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The coordination chemistry of 1,2,4,5-tetrazines

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Contents

Abstract

1,2,4,5-Tetrazine and its 3,6-disubstituted derivatives exhibit a particular coordination chemistry, characterized by electron and charge transfer phenomena and by the ability of these heteroatom-rich ligands to bridge metal centers in various ways. A very low-lying π^* orbital localized at the four nitrogen atoms is responsible for intense low-energy charge transfer absorptions, electrical conductivity of coordination polymers, unusual stability of paramagnetic radical or mixed-valent intermediates and for often well-resolved EPR hyperfine structure in the radical complexes. Substituted 1,4-dihydro-1,2,4,5-tetrazines have also been used as bridging ligands. The structural consequences of electron transfer as well as the capability for efficient and variable metal–metal bridging render the tetrazines as valuable components of supramolecular materials. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Bridging ligands; Electronic structure; Heterocycles; Radical ligands; Tetrazines

1. Introduction

Pyridines and their coupling products such as the 2,2′- and 4,4′-bipyridines have been among the most frequently used organic ligands in coordination chemistry. However, the pyridine ring is only one member of the azine heterocycles, in which one or more CH group of benzene, the prototypical aromatic compound, is re-

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Abbreviations: [9]aneS$_3$, 1,4,7-trithiacyclononane; acac, acetylacetonate (2,4-pentanedionate); 3,3′-bptz, 3,6-bis(3-pyridyl)-1,2,4,5-tetrazine; 4,4′-bptz, 3,6-bis(4-pyridyl)-1,2,4,5-tetrazine; bctz, 3,6-bis(carbomethoxy)-1,2,4,5-tetrazine; bmtz, 3,6-bis(2-pyrimidyl)-1,2,4,5-tetrazine; bptz, 3,6-bis(2-pyridyl)-1,2,4,5-tetrazine; bpy, 2,2′-bipyridine; Cl$_2$tz, 3,6-dichloro-1,2,4,5-tetrazine; (CN)4Pc, tetracyanophthalocyaninato(2-); COD, 1,5-cyclooctadiene; CV, cyclic voltammetry; Cym, cymene (1-isopropyl-4-methylbenzene); EC, electrical conductivity; EPR, electron paramagnetic resonance; IR, IR vibrational spectroscopy; Me$_2$tz, 3,6-dimethyl-1,2,4,5-tetrazine; Me$_8$Pc, octamethylphthalocyaninato(2-); Mes, mesityl (2,4,6-trimethylphenyl); MO, molecular orbital (calculations); nbd, norbornadiene; 2,3-Nc, 2,3-naphthalocyaninato(2-); (NH$_2$)$_2$tz, 3,6-diamino-1,2,4,5-tetrazine; NMR, nuclear magnetic resonance; OPTAP, octaphenyltetraazaporphinato(2-); Pc, phthalocyaninato(2-); p*K*, p*K* determination; pK_{BH^+}, dissociation constant of the acid BH^+ conjugated to base B; RR, resonance Raman spectroscopy; TA, thermal analysis; TBP, 5,10,15,20-tetrakis(3,5-di-*tert*-butyl-4-hydroxyphenyl)porphinato; tz, 1,2,4,5-tetrazine; X-ray, structure analysis by X-ray diffraction.

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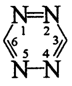
placed by π-accepting and σ-donating sp^2 N atoms. Increasing such replacement leads via diazines (pyridazine, pyrimidine, pyrazine [1,2]) and the triazines to the tetrazines $C_2H_2N_4$ of which the 1,2,4,5 isomer ('*s*-tetrazine', tz) is the most stable form [3]. The obvious attraction of tz or its derivatives for coordination chemistry are the multiple metal binding sites, however, relatively few such compounds were studied and described before 1985 [4–7]. Prejudice regarding the synthetic availability and the thermal or photochemical stability of such systems (via anticipated N_2 extrusion as in Diels–Alder reactions [8]) has long contributed to the relative scarcity of well-defined coordination compounds of tetrazine derivatives. Only during the last decade have such ligands become more common because of their specific electronic and structural properties. Whereas the former are related to the strong π accepting nature of tetrazines due to a low lying π* MO, their structural attraction is based on efficient metal–metal bridging capacity.



tz

Formula1

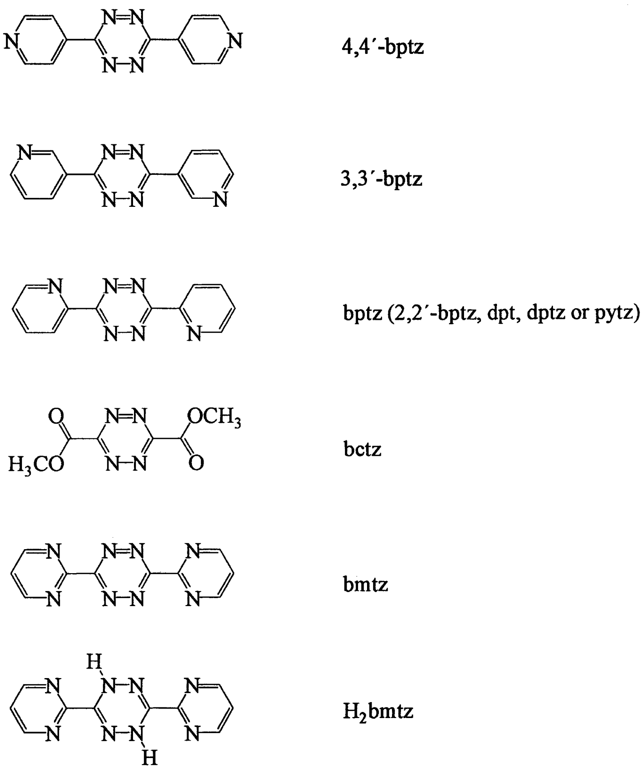
It is the purpose of this article to review the available reports on coordination compounds with 1,2,4,5-tetrazine ligands. Not only tz itself but also in 3,6-position functionally substituted derivatives and partially hydrogenated (e.g. '1,4-dihydro') forms have been employed. While the stable radical anion intermediates of 1,2,4,5-tetrazine derivatives are also being described as ligands, the stable, potentially metal-coordinating [9,10] but only partially π-conjugated verdazyl (3,4-dihydro-1,2,4,5-tetrazine-1(2*H*)-yl) neutral radicals are outside the scope of this article.

verdazyl

Formula2

2. Survey of ligands and their complexes

1,2,4,5-Tetrazines are typically pink compounds which, in spite of their formally 'aromatic' structure, are readily reduced to 1,4-dihydro derivatives [3,11]. The parent tz has rarely been used in coordination chemistry, probably due to its difficult preparation and handling (m.p. 99 °C, subl.). Of the easier accessible 3,6-disubstituted forms, the bis-pyridyl (di-pyridinyl) derivatives bptz (also referred to as dpt, dptz or pytz) were used more frequently; the bis(4-pyridyl) [12], bis(3-pyridyl) [13] and especially the bis(2-pyridyl) [14] isomer (4,4′-bptz, 3,3′-bptz, and bptz, respectively) have become popular ligands in recent years. The latter is a potentially bis-chelating bridging ligand, as are esters of 1,2,4,5-tetrazine-3,6-dicarboxylic acid such as bctz [15]. The 3,6-bis(2-pyrimidyl)-1,2,4,5-tetrazine (bmtz) [16] is a potentially tetrakis-chelating ligand, however, it can also act as a bis-chelating bridge, either in its neutral (bmtz), radical anionic ($bmtz^{\bullet -}$) or 1,4-dihydro form (H_2bmtz) [17].



