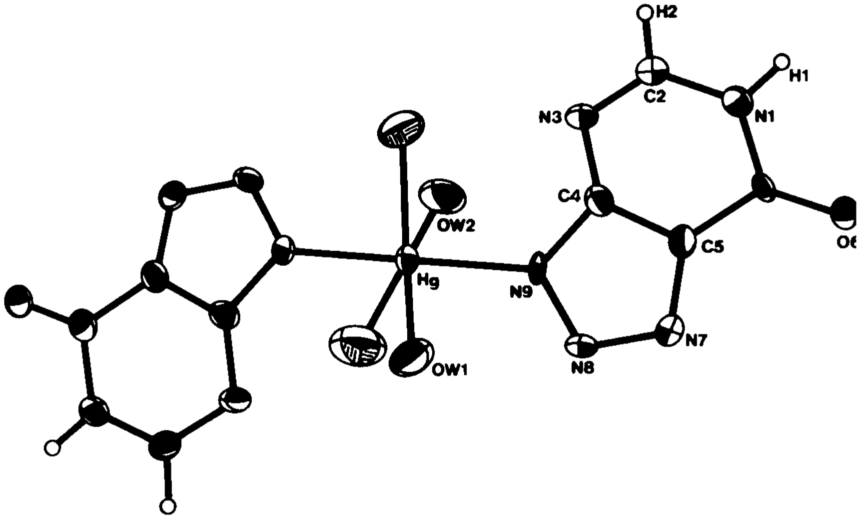
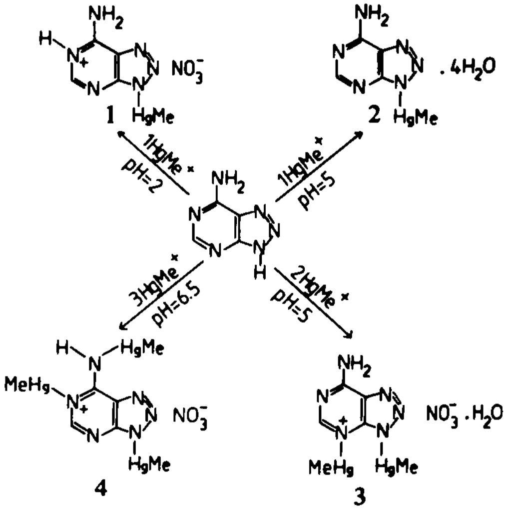


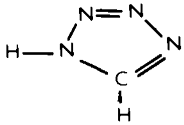
FIG. 17. View of the coordination about mercury in tetraaquabis(8-azahypoxanthinato)mercury(II).



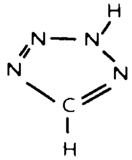
SCHEME 2. Reactions between methylmercury(II) hydroxide and 8-azaadenine.

III. Tetrazole and Tetrazolate Complexes

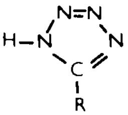
In this section ligands containing the tetrazole ring system are considered. These include the parent tetrazole, various nitrogen- and/or carbon-substituted tetrazoles, 1,5-pentamethylenetetrazole, and the cyclized tautomer of 2-azidopyridine. Although a few examples are mentioned in passing, thiones such as 1,2,3,4-tetrazoline-5-thione and dehydrodithione are generally excluded since they most commonly function as sulfur donors and because they have recently been extensively covered in a review by Raper (*168*) dealing with heterocyclic thione donors. Substituted tetrazoles were first prepared in 1885 by Bladin (*24*), who went on to isolate the parent tetrazole and a series of silver salts in 1892 (*25*). Tetrazoles are quite strong acids; the parent tetrazole has a pK_a value of $\sim$4.8 (*134*), similar to that of acetic acid, and readily forms salts with transition metal ions. Tetrazolate salts and complexes are frequently heat and shock sensitive, and several have found commercial use as explosives or detonators. The parent tetrazole exists in two tautomeric forms (structures **30a** and **30b**), of which the 1H form (structure **30a**) is dominant. Monosubstituted tetrazoles exist in three isomeric forms (structures **31**, **32**, and **33**) with substituents on carbon, nitrogen-1, and nitrogen-2, respectively. The carbon-substituted forms, like the parent, exist as tautomeric mixtures of 1H



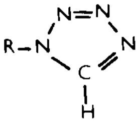
30a



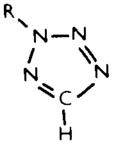
30b



31

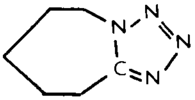


32



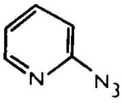
33

and 2H forms. In addition to simple alkyl and aryl groups, substituents include a variety of functional groups, notably CF_3, halide, NH_2, CN, $CONH_2$, and COOH. Disubstituted tetrazoles, which lack an acidic proton and can only coordinate as neutral molecules, are characterized by rather weak base strength (*162*). Examples include the 1,5-polymethylenetetrazoles, of which 1,5-pentamethylenetetrazole (structure **34**) is the most important example, and 2-azidopyridine

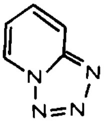


34

(structure **35a**), which coordinates as the cyclized tautomer, structure **35b**. 1,5-Pentamethylenetetrazole (metrazole or cardiazole), first reported by Schmidt in 1925 (*189*), has important medicinal uses as a

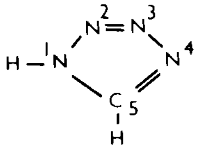


35a



35b

stimulant for the central nervous system; its coordination chemistry was reviewed in 1969 (*162*). Early work on the synthesis and properties of tetrazoles has been summarized in a review by F. R. Benson (*22*). The generally accepted numbering scheme for tetrazoles which is used throughout this section is given in structure **36**. Abbreviations employed for the various ligands are tetrazole (ttaH), tetrazolate anion (tta), 1,5-pentamethylenetetrazole (1,5-pmtta), and the cyclic form of 2-azidopyridine (pytta).

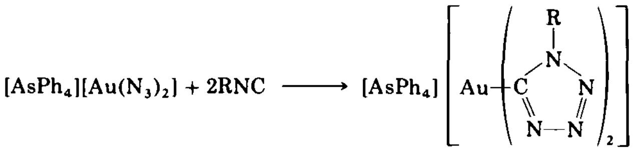


36

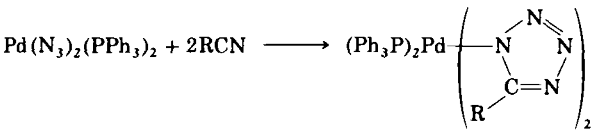
A. SYNTHESIS

Tetrazoles combine readily with transition metal halides to form adducts, many of which are polymeric and deposit from solution as insoluble precipitates (*32, 50, 73, 83*). Reactions between hydrated metal perchlorates or tetrafluoroborates and tetrazoles—1,5-pentamethylenetetrazole and 1- or 2-substituted tetrazoles—usually in the presence of a dehydrating agent, lead to formation of the complex salts $[M(1,5\text{-pmtta})_6][Y]_2$, $[M(1\text{-R-ttaH})_6][Y]_2$, and $[M(2\text{-R-ttaH})_6][Y]_2$ ($M = Mn, Fe, Co, Ni, Cu$, or Zn; $Y = ClO_4$ or BF_4) (*51, 70, 213*). Tetrazole complexes of chromium, molybdenum, and tungsten have been obtained by thermal or photolytic displacement of CO or weakly coordinated MeCN and THF ligands from the hexacarbonyls and their substitution products (*79, 80, 160, 220*). Complex formation between transition metal carbonyls or halides and 2-azidopyridine is accompanied by cyclization of the ligand to the tetrazole form (*160*). Tetrazole and 5-substituted tetrazoles are acidic and readily form alkali metal salts which react with transition metal halides to form tetrazolate complexes (*18, 204*). The latter products can frequently be obtained directly by treatment of the metal salts with the free tetrazole in the presence of base, usually hydrazine (*141*), triethylamine (*172*), or potassium hydroxide (*136*). In some instances the use of added base is unnecessary (*69, 77, 119*). Salts of 1- or 2-substituted tetrazoles, prepared from the free tetrazoles and lithium alkyls, also react with transition metal halides to afford tetrazolate complexes (*75*).

Reactions between 5-cyanotetrazole and transition metals, when performed in boiling acetone, lead to hydrolysis of the cyano group and formation of 5-carbamyl tetrazolate complexes (*68*). Complexes containing 1- or 5-substituted tetrazolate anions can also be obtained by 1,3-dipolar cycloaddition of organic isonitriles (RNC) (*15*) or nitriles (RCN) (*61*), respectively, to coordinated azide ligands [Eqs. (3) and (4)].



(3)



(4)

Alternatively, the azide anion can be added to coordinated organic isonitrile (*211*) or nitrile (*60*) ligands to give the same products. Coordination of RCN ligands greatly increases their susceptibility to attack by azide anions; reactions typically go to completion in 15 minutes at 25°C (*60*).

B. Structural Properties

Early workers, noting the isoelectronic nature of tetrazolate and cyclopentadienide anions, looked for evidence of structures containing η^5-tetrazolate ligands. Initial claims of success (*89*) were later withdrawn (*90*) and to date all established structures involve localized M–N bonds between metal centers and tetrazoles or tetrazolate anions. However, η^5-coordinated tetrazolate ligands have been proposed as intermediates in the N-1 to N-2 isomerization of some cobalt(III) tetrazolate complexes (*164*). Choice of coordination positions on the tetrazole rings is governed by electronic and steric considerations, which in turn are dictated by the nature and position of the substituent groups on the rings. Although complexes containing the parent tetrazole (ttaH) and tetrazolate anion (tta^-) are known, there is very little firm evidence concerning the point of coordination of these ligands. 1-Substituted tetrazoles are thought to coordinate through the N-4 position (*70*) and this arrangement has been confirmed by X-ray diffraction methods for $ZnCl_2(1\text{-Me-ttaH})_2$ (*6*). The triple tetrazole bridges in the complexes $(OC)_3Mo(\mu\text{-1-R-ttaH})_3Mo(CO)_3$ (R = Me, cyclohexyl) are thought to involve N-3/N-4 coordination (*74*). 1-Substituted tetrazolate anions, which are usually formed *in situ* by the interaction of azide and isocyanide groups, must coordinate through the ring carbon (*15, 65*) and this mode of bonding has been confirmed for $[AsPh_4][Au(1\text{-}Pr^i\text{-tta})_4]$ by diffraction methods (*66*). Relatively little is known about the coordination preferences of 2-substituted tetrazoles and tetrazolate anions. However, an X-ray diffraction study on the complex salt $[Ni(2\text{-Me-ttaH})_6][BF_4]_2$ has established N-4 coordination for the 2-methyltetrazole ligands (*213*).

