

# Principles of Mononucleating and Binucleating Ligand Design

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## 1. Introduction

Although multimetallic complexes were known early in the development of modern coordination chemistry, it is only over the past 30 years that special attention has been devoted to their preparation and properties. As was the case for analogous

organometallic compounds, the 1970s were a period of high expectations for multimetallic coordination complexes. It was generally assumed that properly designed multimetallic systems would provide new reactivity patterns and physical properties that could not be achieved with similar monometallic complexes. Multimetallic systems were expected to have greater oxidizing and reducing power, the neighboring metals

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were expected to “cooperate” in promoting reactions, and electronic interactions between metals might lead to distinct physical properties. These and other expectations led to the rapid development of the field that, in its initial phase, provided a variety of polynucleating ligands. The physical properties of the complexes were reported sometimes in great detail. In some cases special physical properties were observed, but the systems yielded few examples of unique reactivity patterns. Under these circumstances one would have expected interest in the area to subside after the initial burst of activity. Enthusiasm for the area, however, has been maintained by one major factor, the rapid growth in the understanding of the functions, reactivities, and structures of metalloproteins.

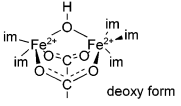
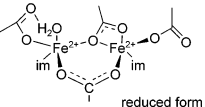
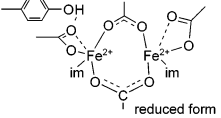
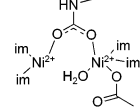
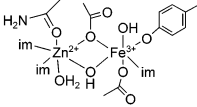
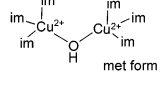
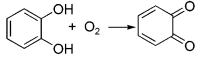
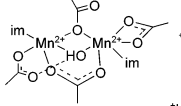
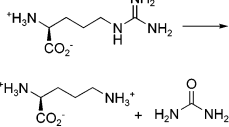
It was especially disconcerting to coordination chemists, particularly those who worked on multimetallic systems, to find that Nature had constructed numerous multimetallic protein complexes that perform an extraordinary array of catalytic transformations, few of which had been anticipated or reproduced in nonprotein systems. These continuing biological discoveries have inspired coordination chemists to persist in developing the area from an inorganic viewpoint. The task of finding functional analogues for these proteins can be a daunting task in most cases because the function performed by the protein is not only controlled by the immediate coordination sphere but is also affected by the larger protein structure. Even so, the study of analogues of metalloproteins can be instructive even if the biological function is not entirely reproduced because such studies help to define the parameters which may guide reactivity in the protein.

Table 1 lists a selection of bimetallic binding sites in various proteins, and the transformations that occur at these sites are indicated. There are many other bimetallic metalloprotein systems, but the list in Table 1 serves to illustrate a number of features of the binding sites. First, the bimetallic protein complexes are constructed using a limited number of ligands. Second, many of the transformations that occur are unlikely to be observed in a simple bimetallic analogue without the surrounding protein structure. It is, however, instructive to determine the relative contributions to reactivity provided by the various elements of the metalloprotein. Unlike biological systems, coordination chemistry can provide multimetallic complexes with a greater variety of ligands, structures, and metals. Consequently, it is possible to consider reactivity patterns unavailable in biological systems.

### 1.1. Scope

This review is concerned with the design of binucleating ligands, that is ligands that form bimetallic complexes. An extraordinary number of these ligands have been studied, and it seemed advisable to describe the essential features of the different types of ligands rather than to provide a comprehensive list. Nonetheless, the reader should be able to access a particular ligand from the references given. The binucleating ligands are categorized by the

**Table 1. A Selection of Proteins that have Bimetallic Sites and Their Functions**

Protein	Structure	Function	Reference
Hemerythrin		reversible dioxygen binding	1
Methane Monooxygenase		catalyzes reaction: $\text{CH}_4 + \text{O}_2 \rightarrow \text{CH}_3\text{OH}$	2, 3
Ribonucleotide Reductase		catalyzes reduction of ribonucleotides to deoxyribonucleotides	4, 5
Urease		catalyzes reaction: $\text{H}_2\text{N}-\text{C}(=\text{O})-\text{NH}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{NCOO}^- + \text{NH}_4^+$	6
Purple acid Phosphatase		catalyzes the hydrolysis of activated phosphoric acid esters and anhydrides like ATP at pH range from 4-7	7
Catechol Oxidase		Catalyzes reaction: 	8
Arginase		Catalyzes reaction: 	9, 10

bridging group that spans the two metals. Emanating from the bridging group are chelate rings, which can adopt various topologies depending on the chelate ring size. Consequently, the review begins with a brief description of the characteristics of chelate rings, particularly those that bear aliphatic backbones.

Most of the work described here encompasses the period from about 1970. The review deals mainly with the structures of the bimetallic complexes, the preparations of some of the ligands, and a description of some of the interesting chemistry or properties of the complexes. No extensive discussion of the electrochemistry, magnetic properties, or electronic spectroscopy of these bimetallic complexes will be given here.

## 2. Monometallic Ligand Design

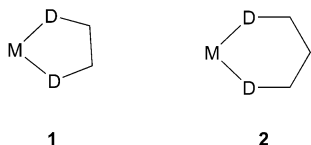
### 2.1. Chelate Rings

It is well known that five-membered chelate rings, **1**, are generally the most stable. The D–M–D bite angle is usually about 86°. The analogous six-membered chelate rings, **2**, are somewhat less stable, and the chelate bite angle, D–M–D, is usually about

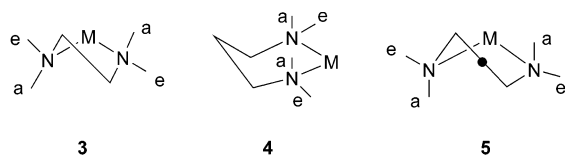
**Table 2. Free Energy of Activation ( $\Delta G^\ddagger$ ) for Inversion of Tertiary Amines, Phosphines, Arsines, and Sulfonium Ions**

compound	rate of inversion	$\Delta G^\ddagger$ (kcal/mol)
NR <sup>1</sup> R <sup>2</sup> R <sup>3</sup>	rapid	~3–7
PR <sup>1</sup> R <sup>2</sup> R <sup>3</sup>	slow	~30
AsR <sup>1</sup> R <sup>2</sup> R <sup>3</sup>	very slow	~45
+SR <sup>1</sup> R <sup>2</sup> R <sup>3</sup>	slow	~28

90°. Larger chelate ring sizes are much less stable



because of entropy considerations. When the chelate rings, **1** and **2**, are made up by aliphatic groups and the donor atoms, D, are amine groups, the rings adopt distinct conformations,<sup>11</sup> **3**, **4**, and **5**. The

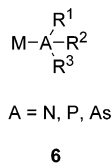


puckered conformation, **3**, is chiral, and the nitrogen substituents adopt axial (a) and equatorial (e) dispositions. The six-membered ring can adopt two main conformations, the achiral chair, **4**, and the chiral skew, **5**. It will be noted that both **4** and **5** dispose the substituents borne by the nitrogen atoms in axial and equatorial orientations, but for **4** the axial groups are *cis*-parallel. The conformation **5** resembles **3**. If the nitrogen atoms are replaced by tertiary phosphines or arsines, similar ring conformations are obtained. Replacement of the nitrogen atoms by divalent oxygen or sulfur groups gives the same ring conformations, and the oxygen or sulfur substituents can adopt similar axial or equatorial dispositions.

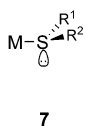
## 2.2. Coordinated Ligand Chirality

Tertiary amines, phosphines, arsines, and sulfonium ions are chiral and have different rates of inversion (Table 2).<sup>12–14</sup>

When tertiary amines, phosphines, and arsines are coordinated to a metal, **6**, the donor atom, A, becomes a quaternary-like chiral center. Secondary sulfides

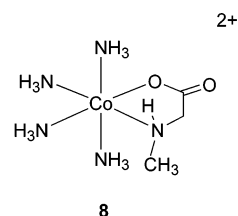


coordinated to a metal, **7**, form a tertiary chiral center.



Although sulfonium salts are slow to racemize (Table 2), the analogous metal complexes formed from sulfides, **7**, invert their configurations rapidly,<sup>15</sup> having an inversion barrier of about 5 kcal/mol for the Pd<sup>2+</sup> and Pt<sup>2+</sup> complexes. The tertiary phosphines and arsines become even more stable to thermal racemization upon coordination to a metal.<sup>16</sup>

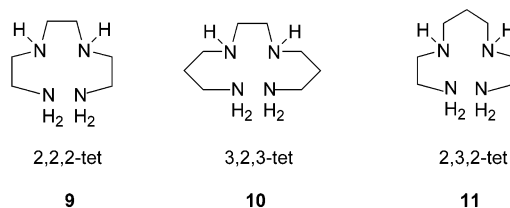
The chiral stability of coordinated tertiary amines is of special interest. The Co<sup>3+</sup> complex, **8**, is chiral by virtue of the stereochemistry of the sarcosine nitrogen atom. The complex, **8**, was resolved and found to be stable in water at pH < 4.3. Under more basic conditions, N–H proton exchange occurs, leading to the formation of a “tertiary” amine intermediate which is capable of rapid inversion of chirality.<sup>16</sup>



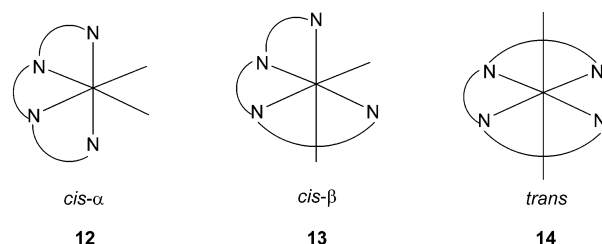
The chirality and chiral stability of amines, phosphines, arsines, and sulfides have important consequences in controlling the topology of multidentate chelates. Considering this donor atom chirality, the conformations of chelate rings, and chelate bite angles, the topologies of octahedral complexes bearing multidentate ligands can be predicted with some, but not complete, confidence. The essential considerations in predicting topology are illustrated by considering the isomers of octahedral complexes that can form from linear quadridentate ligands.

