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Tripodal Tetraamine Ligands Containing Three Pyridine Units: The *other* Polypyridyl Ligands

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The chemistry of tripodal ligands containing three (2-pyridyl)-alkyl arms attached to an aliphatic N atom (tripyridyl tripodal ligands) is reviewed. An outline of the variety of such ligands is given and methods for their synthesis are detailed. The structures of metal complexes containing tripyridyl tripodal ligands are briefly discussed, with particular emphasis on the structures adopted by complexes containing metal ions of varying coordination number. A brief overview of the complexes of tpa, the most widely used tripyridyl tripodal ligand, and its derivatives, is given. The electronic properties of tripyridyl tripodal ligands are detailed, as determined from spectroscopic, NMR, magnetochemical, electrochemical and p*K*a measurements on their metal complexes. Some examples of the reactivity of complexes containing tripyidyl tripodal ligands are given which outline the importance of both steric and electronic effects of the ligands in determining the reactivity of the metal complexes.

Introduction

Multidentate ligands containing two or more pyridine donor units play a significant role in modern coordination chemistry. While it is tempting, and indeed technically correct from a purely English standpoint, to use the term "polypyridyl" to describe such ligands, the currently understood definition of the word "polypyridyl" refers only to a relatively small subset of these ligands. Probably the earliest definition appears to be that of Burstall, who, in 1938 stated that "Polypyridyls are bases in which two or more pyridine rings are linked (but not fused) together."[1] Such a definition was originally used to describe common ligands such as 2,2′-bipyridine (bipy), 2,6′,2′′-terpyridine (terpy) and higher homologues, in which pyridine units are joined by a single C–C bond about which free rotation is possible. It has now grown to include systems such as 1,10-phenanthroline and its derivatives in which separate pyridine rings are fused to a common benzene ring, thereby imparting a significant degree of rigidity both in terms of the loss of rotational freedom of the pyridine rings and also in the positioning of their donor N atoms. Excluded from the above definition are ligands containing two or more pyridine units which are not directly linked. An important class of these are tetradentate tripodal ligands containing three 2-pyridyl-appended alkyl arms connected to a central N atom (Figure 1). These ligands, hereinafter referred to as tripyridyl tripodal ligands, have become widely used in coordination chemistry since the initial report of the first example, tpa, by Anderegg and Wenk in 1967.[2] The importance of such ligands can be appreciated by considering the wide variety of tpa complexes that have been prepared, and the applications that these complexes have found. Tpa complexes containing all transition metals except Ti, Zr, Hf, Nb, Ta, Tc and (somewhat surprisingly) Ag have been reported; such complexes have been variously used as enzyme models,[3] oxidation,[4] oxygenation,[5] hydroxylation,[6] epoxidation,[7] aziridination,[8] atom-transfer radical addition[9] and atom-transfer radical polymerisation[10] catalysts, spin-crossover species,[11] and phosphodiester cleavage agents[12] in addition to their inherent interest as novel chemical species in their own right. This review discusses tripyridyl tripodal

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ligands and their metal complexes. The structure of these ligands allows tremendous scope for derivatisation of the basic ligand skeletons, and as a result an enormous number of such ligands, and their metal complexes, have been reported – indeed there are nearly 1000 complexes containing the unsubstituted tpa ligand alone! Therefore, this review does not attempt to be comprehensive; while outlining and discussing some important individual complexes containing tpa and its derivatives, it focuses primarily on studies involving metal complexes of *series* of tripyridyl tripodal ligands. The ligands within these series differ either in the lengths of the aliphatic chains or in the nature and number of substituents on the pyridine rings. In many cases, these small changes in the ligand structure give rise to significant differences in the structures, physical properties and reactivities of the metal complexes. This review attempts to highlight and summarise systematic studies which quantify these effects. It also complements other reviews on related ligand systems.[13,14]

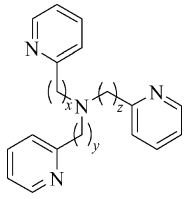


Figure 1. The general structure of the tripyridyl tripodal ligands.

General Structure of Tripyridyl Tripodal Ligands

Tripyridyl tripodal ligands have the general structure outlined in Figure 1 in which three (2-pyridyl)-alkyl arms are attached to a central aliphatic nitrogen atom. In the absence of sterically bulky substituents, such an arrangement of nitrogen atoms allows these ligands to potentially bind to a transition-metal ion in a tetradentate fashion. While ligands containing (3- and 4-pyridyl)-alkyl chains are also possible, the positioning of the nitrogen atom in the pyridine rings of such ligands precludes coordination of all four nitrogen atoms to a single metal ion.

The great variety of these ligands results from two structural features, namely the length of the aliphatic chains, and the different possible substituents that can be incorporated at both the aliphatic and pyridine carbon atoms. The aliphatic chains can potentially have any combination of lengths, ranging from all three the same ($x = y = z$), in which case a nominally C_{3v} symmetric ligand obtains, to all three different ($x \neq y \neq z$), and systematic variation of the chain lengths gives homologous series of ligands.

The "simplest" tripyridyl tripodal ligand is tris(2-pyridyl)-amine ($x = y = z = 0$, Figure 2). Coordination of all four nitrogen atoms in this ligand to a single transition-metal ion would result in the formation of three four-membered chelate rings. However, the geometrical constraints of this ligand appear to preclude such a coordination mode. While there are examples of complexes in which this ligand coordinates in a tridentate fashion through the three pyridine nitrogen atoms[15–18] the fact that it does not act as a tetradentate ligand means that it lies outside the scope of this review and therefore will not be discussed further. Incorporation of a single methylene chain gives the ligand L1 ($x = 1$, $y = z = 0$; Figure 2). This ligand also appears not to be sufficiently flexible to allow coordination of all four nitrogen atoms as it only exhibits bidentate coordination through two pyridine nitrogen atoms in its structurally characterised complexes.[19] It can also act as a bridging ligand in a number of coordination polymers.[19] The ligand L2 ($x = y = 1$, $z = 0$) appears to be the simplest tripyridyl tripodal ligand which can act as a tetradentate ligand; it coordinates through all four nitrogen atoms in the oxo-bridged dimer $[(L2)BrFeOFeBr(L2)]^{2+}$.[20]

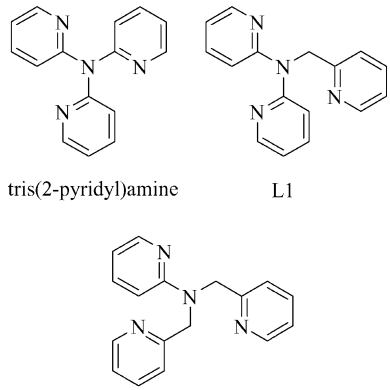


Figure 2. Structures of ligands having at least one 2-pyridyl unit directly attached to the aliphatic N atom.

The four tripyridyl tripodal ligands having x, y and z = 1 or 2, and their numerous substituted derivatives, are by far the most widely studied as they give rise to five- and six-membered chelate rings respectively, on coordination to a metal ion. The ligand having $x = y = z = 1$ has the IUPAC name 1-pyridin-2-yl-*N*,*N*-bis(pyridin-2-ylmethyl)methanamine, but is more commonly known as tris(2-pyridylmethyl)-amine, and is abbreviated variously as tpa or tmpa. This is easily the most commonly used of the tripyridyl tripodal ligands, and many substituted derivatives are also known. The three other members of the homologous series with x, y and z = 1 or 2 are tris[2-(2-pyridyl)ethyl]amine ($x = y = z = 2$; tepa), and the "asymmetric" ligands bis[(2-pyridyl)-methyl]-2-[(2-pyridyl)ethyl]amine ($x = y = 1$, $z = 2$; pmea) and bis[2-(2-pyridyl)ethyl]-2-[(2-pyridyl)methyl]amine ($x = y = 2$, $z = 1$; pmap). These ligands are depicted in Figure 3. There are no reports of tripyridyl tripodal ligands having x, y, or $z > 2$, presumably owing to the instability of the large chelate rings that would be formed on coordination to a metal ion.

Substitution at any available pyridyl carbon atom of a tripyridyl tripodal ligand can lead to a myriad of different possible ligands, and such an approach is particularly useful in altering either the steric or electronic characteristics of a particular tripodal ligand. Incorporation of electron donat-

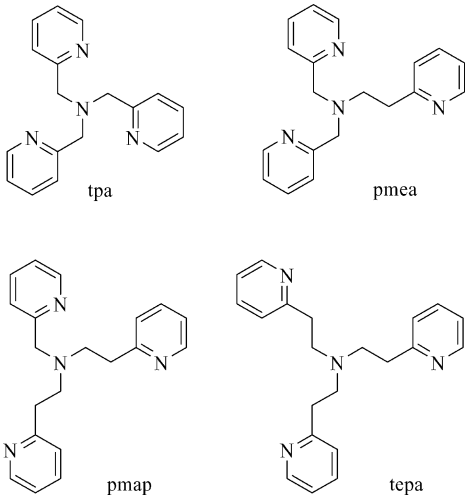


Figure 3. Structures of tpa, pmea, pmap and tepa, the most common tetradentate tripodal pyridyl ligands.

ing or withdrawing groups on one or more pyridine rings can substantially alter the donor properties of the ring nitrogen atom, while introduction of bulky groups, particularly at the 6-position of a pyridine ring (adjacent to the nitrogen atom), can have significant effects on the structure of the resulting metal complex. These aspects will be discussed below. Substitution at the aliphatic carbon atoms is also possible, but has been much less exploited.

Additional coordinating moieties including 2,2′-bipyridine,[21] cyclen,[22] and crown ether[23,24] derivatives, can also be introduced on the parent tripodal ligand skeleton. Arguably the most important example of this is the series of porphyrin-appended tpa ligands developed by Karlin and co-workers[25] which have been used to prepare Fe/Cu complexes which function as cytochrome *c* oxidase models. The structure of one of these ligands, ^{6}L,[26] is given in Figure 4. Tpa units have also been linked together, either directly,[27] or through phenyl[28] alkyl[29,30] ketone[30] or ether[31] linkages between carbon atoms on the pyridine rings. An aesthetically pleasing illustration of one of the ways in which tpa units can be linked is given by the ligand SYMM[31] shown in Figure 5, which binds three Cu^{II} ions

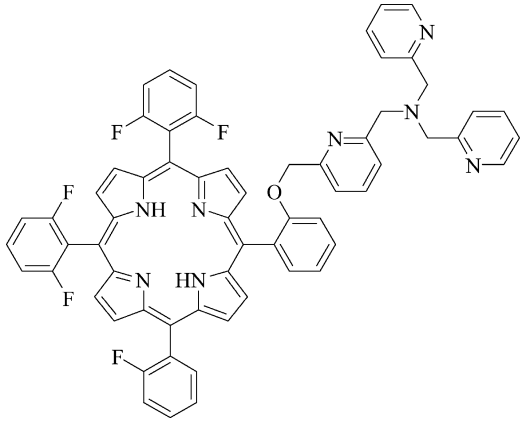


Figure 4. The ^{6}L ligand.

using all but the central N atom. There are at present no examples of linkages between tpa units involving the methylene carbon atoms.