There also appears to be very little hard evidence concerning the coordination sites on 5-substituted tetrazoles. However, much is known about structures of complexes containing 5-substituted tetrazolate anions. Molecular orbital calculations indicate that N-1 and N-2 coordination arrangements are virtually equivalent electronically and energetically (*109, 141*), with perhaps a slight preference for N-1 coordination (*204*). However, steric factors favor N-2 coordination particularly if the ring substituent is large or the coordination site is crowded. Thus X-ray diffraction studies reveal N-1 coordination for square-planar *cis*-$Pd(5\text{-Me-tta})_2(PMe_2Ph)_2$ (*4*) but N-2 coordination for *trans*-$Pd(5\text{-Ph-tta})_2(PPh_3)_2$ (*115*) and several octahedral cobalt(III) complexes, including $[Co(5\text{-Me-tta})(NH_3)_5][ClO_4]_2$ (*157*) and $[Co(5\text{-CN-tta})(NH_3)_5][ClO_4]_2$ (*84*), where the coordination sphere is more congested. In several instances syntheses afford mixtures of N-1- and N-2-coordinated linkage isomers (*141*) and in others N-1 → N-2 isomerizations are observed (*60, 164*). Structures involving bridging through the least sterically hindered N-2 and N-3 positions of the 5-Ar-tta^- ligands have been proposed for a series of polymeric 5-aryl tetrazolate complexes of iron (*176*), cobalt (*177*), and nickel (*175*), and a structure of this type has been confirmed by X-ray diffraction methods for the binuclear silver(I) complex $[Ag(5\text{-CF}_3\text{-tta})(PPh_3)_2]_2$ (*159*). The N-3 site is the least sterically hindered coordination point on the 1,5-pentamethylenetetrazole ligand (*51*) and is likely to be the one used in the crowded octahedral complex cations $[M(1,5\text{-pmtta})_6]^{2+}$. However, an X-ray diffraction study has established N-4 coordination for the monodentate 1,5-pmtta ligands in the binuclear complex $[Ag(NO_3)(1,5\text{-pmtta})_2]_2$ (*27*). The bridging 1,5-pmtta ligands in the same complex are coordinated through N-3 and N-4 positions (*27*). For complexes of 2-azidopyridine (*160*), coordination at the N-3 position on the cyclized ligand seems probable on steric grounds.

Generally monodentate N-1-, N-2-, or C-5-coordinated tetrazolate anions appear to adopt planar, regular pentagonal structures with

TABLE III

X-RAY DIFFRACTION STUDIES ON TETRAZOLE AND TETRAZOLATE COMPLEXES

Complex	Tetrazole- and tetrazolate-bonding mode	Reference
	Tetrazole Complexes	
$[Ni(2\text{-}Me\text{-}ttaH)_6][BF_4]_2$	Monodentate/N-4	*213*
$[Cu(1\text{-}Me\text{-}ttaH)_6][BF_4]_2$	Monodentate/N-4	*220a*
$\{Ag(NO_3)(1,5\text{-}pmtta)_2\}_2$	Monodentate/N-4; bridging/N-3/N-4	*27*
$ZnCl_2(1\text{-}Me\text{-}ttaH)_2$	Monodentate/N-4	*6*
	Tetrazolate Complexes	
$Ni(5\text{-}O_2N\text{-}tta)_2(H_2O)_4$	Monodentate/N-2	*43a*
$[Co(5\text{-}Me\text{-}tta)(NH_3)_5][ClO_4]_2$	Monodentate/N-2	*67* *157*
$[Co(5\text{-}CN\text{-}tta)(NH_3)_5][ClO_4]_2$	Monodentate/N-2	*84*
$[Co(5\text{-}R\text{-}tta)(NH_3)_5][Br]_2$ ($R = NH_2—C{=}NH$)	Chelate/N-1, =NH	*84*
$Co(5\text{-}CF_3\text{-}tta)(dmg)_2(PBu^n_3)$	Monodentate/N-2	*204*
cis-$Pd(5\text{-}Me\text{-}tta)_2(PPhMe_2)_2$	Monodentate/N-1	*4*
trans-$Pd(5\text{-}Ph\text{-}tta)_2(PPh_3)_2$	Monodentate/N-2	*115*
$Cu_2(5\text{-}CF_3\text{-}tta)_2(dppe)_3$	Monodentate/N-2	*81*
$\{Ag(5\text{-}CF_3\text{-}tta)(PPh_3)_2\}_2$	Bridging/N-3/N-4	*159*
$[AsPh_4][Au(1\text{-}Pr^i\text{-}tta)_4]$	Monodentate/C-5	*66*

mean bond lengths of ~1.32 Å, indicating extensive electron delocalization within the ring (*4, 66, 204*). However, the complexes $Cu_2(5\text{-}CF_3\text{-}tta)_2(dppe)_3$ (*81*) and $\{Ag(5\text{-}CF_3\text{-}tta)(PPh_3)_2\}_2$ (*159*) contain monodentate and bridging tetrazolate ligands, respectively, in which there are significant variations in interatomic distances within the rings. Metal–carbon and metal–nitrogen bond lengths are consistent with the presence of single metal–ligand σ bonds (*66*).

A list of crystallographically determined structures containing coordinated tetrazole moieties is given in Table III.

C. SPECTROSCOPIC STUDIES

1. *Vibrational Spectra*

Infrared spectra have been recorded for the parent tetrazole (ttaH), its sodium salt, and a range of transition metal derivatives (*94*). In subsequent work the infrared spectra of sodium tetrazolate and of the copper complex $Cu(tta)_2 \cdot H_2O$ were assigned and a vibrational analysis was reported for the tetrazolate anion (*77*). Infrared data have been assigned for 1-methyltetrazole, its lithium salt, and the nickel(II) complex, Ni(1-Me-tta)$_2$; ν(Ni–C) and ν(Ni–N) occur at 456 and 298 cm^{-1}, respectively (*76*). Characteristic infrared frequencies have been recorded for 1-substituted tetrazolate ligands in a range of palladium, platinum, and gold complexes (*15*). Vibrational spectra have been recorded and assigned for a series of alkyltetrazole complex salts [M(1-R-ttaH)$_6$][BF$_4$]$_2$ (M = Mn, Co, Ni, Cu, and Zn) (*70, 138*) and adducts CuX$_2$(1 or 2-R-ttaH)$_2$ (X = Cl, NCS) (*50a*). Bands assigned to ν(M–N) follow the expected Irving–Williams sequence (*70*). Infrared spectra (4000–200 cm^{-1}) have been recorded and assigned for 1-alkyltetrazoles and the complex iron(II) cations, [Fe(1-R-ttaH)$_6$]$^{2+}$, including high- and low-spin forms of [Fe(1-Pr-ttaH)$_6$][BF$_4$]$_2$ (*71*). Similar data have been reported for 5-phenyltetrazole, its sodium salt, and complexes with chromium(III), cobalt(II), nickel(II), copper(II), and zinc(II); assignments are given for the free tetrazole and the sodium salt (*119*). The presence of a band at ~1250 cm^{-1}, arising from bending of an unsubstituted =N—N=N— group, is reported to be a diagnostic test for N-1 coordination of 5-R-tta$^-$ ligands (*87*). The infrared spectra of 5-aminotetrazole, its sodium salt, and a copper(II) derivative have been recorded and assigned (*36, 103*). Bi- and tridentate bonding modes have been proposed on the basis of infrared data for 5-cyanotetrazolate ligands in the complexes M(5-CN-tta)$_2$·3H$_2$O and M(5-CN-tta)$_2$(5-CN-ttaH)·2H$_2$O (M = Fe, Co, Ni, and Cu) (*69*). Infrared data have been tabulated for sodium salts and iron(II) complexes of the 5-substituted tetrazolate anions, 5-R-tta$^-$ (R = Cl, NO$_2$, or CF$_3$) (*89*). Vibrational spectra (5000–180 cm^{-1}) have been reported for a range of 1,5-pentamethylenetetrazole complex salts [M(1,5-pmtta)$_6$][ClO$_4$]$_2$ (M = Mn, Fe, Co, Ni, Cu, and Zn), [Cu(1,5-pmtta)$_4$][ClO$_4$]$_2$, and [Cu(1,5-pmtta)$_2$]-[ClO$_4$] (*51, 53*). Similar data have been recorded for the free 1,5-pmtta ligand and its silver(I) complex [Ag(1,5-pmtta)$_2$][NO$_3$] (*163*).

Far infrared data have been reported and ν(M–N) frequencies assigned for a variety of cobalt, nickel, copper, zinc, cadmium, and mercury tetrazolate complexes (*153*). An inverse relationship between the basicity of the tetrazolate anions and the values of ν(M–N) has been interpreted as evidence of significant M → L π bonding (*153*).

The complexes *cis*-Pd(5-CF$_3$-tta)$_2$(PR$_3$)$_2$ show ν(Pd–N) and ν(Pd–P) absorptions in the ranges 300–380 and 370–460 cm^{-1}, respectively (*170*).

2. *Electronic Spectra*

High D_q values, comparable with those of 2,2′-dipyridyl, found for the complex cations [M(1-R-ttaH)$_6$]$^{2+}$ indicate very high ligand-field strengths for monodentate 1-alkyltetrazoles (*70*). The iron(II) spin crossover compound $[Fe(1\text{-}Pr\text{-}ttaH)_6][BF_4]_2$ has been particularly thoroughly investigated (*49, 71*). The thermally induced high-spin ($^5T_{2g}$) to low-spin ($^1A_{1g}$) transition and the phenomenon of light-induced excited state spin state trapping have been followed and analyzed using data from single-crystal spectra measured between room temperature and 8 K (*49, 90a*). Similar behavior has been noted for the mixed crystals $[Zn_{1-x}Fe_x(1\text{-}Pr\text{-}ttaH)_6][BF_4]_2$ (*90a*). The D_q values of 806 and 833 cm^{-1} reported for 1-methyl and 1-cyclohexyl tetrazolate anions in the nickel(II) complexes $Ni(1\text{-}R\text{-}tta)_2$ are less than the values for H_2O and NH_3 in $[Ni(H_2O)_6]^{2+}$ and $[Ni(NH_3)_6]^{2+}$, respectively (*76*). However, a D_q value of 1140 cm^{-1} found for $Ni(5\text{-}CF_3\text{-}tta)_2 \cdot 4H_2O$ places the 5-trifluoromethyl tetrazolate anion above NH_3 in the spectrochemical series (*90*). 5-Phenyl and 5-benzyl tetrazolate anions are similar in ligand-field strength (*119*). Electronic spectra have been recorded and assigned for copper(II) complexes with a variety of 5-substituted tetrazolate anions (*119*). The D_q values of 2203 and 2257 cm^{-1} calculated for N-1- and N-2-coordinated isomers of $[Co(5\text{-}Me\text{-}tta)(NH_3)_5][ClO_4]_2$ appear to confirm that, although the nitrogen N-1 of tetrazolate anions is more nucleophilic than nitrogen N-2 (*204*), steric hindrance at the N-1 position arising from the presence of the 5-methyl substituent favors N-2 coordination (*87*).