## 2.3. Linear Quadridentate Ligand Complex Topology

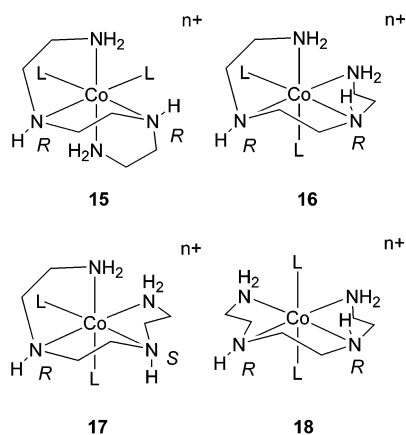
The three linear quadridentate amine ligands, **9–11**, provide an interesting contrast in the topologies they adopt for octahedral complexes. These



ligands can, in principle, assume the three topologies, **12** (*cis*- $\alpha$ ), **13** (*cis*- $\beta$ ), and **14** (*trans*). The octahedral



cobalt(III) complexes of the ligand, 2,2,2-tet provide four isomers, **15–18**.<sup>17–18</sup>

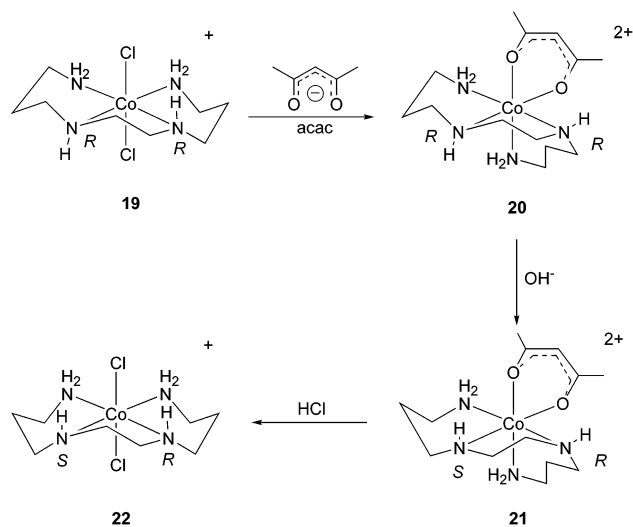


These isomers are formed by complex series of reactions that involve changes in the L-ligands, changes in solvent, and control of the pH of the medium. Simply considering cumulative bite angle strain, the order of stability would be expected to follow the order  $cis-\alpha > cis-\beta > trans$ , but, as noted, the relative stability depends on the nature of L and on the solvent. Each of the isomers, **15–18**, is chiral. These have been separated.<sup>17–18</sup>

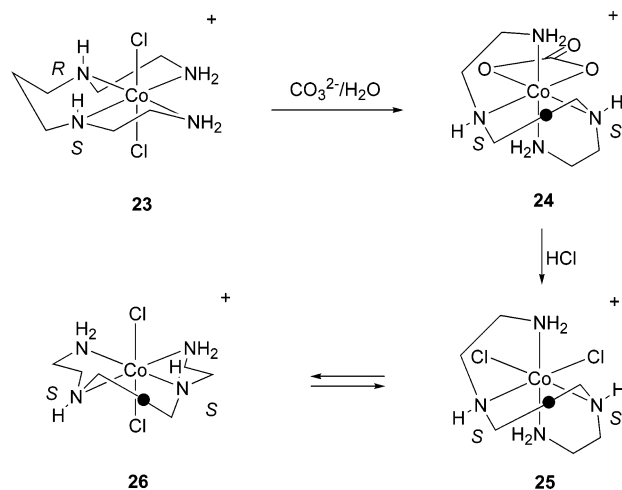
The chiralities of the coordinated secondary nitrogen atoms play a crucial role in fixing the conformations of the chelate rings and, in certain cases, in controlling the topology. The  $cis-\alpha$  isomer, **15**, as drawn in the shown topological enantiomer,<sup>19</sup> requires that the chirality of the nitrogen atoms be in the *R* absolute configuration. The *S,S* configuration of the nitrogen atoms would give the opposite enantiomer of the topology. The  $cis-\alpha$  topology cannot support the *meso* (*R,S*) configuration of coordinated nitrogen atoms. The *R,S* nitrogen configuration is accessible for the  $cis-\beta$  topology that can also support the *R,R* configuration. The  $cis-\beta$  isomer of the topological chirality illustrated, **16**, cannot form when the secondary nitrogen configurations are *S,S*. It will be noted that in rearranging from **16** to **17** the planar-disposed chelate rings flip their conformations. The *trans* topology is formed when the coordinated secondary nitrogen atoms are in the *R,R* (or *S,S*) configuration. The *trans* isomer, **18**, is chiral because of the ring puckering and the secondary nitrogen configurations. The *meso* (*R,S*) *trans* topology has not been isolated for the 2,2,2-tet ligands, possibly because of the high strain generated by this structure.

The cobalt(III) complexes of the 3,2,3-tet, **10**, ligands provide markedly different topologies, as illustrated in the reaction sequence **19–22**.<sup>20</sup> Unlike the case of cobalt(III) complexes of the 2,2,2-tet ligand, the racemic *trans* topology, **19**, is preferred for the 3,2,3-tet ligand. The *trans* isomer **19** was separated into its enantiomers and converted to the  $cis-\beta$ -(*R,R*) isomer, **20**, by reaction with acac. This *R,R* (or *S,S*)  $cis-\beta$ -isomer is more stable than the *R,S*  $cis-\beta$ -isomer **21**. Conversion of **21** to **22** gives the *R,S* *trans*-isomer. The overall behavior of the 3,2,3-tet cobalt(III) complexes contrasts sharply with the 2,2,2-tet analogues. The 3,2,3-tet ligand prefers a *trans* topology and allows for both *R,R* (or *S,S*) and *R,S* *trans* isomers, and the  $cis-\alpha$  topology was not detected. The presumed instability of the  $cis-\alpha$ -isomer

is probably related to intramolecular interligand interactions when the chelate rings are *cis* disposed. It will also be noted that cumulative bite-angle strain is absent in the *trans* disposed 3,2,3-tet ligand.



The cobalt(III) complexes of the 2,3,2-tet, **11**, also have little bite-angle strain in the *trans* topology and generally are found to prefer this isomerism.<sup>21</sup> Racemic *trans* complexes, **19**, of the 3,2,3-tet ligand were found to be more stable than the *meso* (*R,S*) isomer, **22**, but for the *trans* 2,3,2-tet ligand complex the *meso* (*R,S*) isomer, **23**, is more stable than the racemic analogue, **26**. The topological isomers that have been observed for the dichloro-cobalt(III) complexes of the ligand 2,3,2-tet are shown, **23** to **26**. Reaction of **23** with carbonate ions leads to the formation of the  $cis-\alpha$  topology, **24**, where, of necessity, the coordinated secondary nitrogen atoms are in racemic (*R,R* or *S,S*) configurations. Addition of HCl to **24** gives the  $cis-\alpha$ , **25**, and *trans*, **26**, dichloro isomers. The *trans* isomer is racemic and less stable than the *meso* *trans* isomer, **23**. The 2,3,2-tet ligand does not form racemic  $cis-\beta$  complexes because the six-membered chelate ring is forced to adopt a strained conformation in this topology.



For the three amines 2,2,2-tet, 3,2,3-tet, and 2,3,2-tet, the relative stabilities of the cobalt(III) topological isomers can be summarized as follows

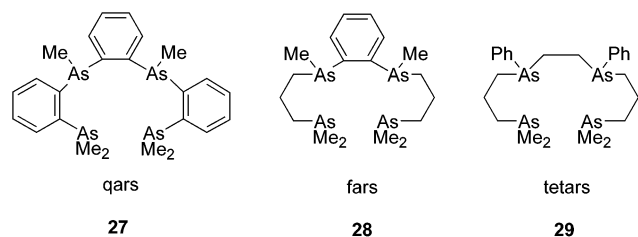
2,2,2-tet:  $R,R$ -*cis*- $\alpha \geq R,R$ -*cis*- $\beta > R,S$ -*cis*- $\beta > R,R$ -*trans*  $\gg R,S$ -*trans*

3,2,3-tet:  $R,R$ -*trans*  $> R,R$ -*cis*- $\beta > R,S$ -*cis*- $\beta > R,S$ -*trans*  $\gg R,R$ -*cis*- $\alpha$

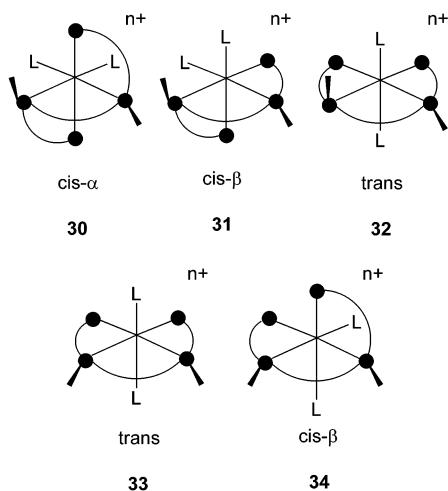
2,3,2-tet:  $R,S$ -*trans*  $> R,R$ -*trans*  $> R,R$ -*cis*- $\alpha \gg R,R$ -*cis*- $\beta$  and  $R,S$ -*cis*- $\beta$

*R,S*-*cis*- $\alpha$  is not possible for any of the tetramines. Although several factors can affect the topological preference, the interplay between chelate ring size, ring conformation, and secondary nitrogen chirality can have a decisive role in determining topology.

These considerations are illustrated by the topologies observed for the quadridentate arsine ligands,<sup>22–23</sup> **27–29**. Each of these linear quadridentate ligands



can exist in stable racemic (*R,R* or *S,S*) or meso (*R,S*)-configuration of the inner tertiary arsenic atoms. As for the case of the linear tetramine ligands, the chirality of the inner tertiary arsine atoms plays an important role in controlling the topology of their octahedral complexes. The possible octahedral topologies **30–32** for the racemic ligands and the topologies **33** and **34** for the meso ligands are illustrated. As follows from the discussion of the linear tetramines, these analogous racemic tetraarsine complexes can produce *cis*- $\alpha$ , *cis*- $\beta$ , and *trans* topologies whereas the meso ligands give only the *trans* and *cis*- $\beta$  isomers. Since the tertiary arsines are configurationally stable, the chirality of the inner arsenic atoms fixes the chirality of the topological disposition of the chelate rings. Thus, for example, the enantiomerically pure complex *cis*- $\alpha$ -[Co(tetars)Cl<sub>2</sub>]<sup>+</sup> having the topological enantiomer shown in **30** has the *S,S* configuration of the inner arsenic atoms.<sup>22,23</sup> Pure *S,S*-tetars, when reacted to give the *cis*- $\alpha$ -[Co(tetars)Cl<sub>2</sub>]<sup>+</sup> complex, gives only one diastereomer.<sup>22–23</sup>



**Table 3. Equilibrium Ratios of Topological Isomers of Complexes of the Type [Co(tetraarsine)Cl<sub>2</sub>]<sup>+</sup>**

compound	solvent	isomer equilibrium, %		
		<i>cis</i> - $\alpha$	<i>cis</i> - $\beta$	<i>trans</i>
[Co( <i>R,R,S,S</i> -fars)Cl <sub>2</sub> ] <sup>+</sup>	1 M HCl	60	40	0
	CH <sub>3</sub> OH	20	20	60
[Co( <i>R,S</i> -fars)Cl <sub>2</sub> ] <sup>+</sup>	1 M HCl		15	85
	CH <sub>3</sub> OH		0	100
[Co( <i>R,R,S,S</i> -qars)Cl <sub>2</sub> ] <sup>+</sup>	1 M HCl	100	0	0
	CH <sub>3</sub> OH	100	0	0
[Co( <i>R,S</i> -qars)Cl <sub>2</sub> ] <sup>+</sup>	1 M HCl		30	70
	CH <sub>3</sub> OH		0	100
[Co( <i>R,R,S,S</i> -tetars)Cl <sub>2</sub> ] <sup>+</sup>	1 M HCl	80	20	0
	CH <sub>3</sub> OH	75	5	20
	CH <sub>3</sub> CN	85	15	0
[Co( <i>R,R,S,S</i> -tetars)Cl <sub>2</sub> ] <sup>+</sup>	1 M HCl		0	100
	CH <sub>3</sub> OH		0	100
	CH <sub>3</sub> CN		0	100

The thermodynamic isomeric distribution of complexes of the type [Co(tetraarsine)Cl<sub>2</sub>]<sup>+</sup>, tetraarsine is **27–29**, in various solvents is shown in Table 3.<sup>22–23</sup> The solvent temperature is the boiling point of the solvent.

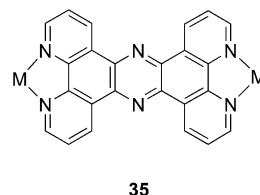
The complex [Co(*R,R,S,S*-qars)Cl<sub>2</sub>]<sup>+</sup>, unlike the other two racemic analogues, only provides the *cis*- $\alpha$  topology because of the presence of three consecutive rigid five-membered rings. It is clear from the data in Table 3 that the topology adopted depends on the solvent medium, the chelate ring size, and the relative stereochemistry of the two inner arsenic atoms. It will be noted that the two racemic ligands, fars and tetars, which are analogous to 3,2,3-tet, have a tendency to give *cis*-cobalt(III) complexes unlike 3,2,3-tet, which prefers the *trans* topology. This difference is probably connected with the larger radius of arsenic. The larger radius tends to favor an angular disposition of chelate rings and has been noted for quadridentate ligand cobalt complexes bearing inner sulfur atoms.<sup>24</sup>

The principles outlined here for monometallic complexes can be transferred to analogous bimetallic systems provided the particular constraints imposed by bridging ligands are recognized.