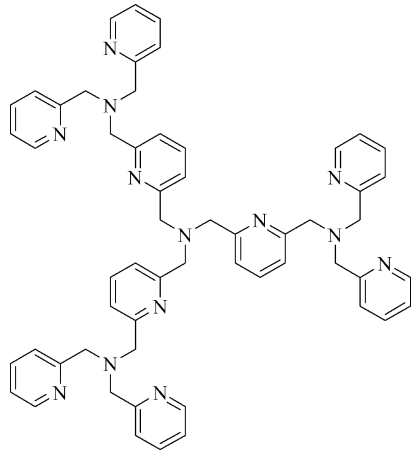
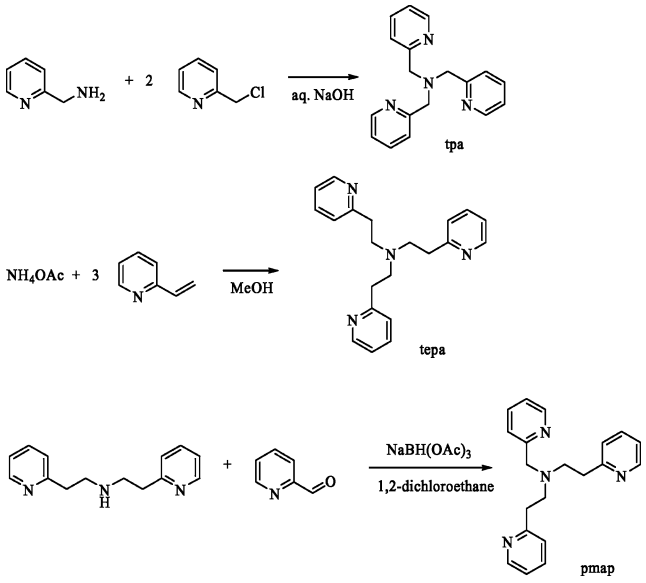


Figure 5. The SYMM ligand.

Synthesis of Tripyridyl Tripodal Ligands

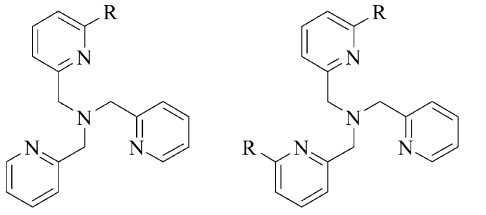
The main method for the synthesis of tripyridyl tripodal ligands is alkylation of either ammonia or a primary (2-pyridyl)alkylamine with an appropriate pyridine precursor. For example, tepa is prepared from the reaction of 2-vinylpyridine with ammonium acetate ,[32–36] while tpa is prepared by the reaction of 2-(aminomethyl)pyridine with two equivalents of 2-(chloromethyl)pyridine.[2,37] The latter procedure can be adapted for the synthesis of "asymmetric" ligands, and both pmea and pmap (Figure 3) are prepared by this general method,[36,38,39] with 2-vinylpyridine being used as the alkylating agent in the synthesis of the latter.[36,40] Alternative syntheses of both pmea and pmap starting from the appropriate secondary bis(2-pyridylalkyl)-amine have also been reported; the reaction of 2-vinylpyridine with bis(2-pyridylmethyl)amine yields pmea, while pmap is prepared via reductive amination of bis(2-pyridylethyl)amine with 2-pyridinecarbaldehyde using sodium triacetoxyborohydride as the reducing agent.[41] Some of these synthetic methods are outlined in Scheme 1.

Given the relative unreactivity of the pyridine ring towards substitution reactions, and the difficulty of specifically directing such reactions to one, two or all three of the pyridine rings, direct substitution of the tripodal ligand is not used to prepare ligands containing substituents on the pyridine rings. The synthesis of such ligands is most conveniently carried out using variations of the above methods with the appropriately substituted precursors. For example, the mono-, di- and trimethyl tpa ligands shown in Figure 6 can be prepared using 2-chloromethyl-6-methylpyridine as the alkylating agent towards the appropriate amine[42,43] while the synthesis of 6-Metpa involving reductive amination of 6-methyl-2-pyridinecarboxaldehyde has also been reported.[39] Synthesis of the amino substituted ligands



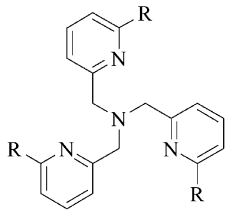
Scheme 1. Some synthetic methods used in the synthesis of tripyridyl tripodal ligands.

mapa, bapa and tapa (Figure 6) generally proceeds through hydrolysis of the appropriate pivaloylamido-substituted species mppa, bppa and tppa, respectively.[44–47]



R = CH_3: 6-Metpa
R = NH_2: mapa
R = $NHCH_2tBu$: mnpa
R = NHC(O)*t*Bu: mppa

R = CH_3: 6-Me_2tpa
R = NH_2: bapa
R = $NHCH_2tBu$: bnpa
R = NHC(O)*t*Bu: bppa



R = CH_3: 6-Me_3tpa
R = NH_2: tapa
R = $NHCH_2tBu$: tnpa
R = NHC(O)*t*Bu: tppa

Figure 6. Series of 6-methyl-, 6-amino- and 6-amido-substituted tpa ligands.

Ligands containing substituents on the aliphatic carbon atoms are less numerous than those substituted on the pyridine rings, and again are generally prepared using the appropriately substituted precursor. As the methylene protons of the unsubstituted tripyridyl tripodal ligand are prochiral, substitution of one of these can lead to the formation of chiral ligands such as those shown in Figure 7. These have been isolated in their homochiral forms using resolved chiral precursors.[37,48–50]

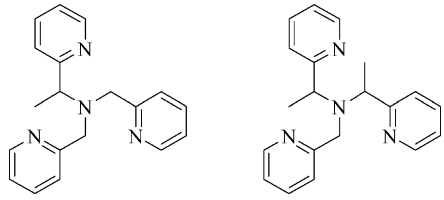


Figure 7. Tpa derivatives substituted at the aliphatic carbon atoms.

Structures of Metal Complexes Containing Tripyridyl Tripodal Ligands

Given the long history of some of their aliphatic counterparts (tren, for example, was first prepared in 1896[13]), it is somewhat surprising that the synthesis of the first tripyridyl tripodal ligand, tpa, was reported as recently as 1967.[2] However, since this time the coordination chemistry of such ligands has been extensively studied, and they have been widely used as ligands towards the majority of the transition metals and lanthanide ions, as well as most of the Group 1 and Group 2 metals and some actinides.

As mentioned above, tpa is the most widely studied tripodal pyridyl ligand and a relatively detailed outline of its coordination modes (and those of its derivatives) is appropriate. There are no structurally characterised examples of four-coordinate transition-metal complexes of the type $[M(tpa)]^{n+}$; the bite angles in the tpa ligand are not sufficiently large to allow tetrahedral coordination of a single metal ion, and the preferred trigonal-pyramidal arrangement of the tpa donor atoms always allows unhindered approach of another ligand from the bottom side of the basal plane. However, the introduction of sterically demanding substituents at the 6-position of the tpa ligand can block this access. This is illustrated by the isolation and structural characterisation of the four-coordinate Cu^I complexes containing 6-substituted tpa derivatives shown in Figure 8.[51–53]

The metal ions display approximate trigonal-pyramidal geometries in each case, as shown by their τ_4 values of 0.77, 0.86 and 0.84, respectively (the structural parameter τ_4 is defined by the equation $\tau_4 = [360° - (\alpha + \beta)]/141°$, where α and β are the two largest X–M–X angles in the four-coordinate complex; τ_4 ranges from 0 for perfect square-planar geometry to 1.00 for perfect tetrahedral geometry, with $\tau_4 = 0.85$ for perfect trigonal-pyramidal geometry[54]). Not surprisingly, tris(2-quinolylmethyl)amine (tmqa, Figure 9), the quinolyl analogue of tpa, has similar steric features, and the complex $[Cu(tmqa)]ClO_4$ also exhibits a four-coordinate trigonal-pyramidal geometry about the Cu^I ion, with τ_4 values of 0.77 and 0.83 for the two independent molecules in the asymmetric unit.[55]

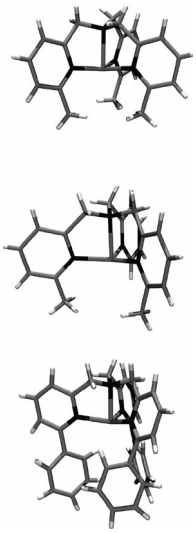


Figure 8. Diagrams of the cations of the four-coordinate Cu^{I} complexes $[Cu(6\text{-}Me_3tpa)]ClO_4$[51] (top), $[Cu(6\text{-}Me_2tpa)]BPh_4$[52] (middle) and $[Cu(6\text{-}Ph_3tpa)]BPh_4$.[53]

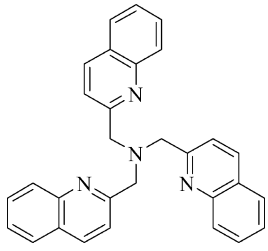


Figure 9. The tmqa ligand.

Square-planar geometry about a metal ion cannot be accommodated by the tpa ligand, and d^8 metal ions such as Pt^{2+} and Pd^{2+}, which prefer such a geometry, instead form complexes such as $[Pt(tpa)Cl]^{+}$[41] and $[Pd(tpa)Cl]^{+}$ (Figure 10)[41,56] in which the tpa ligand binds in a hypodentate[57,58] fashion as a tridentate ligand, with one pyridine remaining unbound. This tridentate coordination mode is also seen in a number of complexes having higher coordination numbers, most notably the six-coordinate $[Ru(tpa)_2]^{2+}$[59] (Figure 10) and $[Fe(tpa)_2]^{2+}$[60] cations which both contain two hypodentate tpa ligands. Hypodentate coordination can also be induced by the introduction of bulky substituents at the 6-position of one or more pyridine rings of the tpa ligand, and examples of this are surprisingly common, with over 30 structurally characterised complexes known.

Five-coordinate complexes containing tpa and its derivatives are relatively numerous, and such complexes generally adopt a trigonal bipyramidal, rather than square pyramidal, geometry owing to the steric requirements of the tripodal ligands.[13] The tmqa ligand again provides the notable exception to this, with the cation of the Cu^{II} complex $[Cu(tmqa)Cl]PF_6.MeCN{\cdot}0.5Et_2O$[61] displaying an essentially square-pyramidal structure as evidenced by the τ_5 value of 0.06 [$\tau_5 = (\beta - \alpha)/60$, where again α and β are the two largest X–M–X angles; $\tau_5 = 0$ for perfect square-pyramidal geometry, while $\tau_5 = 1.00$ for perfect trigonal-bipyramidal geometry[62]]. Six-coordinate complexes containing tpa and derivatives are common. These have the general formula $[M(tpa)X_2]^{n+}$, where X_2 can be either two monodentate or a single bidentate ligand, and generally display distorted octahedral geometries. It is worth noting that the sites occupied by the X_2 ligand(s) are not chemically equivalent; one lies opposite the tertiary aliphatic nitrogen atom, while the other is *trans* to a pyridine nitrogen atom. This becomes apparent when an asymmetric bidentate ligand is coordinated at the X_2 sites, thereby giving rise to two geometric isomers (Figure 11).[63,64] These isomeric possibilities often remain unremarked upon, which is surprising given that such isomers can have significantly different chemical and physical properties, and it is crucial that solution studies are carried out in situations where such isomers are possible in order to confirm their presence or absence.

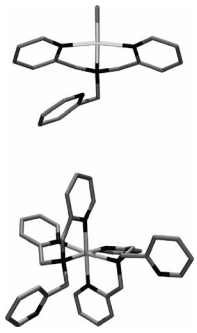


Figure 10. Hypodentate coordination of the tpa ligand in the cations of $[Pd(tpa)Cl]Cl{\cdot}2H_2O$[41] (top) and $[Ru(tpa)_2](PF_6)_2{\cdot}0.5CH_2Cl_2$.[59] H atoms have been omitted for clarity.

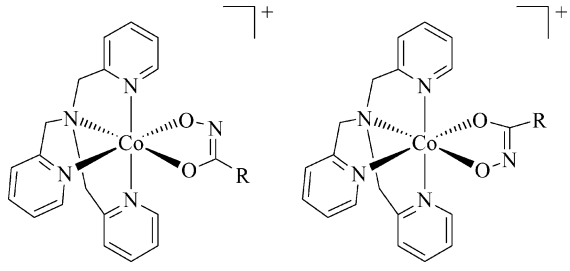


Figure 11. The two possible geometric isomers of Co^{III} tpa complexes containing bidentate hydroximate ligands; R = Me, Et, Ph.[64]

Seven- and eight-coordinate complexes containing tpa have also been structurally characterised. Examples of the latter include $[Fe(tpa)_2](BPh_4)_2$[60] and $[Mn(tpa)_2](ClO_4)_2$,[65] which contain two tetradentate tpa ligands per metal ion.