Electronic spectra have been recorded for the 1,5-pentamethylenetetrazole adducts $MX_2(1,5\text{-}pmtta)$ (M = Mn, Fe, Co, Ni, and Cu; X = Cl and Br) (*32*) and for the complex salts $[M(1,5\text{-}pmtta)_6][ClO_4]_2$ (M = Fe, Co, Ni, and Cu) (*51, 52*). Data for the complex salts indicate that 1,5-pentamethylenetetrazole is a stronger ligand than ethylenediamine in the nickel(II) system but only slightly stronger than water in cobalt(II) complexes (*51*).

3. Nuclear Magnetic Resonance Spectra

The isomeric purity of the N-2-coordinated cobalt(III) tetrazolate complexes $Co(5\text{-}R\text{-}tta)(dmg)_2(PR'_3)$ has been confirmed by ^1H, ^{13}C, ^{19}F, and $^{31}P\{^1H\}$ NMR. Evidence of interannular conjugation, implying coplanarity of aryl and tetrazolate rings, is provided by the proton NMR spectra of the aryl tetrazolate derivatives $Co(5\text{-}Ar\text{-}tta)(dmg)_2(PR'_3)$ (Ar = Ph,3-FC_6H_4, and 4-FC_6H_4) (*204*). The N-2-coordinated complexes $[Co(5\text{-}R\text{-}tta)(NH_3)_5][ClO_4]_2$ have been characterized by ^1H, ^{13}C, and ^{15}N NMR using samples enriched selectively at each ring position (*7*). Formation and interconversion of N-1- and N-2-coordinated isomers of the palladium and platinum complexes $M(5\text{-}R\text{-}tta)_2(PR'_3)_2$

and $PtH(5\text{-}R\text{-}tta)(PR'_3)_2$ ($R = Me$ or CF_3) have been investigated by ^1H and ^{19}F NMR (*141, 170*).

4. *Electron Paramagnetic Resonance Spectra*

EPR data have been reported for 5-aryl tetrazolate salts of copper(II); $\langle g \rangle$ values are in the range 2.12–2.15 and the $g_\perp$ and $g_\parallel$ values are similar to those recorded for copper(II) complexes of other N donors. Related cobalt and nickel complexes gave complex or unresolved spectra (*119*). EPR data have been analyzed for the complex salts $[Mn(1,5\text{-pmtta})_6][ClO_4]_2$ and $[Cu(1,5\text{-pmtta})_n][ClO_4]_2$ ($n = 4$ and 6). For the copper complexes, copper and nitrogen hyperfine splittings were observed (*118*).

An electron spin resonance study (4–300 K) of $[Cu(1\text{-Me-ttaH})_6][BF_4]_2$ reveals that the two crystallographically inequivalent Cu(II) sites are subject to different Jahn–Teller effects arising from differences in the symmetries of the two sites (*220a*).

5. *Mössbauer Spectra*

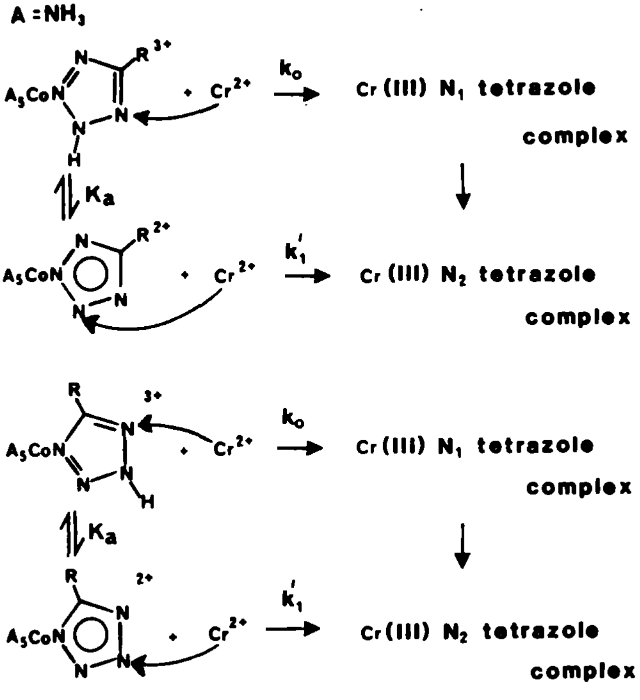
The ^{57}Fe Mössbauer spectra of the iron(II) spin-crossover complex $[Fe(1\text{-Pr-ttaH})_6][BF_4]_2$ have been recorded; the high-spin form shows a quadrupole doublet at room temperature, the low-spin form generates a single-line spectrum. Similar data have been obtained using other 1-alkyl tetrazoles (*138*). The absence of quadrupole splitting and the small isomer shift observed in the Mössbauer spectra of the iron(II) complexes $Fe(5\text{-}R\text{-}tta)_2 2H_2O$ ($R = CF_3$, Cl, or NO_2) were originally interpreted as evidence of a sandwich structure with metal–ligand π bonding (*89*). ^{197}Gold Mössbauer isomer shifts for $[AsPh_4][Au(1\text{-Cy-tta})_4]$ and $[AsPh_4][Au(1\text{-Cy-tta})_2]$ occur at the very low end of the scale, near those found for gold halogen complexes and far below those recorded for gold cyanide and methyl complexes. These results suggest that, unlike cyanide and methyl groups, C-bonded tetrazolate anions are poor σ donors and do not participate to any great extent in metal to ligand π bonding (*11*).

D. GROUP SURVEY

To date no tetrazole complexes appear to have been reported for the following triads: scandium, yttrium, and lanthanum; titanium, zirconium, and hafnium; and vanadium, niobium, and tantalum.

1. Chromium, Molybdenum, and Tungsten

The air- and moisture-sensitive light blue-green paramagnetic ($\mu_{\text{eff}} = 4.55$ BM) 1,5-pentamethylenetetrazole adduct, $CrCl_2$(1,5-pmtta)$_2$, obtained from the free ligand and anhydrous $CrCl_2$, is oxidized to chromium(III) chloride even in dry air (*32*). Reactions of chromium(III) perchlorate with sodium salts of 5-aryltetrazoles afford chromium(III) products Cr(5-Ar-tta)$_2$(OH)·4H_2O. Magnetic moments (3.06–5.33 BM), electronic spectra, and EPR data are consistent with the presence of octahedral chromium(III) ions (*119*). Ligand substitution reactions of $Cr(CO)_6$ and $Cr(CO)_5$(THF) afford Cr(5-Ph-ttaH)$(CO)_5$ (*220*), Cr(1-Ph-ttaH)$(CO)_5$ and Cr(1-Ph-ttaH)$_2(CO)_4$ (*79*), and Cr(pytta)$(CO)_5$ (*160*). Chromium(III) tetrazolate complexes, [Cr(5-R-tta)$(H_2O)_5$][ClO_4]$_2$, are formed when the cobalt(III) complexes [Co(5-R-tta)$(NH_3)_5$][ClO_4]$_2$ are reduced by $[Cr(H_2O)_6]^{2+}$ (Scheme 3) (*7*). An attempt to prepare η^5-tetrazole complexes by treatment of *fac*-Mo(CO)$_3$(MeCN)$_3$ with 1-aryl- or 1-alkyltetrazoles, 1-R-ttaH (R = Me, Cy, or Ph), gave instead the



SCHEME 3. Mechanisms for reduction of N-1- and N-2-coordinated tetrazolate complexes [Co(5-R-tta)$(NH_3)_5$][ClO_4]$_2$ by chromium(II).

tetrazole-bridged binuclear complexes $(OC)_3Mo(1\text{-}R\text{-}ttaH)_3Mo(CO)_3$; a mononuclear product, $Mo(CO)_3(1\text{-}Ph\text{-}ttaH)_3$, was also described (*74*). The photolytic reaction of $W(CO)_6$ with 1-phenyltetrazole yields $W(1\text{-}Ph\text{-}ttaH)(CO)_5$ and $W(1\text{-}Ph\text{-}ttaH)_2(CO)_4$ (*79, 80*). The carbonyls $M(CO)_6$ (M = Cr, Mo, or W) react with sodium tetrazolates Na[5-R-tta] to afford the salts $Na[M(5\text{-}R\text{-}tta)(CO)_5]$ ($R = CF_3$, MeS, or Ph) (*220*). The reaction of 2-azidopyridine with $W(CO)_5THF$ is accompanied by cyclization of the ligand to yield the pyridinotetrazole complex $W(CO)_5(pytta)$ (*160*).

2. *Manganese, Technetium, and Rhenium*

Salts $[Mn(1\text{-}R\text{-}ttaH)_6][BF_4]_2$ have been isolated by treatment of $Mn(BF_4)_2$ with the free tetrazoles, 1-R-ttaH (R = Me, Et, or Pr^i) (*70*); the related pentamethylenetetrazole derivative, $[Mn(pmtta)_6][ClO_4]_2$, is similarly obtained from the free ligand and anhydrous manganese perchlorate (*51*). The latter product has a magnetic moment μ_{eff} = 5.90 BM (*51*) and displays an EPR spectrum indicative of almost regular octahedral symmetry and highly ionic (91%) metal–ligand bonds (*118*). Far infrared bands at approximately 302–285 and 238–198 cm^{-1} have been assigned to M–L stretch and L–M–L deformation modes, respectively (*53*). The stable, isolable adducts $MnX_2(pmtta)$ display electronic spectra and magnetic data ($\mu_{eff} = \sim 5.5$ BM) consistent with octahedral coordination and presumably possess polymeric structures with bridging halide (X = Cl or Br) and/or pentamethylenetetrazole ligands (*32*). The 1:2 adduct obtained from $MnCl_2$ and 2-azidopyridine contains the cyclized (tetrazole) form of the ligand (*160*). The 5-cyanotetrazole complexes $Mn(5\text{-}CN\text{-}tta)_2 \cdot 2H_2O$ and $Mn(5\text{-}CN\text{-}tta)_2(5\text{-}CN\text{-}ttaH) \cdot 2H_2O$ are both thought to contain octahedral MnN_6 chromophores with the tetrazole functioning as a bridging bi- or tridentate ligand (*69*). Reactions of manganese(II) salts with 5-cyanotetrazole in acetone gave the 5-carbamyltetrazole derivatives $Mn\{5\text{-}NH_2 \cdot C(O)\text{-}tta\}_2$ and $Mn\{5\text{-}NH_2 \cdot C(O)\text{-}tta\}_2 \cdot 2H_2O$ (*68*).

To date no tetrazole complexes of technetium and rhenium have been reported.