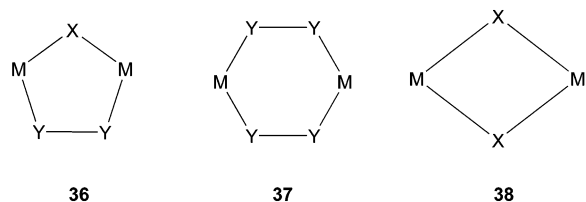
### 3. Bimetallic Ligand Systems

#### 3.1. Bridging Units

It is convenient to classify binucleating ligands by the bridging groups that are used to assemble bimetallic complexes. A list of bridging groups is given in Table 4. This list excludes bridges that cause large metal–metal separations such as **35**. The bridges in Table 4 give metal–metal separations of 3.0–4.0 Å, and these, by convention, are referred to as bridging groups, although there is no reason to exclude the bimetallic system **35**, for example. Further, bridges which span metal–metal-bonded systems are usually excluded when binucleating ligands are discussed. We also exclude these here.



The bridging ligands in Table 4 are of three types: those that have single-atom bridges, those with two-atom bridges, and bimetallic complexes with three-atom bridges. Bimetallic complexes formed with one- or two-atom bridges are of the type **36**–**38**. The bridging structures **36** and **37** are formed without significant strain, but the bridging system **38** carries considerable strain because of angle deformations. Carboxylates and amidinates form three-atom bridges that are formed without significant strain.



Carboxylate bridging is a very common method of forming bimetallic complexes. Usually, the two metals are in a *syn, syn* disposition, but the *syn, anti* and *anti, anti* metal arrangements are known. The analogous amidinates have been less extensively studied. In principle, the amidinate ligand could display the three metal dispositions observed for the carboxylate bimetallic bridge, but so far only *syn, syn* bimetallic bonding has been observed. The pyrazolate and triazolate ligands can form strong bridges to metals. In the case of the triazolate ligand, in principle, three metals could be incorporated. Trimetal bridging is sometimes observed,<sup>25,26</sup> but in most cases, so far, the 1,2-bimetallic bridging mode is obtained. The neutral diazine bridging ligands oxadiazole, thiadiazole, and pyridazine also form bimetallic complexes, but it is likely that they are less stable than the pyrazolate and triazolate bridging ligands because the latter two carry negative charges. Naphthyridine can be regarded as a neutral analogue of the amidinate ligand, and because the two metal–ligand bonds are parallel, the two metals are expected to interact strongly with each other. Perhaps the most studied bridging ligand is the phenolate anion because of the ease of incorporation of ligand substituents at the ortho position. The alkoxide bridge has also been extensively used. The aryl- or alkanethiolate bridges have been employed in only a few binucleating ligands.

The ease of synthesis of multidentate binucleating ligands depends on the bridging unit. The phenolate and alkoxide bridges are generally the least challenging. The diaza heterocyclic bridges are elaborated from the carbon atoms attached to the bridging nitrogen atoms. The ease of preparation depends on the nature of the chelate elaboration required and on the heterocycle bridge. The amidinate ligand is relatively easy to elaborate from the two nitrogen atoms, but such substitution is not possible for the carboxylate groups. Elaboration from the carboxylate R group is difficult because of the chelate ring sizes required to span to the two metals bridged by the carboxylate oxygen atoms.

### 3.2. Binucleating Carboxylate Bridging Ligands

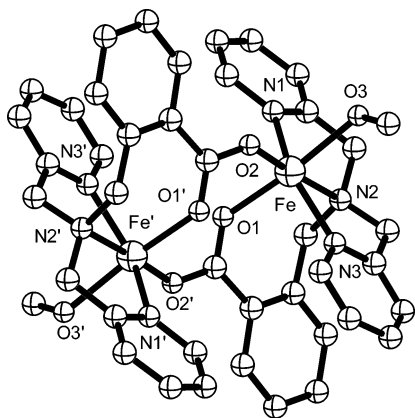
Unlike the other bridges, the synthesis of binucleating ligands bearing one or two carboxylate ligands

**Table 4. Some Bimetallic Bridging Units**

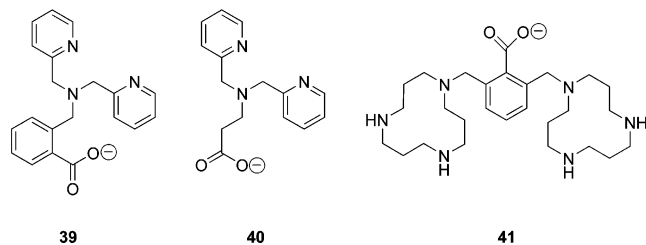
Bridging unit name	Bridging unit	Metal binding mode
Carboxylate		 <i>syn, syn</i> <i>syn, anti</i> <i>anti, anti</i>
Formamidinate		<i>syn, syn</i>
Pyrazolate		<i>syn, syn</i>
Triazolate		<i>syn, syn</i>
Oxadiazole		<i>syn, syn</i>
Thiadiazole		<i>syn, syn</i>
Pyridazine and Phthalazine		<i>syn, syn</i>
1,8-Naphthyridine		<i>syn, syn</i>
Phenolate, Alkoxide		<i>syn, syn</i>
Thiophenolate, Thiolate		<i>syn, syn</i>
Disulfide		<i>syn, syn</i>

is not a simple matter. The major challenge is to construct ligands that will incorporate the carboxylate group as a bridge and also allow ligands substituted to the carboxylate to bind to the metals. This problem is yet to be solved, although some interesting work in this direction has been reported.

Perhaps the simpler of these ligands are binucleating multidentate ligands bearing only one carboxylate bridge. Three such ligands, **39**,<sup>27</sup> **40**,<sup>28</sup> and **41**,<sup>29</sup> have been prepared, and a number of di-Fe<sup>2+</sup> complexes have been structurally characterized. The complex [Fe<sub>2</sub>(**39**)<sub>2</sub>(CH<sub>3</sub>OH)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> has the solid-state structure shown in Figure 1.<sup>27</sup> As can be seen, the two iron atoms are bridged by the carboxylates and the iron atoms are bonded *syn, anti*. Interestingly, the Fe–O bond lengths are 1.99(1) Å for *syn* bonding

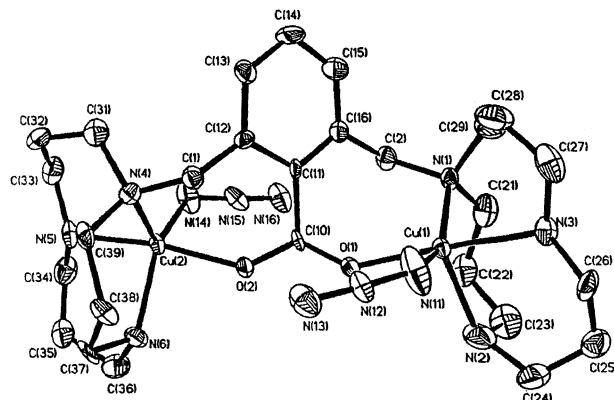


**Figure 1.** Crystal structure of  $[\text{Fe}_2(\mathbf{39})_2(\text{CH}_3\text{OH})_2]^{2+}$ . (Reprinted with permission from ref 27. Copyright 1996 The Royal Society of Chemistry.)



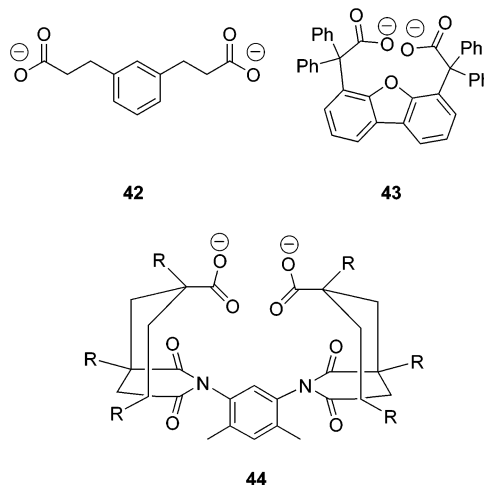
and 2.09(1) Å for the *anti* iron–oxygen bonds. This difference was ascribed<sup>27</sup> to the higher base strength of *syn* carboxylate lone pairs. The analogous ligand, **40**, gives a bimetallic di- $\text{Fe}^{2+}$  complex,  $[\text{Fe}_2(\mathbf{40})_2(\text{H}_2\text{O})_2\text{O}](\text{ClO}_4)_2$ , where the metal atoms are supported by an oxo bridge and the carboxylates act as unidentate ligands.<sup>28</sup> These different structures may be related to the shorter and more flexible amino acid link, or the structures isolated may simply be the least soluble of the species equilibrating in solution. The di- $\text{Cu}^{2+}$  complex of the ligand **41**,  $[\text{Cu}_2(\mathbf{41})(\text{N}_3)_2]\text{ClO}_4$ , has the structure shown in Figure 2.<sup>29</sup> The notable feature of this structure is the *anti,anti* bonding of the carboxylate that probably arises because chelation does not allow for *syn* bonding. This structure illustrates that very large chelate rings are required in order to obtain *syn,syn* carboxylate bridging in multidentate binucleating ligands. It is probable that unless these large rings possess rigidity, polymeric structures will form.

The respiratory protein hemerythrin (Table 1) carries two (*syn,syn*) carboxylate bridges, and several attempts have been made to generate dicarboxylate ligands, which will reproduce the metal binding in the protein. Lippard developed a number of these ligands, and three of these are shown, **42**–**44**. The ligand **42**<sup>30,31</sup> is very flexible and potentially could form oligomeric or polymeric complexes. Nonetheless, several bimetallic di-iron complexes have been isolated where the two carboxylates bridge the two metals. The ligand **43**<sup>32,33</sup> is clearly more rigid than **42**. It was asserted<sup>32</sup> that the phenyl groups in **43** serve to preorganize the carboxylate groups through nonbonding interactions and that they enhance crystallinity and solubility of the complexes. Ligand **44**, which was developed by Rebek<sup>34</sup> for other purposes, is an especially rigid system where the two carboxylate groups are constrained to point at each other.



**Figure 2.** Crystal structure of  $[\text{Cu}_2(\mathbf{41})(\text{N}_3)_2]^+$ . (Reprinted with permission from ref 29. Copyright 2000 Elsevier.)

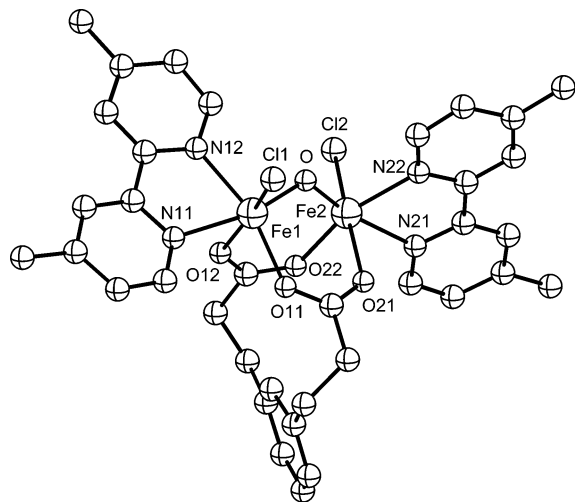
Lippard used this basic ligand type with a variety of R groups to form dicarboxylate bridging bimetallic complexes.<sup>35–45</sup> The ligand **44** is expected to form especially stable bimetallic complexes because the two carboxylates are sterically constrained to orient in a geometry ideally suited for (*syn,syn*) bridging.