In addition to the geometric isomers shown in Figure 11 which arise from the non-equivalence of the two remaining coordination sites about a six-coordinate metal ion, the symmetry of the tripyridyl tripodal ligand can also give rise to other isomeric possibilities. For example, geometric isomers exist in six-coordinate complexes containing pmea and pmap due to the different possible positioning of the five- and six-membered chelate rings relative to the two coordination sites not occupied by the tripodal ligand.[66] Simi-

larly, the introduction of substituents on one or two pyridine rings leads to different possible positionings of these substituents relative to other atoms in the complex. Therefore, two possible such isomers exist for the complex [Co(6-Metpa)(O_2CO)]$^+$, in which the Me substituent sits in either the equatorial or axial plane.[67] The isomeric possibilities for both situations are depicted in Figure 12. Numerous isomers are also possible in square-pyramidal five-coordinate complexes as a result of the axial or equatorial positionings of the aliphatic N atom, the five- or six-membered chelate rings and/or the substituted pyridine rings.

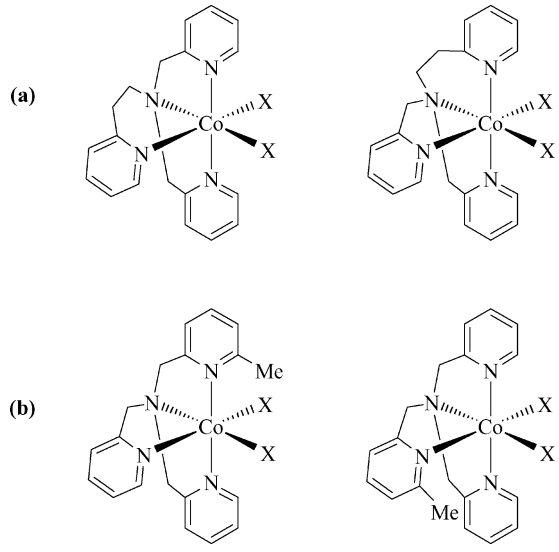


Figure 12. Isomeric possibilities in six-coordinate complexes arising from (a) the different relative positionings of five- and six-membered chelate rings, and (b) the different relative positionings of pyridine substituents.

Significant changes in complex geometries are observed on increasing the length of the aliphatic chains in the tripodal ligands, and complexes containing pmea, pmap, tepa and their derivatives display some distinct differences with respect to the geometries about the metal ion when compared to their tpa analogues. For example, the four-coordinate Cu^I complexes [Cu(L)]$^+$ (L = pmea,[36] pmap[36] and tepa[33]) are all easily prepared, without the requirement to introduce bulky substituents on the pyridine rings. There is a gradual decrease in the value of τ_4 across the series [Cu(tepa)]$^+$ (0.84), [Cu(pmap)]$^+$ (0.75), [Cu(pmea)]$^+$ (0.72) signifying a change from almost perfect trigonal pyramidal to a more see-saw geometry, presumably as a result of the decreasing flexibility of the ligands. In contrast to trigonal bipyramidal [Cu(tpa)Cl]$^+$ the five-coordinate complexes [Cu(tepa)Cl]$^+$,[68] [Cu(pmap)Cl]$^+$[36] and [Cu(pmea)Cl]$^+$[36] display essentially square-pyramidal geometries [τ_5 values of 0.19, 0.08 and 0.14/0.12 (two cations in the asymmetric unit) respectively], with the Cl ligand lying *trans* to the aliphatic N atom in all cases.

Introduction of substituents on the pyridine rings, particularly at the 6-position, can have significant structural implications on the resulting metal complexes. For example, while [Cu(tpa)Cl]$^+$ displays essentially perfect trigonal-bipyramidal geometry (τ_5 = 1.00)[68] the complexes [Cu(L)Cl]$^+$ (L = 6-Metpa, 6-Me_2tpa, 6-Me_3tpa) containing methylated tpa ligands exhibit geometries which tend much more towards square pyramidal (τ_5 = 0.16/0.24, 0.06 and 0.34, respectively).[69] However, when the substituent(s) on the pyridine ring(s) is/are capable of hydrogen bonding with the remaining ligand in a five-coordinate complex, then this effect is not so marked. Thus [Zn(tpa)Cl]$^+$ is essentially trigonal bipyramidal (τ_5 = 0.93, 0.99/0.94)[70,71] as are the amino-substituted complexes [Zn(L)Cl]$^+$ (L = mapa, tapa, mnpa, bnpa, tnpa; τ_5 = 0.83, 1.00, 0.80, 0.82 and 0.94 respectively).[45,72] In six-coordinate complexes, where such large geometric changes are not possible, increasing substitution of the pyridine rings can significantly affect M–N bond lengths. This is demonstrated in the complexes [Co(L)-O_2CO]$^+$ (L = tpa, 6-Metpa, 6-Me_2tpa, 6-Me_3tpa), where the increasing Co–N_{av} distances (1.915 Å, 1.936 Å, 1.950 Å and 1.982 Å, respectively; Table 1) appear to arise as a result of unfavourable steric interactions of the ligand methyl groups.[67] Incorporation of substituents at the 6-position of the pyridine rings which can potentially bind to the metal ion also influences the nature of the complexes obtained. For example, reaction of mppa, bppa and tppa (Figure 6) with $RuCl_3 \cdot 3H_2O$ in either MeOH or EtOH in the presence of Et_3N gives the Ru^{II} complexes [Ru(mppa)Cl]$^+$, [Ru(bppa)Cl]$^+$ and [Ru(tppa)Cl_2], respectively, while in the absence of Et_3N the final reaction gives the hypodentate Ru^{III} complex *mer*-[Ru(tppa)Cl_3] in which the tppa ligand is tridentate. While the tppa ligand in [Ru(tppa)Cl_2] coordinates to the Ru^{II} ion in a tetradentate fashion, both mppa and bppa act as pentadentate ligands in their Ru^{II} complexes, with an amide O atom binding to the metal centre *trans* to the aliphatic N atom in both cases (Figure 13). Under the same reaction conditions in the absence of Et_3N, the reduced amino ligands mnpa, bnpa and tnpa all give the dichloro Ru^{III} complexes [Ru(L)Cl_2]$^+$ in which the tripyridyl tripodal ligands are bound in a tetradentate fashion.[73]

Table 1. UV/Vis and ^{59}Co NMR spectroscopic data (aqueous solution) for [Co(L)(O_2CO)]$^+$ complexes containing tripyridyl tripodal ligands.

L	λ_{max} [nm]	Δ [cm^{-1}]	δ^{59}Co/ppm	Co–N_{av} [Å]
tpa	487, 348	22172	7965	1.915
pmea	500, 357	21599	8509	1.926
pmap	515, 360	21077	9096	1.961
tepa	526, 384	20425	10121	1.995
tpa	487, 348	22172	7965	1.915
6-Metpa	502, 355	21562	8606	1.936
6-Me_2tpa	516, 365	20976	9162	1.950
6-Me_3tpa	544, 379	19970	10251	1.982

The chelate rings formed in complexes containing tripyridyl tripodal ligands contain two sp^2-hydridised atoms, and this can confer significant rigidity on these chelate rings when compared to their aliphatic counterparts. For example, VT ^{1}H and ^{13}C NMR spectra of [Co(pmea)(O_2CO)]$^+$ give evidence for a fluxional process involving inversion of

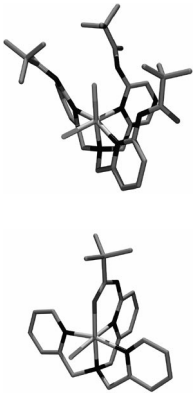


Figure 13. Structures of $[Ru(tppa)Cl_2]$ (top) and the $[Ru(mppa)Cl]^+$ cation. H atoms have been omitted for clarity.

the unique six-membered chelate ring. $\Delta G^{\ddagger}$ for this process at 25 °C is 58 kJ mol^{-1}, significantly greater than values measured for the normally more rigid aliphatic five-membered rings (ca. 40 kJ mol^{-1}), attesting to the considerable rigidity of the ligand chelate rings in this complex.[66]

The use of tripyridyl tripodal ligands is not limited solely to the synthesis of complexes containing a single metal ion. Tpa and its substituted derivatives in particular have been used in the synthesis of numerous homo- and heteromultimetallic complexes. Species as diverse as C_2H_4,[74] CN^-,[75] $NH_2C(O)NH^-$,[76] peroxycarbonate,[77] $P_2O_7^{4-}$,[78] and S_2^{2-}[79] have been used as bridging ligands in binuclear complex cations of the type $[M(Rtpa)X(Rtpa)M]^{n+}$ (Rtpa = tpa or any tpa-derived ligand), while complexes containing the trinuclear cations $\{[U(tpa)(\mu\text{-}O)I]_3(\mu_3\text{-}I)\}^{2+}$,[80] $[Fe_3(\mu\text{-}O)_3(tpa)_3]^{3+}$[81] and $[Fe_3(\mu\text{-}O)_3(5\text{-}Ettpa)_3]^{3+}$,[82] $[(M(tpa))_3(\mu_3\text{-}CO_3)]^{4+}$ (M = Cu^{2+},[83] Zn^{2+}[83,84] (Figure 14)) and $[(Cu(tpa))_3(ta)]^{3+}$[85] (ta = trianion of trimesic acid) have also been structurally characterised. The tetracopper complex cations $[(Cu(tpa))_4M(CN)_4]^{6+}$ (M = Ni, Pt), in which the $[M(CN)_4]^{2-}$ unit acts as a quadruply bridging ligand, have been structurally characterised as their perchlorate salts (M = Ni, Figure 14),[86] while the $[Fe(CN)_6]^{4-}$ unit is used to bridge six $[Cu(tpa)]^{2+}$ fragments in the hexacopper complex $[(Cu(tpa))_6Fe(CN)_6](ClO_4)_8\cdot 3H_2O$ (Figure 14).[87]

Figure 14. Structures of the $[(Zn(tpa))_3(\mu_3\text{-}CO_3)]^{4+}$ (top), $[(Cu(tpa))_4Ni(CN)_4]^{6+}$ (middle) and $[(Cu(tpa))_6Fe(CN)_6]^{8+}$ cations. H atoms have been omitted for clarity.

Complexes Containing tpa and Derivatives: A Brief Overview

Although tpa was first reported in 1967, the first complexes containing tpa were not prepared until 1969,[88] while X-ray structural characterisation of a tpa complex was not achieved until 1982, when $[Cu(tpa)Cl]PF_6$ was shown to adopt a trigonal-bipyramidal geometry (τ_5 = 1.00).[68] The values of formation constants for M^{2+} ions with tpa in aqueous solution follow the order predicted by the Irving–Williams series, with log K_f values as follows: Mn^{2+}, 5.62; Fe^{2+}, 8.65; Co^{2+}, 11.68; Ni^{2+}, 14.60; Cu^{2+}, 16.15; Zn^{2+}, 11.00.[89] These values are similar to those obtained using tren, the aliphatic analogue of tpa, indicating that both ligands have comparable affinities for transition-metal ions despite the greater basicity of the aliphatic N donor atoms in tren.