3. *Iron, Ruthenium, and Osmium*

Ferrous tetrafluoroborate reacts with 1-alkyltetrazoles, 1-R-ttaH (R = Me, Et, Pr^n, or Pr^i), to yield octahedral iron(II) salts $[Fe(1\text{-}R\text{-}ttaH)_6][BF_4]_2$, which undergo reversible transitions from white, high-spin ($^5T_{2g}$) to purple, low-spin ($^1A_{1g}$) form at temperatures ranging from

140 to 80 K (*71*). Variable-temperature Mössbauer, magnetic susceptibility, and far infrared studies have been reported for these salts and have shown that the spin transition in the *n*-propyltetrazole derivative induces a first-order phase transition with structural reordering in the vicinity of the iron centers (*138*). The phenomena of thermally induced spin transition and light-induced excited state spin trapping in $[Fe(1\text{-}Pr^n\text{-}ttaH)_6][BF_4]_2$ have been investigated by single-crystal optical absorption spectroscopy. The magnetic susceptibility of the light-induced high-spin state has been measured (*49*). Dehydration of ferrous perchlorate by 2,2-dimethoxypropane in the presence of pentamethylenetetrazole affords the related salt $[Fe(pmtta)_6][ClO_4]_2$ (*51*), for which the magnetic moment ($\mu_{eff} = 5.20$ BM), electronic spectra (*51*), and far infrared data (*53*) have been reported. Magnetic moment and electronic (reflectance) spectra data for the insoluble yellow pentamethylenetetrazole adduct $FeCl_2(pmtta)_2$ indicate the presence of a polymeric structure with octahedral iron centers linked by bridging tetrazole ligands (*32*). Anhydrous ferrous chloride complexes 2-azidopyridine to form the pyridinotetrazole adduct $FeCl_2(pytta)_3$ (*160*).

Nonstoichiometric iron(III) tetrazolate precipitates, prepared by mixing ferrous salts and tetrazole in water, methanol, or ethyl acetate, react very vigorously with water after dehydration over P_2O_5 (*94*). In an attempt to prepare a tetrazole analog of ferrocene, hydrated ferrous chloride was allowed to react with sodium tetrazolate salts Na[5-R-tta] containing electron-withdrawing groups (R = NO_2, CF_3, or Cl). The products $Fe(5\text{-}R\text{-}tta)_2\cdot 2H_2O$ isolated from these reactions were first assigned sandwich structures involving tetrahedral coordination of iron(II) to π electron density associated with four N–N double bonds (*89*). However, subsequent consideration of reflectance spectra led to their reformation as polymeric species with octahedral iron centers coordinated to terminal aquo and bridging tetrazolate ligands (*90*). Rather similar structures involving bi- or tridentate 5-cyanotetrazolate ligands have been proposed for the iron(III) complexes $Fe(5\text{-}CN\text{-}tta)_2\cdot 2H_2O$ and $Fe(5\text{-}CN\text{-}tta)_2(5\text{-}CN\text{-}ttaH)\cdot 2H_2O$ (*69*). Viscous red solutions that form when dilute anaerobic solutions of "$Fe(NH_4)_2SO_4\cdot 6H_2O$" are treated with a large excess of Na(5-Ar-tta) (Ar = Ph or *p*-tolyl) have been shown to contain complex anions of stoichiometry $[Fe(5\text{-}Ar\text{-}tta)_3]^-$, which are believed to be polymeric species with triple N-2/N-3 tetrazolate bridges (*176*). 2-Azidopyridine reacts with $RuCl_2(SbPh_3)_3$ and $RuX_2(PPh_3)_3$ (X = Cl or Br) to yield pyridinotetrazole derivatives $RuCl_2(pytta)_2(SbPh_3)_2$ and $RuX_2(pytta)_2(PPh_3)_2$; the latter products afford $RuX_2(pytta)(CO)(PPh_3)_2$ on carbonylation (*160*). The ruthenium tetrazolate complex $Ru(5\text{-}CF_3\text{-tta})_2(Ph_2PCH_2PPh_2)_2$ has been obtained from the corresponding dichloride and $Na(5\text{-}CF_3\text{-tta})$ (*14, 18*), and by the 1,3-cycloaddition of CF_3CN to the azide $Ru(N_3)_2(Ph_2PCH_2PPh_2)_2$ (*18*). Labeling experiments indicate that a transient cyclic $\overline{\text{Ru—N=N—N=N}}\text{—O}$ intermediate is involved in the reaction between $[RuCl(NO)(py)_4]^{2+}$ and N_3^- (*30*). Reactions between $[RuCl(NO)(Me_2AsC_6H_4AsMe_2)_2]Cl$ and azide anions or between $Ru(N_3)Cl(Me_2AsC_6H_4AsMe_2)_2$ and NO^+ proceed via similar cyclic N_4O intermediates (*56*).

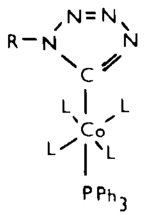
To date there appear to be no examples of osmium tetrazolate complexes.

4. *Cobalt, Rhodium, and Iridium*

Stability constants of cobalt(II) complexes with 5-methyltetrazole have been determined by potentiometry (*125*). A series of papers report solution studies on cobalt(II) complexes of aminoalkyltetrazoles (*62, 63, 122*). The complex salts $[Co(1\text{-R-ttaH})_6][BF_4]_2$ (R = Me, Et, or Pr) (*70*) and $[Co(pmtta)_6][ClO_4]_2$ (*51*) have been prepared, and characterized by magnetic and spectroscopic methods. Magnetic moment and electronic (reflectance) spectra recorded for cobalt(II) pentamethylenetetrazole adducts confirm octahedral and tetrahedral structures for pink $[CoCl_2(pmtta)]_n$ and blue $CoBr_2(pmtta)_2$, respectively (*32*). Magnetic data and vibrational and electronic spectra have been reported for the cobalt(II) adducts $CoCl_2(ttaH)_{1.5}$, $CoCl_2(5\text{-}NH_2\text{-ttaH})_2$, and $Co(NO_3)_2(5\text{-}NH_2\text{-ttaH})_2$ (*124, 153*); for the first of these a polymeric structure has been proposed (*124*). The vibrational spectrum of an impure sample of $Co(tta)_2$ has been reported and assigned (*94*). The yellow amorphous precipitate, $Co(5\text{-}CF_3\text{-tta})_2 \cdot 6H_2O$, obtained from $Co(NO_3)_2 \cdot 6H_2O$ and sodium 5-trifluoromethyl tetrazolate (*104*) is believed to contain at least one coordinated $5\text{-}CF_3$-tta anion, since the D_q value recorded is considerably larger than that of the $[Co(H_2O)_6]^{2+}$ cation (*90*). Formation constants for the adducts $CoCl_2(1\text{-R-ttaH})$ and $CoCl_2(1\text{-R-ttaH})_2$ in THF are reported to be 135 ± 5 and $3.3 \pm 0.1 \times 10^3$, respectively, for R = Me, and 145 ± 25 and $3.3 \pm 0.5 \times 10^3$, respectively, for R = Cy (*83*). Cobalt(II) tetrazolate complexes synthesized, and characterized by vibrational and electronic spectroscopy include the monohydrate $Co(5\text{-R-tta})_2 \cdot H_2O$ (R = p-ClC_6H_4, p-$MeOC_6H_4$, o-ClC_6H_4, or p-$Cl\text{-}C_6H_4CH_2$) (*119*), the trihydrate $Co(5\text{-CN-tta})_2 \cdot 3H_2O$ (*69*), the adduct $Co(5\text{-CN-tta})_2(5\text{-CN-ttaH}) \cdot 2H_2O$ (*69*), and the 5-carbamyl tetrazolate complexes $Co(5'\text{-R-tta})_2$ and $Co(5'\text{-R-tta})_2 \cdot 2H_2O$ [$R' = C(O)NH_2$] (*68*). Viscous yellow solutions that form when dilute solutions of

$Co(NO_3)_2\cdot6H_2O$ are treated with a large excess of sodium 5-phenyl tetrazolate are thought to contain a polymeric complex $[Co(5\text{-}Ph\text{-}tta)_2(H_2O)_2]_n$ with a molecular weight in the region 10^4 to 10^5. A rigid linear chain structure with double tetrazolate bridges is proposed (*177*).

Reactions between cobalt(III) complexes $CoCl(dmg)_2L$ and sodium salts of tetrazoles Na(5-R-tta) do not always give isolable products. However, yellow or brown crystalline complexes $Co(5\text{-}R\text{-}tta)(dmg)_2L$ ($L = PBu^n_3$, R = Me, CF_3, Bz, Ph, *m*- or *p*-F-C_6H_4, or NMe_2; $L = PMePh_2$, R = Me, Bz, or *p*-F-C_6H_4; L = py, R = Ph) were obtained by this route and were shown by NMR to involve exclusively N-2-coordinated tetrazolate anions. This mode of coordination was confirmed for $Co(5\text{-}CF_3\text{-}tta)(dmg)_2(PBu^n_3)$ by an X-ray diffraction study (*204*). Since quantum mechanical (MINDO/3) calculations reveal that N-1 is more nucleophilic than N-2, stereochemical factors must be decisive in determining the tetrazolate coordination mode (*204*). In marked contrast to all previous alkylations of tetrazolate complexes, alkylation of the above-mentioned cobalt(III) derivatives gave exclusively 1,5-disubstituted tetrazoles with no evidence of the 2,5 isomers (*204, 205*). Kinetic and mechanistic studies on the alkylation process indicate nucleophilic attack by the alkyl halide on the coordinated tetrazolate to form an intimately associated charged intermediate which subsequently undergoes a dissociative interchange of halide and 1,5-disubstituted tetrazole producing $CoX(dmg)_2PBu^n_3$ and the free tetrazole (*205*). Octahedral cobalt(III) azides $CoN_3(L_4)PPh_3$ (L_4 = tetradentate Schiff base, L_2 = dmg) undergo 1,3-dipolar cycloadditions with organic isonitriles (*65*) and electron-deficient nitriles (*109*) to form C-coordinated 1-alkyl tetrazolate (**37**) and N-2-coordinated 5-alkyl tetrazolate



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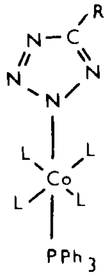