Formula3

Table 1 summarizes the reported systems together with the kinds of studies performed; selected aspects of particular interest are discussed in the following sections.

3. Structural diversity

Independently of the special electronic situation with the very low-lying π*MO (see Section 4), the presence of at least four nitrogen donor atoms in tz and its derivatives allows for a potentially rich coordination chemistry. Metal complexes of the simplest kind, $(\eta^1\text{-tz})ML_n$ (**I**), are rare [6,20–22], the most common arrangement with tz itself involving it as a bridging ligand via the 1- and 4-positions (Table 1). Discrete dinuclear complexes $[(\mu,\eta^1:\eta^1\text{-tz})(ML_n)_2]$ (**II**) or linear coordinaton oligomers and polymers $[(\mu,\eta^1:\eta^1\text{-tz})(ML_n)]_\infty$ (**III**) may result. The latter motif has been

Table 1
Survey of complexes of the tetrazine ligands

ML_x	*m*	*n*	*k*	*p*	Principal methods of study	Reference
1,2,4,5-Tetrazine (tz) and derivatives $\{(tz)_m[ML_x]_n\}_p^k$						
$Cr(CO)_5$	1	1	0	1	IR, NMR	[6]
$Cr(CO)_5$	1	2	0	1	IR, NMR	[6]
$Mo(CO)_5$	1	2	0; −	1	IR, NMR; EPR, MO	[6,18]
$W(CO)_5$	1	2	0; −	1	IR, NMR; EPR, MO	[6,18]
MnPc	1	1	0	∞	IR, UV–vis, EC, TA	[19]
Mn(2,3-Nc)	1	1	0	∞	IR, UV–vis, EC, TA	[19]
FePc	1	1	0	∞	IR, UV–vis, EC, TA, Mößbauer	[7,19,20]
FePc	Me_2tz	1	0	∞	IR, UV–vis, EC, Mößbauer	[24a]
$Fe(Me_8Pc)$	1	1	0	∞	IR, UV–vis, EC, TA, Mößbauer	[24a]
$Fe[(CN)_4Pc]$	1	1	0	∞	IR, UV–vis, EC, TA, Mößbauer	[24a]
FePc	2	1	0	1	Mößbauer	[20]
Fe(2,3-Nc)	1	1	0	∞	IR, UV–vis, EC, TA, Mößbauer	[19,20]
$Fe(CN)_5$	1	1	3−	1	IR, UV–vis, CV	[21,22]
$Fe(CN)_5$	1	2	4−, 5−,	1	IR, UV–vis, CV, EPR^{a}	[21,22]
			6−, 7−	1	Mößbauer	
RuPc	1	1	0	∞	IR, UV–vis, EC, TA	[19,20]
RuPc	Me_2tz	1	0	∞	IR,UV–vis, EC	[24a]
RuPc	$(NH_2)_2tz$	1	0	∞	IR, UV–vis, EC	[24b]
RuPc	Cl_2tz	1	0	∞	IR, UV–vis, EC	[24b]
RuPc	2	1	0	1	EC, TA	[20]
Ru(2,3-Nc)	1	1	0	∞	IR, UV–vis, EC, TA	[23]
$Ru(Me_8Pc)$	1	1	0	∞	EC	[24a]
Ru(OPTAP)	2	1	0	1	IR, UV–vis, NMR	[25]
Ru(OPTAP)	3	2	0	1	IR, UV–vis, NMR	[25]
OsPc	1	1	0	∞	UV–vis, EC, TA	[19,26]
OsPc	2	1	0	1	IR, UV–vis, NMR, EC	[26]
$OsHCl(P^iPr_3)_2(CO)$	1	2	0	1	IR, UV–vis	[27]
3,6-Bis(4-pyridyl)-1,2,4,5-tetrazine (4,4′-bptz) $\{(4,4'\text{-}bptz)_m[ML_x]_n\}_p^k$						
$W(CO)_5$	1	2	0, −	1	IR, UV–vis, CV, EPR, MO ^{a}	[12,28]
$W(CO)_3(P^iPr_3)_2$	1	2	0, -	1	IR, UV–vis, CV, EPR	[29a]
FePc	1	1	0	∞	IR, EC, TA, Mößbauer	[24]
Ru(TBP)	2	1	0,+	1	UV–vis, CV, NMR, EPR	[29b]
Ru(TBP)	1	1	0,+	∞	UV–vis, CV, NMR, EPR	[29b]
$OsCl(bpy)_2$	1	1	+	1	CV ^{b}	[30]
$Ag(NO_3)$	1	1	0	∞	IR, X-ray	[31]
$Ag(MeCN)(PF_6)$	1	1	0	∞	IR, X-ray	[31]
$Ag(MeCN)(BF_4)$	1	1	0	∞	IR, X-ray	[31]
$Cd(NO_3)_2$	3	2	0	∞	X-ray	[32]
3,6-Bis(3-pyridyl)-1,2,4,5,-tetrazine (3,3′-bptz) $\{(3,3'\text{-}bptz)_m[ML_x]_n\}_p^k$						
$Ag(CF_3SO_3)$	1	1	0	∞	X-ray	[33]
$Ag(MeNO_2)_2(PF_6)$	3	2	0	∞	X-ray	[33]
$Ag(MeCN)_3(PF_6)$	1	1	0	∞	X-ray	[33]
$Zn(MeOH)(NO_3)_2$	3	2	0	∞	X-ray	[13]
$Zn(EtOH)(NO_3)_2$	3	2	0	∞	X-ray	[13]
$Zn(NO_3)_2$	3	2	0	∞	X-ray	[13]
$Cd(MeOH)_2(NO_3)_2$	1	1	0	∞	X-ray	[13]
$Cd(NO_3)_2$	3	2	0	∞	X-ray	[13]
3,6-Bis(2-pyridyl)-1,2,4,5-tetrazine (bptz) $\{(bptz)_m[ML_x]_n\}_p^k$						
$Cr(CO)_4$	1	1	0	1	IR, UV–vis, CV	[34]
$Cr(CO)_4$	1	2	−	1	EPR	[18]
$Mo(CO)_4$	1	1	0	1	IR, UV–vis, NMR, CV ^{a,c}	[34–37]
$Mo(CO)_4$	1	2	0, −	1	IR, UV–vis, NMR, CV, EPR, MO ^{a,c}	[14,18,34–37]
$W(CO)_4$	1	2	0,−	1	IR, UV–vis, CV, EPR	[14,18,34]
$MnCl_2$	1	1	0		Solubility	[4]
$Mn(CO)_3Br$	1	2	0	1	IR, UV–vis	[14]
3,6-Bis(2-pyridyl)-1,2,4,5-tetrazine (bptz) $\{(bptz)_m[ML_x]_n\}_p^k$						
TcO_2	2	1	+	1	IR, UV–vis, EC	[38]
$TcOCl_3$	1	2	0	1	IR, UV–vis, EC	[38]
$TcOCl_2(OEt)$	1	2	0	1	IR, UV–vis, EC	[38]

Table 1 (*Continued*)