As mentioned in the introduction, complexes containing tpa and its substituted derivatives have found use in a variety of areas of chemistry. The high affinities of such ligands for transition-metal ions, coupled with their relative resistance to oxidation, reduction and other decomposition reactions, make them ideal for use in complexes containing metal ions in a range of oxidation states. Although at first glance, the synthesis of mononuclear complexes of tpa and its derivatives might appear relatively straightforward and predictable, one need only consider the remarkable variety of complexes obtained on mixing various simple Fe^{II} salts with tpa to show that this is not the case. For example, while reaction of tpa with anhydrous $FeCl_2$ gives the expected six-coordinate $[(tpa)FeCl_2]$ complex,[90] the same reaction with $Fe(CF_3SO_3)_2\cdot 2MeCN$ gives variously six-coordinate low-spin $[(tpa)Fe(MeCN)_2](CF_3SO_3)_2$, six-coordinate high-spin $[(tpa)Fe(OSO_2CF_3)_2]$, six-coordinate hypodentate $[Fe(tpa)_2](CF_3SO_3)_2$ and eight-coordinate $[Fe(tpa)_2](BPh_4)_2$, depending on the mole ratio of Fe^{II} to tpa, the solvent, and the counterion.[60] In addition to the usual "classical" coordination complexes, a number of organometallic complexes containing tpa and derivatives have also been reported. Notable examples include the metallacyclic Co^{III} complex $[Co(tpa)(CH_2NH_2)](BPh_4)_2.(CH_3)_2CO$, formed from photodecarboxylation of the $[Co(tpa)gly]^{2+}$ cation (Figure 15),[91] the Cr^{III} alkyl complex $[Cr(tpa)(Me)_2]BPh_4\cdot 0.5CH_2Cl_2$, prepared by treatment of $[Cr(tpa)Cl_2]^+$ with MeMgCl,[92] the Rh^{III} metallaoxetane and metalladioxolane complexes $[(6\text{-}Metpa)Rh(\kappa^2C^1,O\text{-}CH_2CH_2O\text{-})]BPh_4\cdot 1.5H_2O$[93] and $[(tpa)Rh(\kappa^2C^1,O^2\text{-}CH_2CH_2OO\text{-})]$-

$BPh_4 \cdot 0.5MeCN \cdot 0.5ClCH_2CH_2Cl \cdot 0.5Et_2O$ (Figure 16),[94] and the $\eta^1:\eta^1$-ethylene-bridged Ir^{III} dimers $[(Rtpa)(MeCN)Ir(C_2H_4)Ir(MeCN)(Rtpa)](PF_6)_4$ (Rtpa = 6-Me_2tpa, 6-Me_3tpa).[95]

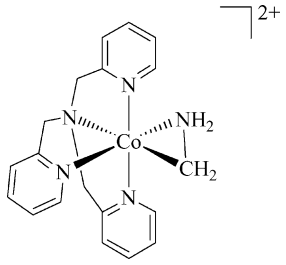


Figure 15. The $[Co(tpa)(CH_2NH_2)]^{2+}$ cation.

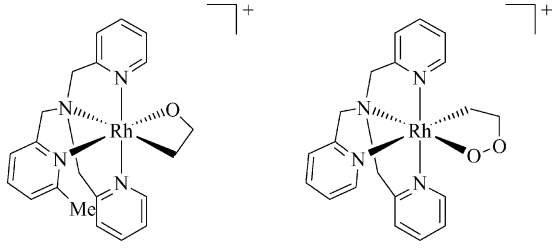


Figure 16. The cations of structurally characterised Rh^{III} metallaoxetane and metalladioxolane complexes.

Dimeric complexes containing $M(tpa)^{n+}$ units bridged by bis(bidentate) benzoquinone-derived ligands (Figure 17) have been found to display interesting electronic behaviour. For example, the complex $[(tpa)Fe(THBQ)Fe(tpa)](BF_4)_2$ (THBQ = the dianion of 2,3,5,6-tetrahydroxy-1,4-benzoquinone) undergoes a spin-crossover process around 250 K with thermal hysteresis (width ca. 10 K) as well as exhibiting ferromagnetic coupling below 45 K,[96] while the closely related complex $[(tpa)Fe(DBQ)Fe(tpa)](BF_4)_2$ (DBQ = the dianion of 2,5-di-*tert*-butyl-3,6-dihydroxy-1,4-benzoquinone) undergoes spin-crossover at room temperature.[11] The Co^{III}–Co^{III} dimer $[(tpa)Co(DHBQ)Co(tpa)](PF_6)_3$ contains the $DHBQ^{3-}$ radical as a bridging ligand (DHBQ = the dianion of 2,5-dihydroxy-1,4-benzoquinone), and this complex undergoes both thermal and light-induced valence tautomerism to give a product formulated as a Co^{III}–Co^{II} dimer with a $DHBQ^{2-}$ bridging ligand. Interestingly, the thermal process displays hysteresis, which is thought to be a result of π–π interactions between the pyridyl rings on adjacent cations.[97] Another radical, in this case the chloranilate radical $CA^{\cdot 3-}$, is found to act as a bridging ligand in both the Co^{II}–Co^{II} and Co^{III}–Co^{III} dimers $[(tpa)Co(CA)Co(tpa)](BF_4) \cdot 2Et_2O$[98] and $[(tpa)Co(CA)Co(tpa)](BF_4)_3 \cdot 4MeCN$.[99]

Tpa and its derivatives have found particular use in the synthesis of transition-metal complexes as models for biomolecules, and the extensive work of Karlin, using Cu complexes,[100] and Que, using Fe complexes,[101] deserves special mention in this regard. X-ray structural characterisation of the first copper–dioxygen complex $[(tpa)Cu(O_2)Cu(tpa)](PF_6)_2 \cdot 5Et_2O$ by Karlin and co-workers in 1988 added significant impetus to the study of Cu-containing biomolecules and ultimately led to important advances in the bioinorganic model chemistry of copper. In this complex the Cu^{II} ions are bridged by a *trans*-1,2-O_2^{2-} peroxo unit, as shown in Figure 18.[102] Interestingly, when the ligand 6-Me_2tpa is used under the same conditions, the bis(μ-oxo)Cu^{III} dimer $[(6\text{-}Me_2tpa)Cu(O)_2Cu(6\text{-}Me_2tpa)](PF_6)_2 \cdot 2(CH_3)_2CO$ (Figure 18) is isolated.[52] Also of note is the mononuclear hydroperoxo complex $[Cu(bppa)(OOH)]ClO_4$, formed on treatment of $[Cu(bppa)]ClO_4$ or $[Cu(bppa)(CH_3COO)]ClO_4$ with excess H_2O_2 at room temperature. This unusual stability of this complex is believed to be due to intermolecular hydrogen bonding of the hydroperoxo ligand with the amide N–H protons of the bppa ligand, as well as protection of the hydroperoxo ligand by the hydrophobic *tert*-butyl groups of bppa.[103]

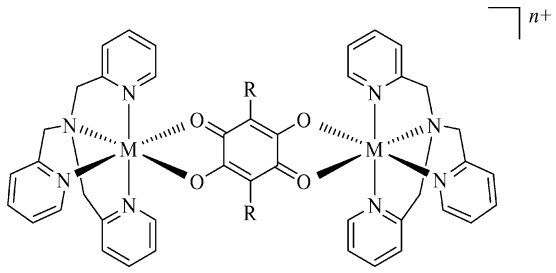


Figure 17. The general structure of benzoquinone-bridged dimers. R = *tert*-butyl, H, OH, Cl. M = Fe, Co. Note that isomers which differ in the relative positionings (mutually *cis* or *trans*) of the tertiary aliphatic N atoms of tpa are possible and examples of each have been structurally characterised.

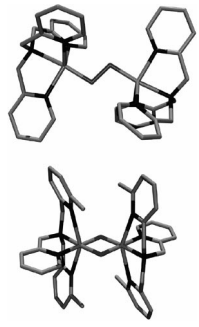


Figure 18. Views of the $[(tpa)Cu(O_2)Cu(tpa)]^{2+}$ (top) and $[(6\text{-}Me_2tpa)Cu(O)_2Cu(6\text{-}Me_2tpa)]^{2+}$ cations. H atoms are omitted for clarity.

Tpa derivatives have also been found to support high-valent iron-oxo species. The first structurally characterised bis(μ-oxo) Fe^{III} dimer, $[(6\text{-}Me_3tpa)Fe(O)_2Fe(6\text{-}Me_3tpa)](ClO_4)_2 \cdot 2THF$, was prepared by Que and co-workers in 1995,[104] and they subsequently prepared and structurally characterised the Fe^{III}–Fe^{IV} dimer $[(5\text{-}Et_3tpa)Fe(O)_2Fe(5\text{-}Et_3tpa)](ClO_4)_3 \cdot 2CH_3C(O)C_2H_5 \cdot CH_3OH$[105] which was shown to be valence delocalised. The monomeric Fe^{IV} complex $[Fe(O)(tpa)]^{2+}$ was also prepared by this group in

2003,[106] and recently they also reported the bis(μ-oxo)-Fe^{IV} dimer $[(L^b)Fe(O)_2Fe(L^b)]^{4+}$, L^b = (3,5-Me_2-4-OMe)$_3$-tpa),[107] although neither complex has been characterised by X-ray crystallography. Other high-valent first-row bis(μ-oxo) complexes containing tpa-derived ligands that have been structurally characterised include the mixed-valence Mn^{III}–Mn^{IV} dimer $[(tpa)Mn(O)_2Mn(tpa)](S_2O_6)_{3/2}\cdot 7H_2O$,[108] the Mn^{III}–Mn^{III} dimers $[(Rtpa)Mn(O)_2Mn(Rtpa)]X_2$ (Rtpa = tpa, X = BPh_4^-;[4] Rtpa = 6-Me_2tpa, X = NO_3^-;[109] Rtpa = 6-Me_3tpa, X = ClO_4^-[110]) and the Ni^{III}–Ni^{III} dimers $[(Rtpa)Ni(O)_2Ni(Rtpa)]X_2$ (Rtpa = 6-Me_2tpa, X = BPh_4^-;[111] Rtpa = 6-Me_3tpa, X = BF_4^-[112]). Also of interest is the mixed-valence rhenium dimer [(6-Metpa)$Re(O)_2$Re(6-Metpa)]$(PF_6)_3$, which exhibits a Re–Re distance of 2.426(1) Å, consistent with a Re–Re bond order of 2.5.[113]

Electronic Properties of Tripyridyl Tripodal Ligands

The limited available p*K*a data give an indication of the trends in basicity of the tripyridyl tripodal ligands. Only three pK_a values can be measured for tpa (approximately 2.6, 4.4 and 6.2[2,114] at 20–25 °C) and these have been assigned to deprotonation of the protonated pyridine nitrogen atoms on the basis of both ^{14}N and ^{15}N NMR spectroscopic data.[115] The fact that the aliphatic nitrogen atom displays negligible basicity is confirmed by the observation that the triprotonated, rather than tetraprotonated, ligand is generally isolated from acidic solution.[116–118] Three pK_a values are also obtained for tepa (approximately 3.5, 3.9 and 8.2)[119] although in this case, the fact that the ligand can be isolated as the tetraprotonated salt[32] suggests that the longer ligand arms result in the aliphatic nitrogen atom being appreciably more basic than that in tpa.

Studies of physical properties of transition-metal complexes containing tripyridyl tripodal ligands allow the ligand field strengths of these ligands to be quantified. Of particular importance in this respect are sets of metal complexes which contain ligands which differ only slightly from each other. Two such ligand sets which have been investigated in some detail are tpa; pmea; pmap; tepa (these differ in the number of aliphatic carbon atoms) and tpa; 6-Metpa; 6-Me_2tpa; 6-Me_3tpa (these differ in the number of substituents at the 6-position of the pyridine rings).

The Co^{III} complexes $[Co(L)(O_2CO)]^+$ (L = tpa, pmea, pmap, tepa) have been prepared and structurally characterised as ClO_4^- salts.[66] It can be seen from the structures of these complexes (Figure 19) that the introduction of CH_2 groups into the ligand arms has significant structural effects on the complex cations, the most important of which is an increase in the average Co–N bond lengths across the series, which in turn leads to a weakening of the ligand field exerted by the tripodal ligands. This weakening is manifested in some interesting spectroscopic and NMR behaviour.