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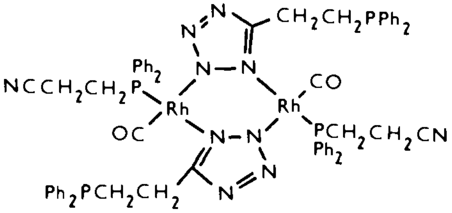
(**38**) complexes, respectively. Anation reactions between $[Co(NH_3)_5(H_2O)][ClO_4]_3$ and the anions 5-R-tta$^-$ in aqueous solution afford the explosive perchlorate salts $[Co(5\text{-}R\text{-}tta)(NH_3)_5][ClO_4]_2$ (R = H, Me, CN, or $CONH_2$), which can be converted by ion exchange into the rather safer tetrafluoroborates $[Co(5\text{-}R\text{-}tta)(NH_3)_5][BF_4]_2$ (*7*). NMR (^1H, ^{13}C, and ^{15}N) and electronic spectra establish that tetrazolate coordination occurs through N-2 (*7*) and this coordination mode has been confirmed for $[Co(5\text{-}Me\text{-}tta)(NH_3)_5][X]_2$ (*67, 157*) and $[Co(5\text{-}CN\text{-}tta)(NH_3)_5][ClO_4]_2$ (*84*). The N-1-bonded isomers $[Co(5\text{-}R\text{-}tta)(NH_3)_5][ClO_4]_2$ (R = Me or Ph) have been prepared by controlled reactions between the nitrile complexes $[Co(RCN)(NH_3)_5][ClO_4]_3$ and azide anions and were precipitated from solution as iodides $[Co(5\text{-}R\text{-}tta)(NH_3)_5]I_2 \cdot H_2O$ (*60*). Prolonged stirring of the reaction mixture prior to precipitation of the iodides leads to formation of the N-2-bonded isomers (*60*). N-1- or N-2-bonded tetrazolate complexes $[Co(5\text{-}Ar\text{-}tta)(NH_3)_5]I_2$ have been obtained by treating the corresponding organonitrile complexes $[Co(ArCN)(NH_3)_5][ClO_4]_3$ successively with azide and iodide anions. Azide attack on the coordinated nitrile has been shown to be first order in complex and first order in azide anion (*87*). Mechanisms involving concerted 1,3-dipolar cycloaddition of azide anion across the nitrile bond or azide attack on the nitrile carbon atom to form an imidoylazide intermediate which subsequently cyclizes have been advanced (*87*). The kinetics of reduction of N-1- and N-2-coordinated tetrazolate complexes $[Co(5\text{-}R\text{-}tta)(NH_3)_5][ClO_4]_2$ by Cr^{II} have been investigated. The reactions are thought to proceed by inner-sphere mechanisms leading to formation of N-1- and N-2-coordinated chromium(III) tetrazolate complexes, $[Cr(5\text{-}R\text{-}tta)(H_2O)_5][ClO_4]_2$ (Scheme 3) (*7*). Kinetics of the linkage isomerization of N-1-coordinated $[Co(5\text{-}Me\text{-}tta)(NH_3)_5]^{2+}$ to the N-2-bonded form have been studied as a function of temperature and pH. Rate constants for isomerization of the protonated (+3) and nonprotonated (+2) complex were found to differ appreciably. A base catalyzed pathway was established for the +2 complex (*164*). The use of $[Co(5\text{-}CN\text{-}tta)(NH_3)_5][ClO_4]_2$ (N-2 isomer) as an explosive has led to the development of a purification technique based upon capillary tube isotachophoresis (*123*). Chemical technology associated with the use of $[Co(5\text{-}CN\text{-}tta)(NH_3)_5][ClO_4]_2$ as an explosive has been reviewed (*128, 132*). A chelate structure (N-1 and exocyclic =NH coordination) has been found by diffraction methods for the 5-amidinotetrazolate complex $[Co(5\text{-}R\text{-}tta)(NH_3)_4]Br_2$ [R = $-C(NH_2){=}NH$] (*84*).

The first rhodium tetrazolate complex $Rh(5\text{-}CF_3\text{-}tta)(PPh_3)_3$ was obtained in 1969 by treatment of $RhCl(PPh_3)_3$ with $Na(5\text{-}CF_3\text{-}tta)$ (*18*). The complex $Rh_2(\mu\text{-}5\text{-}CF_3\text{-}tta)(\mu\text{-}N_3)(5\text{-}CF_3tta)_2(C_5Me_5)_2$, obtained by addition of CF_3CN to the rhodium azide $Rh_2(\mu\text{-}N_3)_2(N_3)_2(C_5Me_5)_2$, contains terminal (N-2) and bridging (N-2/N-3) tetrazolate ligands (*178*). The rhodium azide $Rh(N_3)(CO)(PPh_3)_2$ undergoes 1,3-cycloaddition reactions with amino-, phosphino-, and thionitriles to form the corresponding tetrazolates $Rh(5\text{-}R\text{-}tta)(CO)(PPh_3)_2$ and a range of chelated and/or bridged products (structures **39**, **40**, and **41**) (*61*). Similar



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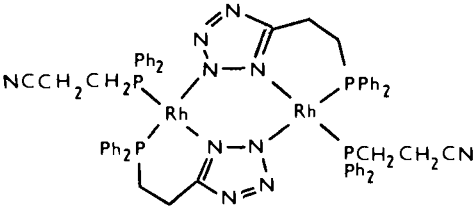

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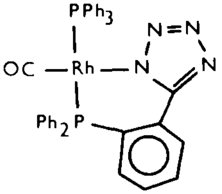

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reactions with $Ir(N_3)(CO)(PPh_3)_2$ have furnished the iridium analogs $Ir(5\text{-}R\text{-}tta)(CO)(PPh_3)_2$ (*61, 114*). Other rhodium tetrazolate complexes include $Rh_3(\mu\text{-}tta)_3(\eta^3\text{-}C_3H_5)_6$ and $Rh_3(\mu\text{-}tta)(\mu\text{-}Cl)Cl(\eta^3\text{-}C_3H_5)_2(CO)_4$ (*156a*).

5. *Nickel, Palladium, and Platinum*

A series of papers describe solution studies on nickel(II) complexes of aminoalkyltetrazoles (*62, 63, 122*). Stepwise stability constants for the $Ni(ClO_4)_2$/5-Me-ttaH system in aqueous solution range from 5.02 (log β_1) to 19.1 (log β_6) (*125*). Disodium ethyl bis(5-tetrazolylazo)acetate trihydrate has been used as a colorimetric agent for nickel (*102*). Vibrational and electronic spectra have been reported for the complex salts $[Ni(5\text{-R-ttaH})_6][BF_4]_2$ (R = Me, Et, or Pr^n) (*70*) and the related 1,5-pentamethylenetetrazole derivative $[Ni(1,5\text{-pmtta})_6][ClO_4]_2$ (*51, 53*). The crystal structure of the first 2-substituted tetrazole complex $[Ni(2\text{-Me-ttaH})_6][BF_4]_2$ reveals coordination at the N-4 position (*213*). Complex formation between nickel(II) salts and various tetrazoles 5-R-ttaH (R = Me, NH_2, Ph, *p*-$MeOC_6H_4$, and *p*-ClC_6H_4) has been studied by spectroscopic methods, but only impure products could be isolated from the blue solutions formed (*48*). Spectroscopic evidence for the formation of a 2:1 tetrazole: nickel perchlorate adduct in dimethyl formamide solution has been reported; stability constants are $\beta_1 = 2.3 \pm 1.5$ and $\beta_2 = 13.1 \pm 0.9$ (*94*). Infrared and stability constant data have been reported for the nickel(II) chloride adducts $NiCl_2(5\text{-R-ttaH})_2$ (R = Me or Cy) (*83*). Vibrational and electronic spectra have been recorded for the adducts $NiCl_2(5\text{-R-ttaH})\cdot 0.5H_2O$ (R = H and Ph·CH=N—NH—) and $NiCl_2(5\text{-}NH_2\text{-ttaH})_2$ (*124, 153*); a polynuclear structure is proposed for $NiCl_2(ttaH)\cdot 0.5H_2O$ (*124*). Polymeric structures with bridging halide ligands and octahedral coordination about the nickel centers have also been proposed for the 1:1 nickel(II) halide: 1,5-pentamethylenetetrazole adducts $NiX_2(pmtta)$ (X = Cl or Br) (*32*). 2-Azidopyridine adopts the tautomeric tetrazole structure (pytta) in the polymeric adducts $NiX_2(pytta)_2$ (X = Cl, or Br) and $NiCl_2(pytta)$, which form when the free ligand reacts with nickel(II) phosphine complexes $NiX_2(PPh_3)_2$. Magnetic and spectroscopic data indicate the presence of octahedral nickel(II) (*160*). A range of blue-violet nickel(II) tetrazolates, $Ni(5\text{-R-tta})_2\cdot H_2O$ (R = H, NH_2, or aryl), prepared from nickel(II) perchlorate and the appropriate sodium tetrazolates, give magnetic moments and electronic and vibrational spectra which do not distinguish unambiguously between octahedral and tetrahedral coordination (*94, 119*). A similar reaction involving the sodium salt of 5-trifluoromethyltetrazole affords a pink product $Ni(5\text{-}CF_3\text{-tta})_2\cdot 4H_2O$, which, after drying over P_2O_5, becomes violet in color (*104*). Electronic spectra are consistent with octahedral nickel(II) σ bonded to H_2O and tetrazolate ligands (*90*). N-2-Coordinated tetrazolate ligands have been confirmed for *trans*-$Ni(5\text{-}O_2N\text{-tta})_2(H_2O)_4$ by X-ray diffraction methods (*43a*). The blue precipitate initially formed on addition of Na(5-Ph-tta) to aqueous solutions of $Ni(NO_3)_2\cdot 6H_2O$ dissolves on standing to give clear, viscous, pink-purple solutions from which a pink-purple solid of stoichiometry $Na[Ni(5\text{-Ph-tta})_3]7H_2O$ was recovered on slow evaporation to dryness. Studies on the viscous solutions indicate the presence of a polymeric anionic species of stoichiometry $[Ni(5\text{-}Ph\text{-}tta)_3]^-$ with a molecular weight in the range $0.75-1.5 \times 10^5$ (*175*). A rodlike structure with triple tetrazolate bridges is proposed (*175*). The reactions of nickel(II) salts with 5-cyanotetrazole in aqueous or aqueous ethanol solutions afford the expected 5-cyanotetrazolate derivatives $Ni(5\text{-}CN\text{-}tta)_2 \cdot 3H_2O$ and $Ni(5\text{-}CN\text{-}tta)_2(5\text{-}CN\text{-}ttaH) \cdot 2H_2O$ (*69*), whereas similar reactions in boiling acetone yield 5-carbamyl tetrazolate complexes $Ni(5\text{-}NH_2 \cdot CO\text{-}tta)_2$ and $Ni(5\text{-}NH_2 \cdot CO\text{-}tta)_2 \cdot 3H_2O$ (*68*). In both types of complex (*68, 69*) the tetrazolate anions are thought to function as bridging tridentate ligands, binding through two tetrazole nitrogens and the cyanide or carbamyl nitrogen. Green nickel(II) complexes containing C-coordinated 1-alkyl tetrazolate anions $Ni(1\text{-}R\text{-}tta)_2$ (R = Me or Cy) have been obtained from $NiCl_2(PEt_3)_2$ and Li(1-R-tta) under strictly anhydrous and anaerobic conditions (*75, 76*). Magnetic and spectroscopic data are consistent with polymeric structures containing octahedral or tetrahedral nickel(II) centers with briding tetrazolate anions coordinated through C-1, N-4, and N-2 or N-3 (*76*). An N-bonded 1-phenyltetrazoline-5-thionato complex $Ni(PhN_4CS)(C_5H_5)(PBu_3)$ has been obtained by addition of PhNCS to the azide $Ni(N_3)(C_5H_5)(PBu_3)_2$ (*185*).