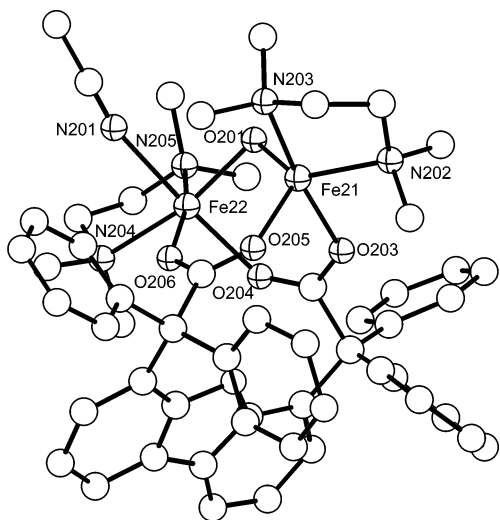
A number of di-iron complexes with ligand **42** have been structurally characterized,<sup>30,31</sup> including the di- $\text{Fe}^{3+}$  complex  $[\text{Fe}_2(\mu\text{-O})(\mathbf{42})(4,4'\text{-Me}_2\text{bipy})_2\text{Cl}_2]$ <sup>31</sup> (Figure 3). In this structure and others, the two carboxylate groups form *syn,syn* bridges to the two iron atoms. The very large chelate ring formed by **42** may attest to the stability of the *syn,syn* diacetate dimetal assembly.

Ligand **43** provides a rigid framework for binding of the two bridging carboxylate ligands as illustrated by the structure of the di- $\text{Fe}^{2+}$  complex  $[\text{Fe}_2(\mu\text{-OH})(\mathbf{43})(\text{TMEDA})_2(\text{CH}_3\text{CN})]\text{BPh}_4$ ,<sup>32</sup> shown in Figure 4 (TMEDA =  $(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$ ). The structure has *syn,syn* carboxylate binding and five- and six-coordinate iron atoms that are bridged by an  $\text{OH}^-$  ligand.

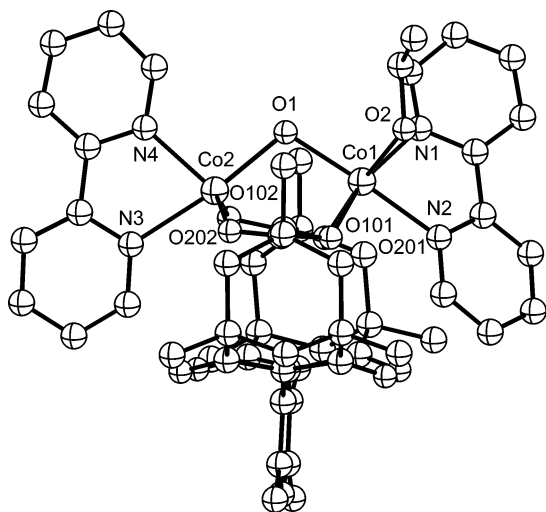
Figure 5 shows the crystal structure of  $[\text{Co}_2(\mu\text{-OH})(\mathbf{44})(\text{bipy})_2(\text{EtOH})]\text{NO}_3$ ,<sup>39</sup> where R in **44** is  $\text{CH}_3$ . In this structure, one  $\text{Co}^{2+}$  ion is five-coordinate and the other is six-coordinate. The carboxylate bridges bind the metals in a *syn,syn* bonding mode. The ligand **44** forms very stable bimetallic complexes.<sup>35–45</sup> What has not yet been reported is a ligand that incorporates structure **44** and carries flanking multidentate ligands



**Figure 3.** Crystal structure of  $[\text{Fe}_2(\mu\text{-O})(\mathbf{42})(4,4'\text{-Me}_2\text{-bipy})_2\text{Cl}_2]$ . (Adapted from ref 31. Copyright American Chemical Society.)

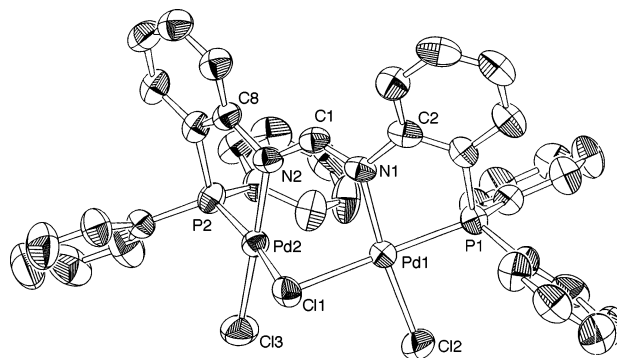


**Figure 4.** Crystal structure of the ion  $[\text{Fe}_2(\mu\text{-OH})(\mathbf{43})\text{-(TMEDA)}_2(\text{CH}_3\text{CN})]^+$ . (Adapted from ref 32. Copyright American Chemical Society.)



**Figure 5.** Crystal structure of the ion  $[\text{Co}_2(\mu\text{-OH})(\mathbf{44})\text{-(bipy)}_2(\text{EtOH})]^+$ , where in  $\mathbf{44}$  R is  $\text{CH}_3$ . (Adapted from ref 39. Copyright American Chemical Society.)

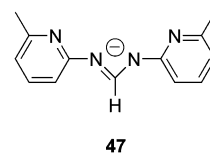
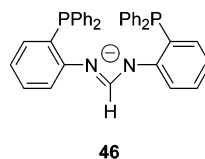
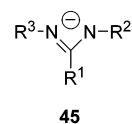
that can bind to the two metals. Such binucleating ligands present formidable synthetic challenges.



**Figure 6.** Crystal structure of  $[\text{Pd}_2(\mu\text{-Cl})(\mathbf{46})\text{Cl}_2]$ . (Adapted from ref 46. Copyright American Chemical Society.)

### 3.3. Binucleating Formamidinate Bridging Ligands

The formamidinate bridge, **45**, has not been used extensively for generating bimetallic complexes. In principle, formamidinate systems should be easier to elaborate into binucleating multidentate ligands than the carboxylate analogues because each of the nitrogen atoms can bear a substituent ( $\text{R}^2, \text{R}^3$ ). Simple elaboration has been reported and is represented by the ligands, **46**<sup>46</sup> and **47**<sup>47</sup>. Several bimetallic complexes of Pd(II) and Pt(II) have been isolated and characterized for the ligand **46**.<sup>46</sup> Figure 6 shows the crystal structure of  $[\text{Pd}_2(\mu\text{-Cl})(\mathbf{46})\text{Cl}_2]$ , where it will be noted that the N, P, Pd, and  $\mu\text{-Cl}$  atoms do not lie in one plane. The ligand **47** does, however, form bimetallic  $\text{Cd}^{2+}$  complexes where the four nitrogen atoms are essentially in one plane. Figure 7 shows a crystal structure of  $[\text{Cd}_2(\mathbf{47})_3]\text{NO}_3$ ,<sup>47</sup> where the cadmium atoms are in pseudooctahedral geometries.

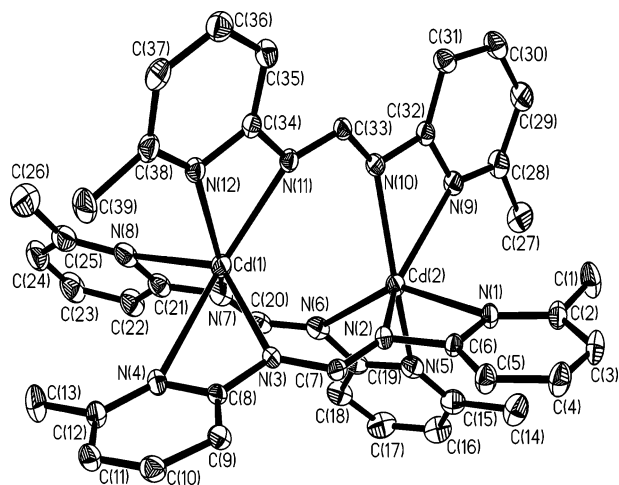


Formamidinate ligands have been used extensively as alternatives to acetate bridges in bimetallic complexes bearing metal–metal bonds.<sup>48</sup> We have arbitrarily chosen to exclude such bimetallic complexes here.

### 3.4. Binucleating Pyrazolate Bridging Ligands

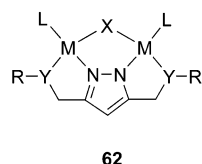
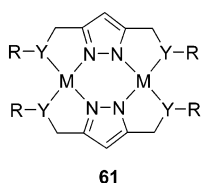
The negatively charged pyrazolate bridge can form five-membered, **36**, or six-membered, **37**, bimetallic ring systems. Generally such bridging structures are without significant strain. The metal–metal separations in these systems range from about 3.5 to 4.0 Å. Although the pyrazolate bridge has several attractive features, including its stability, strainless formation of bimetallic complexes, and resemblance to imidazoles, the synthesis of multidentate binucleating





**Figure 7.** Crystal structure of the ion  $[\text{Cd}_2(\mathbf{47})_3]^+$ . (Reprinted with permission from ref 47. Copyright 2002 Elsevier.)

pyrazole ligands is not simple. Some general routes to the synthesis of multidentate binucleating ligands are given at the end of this section. Table 5 collects a variety of binucleating pyrazolate ligands. All of these ligands incorporate ligand substituents emanating from the 2,4-positions of the pyrazolate ring. Many of these ligands can form either bispyrazolate systems, **61**, or monopyrazolate systems of the type **62**. In the latter case, the di-metal ring is completed by the introduction of an exogenous bridging ligand, X. Because five-membered chelate rings have a bite angle of about  $86^\circ$ , a bimetallic complex of the type **62** will have greater separation of the metals than when six-membered flanking rings are present. No examples of binucleating pyrazole ligands bearing flanking six-membered rings have been reported.

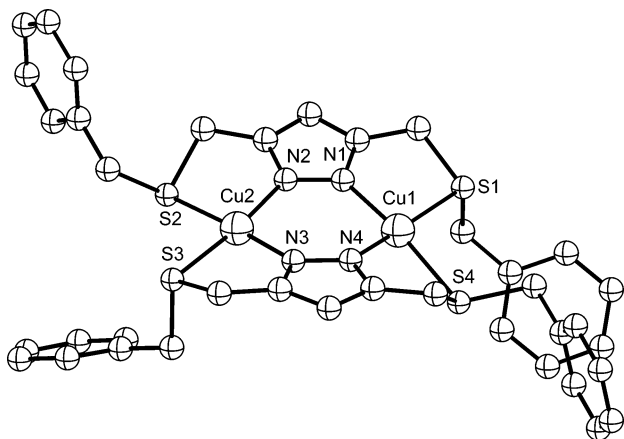


The crystal structure of the di- $\text{Cu}^{2+}$  complex  $[\text{Cu}_2(\mathbf{48})_2](\text{BF}_4)_2 \cdot (\text{CH}_3)_2\text{CO}$  is shown in Figure 8.<sup>49</sup> The  $\text{Cu} \cdots \text{Cu}$  distance was found to be  $3.828 \text{ \AA}$ ; the other bond angles and distances are unexceptional. A similar structure is observed for the complex  $[\text{Ni}_2(\mathbf{50})(\text{CH}_3\text{OH})_4]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ .<sup>51</sup> The di- $\text{Cu}^{2+}$  complex  $[\text{Cu}_2(\mathbf{51})_2(\text{Cl})_2]$  has an interesting crystal structure.<sup>52</sup> Two pyrazolates bridge the copper ions, but one oxime unit of one ligand is bound via the nitrogen atom, whereas the other oxime binds the metal through the oxygen atoms after the O-proton is transferred to the nitrogen atom. The structure is shown in Figure 9. The  $\text{Cu} \cdots \text{Cu}$  distance is about  $3.8 \text{ \AA}$  depending on the crystalline form.