Somewhat unusually for Co^{III} complexes having an N_4O_2 donor atom set, the complexes display a range of colours, from orange (tpa) to purple (tepa), with λ_{max} for the two observed d–d bands in the UV/Vis spectra increasing by approximately 40 nm from $[Co(tpa)(O_2CO)]^+$ to $[Co(tepa)(O_2CO)]^+$ (Table 1). Co^{III} complexes with a N_4O_2 donor set are usually red or red-purple, and given that the geometry of the chelated carbonate ligands in all four complexes is essentially identical, the range of colours of the complexes must arise from differences in the ligand field strengths of the tripodal ligands. This is borne out by the calculated Δ values in Table 1, which vary by 1747 cm^{-1} (ca. 21 $kJ\,mol^{-1}$) across the series of complexes. The ligand field differences are manifested not only in the UV/Vis spectra, but also in the ^{59}Co NMR spectra, data for which are given in Table 1. The greater than 2000 ppm difference in chemical shift across the series of complexes again bears testament to the large differences in ligand field strengths from tpa → tepa. The chemical shift of $[Co(tpa)O_2CO]^+$ is more typical of a CoN_6 system,[120] showing that the tpa ligand has a significant ligand field strength. The relatively weak-field nature of the tepa ligand is attested to by the fact that $[Co(tepa)(O_2CO)]^+$ cannot be prepared by the normal method of air oxidation of a Co^{II} salt in the presence of tepa and HCO_3^-; such a mixture remains pale pink even on prolonged bubbling of air through the solution.

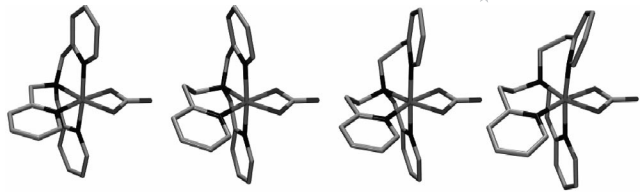


Figure 19. Views of the cations of the Co^{III} complexes $[Co(L)(O_2CO)]^+$. From left to right, L = tpa, pmea, pmap and tepa.

Similar, but somewhat more pronounced trends are observed in the structurally characterised Co^{III} complexes $[Co(L)(O_2CO)]^+$ (L = tpa, 6-Metpa, 6-Me_2tpa, 6-Me_3tpa) the structures of which are shown in Figure 20.[67] Significant differences in the structures of the complex cations result from the introduction of successive methyl groups at the 6-position of the pyridine rings, and a lengthening of the average Co–N distances is again observed.

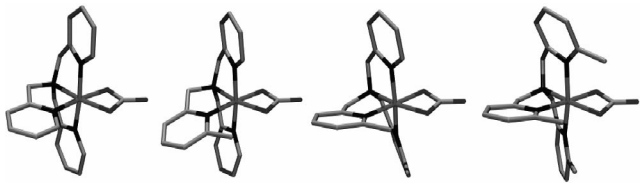


Figure 20. Views of the cations of the Co^{III} complexes $[Co(L)(O_2CO)]^+$. From left to right, L = tpa, 6-Metpa, 6-Me_2tpa and 6-Me_3tpa.

As can be seen in Table 1, λ_{max} for the longest wavelength UV/Vis band increases by 57 nm from $[Co(tpa)(O_2CO)]^+$ to $[Co(6\text{-}Me_3tepa)(O_2CO)]^+$ while Δ values differ by 2202 cm^{-1} (ca. 26 $kJ\,mol^{-1}$) across the set of complexes. The observed trends for both sets of complexes correlate well with the

average Co–N bond lengths (Co–N_{av} in Table 1) which increase significantly with both increasing number of aliphatic carbon atoms and increasing substitution at the pyridine 6-positions. As the Co–N_{av} bond length increases, the value of Δ decreases, implying less efficient metal–ligand orbital overlap. This is confirmed by DFT calculations which show that the decrease in Δ is due to a gradual lowering in energy of the $d_{x^2-y^2}$- and d_{z^2}-derived orbitals across both series of complexes.[121] UV/Vis spectroscopic data have also been obtained for the five-coordinate complexes $[Cu(L)Cl]^+$ (L = tpa, pmea, pmap, tepa)[36,68] but as these complexes display different geometries about the metal ion (see above) these data cannot be so easily used in evaluating ligand field strengths. However, electrochemical data for these complexes show a regular trend, with the complexes becoming more easily reduced across the series $[Cu(tpa)Cl]^+ \rightarrow [Cu(tepa)Cl]^+$. This observation is in agreement with tpa being the strongest field, and tepa the weakest field ligand. The five-coordinate complexes $[Cu(L)N_3]^+$ (L = tpa, mapa, bapa, tapa) also show differences in geometries about the Cu^{2+} ion (τ_5 values of 0.92, 0.87, 0.79 and 0.48, respectively) but there are no obvious trends in the positions of the d–d bands. However, there is a gradual decrease in the wavelength of the $N_3^- \rightarrow Cu^{2+}$ LMCT band across the series $[Cu(tpa)N_3]^+ \rightarrow [Cu(tapa)N_3]^+$, consistent with decreasing ligand field strength from tpa → tapa.[47]

The varying ligand field strengths of the tripyridyl tripodal ligands are also manifested in the spin states of the metal ions in complexes of these ligands. This is most clearly illustrated in Fe^{II} and Fe^{III} complexes of tpa and its methyl-substituted congeners. Whereas the complex $[Fe(tpa)(MeCN)_2]^{2+}$ is low-spin at room temperature, introduction of a single 6-methyl substituent on one of the pyridine rings gives high-spin $[Fe(6\text{-}Metpa)(MeCN)_2]^{2+}$, and both $[Fe(6\text{-}Me_2tpa)(MeCN)_2]^{2+}$ and $[Fe(6\text{-}Me_3tpa)(MeCN)_2]^{2+}$ are also high-spin. Similarly the Fe^{III} complex $[Fe(tpa)(acac)]^{2+}$ is low-spin at room temperature, while $[Fe(6\text{-}Metpa)(acac)]^{2+}$ is high-spin.[42] Such observations are consistent with a decrease in ligand field strength as 6-Me substituents are introduced, as was also observed for the $[Co(L)(O_2CO)]^+$ complexes above. The strong-field nature of the tpa ligand is also manifested in dimeric Fe^{II} complexes of the type $[(tpa)FeXFe(tpa)]^{n+}$, where X is either two single bis(monodentate) bridging ligands or a single bis(bidentate) bridging ligand. For example, when X = $(NC(CH_2)_4CN)_2$ or bptz [bptz = 3,6-bis(2-pyridyl)1,2,4,5-tetrazine] the resulting complexes display LS-LS behaviour between 2 K and ca. 300 K. However, an exception to this is seen when X = H_2bptz; in this case, the complex is HS-HS at room temperature and undergoes a "half crossover" transition to a mixed HS-LS state at 134 K.[122] Interesting electronic effects are also observed in high valent Fe dimers of the type $[LFe(O)_2FeL]^{3+}$ (L = tpa, 6-Metpa, 6-Me_3tpa). These complexes contain an $Fe(O)_2Fe$ "diamond" core and are formally Fe^{III}/Fe^{IV} species. When L = tpa, both metal centres are low spin, leading to a valence-delocalised S = 3/2 ground state.[123] In contrast, when the weaker field 6-Metpa or 6-Me_3tpa ligands are used, both metal centres are high spin, and antiferromagnetic coupling between them gives an S = 1/2 valence localised ground state.[124,125]

The very small number of Fe complexes containing either pmea and pmap appear to be high-spin; the dimeric complex $[(pmap)Fe(tcm)Fe(pmap)](tcm)_2(H_2O)_2$ (tcm = the tricyanomethanide monoanion) displays HS-HS behaviour over the temperature range 2–300 K[122] while, although magnetic data were not obtained, X-ray structural characterisation of $[Fe(pmea)Cl_2]ClO_4\cdot(C_2H_5)_2O$ and $[Fe(pmea)(tbc)]ClO_4\cdot H_2O$ (tbc = the tetrabromocatecholate dianion) reveals Fe–N bond lengths characteristic of high-spin Fe^{III}.[20] Although the above examples show that the ligand field strength of tpa is considerable, it is still incapable of giving rise to low-spin Mn^{II}, as shown by the fact that the complexes $[Mn(tpa)X_2]$ (X = Cl, Br, I) are all rigorously high spin.[126–128] Similarly, the crystallographically characterised (at 298 K) complex $[Cr(tpa)Cl_2]$ displays a significant Jahn–Teller distortion, as well as a room temperature μ_{eff} of 4.6 μ_B, both of which are consistent with a high-spin configuration.[92]

The complexes $[(phen)_2Cr(\mu\text{-}OH)_2Ni(L)]^{3+}$ (L = tpa, 6-Metpa, 6-Me_2tpa, 6-Me_3tpa) show systematic changes in both their structural and physical properties as the number of methyl groups on the tripodal ligand is increased. The Ni–N_{av} bond lengths increase from 2.084 Å to 2.216 Å across the ligand series tpa → Me_3tpa, even though the Ni–N bond to the aliphatic N atom actually decreases in length from 2.087 Å (tpa) to 2.062 Å (Me_3tpa). The Cr···Ni separations also gradually increase across the series [3.062 Å (tpa) to 3.140 Å (Me_3tpa)]. These structural changes are manifested both in the electronic spectra and magnetic behaviour of the complexes. While the bands due to the Cr^{III} centre remain essentially unchanged in wavelength in the UV/Vis spectra of the complexes, the band due to the Ni^{II} ion which is not obscured by Cr^{III} features moves to longer wavelengths as the number of methyl groups on the tripyridyl tripodal ligand increases, with a shift of approximately 400 cm^{-1} per methyl group. These observations parallel those for the Co^{III} complexes discussed above. The complexes also undergo a change from antiferromagnetic to ferromagnetic coupling between the metal centres, with J values of –1.4 cm^{-1} (L = tpa), 0.0 cm^{-1} (L = 6-Metpa), +4.1 cm^{-1} (L = 6-Me_2tpa) and +7.4 cm^{-1} (L = 6-Me_3tpa) observed across the series.[129]

Electrochemical data of metal complexes containing tripyridyl tripodal ligands also reflect the ligand field strength of these ligands (Table 2). Both Co^{III} and Cu^{II} complexes of ligands in the homologous series tpa → tepa exhibit a gradual increase in reduction potentials across this series, implying an increasing stabilisation of the lower of the two possible oxidation states. This is consistent with decreasing ligand field strengths from tpa → tepa. A regular increase in reduction potentials across the series of Cu^{II} complexes containing the ligands tpa → Me_3tpa is also observed, and a similar, though less pronounced, increase is observed in Cu^{II} complexes of the amino substituted ligand series tpa → tapa, results consistent with tpa exerting the strongest field of these ligands.

Table 2. Electrochemical data for series of Co and Cu complexes containing tripyridyl tripodal ligands.