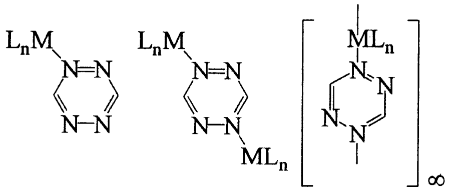
ML_x	m	n	k	p	Principal methods of study	Reference
TcO_3Cl	1	2	0	1	IR, UV−vis, EC	[38]
$TcO_3(Ome)$	1	2	0	1	IR, UV−vis, EC	[38]
$TcO_3(OEt)$	1	2	0	1	IR, UV−vis, EC	[38]
$Re(CO)_3Cl$	1	1	0, −	1	IR, UV−vis, CV, EPR	[40]
$Re(CO)_3Cl$	1	2	0, −	1	IR, UV−vis, CV, EPR	[39]
$Re(CO)_3Br$	1	2	0, −	1	IR, UV−vis, CV, EPR	[39]
$Re(CO)_3Cl/$	1	1				
$Rh(\eta^5\text{-}C_5Me_5)Cl$		1	+, 0, − [d]	1	X-ray, IR, UV−vis, CV, EPR	[40]
$Re(CO)_3Cl/$	1	1				
$Ir(\eta^5\text{-}C_5Me_5)Cl$		1	+, 0, − [d]	1	IR, UV−vis, CV, EPR	[41]
Fe^{2+}				[e]	UV−vis	[5]
$Fe(CN)_4$	1	2	3−, 4−, 5−	1	IR, UV−vis, CV, EPR [a]	[42]
$Ru(bpy)_2$	1	2	6+, 5+, 4+, 3+, 2+	1	UV−vis, CV, EPR, RR	[14,43–50]
$Ru(NH_3)_4$	1	1	2+	1	UV−vis, CV, EPR	[29b,49]
$Ru(NH_3)_4$	1	2	5+, 4+, 3+	1	UV−vis, CV, EPR	[49,51]
$Ru(DMSO)_2Cl_2$	1	1	0	1	IR, UV−vis	[52]
$Ru([9]aneS_3)Cl$	1	2	4+, 3+, 2+	1	UV−vis, CV	[53]
3,6-Bis(2-pyridyl)-1,2,4,5-tetrazine (bptz) $\{(bptz)_m[ML_x]_n\}^k_p$						
$Ru(acac)_2$	1	2	+, 0	1	X-ray, UV−vis, CV	[54]
$Os(bpy)_2$	1	2	5+, 4+, 3+	1	UV−vis, CV, EPR	[55,56]
$Os(\eta^6\text{-}C_6Me_6)Cl$	1	1	+, 0 [d]	1	UV−vis, CV, EPR	[57]
$Os(\eta^6\text{-}C_6Me_6)Cl$	1	2	2+, +, 0 [d]	1	UV−vis, CV, EPR	[57]
Co^{2+}				[e]	UV−vis	[5]
$CoCl_2$	1	1	0		Solubility	[4]
$CoBr_2$	1	1	0		Solubility	[4]
$Rh(nbd)$	1	2	+	1	EPR	[56]
$Rh(\eta^5\text{-}C_5Me_5)Cl$	1	1	+	1	UV−vis, CV	[57]
$Rh(\eta^5\text{-}C_5Me_5)Cl$	1	2	2+, +, 0 [d]	1	UV−vis, CV, EPR	[57,58]
$Ir(\eta^5\text{-}C_5Me_5)Cl$	1	2	2+, +, 0 [d]	1	UV−vis, CV, EPR	[58]
$NiCl_2$	1	1	0		Solubility	[4]
$NiCl_2$	2	1	0	1	IR	[47]
$NiBr_2$	1	1	0		Solubility	[4]
$Ni(MeCN)_2(BF_4)_2$	1	1	0	4	X-ray, magnetism	[59]
$Ni(MeCN)_2(ClO_4)_2$	1	1	0	4	X-ray	[60]
$Ni(MeCN)_2(SbF_6)_2$	1	1	0	5	X-ray, magnetism	[60]
$Pt(Mes)_2$	1	2	2+, +, 0, −, 2−	0	UV−vis, CV, EPR [f]	[61,62]
Cu^{+}				[e]	UV−vis	[5]
$CuCl_2$	1	1	0		Solubility	[4]
3,6-Bis(2-pyridyl)-1,2,4,5-tetrazine (bptz) $\{(bptz)_m[ML_x]_n\}^k_p$						
$CuBr_2$	1	1	0		Solubility	[4]
$Cu(PPh_3)_2$	1	2	2+, +	0	X-ray, UV−vis, CV, EPR, RR [h,f]	[50,63–65]
$Cu(Ph_2P(CH_2)_2PPh_2)$	1	2	2+, +	0	UV−vis, CV, EPR	[56,63a,63c]
$Cu(Ph_2P(CH_2)_6PPh_2)$	1	2	2+,+	0	UV−vis, CV, EPR [f]	[65,66]
$Cu(Ph_2P(CH_2)_8PPh_2)$	1	2	2+, +	0	UV−vis, CV, EPR [f]	[65,66]
$Cu(COD)$	1	2	2+, +	0	UV−vis, CV, EPR	[63c]
$Au(PPh_3)$	1	2	+	0	EPR	[56]
$ZnCl_2$	1	1	0		Solubility	[4]
$Zn(MeCN)(H_2O)(ClO_4)_2$	1	1	0	4	X-ray	[67]
$Zn(MeCN)_2(BF_4)$	1	1	0	4	X-ray	[60]
$Zn(MeCN)_2(ClO_4)$	1	1	0	4	X-ray	[60]
3,6-Bis(2-pyrimidyl)-1,2,4,5-tetrazine (bmtz) $\{(bmtz)_m[ML_x]_n\}^k_p$						
$Fe(CN)_4$	1	2	3−, 4−, 5−	1	IR, UV−vis, CV, EPR	[68,69]
$Ru(bpy)_2$	1	2	6+, 5+, 4+, 3+	1	UV−vis, CV, EPR	[16a]
$Ru(Cym)Cl$	1	2	2+, +	1	UV−vis, CV, EPR	[70]
$Os(Cym)Cl$	1	2	3+, 2+, +	1	UV−vis, CV, EPR	[70]
$Cu(PPh_3)_2$	1	2	2+, +	1	X-ray, UV−vis, CV, EPR [g]	[17]
$\{(H_2bmtz)_m[ML_x]_n]^k_p$						
$Ru(bpy)_2$	1	2	4+	1	UV−vis, CV, pK	[16]
$Ru(Cym)Cl$	1	2	2+	1	UV−vis, CV, pK	[16b]
$Os(bpy)_2$	1	2	4+	1	X-ray, UV−vis, CV	[16b]
$Os(Cym)Cl$	1	2	2+	1	UV−vis, CV, pK	[16b]
$Cu(PPh_3)_2$	1	1	2+	1	X-ray, UV−vis, CV	[17]

Table 1 (*Continued*)

ML_x	m	n	k	p	Principal methods of study	Reference
3,6-Bis(carbomethoxy)-1,2,4,5-tetrazine (bctz) $\{(bctz)_m[ML_x]_n\}_p^k$						
Ru(bpy)$_2$	1	2	2+, +	1	CV, EPR	[15]

[a] Including solvatochromism.
[b] Film on Pt microelectrode.
[c] ^{95}Mo-NMR.
[d] EC processes (halide dissociation).
[e] Color formation in ethanol-water solutions.
[f] Variable frequency EPR.
[g] Radical form.
[h] (2+) and (+) forms.

used abundantly by Hanack and coworkers in the construction of electrically conducting 1D materials **III** where ML_n are typically metallophthalocyanines (Table 1) [7,19,20,23–26,71,72].