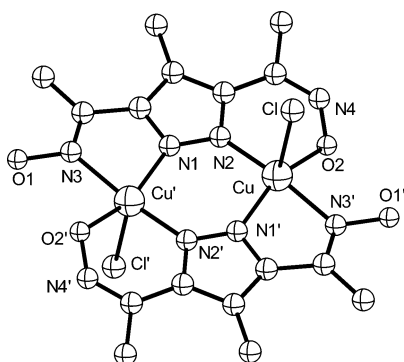
When the ligand has more than four donor atoms, **52–60**, bimetallic complexes of the type **62** are usually formed. The crystal structure of the complex  $[\text{Co}_2(\mu\text{-Cl})(\mathbf{57c})(\text{BPh}_4)_2]^{54}$  (Figure 10) is representative of the structures encountered. In this structure, the  $\text{Co} \cdots \text{Co}$  separation is about  $3.9 \text{ \AA}$  and the cobalt(II) ions adopt distorted trigonal bipyramidal geometries.

**Table 5. Binucleating Pyrazolate Ligands**

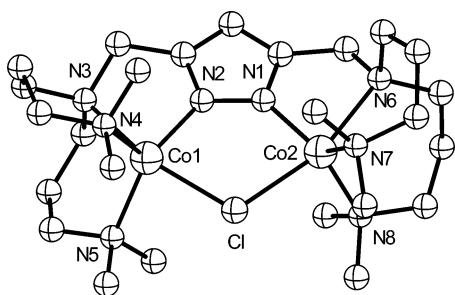
Ligand Number	Ligands	Metal Complexes	Reference
48		di- $\text{Cu}^{2+}$	49
49		di- $\text{Rh}^+$ , di- $\text{Ir}^+$ , di- $\text{Pd}^{2+}$	50
50		di- $\text{Ni}^{2+}$	51
51		di- $\text{Cu}^{2+}$	52
52		di- $\text{Co}^{2+}$ , di- $\text{Ni}^{2+}$	53, 54
53		di- $\text{Mn}^{2+}$ , di- $\text{Cu}^{2+}$	55
	R = $\text{CH}_3$ , $\text{CH}_2\text{CH}_3$		
54		di- $\text{Cu}^{2+}$	56
55		di- $\text{Cu}^{2+}$	57
56		di- $\text{Cu}^{2+}$	58
	a). R = $\text{CH}_2\text{CH}_2\text{N}(\text{CH}_2\text{CH}_3)_2$ b). R = $\text{CH}_2$ -2-pyridine c). R = $\text{CH}_2\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$		
57			
	a). R = $\text{CH}_2\text{CH}_2\text{N}(\text{CH}_2\text{CH}_3)_2$ b). R = $\text{CH}_2\text{CH}_2\text{S}(\text{CH}_2\text{CH}_3)_2$ c). R = $\text{CH}_2\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$ d). R = $\text{CH}_2$ -2-pyridine	di- $\text{Ni}^{2+}$ , di- $\text{Co}^{2+}$ , di- $\text{Zn}^{2+}$ di- $\text{Ni}^{2+}$ di- $\text{Ni}^{2+}$ , di- $\text{Co}^{2+}$ , di- $\text{Zn}^{2+}$ di- $\text{Mn}^{2+}$	59-61 62 54, 59-61 56
58			
	a). X = Y = NH b). X = Y = S c). X = S, Y = NH	di- $\text{Cu}^{2+}$ , di- $\text{Ni}^{2+}$ di- $\text{Cu}^{2+}$ di- $\text{Cu}^{2+}$	63 64 64
59		di- $\text{Ni}^{2+}$	65
60		di- $\text{Ni}^{2+}$	62



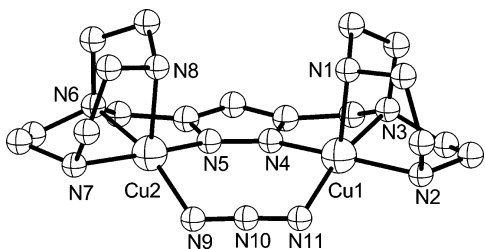
**Figure 8.** Crystal structure of  $[\text{Cu}_2(\mathbf{48})_2]^{2+}$ . (Reprinted with permission from ref 49. Copyright 1997 WILEY-VCH.)



**Figure 9.** Crystal structure of  $[\text{Cu}_2(\mathbf{51})_2\text{Cl}_2]$ . (Reprinted with permission from ref 52. Copyright 1993 The Royal Society of Chemistry.)



**Figure 10.** Crystal structure of  $[\text{Co}_2(\mu\text{-Cl})(\mathbf{57c})]^{2+}$ . (Reprinted with permission from ref 54. Copyright WILEY-VCH.)



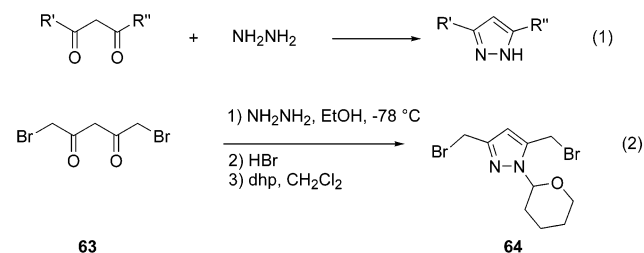
**Figure 11.** Crystal structure of  $[\text{Cu}_2(\mu\text{-}1,3\text{-N}_3)(\mathbf{58a})]^{2+}$ . (Reprinted with permission from ref 63. Copyright 1995 Helvetica Chimica Acta.)

The structures of the bimetallic complexes formed by the ligands in entries **58a–c** are those expected for the particular metal. For example, the structure<sup>63</sup> of  $[\text{Cu}_2(\mu\text{-}1,3\text{-N}_3)(\mathbf{58a})](\text{PF}_6)_2 \cdot \text{H}_2\text{O}$  is shown in Figure 11. Each of the  $\text{Cu}^{2+}$  ions is square pyramidal and

the  $\text{Cu}\cdots\text{Cu}$  separation is large (4.15 Å) at least partly because of the 1,3-binding mode of the azido bridge.

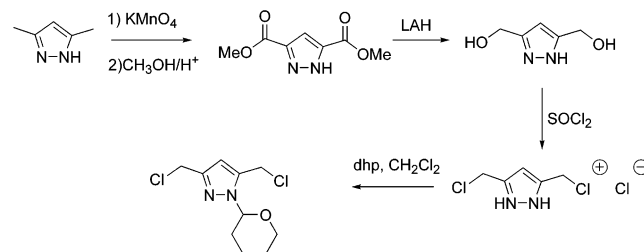
### 3.4.1. Ligand Synthesis

Pyrazoles can be generated by a variety of methods; the most commonly used method is the efficient reaction between a 1,3-diketone and hydrazine (eq 1). Thus, the dibromo compound **63**<sup>66</sup> can be reacted with  $\text{NH}_2\text{NH}_2$  at low temperatures to give the pyrazole, which is stabilized by its tetrahydropyran (thp) derivative, **64**<sup>67</sup> (eq 2). The compound **64**



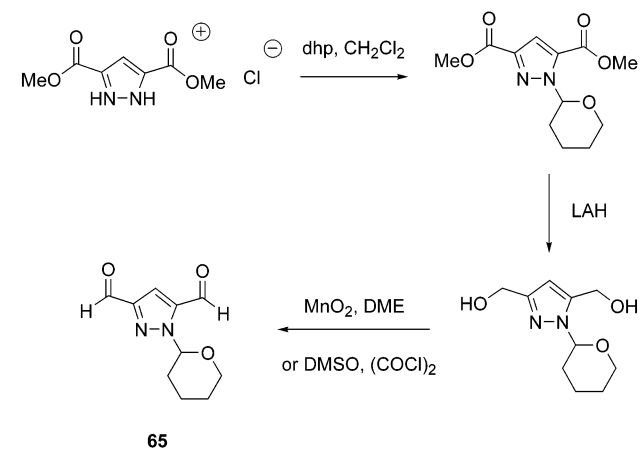
is readily elaborated. More often, the somewhat less reactive chloro analogue of **64** has been employed, that is prepared by the procedures in Scheme 1.<sup>50</sup> The

#### Scheme 1



dichloro salt can be converted to the stable thp adduct<sup>50,67</sup> The analogous dialdehyde **65** is prepared by starting from the dimethylester,<sup>67</sup> Scheme 2. The

#### Scheme 2

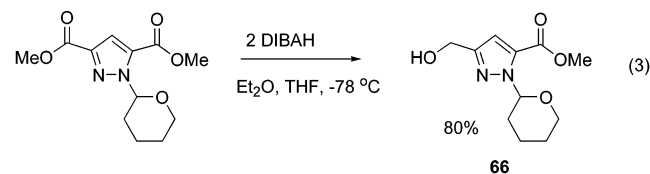


dihalogeno and the dialdehyde compounds are readily elaborated by standard methods. Unsymmetrical substitution of the pyrazole ring has been achieved by selective reduction using diisobutylaluminumhydride (DIBAH) at low temperatures<sup>67</sup> (eq 3). A similar unsymmetrically substituted pyrazole is prepared by

**Table 6. Triazole and Triazolite Ligands**

Ligand Number	Ligands	Metal Complexes	Reference
67		di-Ni <sup>2+</sup> , di-Cu <sup>2+</sup>	72, 73
68		di-Cu <sup>2+</sup>	74, 75
69		di-Cu <sup>2+</sup>	76, 77
70		di-Cu <sup>2+</sup>	78

the cycloaddition procedure<sup>68</sup> (eq 4). The alcohol and ester groups can be manipulated separately to generate unsymmetrical binucleating ligands.<sup>62</sup>

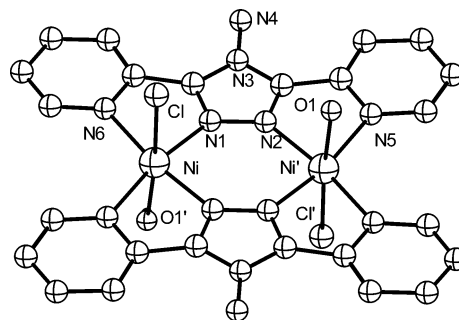


Numerous bimetallic complexes using simple pyrazolate ligands have been reported.<sup>69–70</sup> These bimetallic complexes, which are only supported by the pyrazolate ligands, were extensively used to study oxidative addition reactions with contiguous low-valent metals. These complexes will not be discussed here.

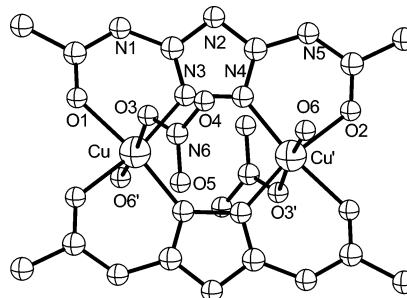
### 3.5. Triazole and Triazolite Bridging Ligands

There is a substantial number of complexes reported for simple triazole and triazolite ligands. A recent review<sup>71</sup> reports on many of these complexes. Fewer examples of multidentate triazole and triazolite ligands have been reported. Table 6 lists a number of these multidentate ligands that are of two types: those with a 4-amino substituent and those with an (acidic) proton. In all multidentate ligand cases so far reported, the two metals bind to the 1,2-disposed nitrogen atoms.

The ligand **67** forms two types of bimetallic complexes, those with bis-ligand–di-metal binding (resembling **61**) and those with mono-ligand–di-metal (resembling **62**) coordination. The first type of complex is displayed by the compound [Ni<sub>2</sub>(**67**)<sub>2</sub>Cl<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]·4H<sub>2</sub>O.<sup>72</sup> Its crystal structure is shown in Figure 12, where the Ni···Ni distance is 4.134(8) Å, the ligands are essentially planar, and the Ni<sup>2+</sup> ions are in an octahedral geometry. The ligand **68** forms a



**Figure 12.** Crystal structure of [Ni<sub>2</sub>(**67**)<sub>2</sub>Cl<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>2+</sup>. (Reprinted with permission from ref 72. Copyright 1984 The Royal Society of Chemistry.)