The palladium(II) adducts, $PdCl_2(1,5\text{-}pmtta)_2$, react with nucleosides to yield mixed ligand complexes $[Pd(1,5\text{-}pmtta)_2(nucl)_2]Cl_2$ (nucl = inosine, guanosine, or cytidine) (*161*). 2-Azidopyridine is bound as the tetrazole tautomer (pytta) in the adduct *cis*-$PdCl_2(pytta)_2$ (*160*). The square-planar palladium(II) tetrazolate complexes $Pd(5\text{-}R\text{-}tta)_2L_2$ (R = Me, CF_3, *cyclo*-Pr, or Ph; L = tertiary phosphine) have been prepared by four different routes—metathesis of the corresponding chlorides with sodium tetrazolate salts, reactions of PdL_4 with free tetrazoles, 1,3-dipolar addition of nitriles RCN to the corresponding azides, and "reduction" of $PdCl_2L_2$ with hydrazine in the presence of free tetrazole (*14, 17, 18, 141, 170*). Spectroscopic measurements, in particular ^1H and ^{19}F NMR, confirm the ambidentate nature of the tetrazolate anion; N-1/N-1, N-2/N-2, and mixed N-1/N-2 isomers can be detected in solution. The mechanisms of linkage and geometric (cis/trans) isomerization in these complexes has been studied by spectroscopic methods (*170*). X-Ray diffraction studies reveal *cis*-phosphine ligands and N-1-coordinated tetrazolate anions for $Pd(5\text{-}Me\text{-}tta)_2(PPhMe_2)_2$ (*4*) (Fig. 18), but *trans*-phosphine ligands and N-2-coordinated tetrazolate anions for $Pd(5\text{-}Ph\text{-}tta)_2(PPh_3)_2$ (*115*) (Fig. 19). The complexes $Pd(5\text{-}R\text{-}tta)_2(PPh_3)_2$ are cleaved by HCl and R′COCl under mild conditions to yield monosubstituted (5-R-ttaH) and disubstituted

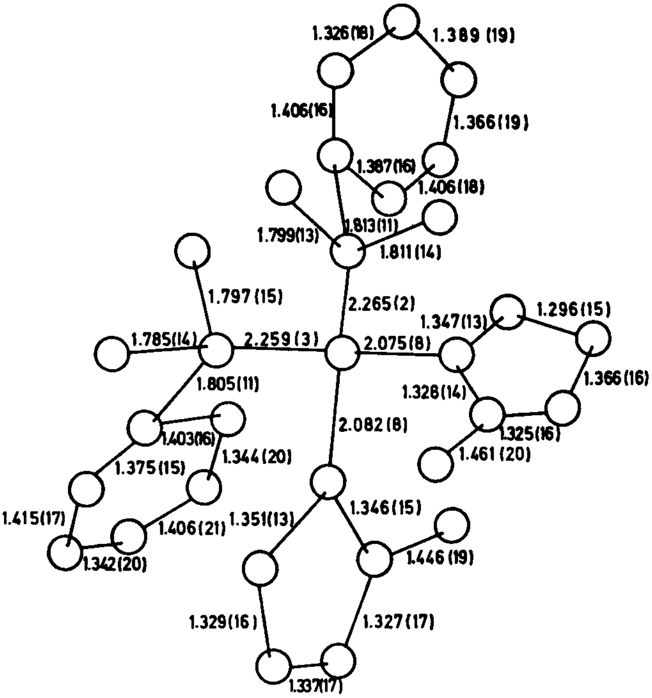


FIG. 18. Molecular structure of *cis*-bis(dimethylphenylphosphine)bis(5-methyltetrazolato)palladium(II).

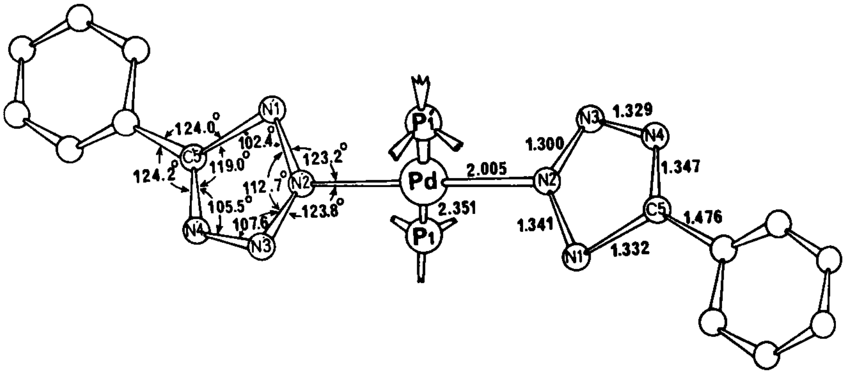
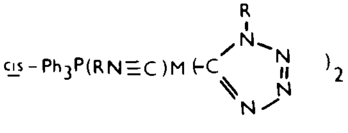


FIG. 19. Molecular structure of *trans*-bis(5-phenyltetrazolato)bis(triphenylphosphine)palladium(II).

(3-R′CO-5-R-ttaH) tetrazoles, respectively (*114*). The azide $Pd(N_3)_2(PPh_3)_2$ also undergoes 1,3-cycloaddition reactions with organic isonitriles (RNC) (*15*) and isothiocyanates (RNCS) (*114*) to afford the complexes **42** and **43** (M = Pd), respectively. N-1-Coordinated tetrazolate chelate complexes **44** and **45** are formed by treatment of the azide $Pd(N_3)_2(PPh_3)_2$ with *o*-cyanopyridine and 2-cyanoethyldiphenylphosphine, respectively (*61*). Chelate ring opening to accommodate bis(diphenylphosphino)ethane ligands converts structure **44** to structure **46** (*61*). A variety of functional organonitriles react with $Pd(N_3)_2(PPh_3)_2$ and $[Pd(N_3)(\mu - N_3)(PPh_3)]_2$ to form terminal and bridging tetrazolate derivatives (structures **47** and **48**), respectively (*61*). Internal 1,3-cycloaddition converts the azide $Pd(N_3)$-



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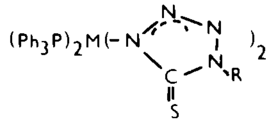

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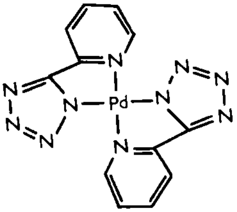

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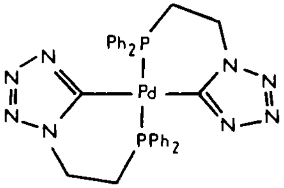

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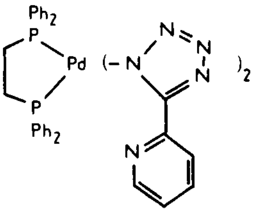

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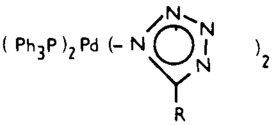

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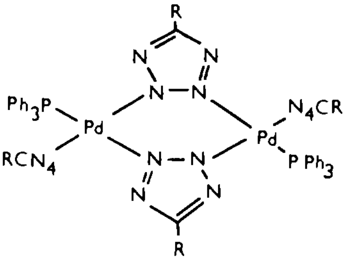

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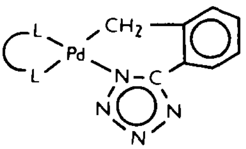

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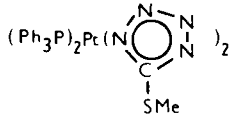
$(CH_2C_6H_4CN\text{-}o)$(dppe) to the chelate tetrazolate complex (structure **49**) (*179*). The azide-bridged complex $[Pd(N_3)(\eta^3\text{-}C_3H_5)]_2$ undergoes 1,3-cycloaddition reactions with CF_3CN and PhNCS to afford the corresponding 5-CF_3tta and PhN_4CS bridged complexes (*37*). Anions of 1-substituted 1,2,3,4-tetrazoline-5-one and -5-thione bond through nitrogen (N-2 or N-4) and sulfur, respectively, in palladium(II) complexes (*16*).

The platinum(II) adduct $PtCl_4(Et\text{-}ttaH)_2$, reported in 1910, provided an early example of a transition metal tetrazole complex (*154*). Other platinum(II) tetrazole adducts include $PtCl_2(1\text{-}R\text{-}ttaH)_2$ (R = Me, Cy, Ph, p-MeC_6H_4, and p-ClC_6H_4) (*23, 83*) or $PtX_2(1,5\text{-}pmtta)_2$ (X = Cl, Br, or I) (*161*). The latter products (X = Cl) add nucleosides (L = cytidine, adenosine, or guanine) to form salts $[Pt(1,5\text{-}pmtta)_2L_2]Cl_2$ (*161*). The platinum(II) complex $Pt(5\text{-}CF_3\text{-}tta)_2$, obtained from K_2PtCl_4 and $Na(5\text{-}CF_3\text{-}tta)$, adds triphenylphosphine to form $Pt(5\text{-}CF_3\text{-}tta)_2(PPh_3)_2$; the same product forms directly from $PtCl_2(PPh_3)_2$ and $Na(5\text{-}CF_3\text{-}tta)$ (*18*). Reactions of $PtCl_2(PPh_3)_2$ with tetrazoles, 5-R-ttaH, in the presence of N_2H_4 afford $Pt(5\text{-}Cy\text{-}tta)_2(PPh_3)_2$ and the hydrides *trans*-$PtH(5\text{-}R\text{-}tta)(PPh_3)_2$ (R = Ph, Cl, or Br) (*141*). Oxidative addition of 5-Ph-ttaH to $Pt(PPh_3)_4$ generates $Pt(5\text{-}Ph\text{-}tta)_2(PPh_3)_2$ (*141*). Treatment of $PtCl_2$(dppe) with tetrazole in methanolic KOH affords $Pt(tta)_2$(dppe) (*136*). NMR studies on several of these complexes indicate the presence of N-1- and N-2-coordinated linkage isomers (*141*). The N-1- and N-2-bonded linkage isomers $Pt(5\text{-}Me\text{-}tta)(CN)(PPh_3)_2$, obtained by addition of MeCN to $Pt(N_3)(CN)(PPh_3)_2$, display fluxional N-1 $\rightleftharpoons$ N-2 $\rightleftharpoons$ N-3 $\rightleftharpoons$ N-4 exchange above 150°C (*19*). Carbon-bonded tetrazolato complexes of platinum(II) have been obtained by azide ion attack on coordinated isocyanide ligands (*211*) and by interaction of azide ligands with free isocyanides (*15*). Confirmation of structure is provided by ^1H NMR and infrared spectra, and by hydrolysis reactions which liberate 1-substituted tetrazoles (*15*). Reactions of functional cyanides, 2-CN-py and $Ph_2PCH_2CH_2CN$, with platinum azide complexes give chelate tetrazolate derivatives analogous to those reported for palladium (vide supra) (*61*). A chelate tetrazolate product is also formed by the thermally induced intramolecular cycloaddition reaction of *cis*-$Pt(N_3)(CH_2C_6H_4CN\text{-}o)(PPh_3)_2$ (*179, 180*). Addition of methyl thiocyanate and methyl isothiocyanate to $Pt(N_3)_2(PPh_3)_2$ affords the isomeric complexes **50** and **43** (M = Pt), respectively (*114*).