I **II** **III**

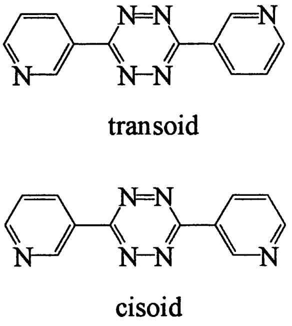
Formula4

The bridging of three or four metal centers by the potentially tetradentate tz or its derivatives has not yet been observed. However, all four N donor atoms of the central tetrazine are engaged in electrophile binding in the structurally characterized $\{(\mu,\eta^2{:}\eta^2\text{-}H_2bmtz)[Cu(PPh_3)_2]_2\}(BF_4)_2$ (H_2bmtz = 1,4-dihydro-3,6-bis(2-pyrimidyl)-1,2,4,5-tetrazine, see Fig. 2) [17].

The 4,4′-bptz derivative belongs to a family of linearly bridging bis(monohapto) ligands such as pyrazine [1,2], 4,4′-bipyridine, bis(4-pyridyl)ethyne or unsubstituted 1,2,4,5-tetrazine. It should be noted, however, that 1,4-dicoordinated tz does not have D_{2h} symmetry. The 4,4′-bptz ligand typically uses the more basic and sterically unencumbered pyridyl nitrogen atoms for metal coordination. It is known to form dinuclear complexes and coordination polymers (Table 1), the latter with linear chain, 3D helical or polyknotted structures [31,32]. A series of silver(I) complexes has shown how the anion determines the arrangement within the crystal [31], a feature which is also evident in nickel(II) oligomers of bptz (cf. below) [60].

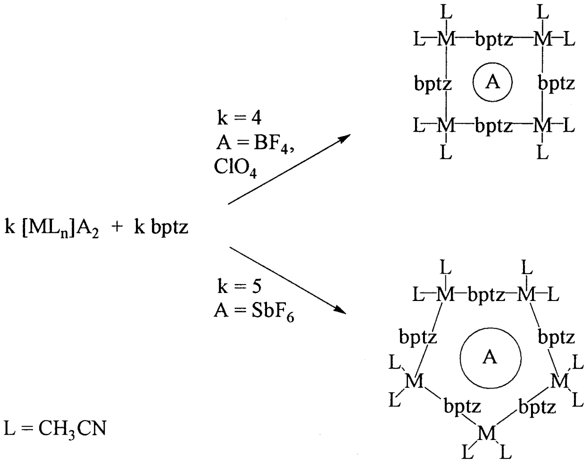
While the 3,3′-bptz ligand cannot bridge linearly via the pyridyl N atoms as does the 4,4′ derivative, it can, however, coordinate in a cisoid or transoid fashion [13,33]. This feature has contributed to various coordination polymeric arrangements such as zigzag chains or noninterpenetrated ladder structures [13,33].

Metal coordination through the less basic and sterically less exposed tetrazine nitrogen atoms has not yet been observed for 4,4′- and 3,3′-bptz ligands; bridging via the pyridine N centers is often accompanied by some twisting around the C–C single bonds between the pyridyl and tetrazine rings [13,31–33].



Formula5

The most frequently used tetrazine ligand bptz and the related bmtz and bctz usually act as transoid-symmetrically bis-chelating ligands ($\mu,\eta^2{:}\eta^2$ coordination). With the exception of a few monomeric compounds and mixed (heterodinuclear) systems such as $[Cl(OC)_3Re(\mu\text{-bptz})Rh(C_5Me_5)Cl](PF_6)$ [40] most of the well characterized species are homodinuclear complexes (Table 1). Depending on the metal fragments there is the possibility of isomerism in those dinuclear compounds, e.g. the *cis*/*trans* (syn/anti) alternative for $Re(CO)_3Cl$ or



Scheme 1.

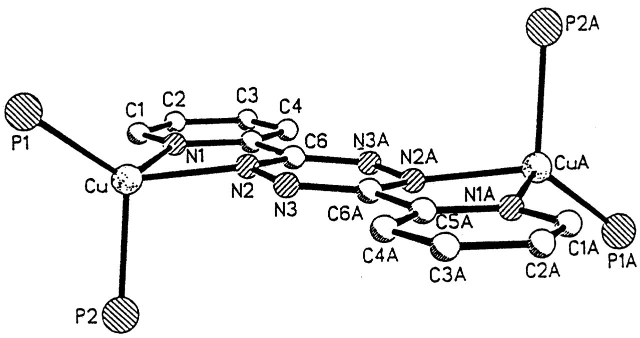


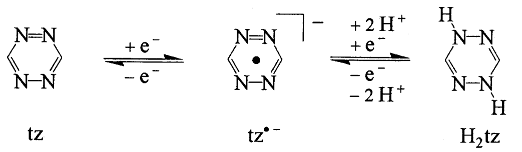
Fig. 1. Molecular structure of the radical cation in $\{(\mu\text{-bptz})[Cu(PPh_3)_2]_2\}(BF_4)$ (P-phenyl rings omitted for clarity) [64].

$^{+}Rh(C_5Me_5)Cl$ complexes [40,57,73] or the rac/meso alternative for $^{2+}Ru(bpy)_2$ compounds [44,73b]. While no coordination polymers were reported with bptz, oligomeric ($n = 4,5$) zinc(II) and nickel(II) complexes were obtained through anion template reactions (Scheme 1) [59,60,67].

The nickel(II) oligomers were also studied with respect to magnetic coupling, each metal is coordinated by two pyridyl and two tetrazine nitrogen atoms from bridging bptz molecules and by two external ligands (acetonitrile) [59,60].

The bptz ligand has also been used in the one-electron reduced (radical anion) form to bridge metal centers [18]. The structural characterization of one such complex $\{(\mu,\eta^2:\eta^2\text{-bptz})[Cu(PPh_3)_2]_2\}(BF_4)$ (Fig. 1) [64] and of the bmtz analogue [17] showed bond parameter changes in agreement with a calculated [50] tetrazine-centered electron acquisition (see Scheme 2):

On going from the 'aromatic' tetrazine parent (with similar C–N and N–N intra-tetrazine bond distances of about 1.34 Å [50]) via the anion radical to the two-electron reduced 1,4-dihydro form the C3–N4 and C6–N1 (+0.05 Å) and especially the N1–N2 and N4–N5 bonds (+0.10 Å) lengthen due to single bond formation [17,64] whereas the N2–C3 and N5–C6 distances shorten to ca. 1.28 Å [11,17,64] through becoming regular double bonds (Scheme 2).



Scheme 2.

The structural pair $\{(\mu,\eta^2:\eta^2\text{-bptz})[Cu(PPh_3)_2]_2\}^{2+/\bullet+}$ [50,64] shows about half such effects, again with the N-N bond length as the most sensitive parameter. In contrast to the radical ligand $bptz^{\bullet-}$ which exhibits approximate coplanarity of pyridyl and tetrazine rings in a dicopper(I) complex (Fig. 1), the 1,4-dihydro state shows significant conformational change (Fig. 2). As cyclical 8π electron systems the 1,4-dihydro-1,2,4,5-tetrazines avoid full π conjugation to an 'anti-aromatic' species [74,75] by significant bending along the axis through N1 and N4 with typical dihedral angles of 140–150° [11]. Replacing NH by $NSiMe_3$ in 1,4-dihydro-1,2,4,5-tetrazine appears to attenuate this deviation from planarity [75].