Complex	$E_{1/2}$/V
$[Co(tpa)(O_2CO)]^+$	–0.541[a]
$[Co(pmea)(O_2CO)]^+$	–0.535[a]
$[Co(pmap)(O_2CO)]^+$	–0.444[a]
$[Co(tepa)(O_2CO)]^+$	–0.244[a]
$[Cu(tpa)Cl]^+$	–0.386[b]
$[Cu(pmea)Cl]^+$	–0.300[b]
$[Cu(pmap)Cl]^+$	–0.200[b]
$[Cu(tepa)Cl]^+$	+0.115[b]
$[Cu(tpa)N_3]^+$	–0.36[c]
$[Cu(mapa)N_3]^+$	–0.37[c]
$[Cu(bapa)N_3]^+$	–0.33[c]
$[Cu(tapa)N_3]^+$	–0.27[c]
$[Cu(tpa)]^{2+}$	–0.32[d]
$[Cu(6\text{-Metpa})]^{2+}$	–0.26[d]
$[Cu(6\text{-Me}_2\text{tpa})]^{2+}$	–0.14[d]
$[Cu(6\text{-Me}_3\text{tpa})]^{2+}$	+0.07[d]

[a] MeCN solvent, relative to decamethylferrocene.[66] [b] DMF solvent, relative to NHE.[36] [c] MeOH solvent, relative to SCE.[47] [d] MeCN solvent relative to $Ag/AgNO_3$. It is probable that these complexes contain a MeCN ligand in the 5th coordination site.[51]

Although the accumulated data show unambiguously that the ligand field strength of the 6-Me_3tpa ligand is the lowest of all the 6-methyl tpa ligands, it does not necessarily follow that this ligand will preferentially stabilise low oxidation state metal ions, as the steric effect of the methyl groups can also be important. This is demonstrated in the Ni^{III} dimer $[(6\text{-Me}_3\text{tpa})Ni(\mu\text{-}O)_2Ni(6\text{-Me}_3\text{tpa})]^{2+}$, which is prepared by oxidation of the Ni^{II} dimer $[(6\text{-Me}_3\text{tpa})Ni(\mu\text{-}OH)_2Ni(6\text{-Me}_3\text{tpa})]^{2+}$ by H_2O_2 at –90 °C. Despite having rather long Ni–N bonds, indicative of the relatively poor electron-donating nature of the ligand, the methyl groups form a protective cleft around the μ-oxo bridging ligands, thereby retarding possible decomposition reactions involving these sites. The analogous tpa and 6-Metpa starting materials fail to show any colour change on addition of H_2O_2 under these conditions, while the 6-Me_2tpa complex gives rise to only a very short-lived (seconds) species, thus attesting to the importance of the methyl groups in stabilising the high-valent Ni^{III} complex.[112]

Zn^{II} complexes of the type $[Zn(L)(OH_2)]^{2+}$ (L = tpa, mapa, bapa, tapa) show a regular decrease in their pK_a values from tpa → tapa, with values of 8.0 (L = tpa), 7.62 (L = mapa), 6.68 (L = bapa) and 5.99 (tapa). This decrease has been ascribed to increased polarisation of the O–H bond of the coordinated water molecule and increased stabilisation of the resulting Zn–OH unit, due to greater H-bonding interactions as the number of amino substituents is increased. Such a regular progression is not observed when the analogous neopentylamino ligands mnpa, bnpa and tnpa are used, as the pK_a of the complex containing the trisubstituted ligand tnpa is less than that containing disubstituted bnpa. However, inspection of the crystal structures of these complexes shows that the observed H-bonding interactions in the complex containing tnpa are in fact weaker than those in the bnpa complex, and this does indeed correlate with the observed pK_a values for the two complexes.[130]

Reactivity of Complexes Containing Tripyridyl Tripodal Ligands

Co^{III} complexes containing chelated carbonate in which the ancillary ligands are tripyridyl tripodal ligands show remarkable stability in aqueous acidic solution. This was first demonstrated for the complex $[Co(tepa)(O_2CO)]ClO_4$, which on standing in 2.7 M $HClO_4$ gave not the expected hydrolysis product $[Co(tepa)(OH_2)_2]^{3+}$ but crystals of the chelated hydrogen carbonate complex $[Co(tepa)(O_2COH)](ClO_4)_2{\cdot}3H_2O$.[131] Subsequent work showed that the $[Co(L)(O_2CO)]^+$ complexes (L = tpa, 6-Metpa, 6-Me_2tpa, 6-Me_3tpa, pmea, pmap) all display significant, but varying, degrees of stability in aqueous acidic solution.[66,67] In 6 M HCl, the tpa complex displays the most rapid rate of hydrolysis ($k_{obsd.} = 1.79 \times 10^{-3}$ s^{-1}) while, with the exception of the pmap complex, the other complexes have $k_{obsd.}$ values between 10^{-4} and 10^{-5} s^{-1} for the hydrolysis reaction at 25.0 °C, which translate to half lives of hundreds of minutes under these conditions. Hydrolysis of the pmap complex is too slow to measure at this temperature; for this complex at 50.0 °C, $k_{obsd.} = 2.5 \times 10^{-5}$ s^{-1}.[132] It should also be noted that, while the tpa, pmea and pmap complexes hydrolyse to their respective diaqua species, the final product of hydrolysis of the tepa complex is Co^{II}, in keeping with the low ligand field strength of this ligand. The extraordinary stability of these complexes in 6 M HCl appears to have a steric, rather than electronic, basis as no correlation between the ligand field strength of the tripyridyl tripodal ligand and the hydrolysis rate is observed. In addition, DFT calculations show that the d_{xz}, d_{yz}, and d_{xy} derived HOMOs contain significant contributions from *p* orbitals on the coordinated O atoms and that these orbitals remain essentially constant in energy across the series of complexes studied, as well as in the rapidly hydrolysed complex $[Co(NH_3)_4(O_2CO)]^+$.[121] As the first mechanistic step in the hydrolysis reaction is protonation at one of these coordinated O atoms,[133] it might be expected that the large differences in hydrolysis rates would be paralleled in the energies of these orbitals. That these energies remain essentially constant provides further evidence that electronic factors do not primarily determine the rate of hydrolysis. The space filling diagrams of the pmap complex in Figure 21 show that the pmap ligand provides significant steric hindrance of the coordinated O atoms; the pyridyl protons at the 6 position of the pyridine rings lie close to one of the O atoms while the CH_2 protons from the aliphatic chain impede access to the other. This means that protonation at the coordinated O atoms is inhibited, thereby leading to relatively slow rates of hydrolysis. Inspection of the space filling model of $[Co(NH_3)_4(O_2CO)]^+$ (Figure 21), a complex which hydrolyses rapidly, further serves to emphasise the degree of hindrance present in the pmap complex.

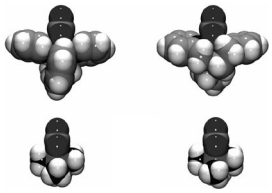


Figure 21. Space filling models of $[Co(pmap)(O_2CO)]^+$ (top) and $[Co(NH_3)_4(O_2CO)]^+$ (bottom) viewed from both sides of the carbonate ligand, showing the differences in accessibility of the coordinated carbonate O atoms.

Cu^I complexes of the type $[Cu(L)]^+$ (L = pmea, pmap, tepa) display widely differing reactivities towards dioxygen. $[Cu(pmea)]^+$ forms the purple $\eta^1:\eta^1$-peroxo-bridged dimer $[(pmea)Cu(O_2)Cu(pmea)]^{2+}$ on treatment with O_2 in propionitrile at –90 °C, while, although being sensitive to O_2, no such complex can be observed for $[Cu(pmap)]^+$ under the same conditions. Interestingly, $[Cu(tepa)]^+$ is stable towards O_2, and a solution of this complex remains yellow even on prolonged treatment with O_2.[36] A range of reactivites towards O_2 is also observed across the series of complexes $[Cu(L)]^+$ (L = 6-Metpa, 6-Me_2tpa, 6-Me_3tpa). While $[Cu(6\text{-}Metpa)]^+$ reacts with O_2 in acetone at –70 °C to give the $\eta^1:\eta^1$ peroxo dimer, both the di- and trimethyl complexes react to give the bis(μ-oxo) dimer $[LCu(O)_2CuL]^{2+}$ under these conditions, with reaction of the latter complex being much slower. Both complexes eventually decompose at low temperature to give various ligand degradation products derived from *N*-dealkylation, ligand hydroxylation and/or oxidation.[51,52,134] Such behaviour is not replicated in the amino-substituted series of complexes $[Cu(L)]^+$ (L = mapa, bapa, tapa); all three complexes react with O_2 at –75 °C in MeOH to give the $\eta^1:\eta^1$-peroxo-bridged dimers $[(L)Cu(O_2)Cu(L)]^{2+}$. It is interesting to note that the $\eta^1:\eta^1$-peroxo-bridged tpa dimer $[(tpa)Cu(O_2)Cu(tpa)]^{2+}$ cannot be prepared in MeOH under these conditions, and it is speculated that the $-NH_2$ substituents of the mapa, bapa and tapa ligands help protect the peroxo ligand from protonation in this solvent.[47]

A number of metal complexes (M = Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}) containing tpa have been found to be effective as catalysts in alkane oxygenation reactions effected by *m*CPBA, with $[Ni(tpa)(OAc)(OH_2)]^+$ exhibiting the highest turnover number of the complexes studied.[135] Subsequent work has shown that the dimeric $[(tpa)Ni(NO_3)_2Ni(tpa)]^{2+}$ and monomeric $[Ni(tepa)(OAc)]^+$ and $[Ni(tepa)(O_2NO)]^+$ complexes all catalyse the oxidation of cyclohexane by *m*CPBA; the tpa complex exhibits a higher turnover number than the tepa complexes, which in turn exhibit greater alcohol/ketone selectivity.[6]

Interest in Fe complexes of tripodal tripyridyl ligands has stemmed, at least in part, from the oxoiron(IV) species that have been isolated in reactions of these with peracetic acid or *t*BuOOH at –40 °C. Reaction of both $[Fe(tpa)(MeCN)_2]^{2+}$ and $[Fe(6\text{-}Metpa)(MeCN)_2]^{2+}$ under these conditions leads to the formation of $[Fe(O)(L)]^{2+}$ (L = tpa, 6-Metpa).[106,136] Both of these Fe^{IV} complexes are low spin, showing that the introduction of a single methyl group on the tpa ligand does not, in contrast to other examples discussed above, lead to a high-spin configuration. The 6-Metpa ligand does, however, exert a weaker ligand field as evidenced by the shift to longer wavelength of features in the near-IR region of the UV/Vis spectrum of the 6-Metpa complex.

Areas for Future Study

The examples given in these pages hopefully serve to emphasise the breadth of the chemistry of, and current interest in, tripodal tripyridyl ligands. Even so, there are areas which, as yet, have undergone little scrutiny and are ripe for study. One such area of current interest is that of coordination polymers. Tripodal tripyridyl ligands containing one long arm should prefer to bind to a transition-metal ion in a tridentate fashion, leaving a pendant pyridine N atom available for coordination to a neighbouring metal ion. In addition, as documented above, tripodal tripyridyl ligands bind in a tridentate fashion to d^8 metal ions, again leaving a pendant pyridine unit capable of bridging to another metal ion. Such approaches to potentially interesting polymeric materials should most certainly be explored. Another area in which surprisingly little work has been done is that of anion receptors. While many impressive systems based on tren have been developed,[137] there appear to be relatively few analogous anion receptors derived from tpa, presumably due to the greater synthetic difficulties inherent in such systems. Although some studies of both triprotonated tpa[118] and metallated tpa derivatives[138–140] as anion receptors have been reported, this remains an essentially unexplored area. Much of the work outlined in this review has involved the synthesis of new tpa derivatives, substituted at the pyridine rings, and the results obtained from such studies show the importance of both the electronic and steric effects that such substitutions impart. However, there has been very little work carried out on the analogously substituted derivatives of pmea, pmap or tepa, and there is certainly significant scope for research using these ligands. In addition, the majority of studies involving complexes of tripodal tripyridyl ligands have utilised first-row transition metals, while the other transition metals, not to mention the lanthanides and actinides, remain underrepresented. But what the examples given above emphasise perhaps more than anything is the degree of electronic control (or "tuning", to use a current buzzword) that can be achieved in tripyridyl tripodal ligands, and it is surely here where we can expect to see major advances in the chemistry of complexes containing these ligands. The ligand field strengths of such ligands can be modulated over a significant range simply by altering the arm length and/or substitution at the pyridyl rings. Given that the spin state of an individual metal ion, and degree of electronic coupling between neighbouring metal ions are, to a large extent, controlled by the electronic nature of the bound ligand, it appears that future studies in which the substituents on the

tripyridyl tripodal ligand are systematically varied will reap significant rewards. The results of these future studies are awaited with interest.