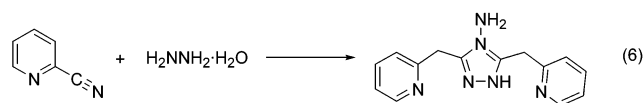
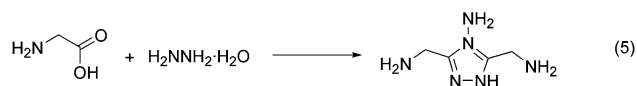


**Figure 13.** Crystal structure of [Cu<sub>2</sub>(**70**)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]. (Reprinted with permission from ref 78. Copyright 1999 The Royal Society of Chemistry.)

complex ion [Cu<sub>2</sub>(**68**)<sub>2</sub>Br<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>2+</sup>, the crystal structure<sup>74</sup> of which is analogous to that shown in Figure 12. The crystal structure of the di-copper(II) complex formed by the triazolite ligand **69**, namely, [Cu<sub>2</sub>(**69**)<sub>2</sub>(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>2-</sup>,<sup>77</sup> is similar to the structure shown in Figure 12. The di-Cu<sup>2+</sup> complex of the ligand **70**, [Cu<sub>2</sub>(**70**)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>], is shown in Figure 13.<sup>78</sup> Each Cu<sup>2+</sup> ion is in a tetragonally elongated octahedral geometry, the Cu···Cu distance is 3.854(6) Å, and as is usually found the anionic ligands (NO<sub>3</sub><sup>-</sup>) are disposed on either side of the ligand plane, and the acyl oxygen atoms act as ligands.

#### 3.5.1. Ligand Synthesis

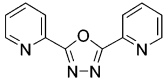
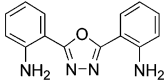
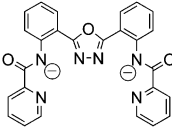
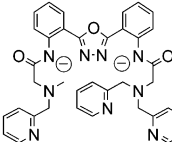
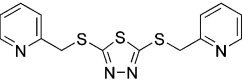
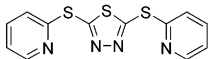
Preparation of 1,2,4-triazoles substituted in the 3- and 5-positions has not been extensively developed. Reactions of carboxylic acids<sup>74</sup> or nitriles<sup>79</sup> with hydrazine can generate the triazoles with substituents at the 3- and 5-positions (eqs 5 and 6).



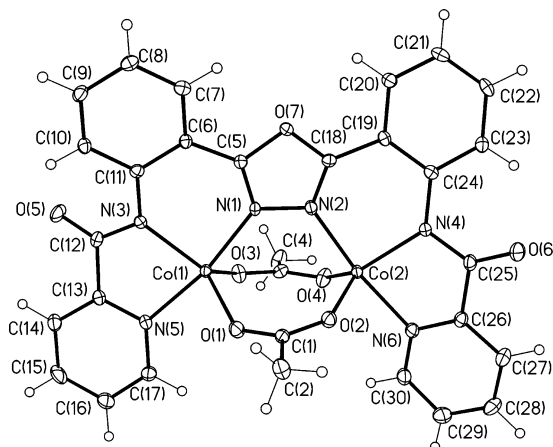
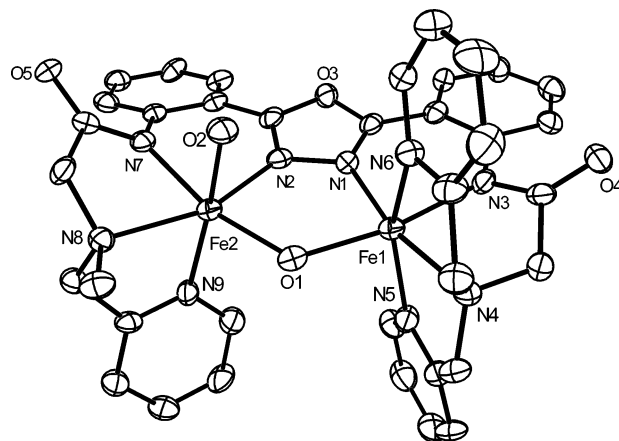
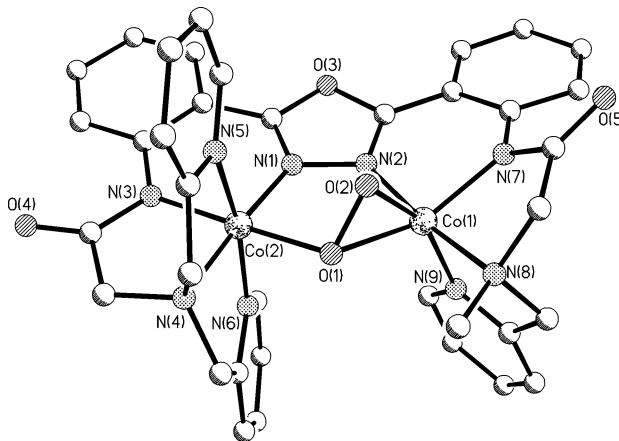
### 3.6. Oxadiazole and Thiadiazole Bridges

Unlike simple pyrazolate, triazolite, and triazole ligands, few reports have appeared on using simple oxadiazoles or thiadiazoles as ligands. Several multidentate oxadiazole and thiadiazole ligands have been prepared, and their complexes have been stud-

**Table 7. Oxadiazole and Thiadiazole Ligands**

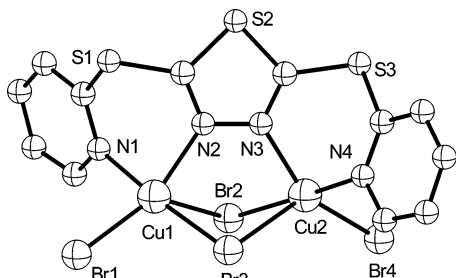
Ligand Number	Ligands	Metal Complex	Reference
71		mono-Pt <sup>2+</sup> mono-Cu <sup>2+</sup> poly-Cu <sup>2+</sup>	80 81 82
72		mono-Cu <sup>2+</sup>	83
73		di-Cu <sup>2+</sup> di-Co <sup>2+</sup> di-Ni <sup>2+</sup>	83
74		di-Co <sup>2+</sup> di-Co <sup>3+</sup> di-Fe <sup>2+</sup>	84, 85
75		di-Cu <sup>2+</sup>	86, 87
76		di-Cu <sup>2+</sup>	86, 87

ied. Some of these are listed in Table 7. It is of interest to note that the ligands **71** and **72** generally form monometallic complexes. The monometallic complexes form even in excess of metal under a variety of conditions. It would appear that for the two ligands **71** and **72**, bimetallic complexes are less stable than for analogous pyrazolate, triazolate, and triazole ligands. The crystal structure of a polymeric multimetallic Cu<sup>2+</sup> complex of **71** has been reported,<sup>82</sup> however. To obtain conventional bimetallic complexes with oxadiazole rings, the multidentate ligand **73** is required.<sup>83</sup> This ligand gives bimetallic complexes of Co<sup>2+</sup>, Cu<sup>2+</sup>, and Ni<sup>2+</sup>, and a crystal structure<sup>83</sup> of [Co<sub>2</sub>(μ-OAc)<sub>2</sub>(**73**)·CH<sub>2</sub>Cl<sub>2</sub>] is shown in Figure 14. Each of the cobalt atoms is in a trigonal bipyramidal geometry, and their separation is 3.781 Å. The complex multidentate ligand **74** readily forms bimetallic complexes of Fe<sup>2+</sup> and Co<sup>2+</sup> of the general formula [M<sub>2</sub><sup>2+</sup>(μ-OH)(**74**)(H<sub>2</sub>O)]ClO<sub>4</sub>.<sup>84,85</sup> The crystal structure of the di-Fe<sup>2+</sup> complex is shown in Figure 15.<sup>88</sup> In some respects, the di-Fe<sup>2+</sup> complex can be regarded as an analogue of hemerythrin (Table 1). Although the complex reacts with O<sub>2</sub>, the products are ill-defined. The analogous di-Co<sup>2+</sup> complex undergoes one-site addition two-metal oxidation reactions<sup>89</sup> with a number of two-electron oxidants including O<sub>2</sub>. The crystal structure of one of these dioxygen adducts<sup>85</sup>

**Figure 14.** Crystal structure of [Co<sub>2</sub>(μ-OAc)<sub>2</sub>(**73**)]. (Adapted from ref 83. Copyright American Chemical Society.)**Figure 15.** Crystal structure of [Fe<sub>2</sub>(μ-OH)(**74**)(H<sub>2</sub>O)]<sup>+</sup>.**Figure 16.** Crystal structure of [Co<sub>2</sub>(μ,η<sup>1</sup>:η<sup>2</sup>-O<sub>2</sub>)(**74**)]<sup>2+</sup>. (Adapted from ref 85. Copyright American Chemical Society.)

[Co<sub>2</sub>(μ,η<sup>1</sup>:η<sup>2</sup>-O<sub>2</sub>)(**74**)](PF<sub>6</sub>)<sub>2</sub>·CH<sub>3</sub>CN is shown in Figure 16. The unusual dioxygen bonding of the bimetallic complex is the first example observed for a di-Co<sup>3+</sup> compound.

The two ligands **75** and **76** form bimetallic complexes readily, especially with Cu<sup>2+</sup> ions. So far, all of the bimetallic complexes are those which bear one ligand to two metal ions with a variety of exogenous bridges. The structure<sup>87</sup> of the compound [Cu<sub>2</sub>(μ-Br)<sub>2</sub>(**76**)Br<sub>2</sub>] is shown in Figure 17. The Cu···Cu distance is 3.556(2) Å.

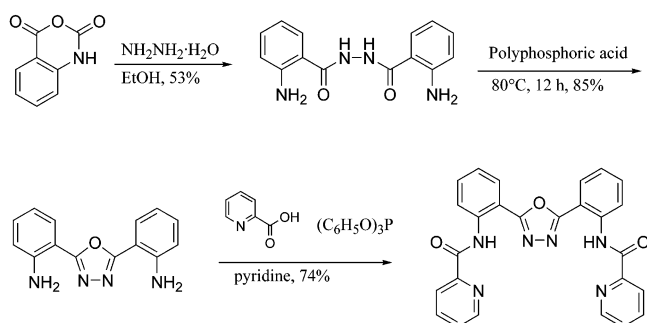


**Figure 17.** Crystal structure of  $[\text{Cu}_2(\mu\text{-Br})_2(\mathbf{76})\text{Br}_2]$ . (Adapted from ref 87. Copyright American Chemical Society.)