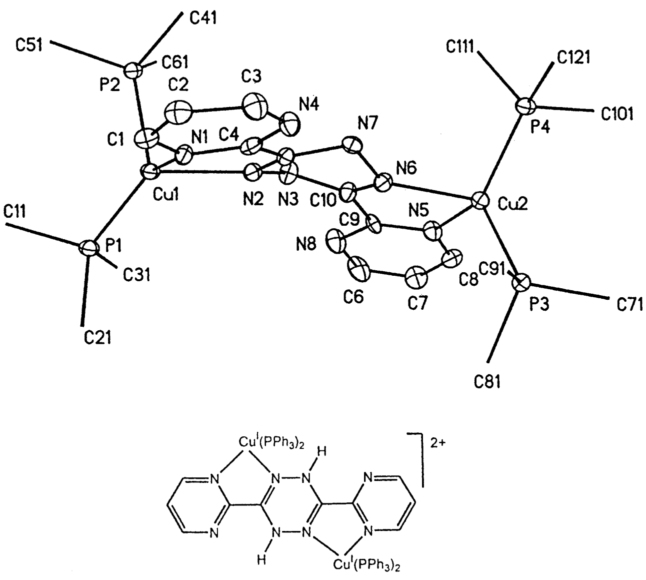
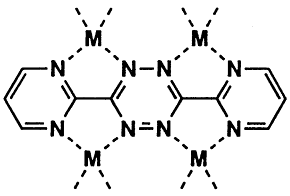


Fig. 2. Molecular structure of the dication in $\{(\mu\text{-}H_2bmtz)[Cu(PPh_3)_2]_2\}(BF_4)_2$ (P-phenyl rings and hydrogen atoms omitted for clarity) [17].

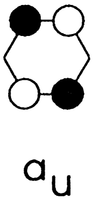


Scheme 3.

The potentially tetrakis-chelating bmtz [16,17] (Scheme 3) has so far been reported only in dinuclear complexes where it acts as transoid bridge (Table 1). In view of related non-tetrazine grid-forming ligands [76] it is a potential component for supramolecular structures, however, its strong tendency to being reduced to the radical anion and further to the 1,4-dihydro form H_2bmtz has so far precluded its wider use. In taking advantage of this facile reduction, discrete dinuclear complexes of the $bmtz^{\bullet-}$ radical anion and H_2bmtz proved to be sufficiently stable, even for crystallization with two $^{+}Cu(PPh_3)_2$ fragments [17]. Whereas the bridging $bmtz^{\bullet-}$ shows the typical [64] intermediate bond distances within the planar tetrazine ring (Scheme 2), the coordinated H_2bmtz (like H_2tz [11] or free H_2bptz [64,77]) exhibits a boat conformation of the central dihydrotetrazine ring (Fig. 2) [17]. The variation of M–N bond distances in complexes of bptz, bmtz and their reduced forms will be discussed in Section 4.

4. Electronic structure of tetrazine ligands

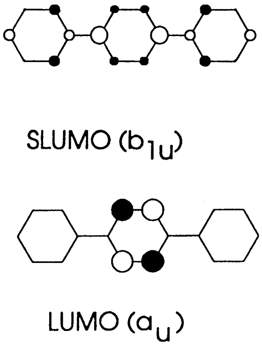
One of the most remarkable aspects of tetrazine chemistry is the presence of a very low-lying π^* molecular orbital. Replacement of four CH groups in the 1,2,4,5-positions of benzene by the more electronegative N atoms results in a particular stabilization of the unoccupied a_u orbital [18] (Scheme 4). In consequence, most 1,2,4,5-tetrazines are almost as reducible as quinones ($E > -1.3$ V vs. ferrocenium/ferrocene) [16a,22,34,78], their anion radical and 1,4-dihydro forms are often more stable than the 'aromatic' parent molecule [16a], ligands ($n \rightarrow \pi^*$) and complexes ($d \rightarrow \pi^*$ transitions) are typically colored [5,14], tetrazine-bridged mixed-valent dimetal systems are strongly coupled [21,22,44,51,53,68], and coordination polymers can exhibit rather high electrical conductivities [7,19,20,23–26,71,72]. The latter two features involve a_u as excellent electron-accepting MO for facilitating the transmission of charge with a radical anion formulation $(L_xM)(\text{tz-ligand})^{\bullet -}(ML_x)$ as intermediate (see Section 3).



Scheme 4.

The energetic stabilization of the a_u MO and its nodal plane at the 3,6-position (the C-substitution sites) result in a remarkable indifference of this MO towards such substitution. Accordingly, the bptz ligands still have as lowest unoccupied MO (LUMO) a virtually tetrazine-localized a_u MO (Scheme 5). Only on very strong perturbation such as diquarternization of 4,4′-bptz at the pyridyl nitrogen atoms could another MO (b_{1u}) be stabilized below the level of a_u, as evident from EPR spectroscopy of the one-electron reduction product (see Fig. 5) [79]. In fact, this second lowest unoccupied MO (SLUMO, b_{1u}) is rather close in energy to the LUMO (a_u) in the bptz and bmtz π systems [16,34].

The highest lying occupied MOs in tetrazines are combinations of nitrogen lone pairs [80]. Due to the presence of four electronegative nitrogen atoms in a conjugated six-membered ring the basicity of individual tetrazine N donor centers is very small ($pK_{BH^+} < 0$) [34,80]. As a consequence, the metal binds to very different azine N donors in bis-chelate complexes of bptz: the pyridyl N is a good donor but only moderate π acceptor center whereas the tetrazine N offers superb π acceptor capacity (for π back-donation from low-valent metals) but poor σ basicity. Accordingly, the bond distances $M-N_{tz}$ or $M-N_{py}$ vary, depending on the metal characteristics. Whereas complexes of bptz with 'innocent' nickel(II) and zinc(II) [59,60,67] have slightly shorter $M-N_{py}$ distances (dominant σ bonding), those complexes which contain Ru^{II}, Cu^{I} and Re^{I} [40,50,54] exhibit distinctly shorter $M-N_{tz}$ bond lengths (significance of π back bonding contributions). A similar phenomenon is observed for dicopper(I) complexes of $bptz^{\bullet -}$ and $bmtz^{\bullet -}$ [17,64] where the negative charge is localized on the tetrazine N atoms; in contrast, $\{(\mu,\eta^2:\eta^2\text{-H}_2\text{bmtz})[\text{Cu(PPh}_3)_2]_2\}(\text{BF}_4)_2$ [17] has unusually long bonds between the copper(I) centers and the imine atoms of the 1,4-dihydro-1,2,4,5-tetrazine ring (which is neither a strong acceptor nor a strong donor).



Scheme 5.

On reduction, the single electron is taken up primarily by the four nitrogen atoms of the tetrazine ring in the a_u MO and the tetrazine N centers should become much more basic. Second electron acquisition at much higher potential would lead to a still further increased pK_{BH^+} value; in fact, this state is usually isolated in the diprotonated (1,4-dihydro) form.