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6. *Copper, Silver, and Gold*

Solution studies on copper(II) complexes with aminoalkyltetrazoles have been described (*62, 63, 122*). Disodium ethyl bis(5-tetrazolylazo)-acetate trihydrate has been employed as a colorimetric agent for copper (*102*). Copper(II) adducts of 1-alkyl- and 2-alkyltetrazoles CuX_2-$(1\text{-R-ttaH})_2$ and $CuX_2(2\text{-R-ttaH})_2$ (X = Cl or SCN; R = Me, Et, vinyl, allyl, hexyl, or octyl) contain N-4- and N-1-coordinated tetrazoles, respectively (*50, 73*). Formation of the copper(II) chloride adducts is an effective method for the isolation and purification of tetrazoles, and for the separation of 1-alkyl and 2-alkyl isomers (*72*). The adducts have been characterized by infrared, EPR, and thermal analysis techniques (*50, 73*). 2-Azidopyridine is coordinated as the tetrazole tautomer in its 1:1 copper chloride adduct (*160*). Other copper(II) adducts include $CuCl_2(ttaH)_{1.5}$, $CuCl_2(5\text{-PhCH{=}N{-}NH{-}ttaH})$ (*124, 153*), and the 1,5-pentamethylenetetrazole derivatives $CuX_2(1,5\text{-pmtta})$ (X = Cl or Br) (*32, 174*). The reactions of $Cu(ClO_4)_2 \cdot 6H_2O$ with 1,5-pentamethylenetetrazole in acetic acid or 2,2-dimethoxypropane solution afford the copper(I) complex $[Cu(1,5\text{-pmtta})_2][ClO_4]$ and the copper(II) complexes $[Cu(1,5\text{-pmtta})_n][ClO_4]_2$ ($n = 4$ or 6). The ease with which the hexacoordinated copper(II) salt forms was unexpected; however, spectroscopic evidence is in favor of this structure rather than the alternative $[Cu(1,5\text{-pmtta})_4][ClO_4]_2 \cdot 2(1,5\text{-pmtta})$, and the complex is isomorphous with other octahedral $[M(1,5\text{-pmtta})_6][ClO_4]_2$ salts (*52*). Far infrared spectra have been reported for all three salts and tentative assignments have been given for metal–ligand stretching and deformation modes (*53*). Electron spin resonance spectra including copper hyperfine splittings have been recorded for $[Cu(1,5\text{-pmtta})_4]$-

$[ClO_4]_2$ and $[Cu(1,5\text{-pmtta})_6][ClO_4]_2$; for the latter complex nitrogen hyperfine splittings are also seen. The data indicate that the Jahn–Teller distortion resonates along all three axes for diluted samples, but gives rise to a permanent tetragonal distortion in the undiluted powder (*118*). Octahedral copper(II) salts $[Cu(1\text{-R-ttaH})_6][BF_4]_2$ (R = Me, Et, or Pr^n) have been synthesized and electronic and vibrational spectra have been reported (*70*). The crystal structure and EPR spectrum (see Section III,C,4) of the 1-methyltetrazole complex have been reported (*220a*). Copper(II) salts react with tetrazole and 5-substituted tetrazoles to yield a wide variety of copper(II) tetrazolate complexes including $Cu(tta)_2 \cdot H_2O$ (*77*), $Cu(5\text{-Ar-tta})_2$ (*119*), $Cu(5\text{-}NH_2\text{-tta})_2$, $Cu(5\text{-}NH_2\text{-tta})_2 \cdot 0.5H_2O$ (*36*), $Cu(5\text{-Ph-tta})_2 \cdot H_2O$, Cu(5-Ph-tta)OH (*47, 119*), Cu(5-Ph-tta)Cl, and the sulfates $Cu_2(5\text{-Ar-tta})_2(SO_4) \cdot 2H_2O$ (*47*). These products are insoluble and tend to precipitate in an impure state, frequently contaminated by the parent copper salt (*36, 47*). Vibrational, electronic (*36, 47, 77, 119*), and EPR (*119*), spectra have been reported for many of these products. Copper(II) salts react with 5-cyanotetrazole in aqueous or alcoholic solution to afford the complexes $Cu(5\text{-CN-tta})_2 \cdot 3H_2O$ and $Cu(5\text{-CN-tta})_2(5\text{-CN-ttaH}) \cdot 2H_2O$ (*69*). However, in boiling acetone solution the same reagents yield the 5-carbamyltetrazole derivatives $Cu(5\text{-}NH_2\text{-CO-tta})_2$ and $Cu(5\text{-}NH_2\text{-CO-tta})_2 \cdot 2H_2O$ (*68*). Electronic spectra and physical properties of the complex $Cu(5\text{-}CF_3\text{-tta})_2 \cdot H_2O$ are consistent with a polymeric structure in which each octahedral copper center is bound to at least five nitrogens (*90, 104*). A binuclear N-2/N-3 tetrazole-bridged structure, similar to that found for the corresponding silver(I) complex (vide infra), has been proposed for the copper complex $Cu(5\text{-}CF_3\text{-tta})(PPh_3)_2$, prepared by 1,3-dipolar addition of CF_3CN to the azide $Cu(N_3)(PPh_3)_2$ (*235*). The same product has been obtained from $CuCl(PPh_3)_2$ and $Na(5\text{-}CF_3\text{-tta})$ (*18*). An X-ray diffraction study (*81*) on the complex $Cu_2(5\text{-}CF_3\text{-tta})_2(dppe)_3$, prepared from the corresponding azide and CF_3CN (*235*), revealed a pair of tetrahedral copper(I) centers linked by a bridging dppe ligand, with each coordinated to a bidentate dppe ligand and a monodentate (N-2) tetrazolate anion (Fig. 20). The binuclear copper(I) derivatives of 1-substituted 1,2,3,4-tetrazoline-5-one and -5-thione $[Cu(YCN_4R)(PPh_3)]_2$ (Y = O or S; R = Me or Ph) contain N-2/N-4-bridging and S- or S/N-4-bridging ligands, respectively (*16*).

The silver(I) salt of tetrazole, Ag(tta), was mentioned by Bladin in 1892 (*25*); more recently, silver(I) tetrazolates Ag(5-R-tta) have been obtained from silver nitrate and the free tetrazole or 5-substituted tetrazole (*78, 94, 134*). The silver salt of 5-nitrotetrazole, $Ag(5\text{-}O_2N\text{-tta})$,

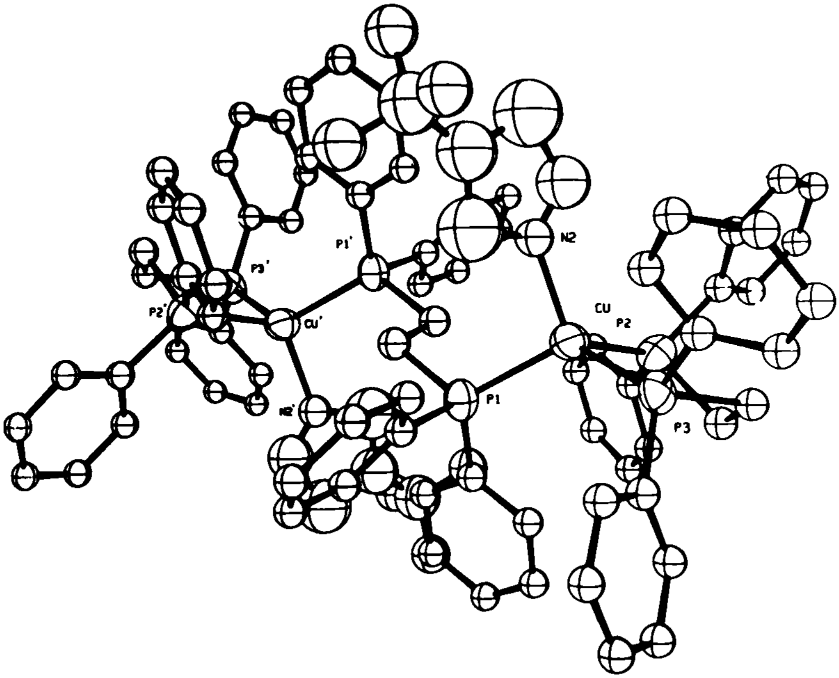
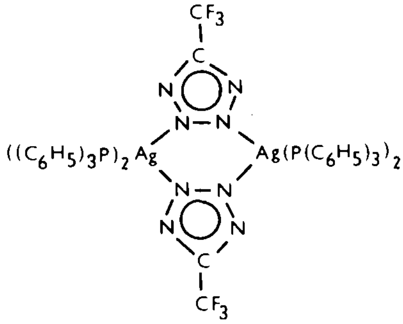


FIG. 20. Perspective view of the molecular structure of $Cu_2(CF_3\text{-tta})_2(Ph_2PCH_2CH_2PPh_2)_3$.

has been proposed as an alternative to lead azide for use in detonators (*12*) and its thermal decomposition characteristics have been examined (*34*). The silver complex $[Ag(5\text{-}CF_3\text{-tta})(PPh_3)_2]_2$, obtained by 1,3-dipolar addition of CF_3CN to $[Ag(N_3)(PPh_3)_2]_2$ (*235*), is binuclear (structure **51**) with N-2/N-3-bridging tetrazolate anions (*159*). Stability



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constants have been measured for a wide range of silver(I) complex cations $[Ag(tetrazole)_2]^+$ (tetrazoles include 8-alkyl-1,5-pmtta, 7,9-dialkyl-1,5-pmtta, 1-cy-5-Me-tta, and various 1,5-polymethylenetetrazoles) (*54, 163*). The 1,5-pentamethylenetetrazole derivative has been isolated as the nitrate salt $[Ag(1,5\text{-pmtta})_2][NO_3]$ (*163*), which has been shown (*27*) to possess a binuclear structure with monodentate (N-4) and bridging (N-3/N-4) tetrazole ligands, and monodentate nitrate anions surrounding distorted tetrahedral silver(I) centers. A 1:1 adduct $Ag(NO_3)(1,5\text{-pmtta})$ has also been reported (*174*). Silver(I) complexes of 1,5-dimethyltetrazole and 1,4-bis(1-methyl-5-tetrazolyl)butane have been studied in nitromethane and methyl cyanide solution, and a salt $[Ag(1,5\text{-}Me_2\text{-tta})_2][ClO_4]$ has been isolated (*31*). Silver(I) salts of 1-substituted tetrazoline-5-ones and -5-thiones are analogous to the corresponding copper(I) derivatives (vide supra) (*16*).