### 3.6.1. Ligand Synthesis

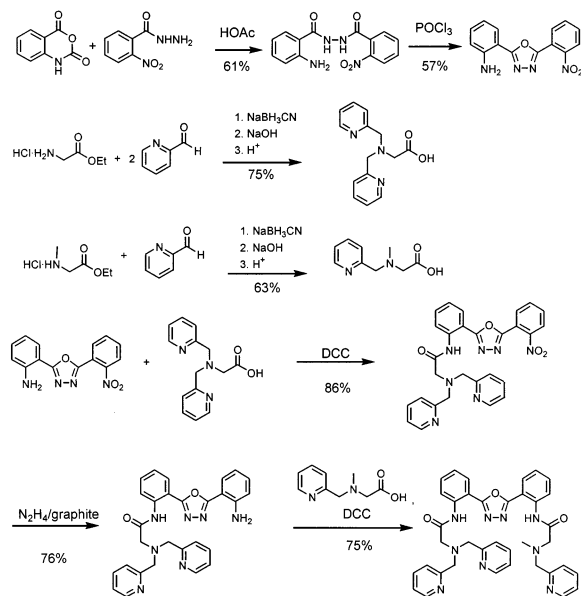
There are two examples where multidentate oxadiazole ligands have been prepared to produce binucleating ligands of modest complexity. Scheme 3

#### Scheme 3



shows a procedure<sup>83</sup> for generating the diprotonated ligand, **73**. The diacylhydrazide can be converted to the oxadiazole with a variety of dehydrating agents, including the one shown, polyphosphoric acid. Scheme 4 shows the synthesis<sup>84</sup> of the diprotonated ligand

#### Scheme 4



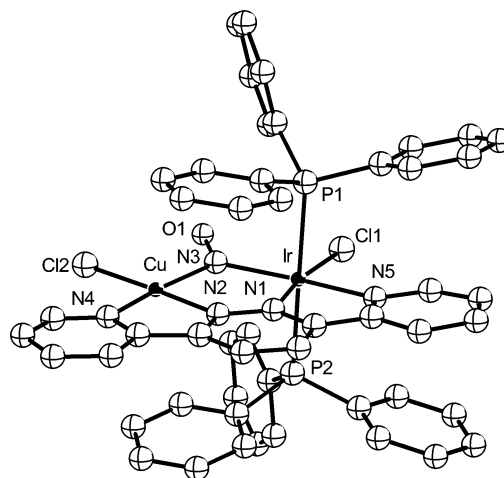
**74**. As will be noted, the two parts of the molecule are distinguished by a nitro group on one phenyl substituent and an amino group on the other. The nitro group is conveniently reduced to the amine with hydrazine/graphite. In addition, Scheme 4 contains

reductive aminations and amino acid coupling procedures commonly used in ligand synthesis.

### 3.7. Pyridazine and Phthalazine Bridging Ligands

Bimetallic complexes with pyridazine and phthalazine bridging ligands have been recently reviewed<sup>90</sup> with special emphasis on macrocyclic systems. Table 8 lists a number of multidentate pyridazine and phthalazine ligands which form bimetallic complexes.

The ligand **77** forms mono- rather than bis-ligand bimetallic complexes, possibly because, in the latter case, substantial steric interactions between the 2-positions of the pyridine groups occur when two of the ligands are incorporated into a planar bimetallic complex. The reported bimetallic complexes are unexceptional, but the heterobimetallic complex  $[\text{IrCl}(\text{PPh}_3)_2(\mu\text{-NO})(\mathbf{77})\text{CuCl}](\text{PF}_6)_2$ , the crystal structure<sup>91</sup> of which is shown in Figure 18, is of special interest.

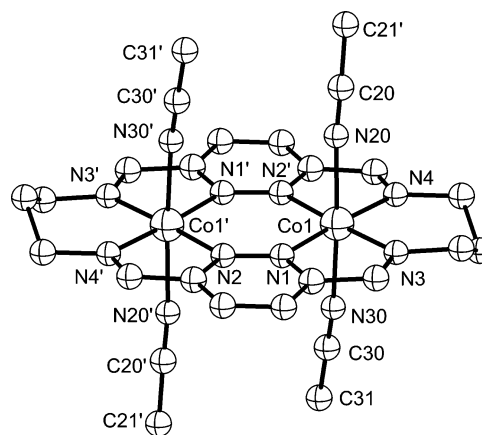


**Figure 18.** Crystal structure of  $[\text{IrCl}(\text{PPh}_3)_2(\mu\text{-NO})(\mathbf{77})\text{CuCl}]^{2+}$ . (Reprinted with permission from ref 91. Copyright 1983 The Royal Society of Chemistry.)

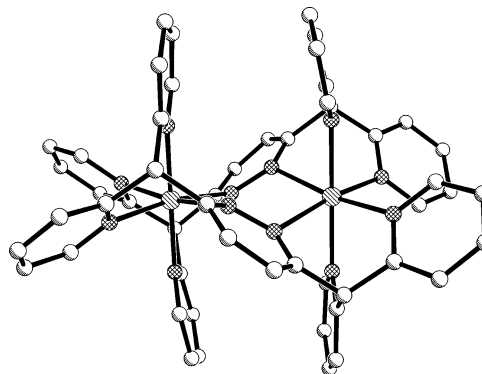
In this complex, the metal oxidation states are  $\text{Ir}^{3+}$  and  $\text{Cu}^{2+}$  and the NO bridging ligand is  $\text{NO}^-$ . The next (anionic) ligand **78** forms a bis-ligand, di- $\text{Cu}^{2+}$  complex where the oxygen atoms of the oxime groups are hydrogen bonded with one hydrogen atom as commonly observed for oxime complexes.<sup>95</sup> The macrocyclic ligand **79** is prepared by templating with  $\text{Pb}^{2+}$ .<sup>96,97</sup> Complexes of other metals are generated by transmetalation. The di- $\text{Cu}^{2+}$  complex of the ligand **79** has been structurally characterized,<sup>96</sup> and as expected, the  $\text{Cu}^{2+}$  ions are in square planar geometries. Certain di- $\text{Co}^{2+}$  complexes provide interesting magnetic behavior. The red complex  $[\text{Co}_2^{2+}(\mathbf{79})(\text{CH}_3\text{CN})_4](\text{ClO}_4)_4 \cdot 1.4\text{CH}_3\text{CN}$  has the crystal structure<sup>90,97</sup> shown in Figure 19. In this complex the ligand adopts a roughly planar structure. The bimetallic complex has a low-spin electronic configuration. In contrast, the yellow tetraaquo analogue  $[\text{Co}_2^{2+}(\mathbf{79})(\text{H}_2\text{O})_4](\text{ClO}_4)_4 \cdot \text{H}_2\text{O} \cdot 2\text{CH}_3\text{CN}$ ,<sup>97</sup> which has a similar structure to the acetonitrile complex (Figure 19), is a high-spin complex. Consistently, the  $\text{Co}^{2+}$  macrocycle bond lengths are about 0.15 Å shorter for the low-spin complex.

**Table 8. Multidentate Pyridazine and Phthalazine Ligands**

Ligand Number	Ligands	Metal Complex	Reference
77		di-Cu <sup>2+</sup> , Cu <sup>2+</sup> -Ir <sup>3+</sup> , di-Ni <sup>2+</sup>	91-94
78		di-Cu <sup>2+</sup>	95
79		di-Cu <sup>2+</sup> di-Pb <sup>2+</sup> di-Co <sup>2+</sup>	96, 97
80		di-Cu <sup>2+</sup> , di-Ni <sup>2+</sup>	98-100
81		di-Cu <sup>2+</sup> , di-Cu <sup>+</sup>	101-103
82		di-Cu <sup>2+</sup>	104, 105
83		di-Cu <sup>2+</sup> , di-Ni <sup>2+</sup> , di-Fe <sup>2+</sup> , di-Zn <sup>2+</sup> , di-Mn <sup>2+</sup>	106-108
84		di-Cu <sup>2+</sup>	109
85		di-Co <sup>2+</sup> , di-Ni <sup>2+</sup> , di-Cu <sup>2+</sup>	110-111
86		di-Cu <sup>2+</sup>	112-113
87		di-Cu <sup>2+</sup>	114
88		di-Cu <sup>2+</sup>	115

**Figure 19.** Crystal structure of  $[\text{Co}_2(\mathbf{79})(\text{CH}_3\text{CN})_4]^{4+}$ . (Reprinted with permission from ref 90. Copyright 2002 The Royal Society of Chemistry.)

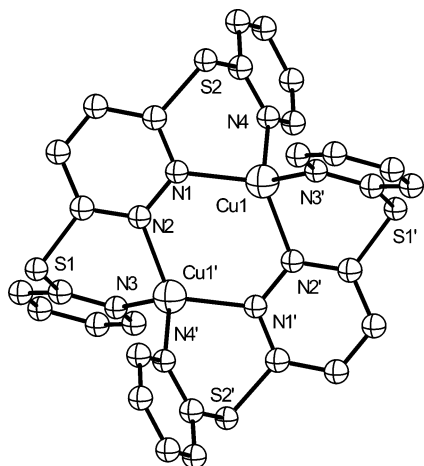
The ligand **80**,  $R = \text{H}$ , forms highly twisted bis-ligand–di-metal complexes of  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$ .<sup>98–100</sup> The crystal structure of  $[\text{Ni}_2(\mathbf{80}, R = \text{H})_2](\text{BF}_4)_4$  is shown in Figure 20, where it will be noted that the

**Figure 20.** Crystal structure of  $[\text{Ni}_2(\mathbf{80}, R = \text{H})_2]^{4+}$ . (Reprinted with permission from ref 98. Copyright 2003 Elsevier.)

pyridazine bridges are twisted in order to accommodate the binding of the terminal pyridine ligands.

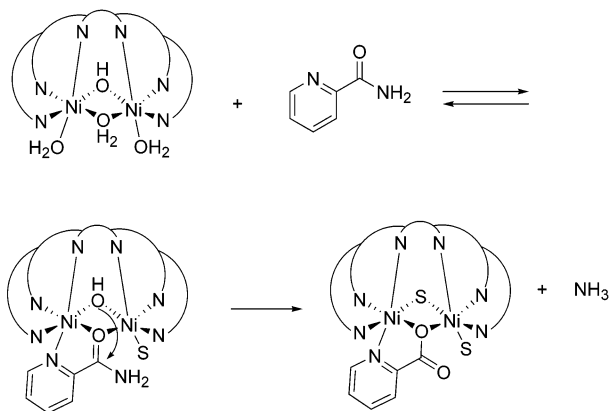
The di-Cu<sup>2+</sup> complexes of the ligands **81** and **82** have structures that contain one of these bridging ligands and one or more exogenous bridging ligands such as hydroxide or halogeno ions. Using the ligand **81**,  $R = 2\text{-pyridyl}$ , a red, air-stable di-Cu<sup>+</sup> complex  $[\text{Cu}_2(\mathbf{81}, R = 2\text{-pyridyl})_2](\text{ClO}_4)_2$  has been structurally characterized<sup>102</sup> (Figure 21). Both Cu<sup>+</sup> ions are bridged by the two pyridazine groups, and the ions are in distorted tetrahedral geometries.

As expected, the phthalazine ligands, **83–88**, form similar bimetallic complexes to those found for the analogous complexes of the related pyridazine ligands. The bimetallic di-Ni<sup>2+</sup> complex  $[\text{Ni}_2(\mu\text{-H}_2\text{O})_2(\mathbf{83}, R = \text{H})(\text{H}_2\text{O})_2](p\text{-toluenesulfonate})_4$  was found to act as a model for urease,<sup>107</sup> by the observation that picolinamide was hydrolyzed by the bimetallic complex. The crystal structure of  $[\text{Ni}_2(\mu\text{-H}_2\text{O})_2(\mathbf{83}, R = \text{H})(\text{H}_2\text{O})_2]^{4+}$  has each Ni<sup>2+</sup> ion octahedrally coordinated, with two bridging water ligands and two terminal water molecules, one each on the two Ni<sup>2+</sup> ions. In ethanol solution, picolinamide is stoichiometrically converted to picolinate by attack of a bridging hydroxide formed after mono-deprotonation of a bridg-



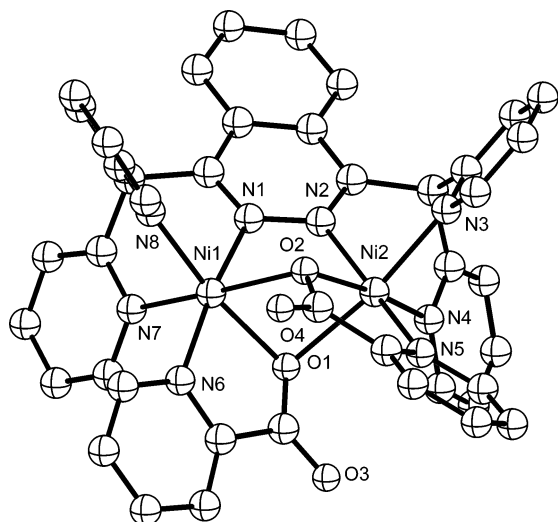
**Figure 21.** Crystal structure of  $[\text{Cu}_2(\mathbf{81}, \text{R} = 2\text{-pyridyl})_2]^{2+}$ . (Adapted from ref 102. Copyright American Chemical Society.)