5. Electrochemistry and electrical conductivity

In agreement with the very low-lying π^*MO of tz and its derivatives these ligands and especially their metal complexes are reduced at easily accessible potentials, according to Scheme 2. Whereas the first electron is typically added reversibly between 0.0 and -1.3 V versus ferrocenium/ferrocene, the distance to the second, sometimes irreversible reduction of the tetrazine species is generally very large, often exceeding 1 V [34,61,81]. In other words, the radical anion (complex) intermediate has an unusually high stability constant $K_c > 10^{17}$ (2) towards disproportionation (1). Most related two-step redox systems exhibit much smaller K_c values [34,82].

The origin of this effect lies in very strong intra-ring Coulombic interactions of the two added charges in A^{2-}.

$$A \underset{E_1}{\underset{-e^-}{\overset{+e^-}{\rightleftharpoons}}} A^{\bullet -} \underset{E_2}{\underset{-e^-}{\overset{+e^-}{\rightleftharpoons}}} A^{2-} \qquad (1)$$

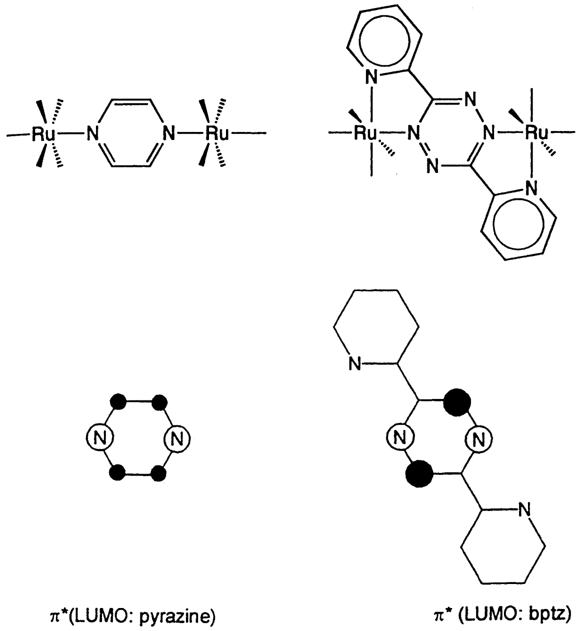
$$K_c = [A^{\bullet -}]^2/[A][A^{2-}] = e^{nF\Delta E/RT} \qquad (2)$$

The propensity of tz and its derivatives to bridge two metal centers has prompted studies of stepwise metal oxidation involving mixed-valent intermediates. According to the established electron-transfer concept (3) [83,84] for the classical mixed-valent dimers derived from the Creutz–Taube ion $[(H_3N)_5Ru(\mu\text{-pz})Ru(NH_3)_5]^{5+}$ (pz = pyrazine, see Scheme 6) the role of the bridging acceptor ligand is to provide a low-lying symmetry-adapted unoccupied orbital for metal–metal communication.

$$\begin{aligned} &(L_xM^+)(\mu\text{-T})(ML_x) \leftrightarrow [(L_xM^+)(\mu\text{-T}^{\bullet -})(^+ML_x)] \\ &\leftrightarrow (L_xM)(\mu\text{-T})(^+ML_x) \end{aligned} \qquad (3)$$

T: tetrazine ligand.

The very strongly stabilized π*MO of tz and the favorable properties of the metal-ligand interface (high LUMO coefficients at the coordinating N centers [44]) have rendered tz and its derivatives as bridging ligands with exceptionally strong metal–metal coupling capacity. Examples include the isolable $[(NC)_5Fe(\mu\text{-tz})Fe(CN)_5]^{5-}$ ($K_c = 10^{19}$ [21,22]) and $[(H_3N)_4Ru(\mu\text{-bptz})Ru(NH_3)_4]^{5+}$ with $K_c = 10^{15}$ [51] (the related Creutz–Taube ion (Scheme 6) has $K_c = 10^{7.3}$, all K_c values from acetonitrile solutions [85]).



Scheme 6.

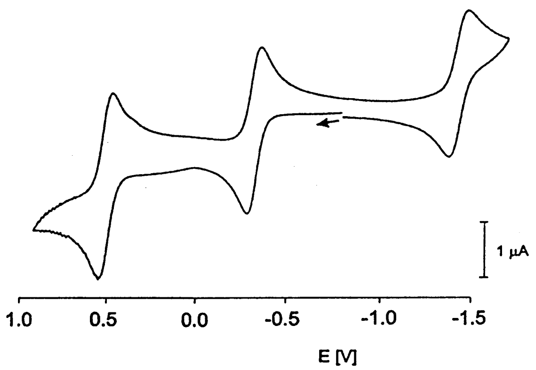


Fig. 3. Cyclic voltammogram of $(NEt_4)_4\{(\mu\text{-bmtz})[Fe(CN)_4]_2\}$ in CH_3CN/0.1 M Bu_4NPF_6 (from [69]).

Other mixed-valent species involving $Fe^{II}Fe^{III}$ [42a,68,69], $Ru^{II}Ru^{III}$ [44,51,53,54], $Os^{II}Os^{III}$ [55] and $Pt^{II}Pt^{III}$ [61] oxidation state combinations have been reported and characterized through typically large K_c values (Fig. 3) and spectroscopic information (e.g. intervalence charge transfer (IVCT) transitions in the near infrared). With the $Pt^{II}Pt^{III}$ (d^8/d^7) combination the splitting of oxidation processes is small due to the occupation of σ (d_z^2) orbitals at the metal atoms but still detectable [61]; the other, d^6/d^5 mixed-valent systems coupled by tetrazine ligands are clearly of the Class III type [86] with fully delocalized valencies as evident e.g. from IR vibrational or Moessbauer spectral data [21,22,42a].

In contrast to the efficient metal–metal coupling via the tetrazine ring, the bridging of two oxidizable metal centers via the pyridyl atoms of 4,4′-bptz in $(\mu\text{-}4,4'\text{-bptz})[W(CO)_3(P^iPr_3)_2]_2$ is not sufficient to allow the detection of a mixed-valent W^o/W^I intermediate [29a,29]. The long metal–metal distance and, more importantly [42,44,83], the non-contribution from the pyridyl rings to the low-lying a_u acceptor orbital are responsible for this effect.

Taken together then, the very low-lying π*MO of the tetrazines can cause both widely separated ligand-centered one-electron reduction processes and similarly separated metal-centered one-electron oxidation steps. Several persistent oxidation states are thus often accessible with soluble complexes of the tetrazine bridging ligands (Fig. 3).

The remarkably increased electrical conductivity of coordination polymers **III** with tz bridges [7,19,20,23–26,71,72] may also be traced to the easily accessible mediating π* system of the bridge according to the formulation (Formula 3).

In those cases where elementary chemical steps (C) are following the electron transfer steps (E) the electrochemical sequences as apparent from cyclic voltammetry can become fairly complicated, reflecting again the strong metal–metal mediating capability of the tz ligands [21,22,44,51,53]. Spectroelectrochemical information is then suitable to analyze the reaction sequence (see Fig. 7 in Section 7). The complexes {(μ-bptz)[Rh(C_5Me_5)Cl]$_2$}(PF_6), M = Rh or Ir, are thus reduced in a characteristic reversible pattern E, EC, EEC, E, E where E is a single electron transfer step and C a chemical reaction (here: reversible chloride dissociation; Fig. 7) [57,58].