[1] F. H. Burstall, *J. Chem. Soc.* **1938**, 1662–1672.
[2] G. Anderegg, F. Wenk, *Helv. Chim. Acta* **1967**, *50*, 2330–2332.
[3] E. E. Chufan, B. Mondal, T. Gandhi, E. Kim, N. D. Rubie, P. Moeenne-Loccoz, K. D. Karlin, *Inorg. Chem.* **2007**, *46*, 6382–6394.
[4] Y. Hitomi, A. Ando, H. Matsui, T. Ito, T. Tanaka, S. Ogo, T. Funabiki, *Inorg. Chem.* **2005**, *44*, 3473–3478.
[5] M. Yamaguchi, H. Kousaka, S. Izawa, Y. Ichii, T. Kumano, D. Masui, T. Yamagishi, *Inorg. Chem.* **2006**, *45*, 8342–8354.
[6] T. Nagataki, K. Ishii, Y. Tachi, S. Itoh, *Dalton Trans.* **2007**, 1120–1128.
[7] R. Mas-Balleste, L. Que Jr, *J. Am. Chem. Soc.* **2007**, *129*, 15964–15972.
[8] K. L. Klotz, L. M. Slominski, A. V. Hull, V. M. Gottsacker, R. Mas-Balleste, L. Que Jr, J. A. Halfen, *Chem. Commun.* **2007**, 2063–2065.
[9] W. T. Eckenhoff, T. Pintauer, *Inorg. Chem.* **2007**, *46*, 5844–5846.
[10] N. V. Tsarevsky, W. A. Braunecker, S. J. Brooks, K. Matyjaszewski, *Macromolecules* **2006**, *39*, 6817–6824.
[11] K. S. Min, A. DiPasquale, A. L. Rheingold, J. S. Miller, *Inorg. Chem.* **2007**, *46*, 1048–1050.
[12] G. Feng, J. C. Mareque-Rivas, R. T. Martin de Rosales, N. H. Williams, *J. Am. Chem. Soc.* **2005**, *127*, 13470–13471.
[13] A. G. Blackman, *Polyhedron* **2005**, *24*, 1–39.
[14] L. M. Berreau, *Comments Inorg. Chem.* **2007**, *28*, 123–171.
[15] Y. Terasaki, T. Fujihara, A. Nagasawa, S. Kaizaki, *Acta Crystallogr., Sect. E* **2004**, *60*, m854–m856.
[16] F. R. Keene, M. R. Snow, P. J. Stephenson, E. R. T. Tiekink, *Inorg. Chem.* **1988**, *27*, 2040–2045.
[17] E. S. Kucharski, W. R. McWhinnie, A. H. White, *Aust. J. Chem.* **1978**, *31*, 2647–2650.
[18] E. S. Kucharski, W. R. McWhinnie, A. H. White, *Aust. J. Chem.* **1978**, *31*, 53–56.
[19] S. P. Foxon, O. Walter, S. Schindler, *Eur. J. Inorg. Chem.* **2002**, 111–121.
[20] M. Merkel, M. Pascaly, B. Krebs, J. Astner, S. P. Foxon, S. Schindler, *Inorg. Chem.* **2005**, *44*, 7582–7589.
[21] K. E. Berg, A. Tran, M. K. Raymond, M. Abrahamsson, J. Wolny, S. Redon, M. Andersson, L. Sun, S. Styring, L. Hammarstrom, H. Toftlund, B. Akermark, *Eur. J. Inorg. Chem.* **2001**, 1019–1029.
[22] S. J. A. Pope, R. H. Laye, *Dalton Trans.* **2006**, 3108–3113.
[23] O. dos Santos, A. R. Lajmi, J. W. Canary, *Tetrahedron Lett.* **1997**, *38*, 4383–4386.
[24] C.-L. Chuang, O. dos Santos, X. Xu, J. W. Canary, *Inorg. Chem.* **1997**, *36*, 1967–1972.
[25] C. F. Martens, N. N. Murthy, H. V. Obias, K. D. Karlin, *Chem. Commun.* **1996**, 629–630.
[26] H. V. Obias, G. P. F. van Strijdonck, D.-H. Lee, M. Ralle, N. J. Blackburn, K. D. Karlin, *J. Am. Chem. Soc.* **1998**, *120*, 9696–9697.
[27] H. Duerr, K. Zengerle, H. P. Trierweiler, *Z. Naturforsch., Teil B* **1988**, *43*, 361–367.
[28] L. Zhu, O. Dos Santos, C. W. Koo, M. Rybstein, L. Pape, J. W. Canary, *Inorg. Chem.* **2003**, *42*, 7912–7920.
[29] M. Kodera, M. Itoh, K. Kano, T. Funabiki, M. Reglier, *Angew. Chem. Int. Ed.* **2005**, *44*, 7104–7106.
[30] D.-H. Lee, N. N. Murthy, K. D. Karlin, *Bull. Chem. Soc. Jpn.* **2007**, *80*, 732–742.
[31] B. Lucchese, K. J. Humphreys, D.-H. Lee, C. D. Incarvito, R. D. Sommer, A. L. Rheingold, K. D. Karlin, *Inorg. Chem.* **2004**, *43*, 5987–5998.
[32] S. K. Brownstein, P. Y. Plouffe, C. Bensimon, J. Tse, *Inorg. Chem.* **1994**, *33*, 354–358.
[33] K. D. Karlin, J. C. Hayes, J. P. Hutchinson, J. R. Hyde, J. Zubieta, *Inorg. Chim. Acta* **1982**, *64*, L219–L220.
[34] M. R. Malachowski, H. B. Huynh, L. J. Tomlinson, R. S. Kelly, J. W. Furbe Jr, *J. Chem. Soc., Dalton Trans.* **1995**, 31–36.
[35] C. M. Che, V. W. W. Yam, T. C. W. Mak, *J. Am. Chem. Soc.* **1990**, *112*, 2284–2291.
[36] M. Schatz, M. Becker, F. Thaler, F. Hampel, S. Schindler, R. R. Jacobson, Z. Tyeklar, N. N. Murthy, P. Ghosh, Q. Chen, J. Zubieta, K. D. Karlin, *Inorg. Chem.* **2001**, *40*, 2312–2322.
[37] J. W. Canary, Y. Wang, R. Roy Jr, L. Que Jr, H. Miyake, *Inorg. Synth.* **1998**, *32*, 70–75.
[38] F. Hojland, H. Toftlund, S. Yde Andersen, *Acta Chem. Scand.* **1983**, *A37*, 251–257.
[39] A. R. Oki, J. Glerup, D. J. Hodgson, *Inorg. Chem.* **1990**, *29*, 2435–2441.
[40] J. Dietrich, F. W. Heinemann, A. Schrodt, S. Schindler, *Inorg. Chim. Acta* **1999**, *288*, 206–209.
[41] D. G. Lonnon, D. C. Craig, S. B. Colbran, *Dalton Trans.* **2006**, 3785–3797.
[42] Y. Zang, J. Kim, Y. Dong, E. C. Wilkinson, E. H. Appelman, L. Que Jr, *J. Am. Chem. Soc.* **1997**, *119*, 4197–4205.
[43] D. C. Bebout, J. F. Bush II, K. K. Crahan, E. V. Bowers, R. J. Butcher, *Inorg. Chem.* **2002**, *41*, 2529–2536.
[44] K. Jitsukawa, M. Harata, H. Arii, H. Sakurai, H. Masuda, *Inorg. Chim. Acta* **2001**, *324*, 108–116.
[45] J. C. Mareque Rivas, E. Salvagni, R. T. Martin de Rosales, S. Parsons, *Dalton Trans.* **2003**, 3339–3349.
[46] S. Yamaguchi, A. Wada, Y. Funahashi, S. Nagatomo, T. Kitagawa, K. Jitsukawa, H. Masuda, *Eur. J. Inorg. Chem.* **2003**, 4378–4386.
[47] A. Wada, Y. Honda, S. Yamaguchi, S. Nagatomo, T. Kitagawa, K. Jitsukawa, H. Masuda, *Inorg. Chem.* **2004**, *43*, 5725–5735.
[48] J. W. Canary, C. S. Allen, J. M. Castagnetto, Y. Wang, *J. Am. Chem. Soc.* **1995**, *117*, 8484–8485.
[49] T. Yamada, S. Shinoda, J.-i. Uenishi, H. Tsukube, *Tetrahedron Lett.* **2001**, *42*, 9031–9033.
[50] T. Yamada, S. Shinoda, H. Sugimoto, J.-I. Uenishi, H. Tsukube, *Inorg. Chem.* **2003**, *42*, 7932–7937.
[51] H. Hayashi, K. Uozumi, S. Fujinami, S. Nagatomo, K. Shiren, H. Furutachi, M. Suzuki, A. Uehara, T. Kitagawa, *Chem. Lett.* **2002**, 416–417.
[52] H. Hayashi, S. Fujinami, S. Nagatomo, S. Ogo, M. Suzuki, A. Uehara, Y. Watanabe, T. Kitagawa, *J. Am. Chem. Soc.* **2000**, *122*, 2124–2125.
[53] C.-l. Chuang, K. Lim, Q. Chen, J. Zubieta, J. W. Canary, *Inorg. Chem.* **1995**, *34*, 2562–2568.
[54] L. Yang, D. R. Powell, R. P. Houser, *Dalton Trans.* **2007**, 955–964.
[55] N. Wei, N. N. Murthy, Q. Chen, J. Zubieta, K. D. Karlin, *Inorg. Chem.* **1994**, *33*, 1953–1965.
[56] Z. H. Zhang, X. H. Bu, Z. A. Zhu, Y. T. Chen, *Polyhedron* **1996**, *15*, 2787–2792.
[57] E. C. Constable, *Prog. Inorg. Chem.* **1994**, *42*, 67–138.
[58] A. G. Blackman, *C. R. Chim.* **2005**, *8*, 107–119.
[59] J. Bjernemose, A. Hazell, C. J. McKenzie, M. F. Mahon, L. P. Nielsen, P. R. Raithby, O. Simonsen, H. Toftlund, J. A. Wolny, *Polyhedron* **2003**, *22*, 875–885.
[60] A. Diebold, K. S. Hagen, *Inorg. Chem.* **1998**, *37*, 215–223.
[61] N. Wei, N. N. Murthy, K. D. Karlin, *Inorg. Chem.* **1994**, *33*, 6093–6100.
[62] A. W. Addison, T. N. Rao, J. Reedijk, J. Van Rijn, G. C. Verschoor, *J. Chem. Soc., Dalton Trans.* **1984**, 1349–1356.
[63] T. W. Failes, C. Cullinane, C. I. Diakos, N. Yamamoto, J. G. Lyons, T. W. Hambley, *Chem. Eur. J.* **2007**, *13*, 2974–2982.
[64] T. W. Failes, T. W. Hambley, *Dalton Trans.* **2006**, 1895–1901.
[65] Y. Gultneh, A. Farooq, K. D. Karlin, S. Liu, J. Zubieta, *Inorg. Chim. Acta* **1993**, *211*, 171–175.
[66] P. M. Jaffray, L. F. McClintock, K. E. Baxter, A. G. Blackman, *Inorg. Chem.* **2005**, *44*, 4215–4225.