The gold(I) and gold(III) azido complexes $Au(N_3)(PPh_3)$, $[AsPh_4][Au(N_3)_2]$, and $[AsPh_4][Au(N_3)_4]$ undergo cycloaddition with isonitriles (RNC) (R = Me, Pr^i, Cy, Ph, Bz, or $p\text{-}MeOC_6H_4$) under mild conditions to afford C-bonded tetrazolate complexes $Au(1\text{-R-tta})(PPh_3)$, $[AsPh_4][Au(1\text{-R-tta})_2]$, and $[AsPh_4][Au(1\text{-R-tta})_4]$, respectively (*15, 17*). Proton NMR and infrared spectra as well as acid hydrolysis to liberate 1-substituted tetrazoles are consistent with the presence of C-5-bound tetrazolate ligands (*15*). Confirmatory evidence has been supplied by an X-ray diffraction study on the square–planar gold(III) complex $[AsPh_4][Au(1\text{-}Pr^i\text{-tta})_4]$ (*66*). Cycloaddition of CF_3CN to $Au(N_3)(PPh_3)_2$ affords $Au(5\text{-}CF_3\text{-tta})(PPh_3)$ (*235*). Tetrazoles react with $Au(O_2CMe)(PPh_3)$ to form the complexes $Au(5\text{-R-tta})(PPh_3)$ (R = H, CF_3, NH_2, NMe_2, or Ph). With 5,5′-bitetrazole and bis(5-tetrazolyl)methane, $Ph_3P{\cdot}Au{\cdot}CN_4{\cdot}CN_4{\cdot}Au{\cdot}PPh_3$ and $Ph_3P{\cdot}Au{\cdot}CN_4{\cdot}CH_2{\cdot}CN_4{\cdot}Au{\cdot}PPh_3$, respectively, were obtained (*110*). Anions of 1-substituted tetrazoline-5-ones and -5-thiones coordinate through nitrogen (N-2 or N-4) and sulfur, respectively, in a range of gold(I) and gold(III) complexes (*16*).

7. *Zinc, Cadmium, and Mercury*

Solution studies on zinc(II) complexes with aminoalkyltetrazoles have been reported (*62, 63, 122*). Zinc halides form 1:2 adducts with 1-alkyl- or 1-aryltetrazoles, $ZnCl_2(1\text{-R-ttaH})_2$ (R = Me, Cy, Ph, or *p*-tolyl) (*23, 83*), and 1,5-pentamethylenetetrazole, $ZnX_2(1,5\text{-pmtta})_2$ (X = Cl, Br, or I) (*32, 174*). An X-ray diffraction study on the 1-methyltetrazole adduct $ZnCl_2(1\text{-Me-ttaH})_2$ reveals distorted tetrahedral geometry with N-4-coordinated tetrazole ligands (*6*). 1-Alkyltetrazoles, 1-R-ttaH (R = Me, Et, or Pr), and 1,5-pentamethylenetetrazole react with zinc salts to form the cationic complexes $[Zn(1\text{-R-ttaH})_6][BF_4]_2$ (*70*) and $[Zn(1,5\text{-pmtta})_6][ClO_4]_2$ (*51*), respectively. Far infrared data have been reported and assignments made (*53 70*); $\nu(Zn-N)$ occurs at $\sim$185 cm^{-1} for the 1-alkyltetrazole complexes (*70*). Stability constants for zinc(II) complexes with the 5-methyl tetrazolate anion have been determined by the potentiometric method ($\log \beta_1 = 1.71$, $\log \beta_6 = 11.9$) (*125*). Zinc complexes, $Zn(5\text{-Ar-tta})_2$, deposit as white precipitates on addition of sodium tetrazolates to aqueous solutions of zinc perchlorate (*119*). 5-Cyanotetrazole reacts with zinc salts in cold aqueous or alcoholic solution to afford the complexes $Zn(5\text{-CN-tta})_2 \cdot 3H_2O$ and $Zn(5\text{-CN-tta})_2(5\text{-CN-ttaH}) \cdot 2H_2O$ (*69*), whereas in boiling acetone solution hydrolysis of the cyanide group occurs and 5-carbamyltetrazole derivatives $Zn(5\text{-}NH_2 \cdot CO\text{-tta})_2$ and $Zn(5\text{-}NH_2 \cdot CO\text{-tta})_2 \cdot 2H_2O$ are formed (*68*).

Cadmium tetrazole complexes examined by far infrared spectroscopy include $CdCl_2(ttaH)_2$, $CdCl_2(5\text{-}NH_2\text{-ttaH})_2$, and $Cd(5\text{-}NH_2\text{-tta})_2 \cdot 0.5H_2O$ (*124, 153*). The synthesis and infrared spectrum of $Cd(tta)_2 \cdot 1.5H_2O$ have also been reported (*94*). The cadminum(II) adducts $CdX_2(1,5\text{-pmtta})_n$ ($X = Cl$, $n = 2$; $X = Br$ or I, $n = 1$), $Cd(SCN)_2(1,5\text{-pmtta})$, and $Cd(ClO_4)_2(1,5\text{-pmtta})$ have been described (*174, 236*).

Interest in mercury(II) tetrazolates, notably $Hg(5\text{-}O_2N\text{-tta})_2$, as detonators (*12, 190*) has prompted thermal decomposition studies on mercury salts of 5-nitrotetrazole (*34*) and 5,5′-azotetrazole (*169*). Cycloaddition of methyl isocyanide to $Hg(N_3)_2(PPh_3)_2$ under mild conditions yields the C-bonded tetrazolate complex $Hg(1\text{-Me-tta})_2$ (*15*). Mercury(II) adducts $HgX_2(1,5\text{-pmtta})$ ($X = Cl$, Br, or CN) and $Hg(NO_3)_2(1,5\text{-pmtta})_2$ have been described (*174, 236*).

IV. Pentazolate and Hexazine Complexes

Although no complexes with cyclic ligands containing five or more adjacent nitrogen atoms are currently known, it seems probable that such species will be synthesized in the future. With a few notable exceptions, coordination to a transition metal imparts additional stability to catenated nitrogen molecules and it therefore seems not unlikely that entities such as the pentazolate anion, *cyclo*-N_5^-, and the hexazine molecule, *cyclo*-N_6—which are isoelectronic with the well-known cyclopentadienyl and benzene ligands, respectively—might be stabilized in this manner. Indeed, recent *ab initio* calculations on the pentazolate anion N_5^- (*151*) and on the hypothetical complexes $[M(\eta^5\text{-}N_5)(CO)_3]^n$ ($M = Cr^0$, $n = -1$; $M = Mn^I$, $n = 0$; $M = Fe^{II}$, $n = +1$) (*150*) suggest combination of the $[M(CO)_3]^{(n+1)+}$ and *cyclo*-N_5^- moieties

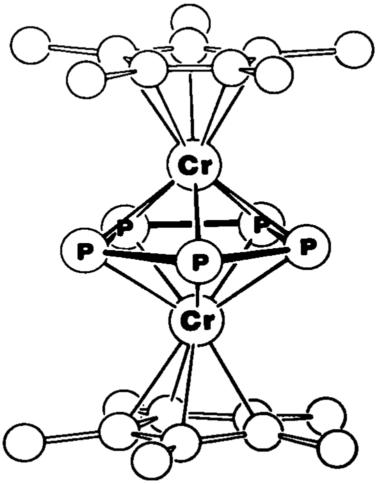

FIG. 21. Molecular structure of $(C_5Me_5)Cr(\eta\text{-}P_5)Cr(C_5Me_5)$.

should be thermodynamically favorable and that the N_5^- ligand should not be susceptible to 1,3-dipolar cycloreversion to form azide anion and liberate dinitrogen. Moreover, the success of organic chemists in synthesizing para-substituted phenylpentazoles, $p\text{-}XC_6H_4\text{-}N_5$ (*140, 212*), one of which, $X = NMe_2$, has been characterized by X-ray diffraction methods (*218*), suggests that suitable sources of the N_5^- ligand may be at hand. Further encouragement for those prepared to accept the challenge of the $\eta^5\text{-}N_5$ ligand has recently been provided by the successful synthesis of the binuclear complex $(\eta^5\text{-}C_5Me_5)Cr(\eta^5\text{-}P_5)Cr(\eta^5\text{-}C_5Me_5)$, which has been shown by X-ray diffraction method to contain a bridging $\eta^5\text{-}P_5$ ligand (Fig. 21) (*187*).

Stabilization of the hexazine, *cyclo*-N_6, molecule by coordination to transition metals also appears to be a realistic medium-term prospect for synthetic chemists. Self-consistent field (SCF) theory calculations suggest that the hypothetical D_{6h} "hexaazabenzene" molecule is likely to be a classic aromatic species, and give a value of 1.288 Å for the equilibrium N–N distance (*186*). Meanwhile, studies on the photolytic decomposition of the platinum(II) azide, *cis*-$Pt(N_3)_2(PPh_3)_2$, have provided the first experimental evidence for the transient existence of hexaazabenzene (*214*). Finally, the recent synthesis and characterization of a binuclear complex $(C_5Me_5)Mo(\eta^6\text{-}P_6)Mo(C_5Me_5)$, in which an η^6-*cyclo*-P_6 ligand bridges the two metal atoms (Fig. 22) (*188*), must raise hopes for the eventual isolation of complexes containing the analogous $\eta^6\text{-}N_6$ ligand.

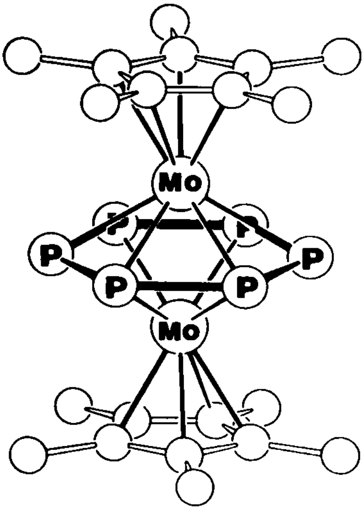

FIG. 22. Molecular structure of $(C_5Me_5)Mo(\mu\text{-}P_6)Mo(C_5Me_5)$.

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