In contrast to the unreduced tz ligands, the 1,4-dihydro forms may be partially re-oxidized to corresponding radical cations which are detectable by EPR [11]. However, the few known metal complexes of 1,4-dihydrotetrazines (Table 1) have not yet been shown to undergo such reversible oxidation.

6. EPR of paramagnetic species

Whereas tetrazine ligand-bridged mixed-valent complexes exhibit EPR spectra corresponding to the individual metal d configurations [21,22,42a,51,69], the one-electron reduced species often display unusually well-resolved EPR spectra because the spin is virtually localized at the four nitrogen centers (a_u as spin-bearing singly occupied MO). Thus, the first partially resolved EPR spectrum of a 'Ru-bpy' type radical complex was observed for {(μ-bptz)[Ru(bpy)$_2$]$_2$}$^{\bullet +}$ [43]. In a symmetrical situation the four tetrazine ^{14}N nuclei ($I = 1$) display a typical widely spaced nonet with ca. 0.5 mT hyperfine splitting (Fig. 5) [18,56,79]. Metal coordination to two of the four tetrazine N atoms usually causes an inequivalence and thus a characteristic divergence of the two sets of ^{14}N hyperfine coupling constants [18,22,56]; the concentration of spin at the coordinating tetrazine N atoms also causes sufficient spin transfer to the metal centers for EPR detection of corresponding hyperfine splitting (Fig. 4) [56,58].

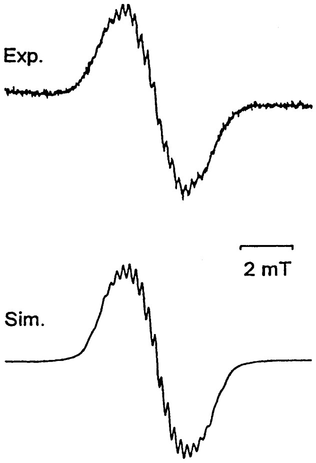


Fig. 4. EPR spectrum of electrogenerated {(μ-bptz)[Rh(C_5Me_5)Cl]$_2$}$^{\bullet +}$ in CH_3CN/0.1 M Bu_4NPF_6 at 293 K with computer simulation (from [58]).

The radical ligand character of paramagnetic complexes obtained by the reduction of tetrazine-bridged dinuclear species is also evident from the relatively small g anisotropy which could be measured in the X band when second and third row transition elements were present [41,46,56,58,61,62]; high-frequency EPR methods were required for dicopper(I) systems [65].

Due to the rather positive reduction potential and the persistence of the resulting radical complexes the bptz ligand can also be used as a substrate for single electron transfer processes with organometallics [87]. The Ti(O^{i}Pr)$_3$Me reagent and bptz thus form a bis-titanium(IV) radical complex as detected by EPR [88].

One-electron reduced tetrazine ligands generally have the virtually tetrazine-localized a_u MO as SOMO. However, on very strong perturbation such as diquarternization of 4,4′-bptz at the pyridyl nitrogen atoms, the b_{1u} MO could be stabilized below the level of a_u. Coordination of two neutral, electron-rich W(CO)$_5$ groups to the pyridyl nitrogen atoms of 4,4′-bptz is not sufficient to stabilize the b_{1u} MO below a_u as evident from the EPR spectrum with hyperfine coupling only to the four ^{14}N nuclei, just like in free 4,4′-bptz$^{\bullet -}$ (Fig. 5, top). However, the binding of two methyl cations results in a totally different EPR response for [Me$_2$(4,4′-bptz)]$^{\bullet +}$, signifying the occupation of the truly delocalized b_{1u} MO by the single electron (Fig. 5, bottom [79]).

7. Spectroscopy and spectroelectrochemistry

The low-lying π* MO (a_u) of tetrazines is an excellent target orbital for low-energy electronic transitions. Thus, even the free tetrazine ligands exhibit distinct colors due to n → π* transitions in the visible. It is no surprise then, that the combination of tetrazine ligands with electron-rich metal complex fragments leads to intense long-wavelength metal-to-ligand charge transfer (MLCT) bands, often extending into the near-infrared region [6,14,21,22]. In fact, the earliest reported use of bptz and related species has been as reagent for the photometric analysis of iron(II) or copper(I) [5]. Transitions are also possible to the stabilized [34] second lowest unoccupied MO (b_{1u}), leading sometimes to various overlapping bands which require deconvolution for analysis (Fig. 6) [89]. In contrast to the non-reduced state, tetrazine radical anions exhibit no significant transitions in the UV–vis or near-infrared regions [61].

The spectroelectrochemical sequence of Fig. 7 illustrates some of the above features. The {(μ-bptz)[Rh^{III}(C_5Me_5)Cl]$_2$}$^{2+}$ ion [57,58] with organometallic rhodium in a 'normal' oxidation state (+III) shows the typical weak n → π* absorption of tetrazines at about 550 nm (intra-ligand transition). On ligand-based one-electron reduction to EPR-detectable (Fig. 4) {(μ-bptz)[Rh(C_5Me_5)Cl]$_2$}$^{\bullet +}$ this band shifts to higher

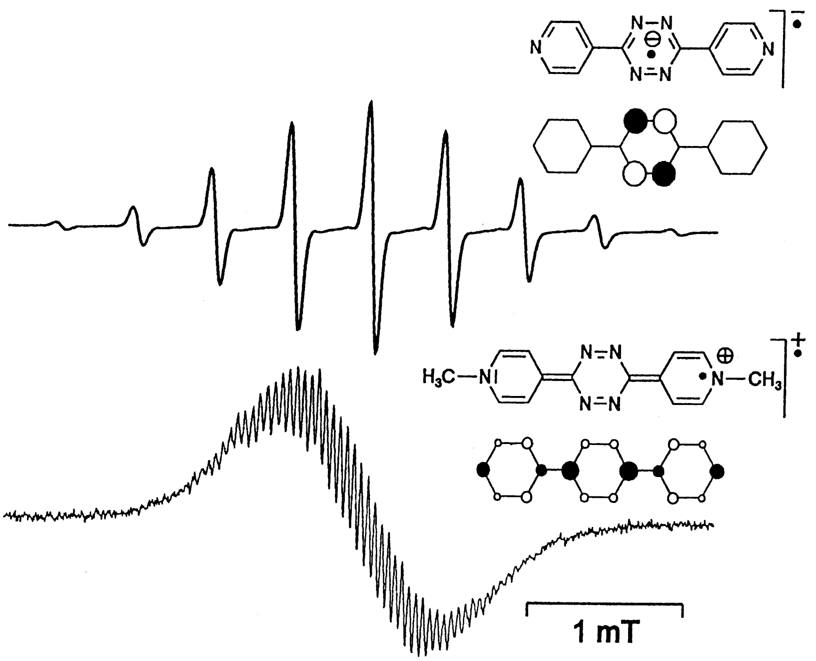


Fig. 5. EPR spectra of 4,4′-bptz$^{\bullet -}$ (top) and Me_2(4,4′-bptz)$^{\bullet +}$ in DMF [79] (reprinted with permission).