[67] S. E. Cheyne, L. F. McClintock, A. G. Blackman, *Inorg. Chem.* **2006**, *45*, 2610–2618.
[68] K. D. Karlin, J. C. Hayes, S. Juen, J. P. Hutchinson, J. Zubieta, *Inorg. Chem.* **1982**, *21*, 4106–4108.
[69] H. Nagao, N. Komeda, M. Mukaida, M. Suzuki, K. Tanaka, *Inorg. Chem.* **1996**, *35*, 6809–6815.
[70] H. Adams, N. A. Bailey, D. E. Fenton, Q.-Y. He, *J. Chem. Soc., Dalton Trans.* **1997**, 1533–1539.
[71] C. S. Allen, C.-L. Chuang, M. Cornebise, J. W. Canary, *Inorg. Chim. Acta* **1995**, *239*, 29–37.
[72] J. C. M. Rivas, R. Prabaharan, R. Torres Martin de Rosales, L. Metteau, S. Parsons, *Dalton Trans.* **2004**, 2800–2807.
[73] K. Jitsukawa, Y. Oka, S. Yamaguchi, H. Masuda, *Inorg. Chem.* **2004**, *43*, 8119–8129.
[74] D. G. H. Hetterscheid, J. Kaiser, E. Reijerse, T. P. J. Peters, S. Thewissen, A. N. J. Blok, J. M. M. Smits, R. De Gelder, B. De Bruin, *J. Am. Chem. Soc.* **2005**, *127*, 1895–1905.
[75] B. S. Lim, R. H. Holm, *Inorg. Chem.* **1998**, *37*, 4898–4908.
[76] S. V. Kryatov, E. V. Rybak-Akimova, A. Y. Nazarenko, P. D. Robinson, *Chem. Commun.* **2000**, 921–922.
[77] A. Wada, S. Yamaguchi, K. Jitsukawa, H. Masuda, *Angew. Chem. Int. Ed.* **2005**, *44*, 5698–5701.
[78] Y. Funahashi, A. Yoneda, C. Taki, M. Kosuge, T. Ozawa, K. Jitsukawa, H. Masuda, *Chem. Lett.* **2005**, *34*, 1332–1333.
[79] M. E. Helton, P. Chen, P. P. Paul, Z. Tyeklar, R. D. Sommer, L. N. Zakharov, A. L. Rheingold, E. I. Solomon, K. D. Karlin, *J. Am. Chem. Soc.* **2003**, *125*, 1160–1161.
[80] L. Karmazin, M. Mazzanti, J. Pecaut, *Inorg. Chem.* **2003**, *42*, 5900–5908.
[81] S. V. Kryatov, S. Taktak, I. V. Korendovych, E. V. Rybak-Akimova, J. Kaizer, S. Torelli, X. Shan, S. Mandal, V. MacMurdo, A. M. i. Payeras, L. Que Jr, *Inorg. Chem.* **2005**, *44*, 85–99.
[82] H. Zheng, Y. Zang, Y. Dong, V. G. Young Jr, L. Que Jr, *J. Am. Chem. Soc.* **1999**, *121*, 2226–2235.
[83] S. Yan, J. Cui, X. Liu, P. Cheng, D. Liao, Z. Jiang, G. Wang, H. Wang, X. Yao, *Sci. China, Ser. B* **1999**, *42*, 535–542.
[84] N. N. Murthy, K. D. Karlin, *J. Chem. Soc., Chem. Commun.* **1993**, 1236–1238.
[85] H. Oshio, H. Ichida, *J. Phys. Chem.* **1995**, *99*, 3294–3302.
[86] M.-L. Flay, H. Vahrenkamp, *Eur. J. Inorg. Chem.* **2003**, 1719–1726.
[87] R. J. Parker, D. C. R. Hockless, B. Moubaraki, K. S. Murray, L. Spiccia, *Chem. Commun.* **1996**, 2789–2790.
[88] M. M. Da Mota, J. Rodgers, S. M. Nelson, *J. Chem. Soc. A* **1969**, 2036–2044.
[89] G. Anderegg, E. Hubmann, N. G. Podder, F. Wenk, *Helv. Chim. Acta* **1977**, *60*, 123–140.
[90] D. Mandon, A. Machkour, S. Goetz, R. Welter, *Inorg. Chem.* **2002**, *41*, 5364–5372.
[91] C. A. Otter, R. M. Hartshorn, *Dalton Trans.* **2004**, 150–156.
[92] N. J. Robertson, M. J. Carney, J. A. Halfen, *Inorg. Chem.* **2003**, *42*, 6876–6885.
[93] B. De Bruin, M. J. Boerakker, J. J. J. M. Donners, B. E. C. Christiaans, P. P. J. Schlebos, R. De Gelder, J. M. M. Smits, A. L. Spek, A. W. Gal, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2064–2067.
[94] M. Krom, R. G. E. Coumans, J. M. M. Smits, A. W. Gal, *Angew. Chem. Int. Ed.* **2001**, *40*, 2106–2108.
[95] B. de Bruin, S. Thewissen, T.-W. Yuen, T. P. J. Peters, J. M. M. Smits, A. W. Gal, *Organometallics* **2002**, *21*, 4312–4314.
[96] K. S. Min, K. Swierczek, A. G. DiPasquale, A. L. Rheingold, W. M. Reiff, A. M. Arif, J. S. Miller, *Chem. Commun.* **2008**, 317–319.
[97] J. Tao, H. Maruyama, O. Sato, *J. Am. Chem. Soc.* **2006**, *128*, 1790–1791.
[98] K. S. Min, A. L. Rheingold, A. DiPasquale, J. S. Miller, *Inorg. Chem.* **2006**, *45*, 6135–6137.
[99] K. S. Min, A. G. DiPasquale, J. A. Golen, A. L. Rheingold, J. S. Miller, *J. Am. Chem. Soc.* **2007**, *129*, 2360–2368.
[100] L. Q. Hatcher, K. D. Karlin, *Adv. Inorg. Chem.* **2006**, *58*, 131–184.
[101] L. Que, *Acc. Chem. Res.* **2007**, *40*, 493–500.
[102] R. R. Jacobson, Z. Tyeklar, A. Farooq, K. D. Karlin, S. Liu, J. Zubieta, *J. Am. Chem. Soc.* **1988**, *110*, 3690–3692.
[103] A. Wada, M. Harata, K. Hasegawa, K. Jitsukawa, H. Masuda, M. Mukai, T. Kitagawa, H. Einaga, *Angew. Chem. Int. Ed.* **1998**, *37*, 798–799.
[104] Y. Zang, Y. Dong, L. Que Jr, K. Kauffmann, E. Münck, *J. Am. Chem. Soc.* **1995**, *117*, 1169–1170.
[105] H.-F. Hsu, Y. Dong, L. Shu, V. G. Young Jr, L. Que Jr, *J. Am. Chem. Soc.* **1999**, *121*, 5230–5237.
[106] M. H. Lim, J.-U. Rohde, A. Stubna, M. R. Bukowski, M. Costas, R. Y. N. Ho, E. Munck, W. Nam, L. Que Jr, *Proc. Natl. Acad. Sci. USA* **2003**, *100*, 3665–3670.
[107] G. Xue, D. Wang, R. De Hont, A. T. Fiedler, X. Shan, E. Munck, L. Que Jr, *Proc. Natl. Acad. Sci. USA* **2007**, *104*, 20713–20718.
[108] D. K. Towle, C. A. Botsford, D. J. Hodgson, *Inorg. Chim. Acta* **1988**, *141*, 167–168.
[109] P. A. Goodson, A. R. Oki, J. Glerup, D. J. Hodgson, *J. Am. Chem. Soc.* **1990**, *112*, 6248–6254.
[110] Y. Gultneh, T. B. Yisgedu, Y. T. Tesema, R. J. Butcher, *Inorg. Chem.* **2003**, *42*, 1857–1867.
[111] J. Cho, H. Furutachi, S. Fujinami, T. Tosha, H. Ohtsu, O. Ikeda, A. Suzuki, M. Nomura, T. Uruga, H. Tanida, T. Kawai, K. Tanaka, T. Kitagawa, M. Suzuki, *Inorg. Chem.* **2006**, *45*, 2873–2885.
[112] K. Shiren, S. Ogo, S. Fujinami, H. Hayashi, M. Suzuki, A. Uehara, Y. Watanabe, Y. Moro-oka, *J. Am. Chem. Soc.* **2000**, *122*, 254–262.
[113] H. Sugimoto, M. Kamei, K. Umakoshi, Y. Sasaki, M. Suzuki, *Inorg. Chem.* **1996**, *35*, 7082–7088.
[114] J. C. Mareque-Rivas, R. Prabaharan, R. T. Martin de Rosales, *Chem. Commun.* **2004**, 76–77.
[115] G. Anderegg, K. Popov, P. S. Pregosin, *Helv. Chim. Acta* **1986**, *69*, 329–332.
[116] D. Britton, R. E. Norman, L. Que Jr, *Acta Crystallogr., Sect. C* **1991**, *47*, 2415–2417.
[117] A. Hazell, J. McGinley, H. Toftlund, *J. Chem. Soc., Dalton Trans.* **1999**, 1271–1276.
[118] H. Sugimoto, H. Miyake, H. Tsukube, *J. Chem. Soc., Dalton Trans.* **2002**, 4535–4540.
[119] E. A. Ambundo, M.-V. Deydier, A. J. Grall, N. Aguera-Vega, L. T. Dressel, T. H. Cooper, M. J. Heeg, L. A. Ochrymowycz, D. B. Rorabacher, *Inorg. Chem.* **1999**, *38*, 4233–4242.
[120] P. Hendry, A. Ludi, *Adv. Inorg. Chem.* **1990**, *35*, 117–198.
[121] G. Cavigliasso, R. Stranger, L. F. McClintock, S. E. Cheyne, P. M. Jaffray, K. E. Baxter, A. G. Blackman, *Dalton Trans.* **2008**, 2433–2441.
[122] S. R. Batten, J. Bjernemose, P. Jensen, B. A. Leita, K. S. Murray, B. Moubaraki, J. P. Smith, H. Toftlund, *Dalton Trans.* **2004**, 3370–3375.
[123] Y. Dong, H. Fujii, M. P. Hendrich, R. A. Leising, G. Pan, C. R. Randall, E. C. Wilkinson, Y. Zang, L. Que Jr, B. G. Fox, K. Kauffmann, E. Münck, *J. Am. Chem. Soc.* **1995**, *117*, 2778–2792.
[124] Y. Dong, L. Que Jr, K. Kauffmann, E. Münck, *J. Am. Chem. Soc.* **1995**, *117*, 11377–11378.
[125] Y. Dong, Y. Zang, K. Kauffmann, L. Shu, E. C. Wilkinson, E. Münck, L. Que Jr, *J. Am. Chem. Soc.* **1997**, *119*, 12683–12684.
[126] C. Duboc, T. Phoeung, S. Zein, J. Pecaut, M.-N. Collomb, F. Neese, *Inorg. Chem.* **2007**, *46*, 4905–4916.
[127] B.-K. Shin, Y. Kim, M. Kim, J. Han, *Polyhedron* **2007**, *26*, 4557–4566.
[128] C. Duboc, T. Phoeung, D. Jouvenot, A. G. Blackman, L. F. McClintock, J. Pecaut, M.-N. Collomb, A. Deronzier, *Polyhedron* **2007**, *26*, 5243–5249.

[129] K. Shiren, S. Fujinami, M. Suzuki, A. Uehara, *Inorg. Chem.* **2002**, *41*, 1598–1605.
[130] J. C. Mareque-Rivas, R. Prabaharan, S. Parsons, *Dalton Trans.* **2004**, 1648–1655.
[131] K. E. Baxter, L. R. Hanton, J. Simpson, B. R. Vincent, A. G. Blackman, *Inorg. Chem.* **1995**, *34*, 2795–2796.
[132] McClintock, L. F., and Blackman, A. G. Unpublished data.
[133] D. A. Buckingham, C. R. Clark, *Inorg. Chem.* **1994**, *33*, 6171–6179.
[134] K. Uozumi, Y. Hayashi, M. Suzuki, A. Uehara, *Chem. Lett.* **1993**, 963–966.
[135] T. Nagataki, Y. Tachi, S. Itoh, *Chem. Commun.* **2006**, 4016–4018.
[136] T. K. Paine, M. Costas, J. Kaizer, L. Que Jr, *J. Biol. Inorg. Chem.* **2006**, *11*, 272–276.
[137] K. Wichmann, B. Antonioli, T. Soehnel, M. Wenzel, K. Gloe, K. Gloe, J. R. Price, L. F. Lindoy, A. J. Blake, M. Schroeder, *Coord. Chem. Rev.* **2006**, *250*, 2987–3003.
[138] S. L. Tobey, E. V. Anslyn, *J. Am. Chem. Soc.* **2003**, *125*, 14807–14815.
[139] S. L. Tobey, B. D. Jones, E. V. Anslyn, *J. Am. Chem. Soc.* **2003**, *125*, 4026–4027.
[140] T. Zhang, E. V. Anslyn, *Org. Lett.* **2006**, *8*, 1649–1652.

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