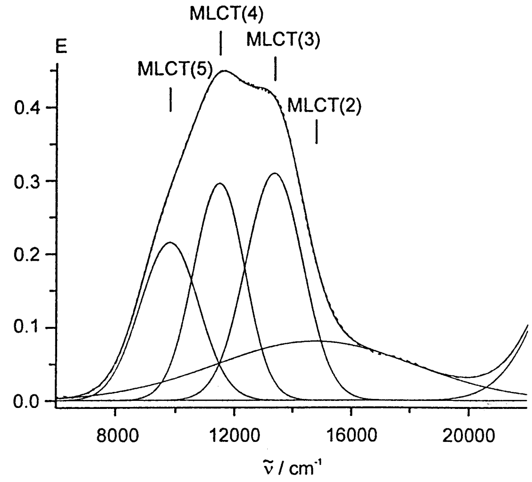


Fig. 6. Deconvolution of the long-wavelength absorption band system in $\{(\mu\text{-bptz})[Fe(CN)_4]_2\}^{4+}$ in isopropanol [89] (the high-energy band MLCT(1) is not shown).

energies as do other bands in the UV region (Fig. 7, top). Chloride-dissociative reduction to $[(C_5Me_5)Rh^I(\mu\text{-bptz})Rh^{III}(C_5Me_5)Cl]^+$ (a metal-based process with bptz serving as intermediate one-electron resevoir [57,58]) produces an intense d(Rh^I)→μ*(bptz) MLCT feature [90] at about 650 nm (Fig. 7, center). The second reductive elimination, a two-electron step, to neutral (μ-bptz)$[Rh(C_5Me_5)]_2$ causes intensification and further bathochromic shift of this MLCT band (Fig. 7, bottom). MLCT bands to higher lying π*MOs such as b_{1u} are less intense due to the more delocalized nature of these MOs [34], providing for smaller overlap at the metal-ligand interface.

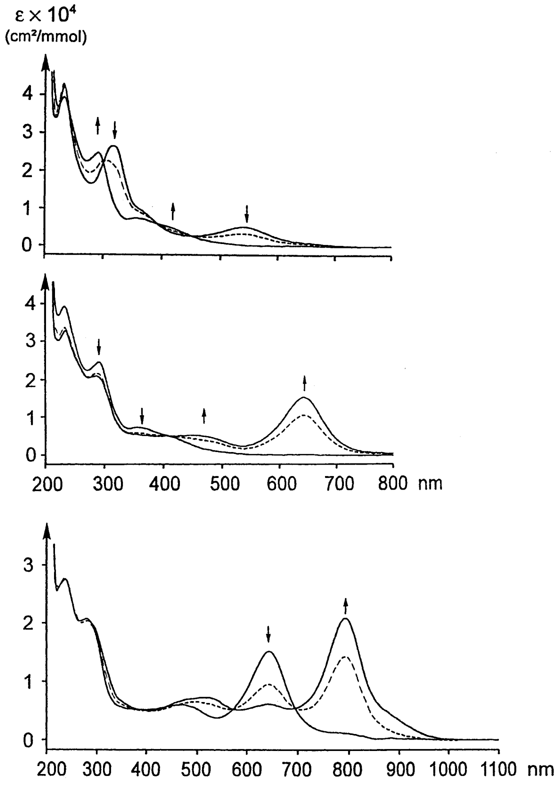


Fig. 7. UV–vis-NIR spectroelectrochemistry of $\{(\mu\text{-bptz})[Rh(C_5Me_5)Cl]_2\}(PF_6)_2$ in CH_3CN/0.1 M Bu_4NPF_6 [57,58]: Spectrum of parent and $\{(\mu\text{-bptz})[Rh(C_5Me_5)Cl]_2\}^{\bullet +}$ (top, $+e^-$), $[(C_5Me_5)Rh(\mu\text{-bptz})Rh(C_5Me_5)Cl]^+$ (center, $+e^-/-Cl^-$) and (μ-bptz)$[Rh(C_5Me_5)]_2$ (bottom, $+2e^-/-Cl^-$).

Indirect evidence for the low basicity of tetrazine ligands comes from an analysis of the 'secondary' d(Ru^{II})→π*(bpy) MLCT bands in complexes {(μ-

L)[Ru(bpy)$_2$]$_2$}$^{4+}$, L = bptz, bmtz [16a,45]. The relatively high energies of these transitions point to stabilized d(Ru) orbitals as a consequence of little σ electron donation from the tetrazine ligands [45]. If L = H$_2$bmtz these secondary MLCT bands allow pK_a values to be photometrically determined [16] (Table 1).

The MLCT bands of mono- and dinuclear complexes of the tetrazine ligands are typically solvatochromic [6,22,28,36,89]. Surprisingly, the dinuclear systems (which do not have a permanent dipole moment) display a stronger response to solvent variation than corresponding mononuclear species [36,42b]. Contributions from polarizability of the whole molecule [36] or local solvation effects (dipole–dipole interactions) at the individual polar metal/ligand binding sites [91] have been invoked to account for such effects.

The capability of tetrazine ligands to stabilize mixed-valent states has also allowed some detailed investigations of the IVCT transitions associated with mixed-valent species. Remarkably, the IVCT band of $[(H_3N)_4Ru(\mu\text{-bptz})Ru(NH_3)_4]^{5+}$ ($K_c = 10^{15}$) occurs at about the same energy as that of the Creutz–Taube ion $[(H_3N)_5Ru(\mu\text{-pz})Ru(NH_3)_5]^{5+}$ (see Scheme 6), however, with much lower intensity [51,54]. Unfavorable metal/ligand/metal orbital overlap in such a rigid bis(chelate) situation has been made responsible for this effect [51,83]; the analogous $[(bpy)_2Ru(\mu\text{-bptz})Ru(bpy)_2]^{5+}$ has a higher IVCT band intensity due to admixture of bpy contributions [50].

Vibrational spectroscopy (IR, resonance Raman) in conjunction with ab initio calculations has been used recently to study bptz, the $\{(\mu,\eta^2{:}\eta^2\text{-bptz})[Cu(PPh_3)_2]_2\}^{2+/\bullet+}$ pair and the $[(bpy)_2Ru(\mu\text{-bptz})Ru(bpy)_2]^{4+}$ species in the ground and excited state, in the reduced and oxidized form [50]. The results confirm the tetrazine-centered LUMO and suggest Class III delocalized formulations for both the MLCT excited state of the Ru^{II}Ru^{II} ion and the mixed-valent Ru^{II}Ru^{III} state [50].

8. Outlook

This review has illustrated the established coordination variety of substituted ‘aromatic’ tetrazine ligands and their unique electronic structure, based on the presence of very low-lying π* orbitals. While 1,2,4,5-tetrazine itself has not been used by many groups, probably due to its non-trivial synthesis, it is a remarkable small bridging ligand, conveying efficient metal–metal interaction as evident from stable mixed-valent intermediates and high electrical conductivity. On the other hand, 3,6-disubstituted tetrazines which are more conveniently accessible through the reaction of nitriles with hydrazine have been shown to form dinuclear complexes, coordination oligomers and polymers with unusual structures and spectroscopic properties. The facile electron uptake by tetrazine ligands has also been responsible for their occurrence as radical anions or 1,4-dihydro forms in well-characterized complexes. However, there are still fields to be explored such as the capability of tetrazine bridging ligands for magnetic coupling or the full use of all available coordination sites in bmtz; in any case, the tetrazine ligands continue to be promising components of functional supramolecular entities in further efforts towards ‘molecular electronics’.

Acknowledgements

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