### Scheme 5

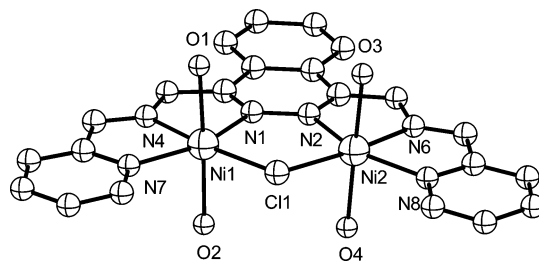


S = solvent; ligand = **83**

ing aquo group (Scheme 5). The crystal structure of the complex  $[\text{Ni}_2(\text{picolinate})_2(\mathbf{83}, \text{R} = \text{H})](p\text{-toluenesulfonate})_2$  is illustrated in Figure 22. The picolinate ligands bind via the pyridine nitrogen atoms, and one carboxylate oxygen atom acts as a bridge. Possibly



**Figure 22.** Crystal structure of  $[\text{Ni}_2(\text{picolinate})_2(\mathbf{83}, \text{R} = \text{H})]^{2+}$ . (Adapted from ref 107. Copyright American Chemical Society.)



**Figure 23.** Crystal structure of  $[\text{Ni}_2(\mu\text{-Cl})(\mathbf{85}, \text{R} = \text{R}' = \text{H})(\text{H}_2\text{O})_4]^{3+}$ . (Adapted from ref 110. Copyright American Chemical Society.)

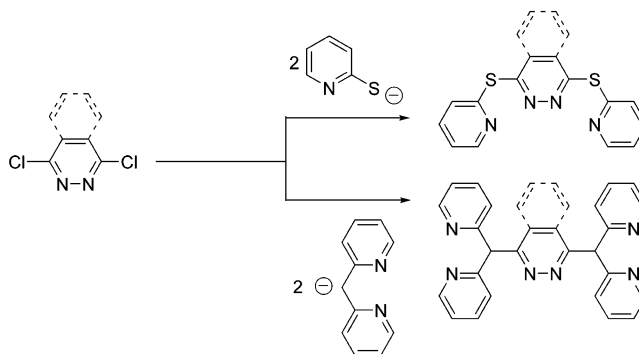
because of this bridging, the  $\text{Ni}\cdots\text{Ni}$  separation is short, 3.079(3) Å.

The two ligands **84** and **85** are related, the former forms<sup>109</sup> a planar bis-ligand–di- $\text{Cu}^{2+}$  complex where the phthalazine units act as bridges and the terminal hydrazine nitrogen atoms act as ligands. The other ligand forms a mono-ligand–di- $\text{Ni}^{2+}$  complex as shown by the crystal structure of the ion,<sup>110</sup>  $[\text{Ni}_2^{2+}(\mu\text{-Cl})(\mathbf{85}, \text{R} = \text{R}' = \text{H})(\text{H}_2\text{O})_4]^{3+}$ , Figure 23. The last three ligands **86–88** give mono-ligand–di-metal complexes with exogenous bridging and terminal unidentate ligands and are structurally similar to the pyridazine analogues.

### 3.7.1. Ligand Synthesis

Syntheses of pyridazine or phthalazine multidentate binucleating ligands follows similar lines. Thus, halogen substitutions of the type shown in Scheme 6 occur with either ring system.<sup>100,103,106,113</sup> Synthesis

### Scheme 6

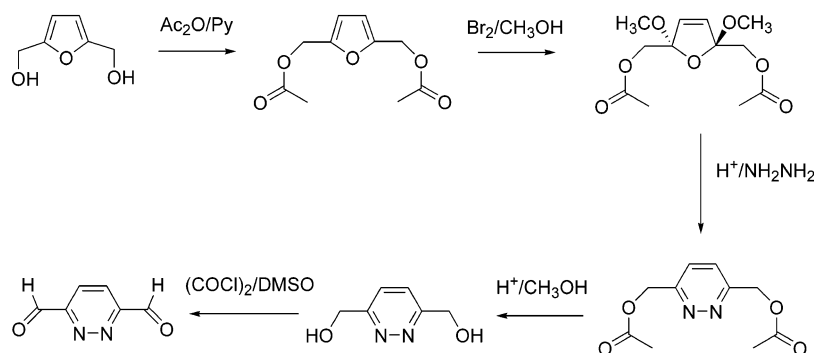


of the 3,6-diformylpyridazine can be accomplished by the sequence of reactions shown in Scheme 7. The formyl groups can be used for elaboration in the usual ways.

### 3.8. 1,8-Naphthyridine Bridging Ligands

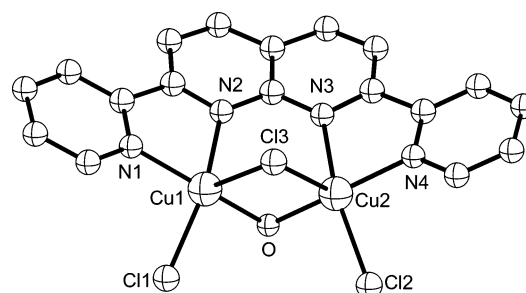
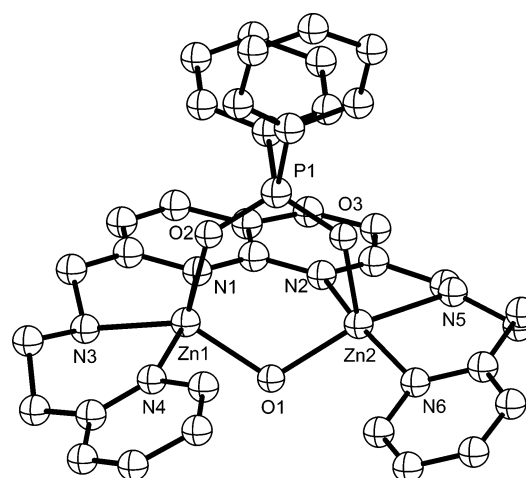
The 1,8-naphthyridine bridge has similar dimensions to that of carboxylate and formamido bridges, and consequently, metal–metal-bonded units can be spanned by the two nitrogen atoms. In many cases, however, the 1,8-naphthyridine group can bridge two metals which do not form metal–metal bonds. As before, only bimetallic systems without metal–metal bonds will be discussed here. Table 9 lists a number of multidentate 1,8-naphthyridine binucleating ligands.

## Scheme 7


**Table 9. Multidentate 1,8-Naphthyridine Bridging Ligands**

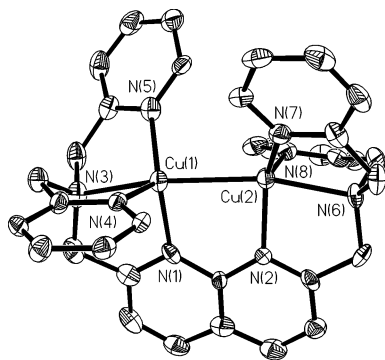
Ligand Number	Ligands	Metal Complex	Reference
89		di-Cu <sup>2+</sup>	116
90		di-Zn <sup>2+</sup> , di-Ni <sup>2+</sup> , di-Cu <sup>2+</sup>	117
91		di-Fe <sup>2+</sup>	118
	R = H, CH <sub>2</sub> CH <sub>3</sub>		
92		di-Cu <sup>+</sup> , di-Cu <sup>2+</sup>	119
93		di-Cu <sup>+</sup>	120

Aside from ligand **89**, the development of these ligands and their complexes is largely due to the work of He and Lippard, who argued that the 1,8-naphthyridine bridge could be regarded as an analogue of the carboxylate bridge but with greater facility for elaboration.<sup>117–121</sup> The di-Cu<sup>2+</sup> complex [Cu<sub>2</sub>(μ-OH)(μ-Cl)(**89**)Cl<sub>2</sub>] has the crystal structure shown in Figure 24.<sup>116</sup> The five-coordinate Cu<sup>2+</sup> ions are separated by 3.022(1) Å in a structure where considerable distortion exists because of the necessity of accommodating the OH<sup>-</sup> and Cl<sup>-</sup> bridges, together with the coparallel bonding of the 2-nitrogen bridge. Double exogenous bridging also occurs for the complex [Zn<sub>2</sub>(μ-OH)(μ-Ph<sub>2</sub>PO<sub>2</sub>)(**90**)](ClO<sub>4</sub>)<sub>2</sub>, the crystal struc-


**Figure 24.** Crystal structure of [Cu<sub>2</sub>(μ-OH)(μ-Cl)(**89**)Cl<sub>2</sub>]. (Adapted from ref 116. Copyright American Chemical Society.)

**Figure 25.** Crystal structure of [Zn<sub>2</sub>(μ-OH)(μ-Ph<sub>2</sub>PO<sub>2</sub>)(**90**)]<sup>2+</sup>. (Adapted from ref 117. Copyright American Chemical Society.)

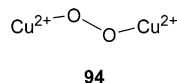
ture of which is shown in Figure 25.<sup>117</sup> In this structure the zinc atoms are in distorted trigonal bipyramidal geometries, the two zinc ions are separated by 3.287(5) Å, and the OH<sup>-</sup> bridge exists under neutral aqueous conditions. The di-Fe<sup>2+</sup> complexes of the type [Fe<sub>2</sub><sup>2+</sup>(μ-OH)(**91**, R = H)OTf](OTf)<sub>2</sub> and [Fe<sub>2</sub><sup>2+</sup>(μ-OH)(**91**, R = Et)](OTf)<sub>3</sub> have been isolated and characterized.<sup>118</sup> An acetonitrile solution of the latter at -40 °C reacts with excess of 30% H<sub>2</sub>O<sub>2</sub> to give what is believed to be an unstable di-Fe<sup>3+</sup>-μ-oxo-hydroperoxide complex analogous to hemerythrin. A dioxygen di-Cu<sup>2+</sup> complex has been detected at -78 °C in CH<sub>2</sub>Cl<sub>2</sub> solution after reaction of the complex [Cu<sup>2+</sup>(**92**)](OTf)<sub>2</sub> with O<sub>2</sub>.<sup>119</sup> The product is believed to have the di-Cu<sup>2+</sup>-O<sub>2</sub> structure, **94**. It is interesting that the di-Cu<sup>+</sup> precursor has the solid-state structure shown (Figure 26) where a short Cu...Cu





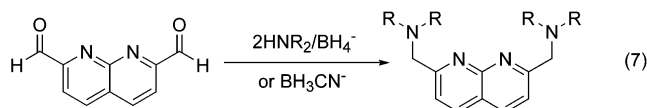
**Figure 26.** Crystal structure of  $[\text{Cu}_2(\mathbf{92})]^{2+}$ . (Reprinted with permission from ref 119. Copyright 2001 WILEY-VCH.)

distance, 2.5947(15) Å, is obtained.<sup>119</sup> Several crystal structures of di- $\text{Cu}^+$  complexes of the ligand **93** have been reported.<sup>120</sup> The  $\text{Cu}\cdots\text{Cu}$  distances range from 2.615 to 2.733 Å for five structures that have a variety of exogenous ligands completing the coordination sphere. One of these di- $\text{Cu}^+$  complexes  $[\text{Cu}_2^+(\mu\text{-O}_2\text{CCPh}_3)(\mathbf{93})\text{OTf}]$  can be oxidized to the mixed-valent  $\text{Cu}^+\text{Cu}^{2+}$  complex  $[\text{Cu}_2(\mu\text{-O}_2\text{CCPh}_3)(\mathbf{93})\text{OTf}]\text{OTf}$ , a transformation that is accompanied by a  $\text{Cu}\cdots\text{Cu}$  distance change from 2.615 to 2.449 Å, respectively.



### 3.8.1. Ligand Synthesis

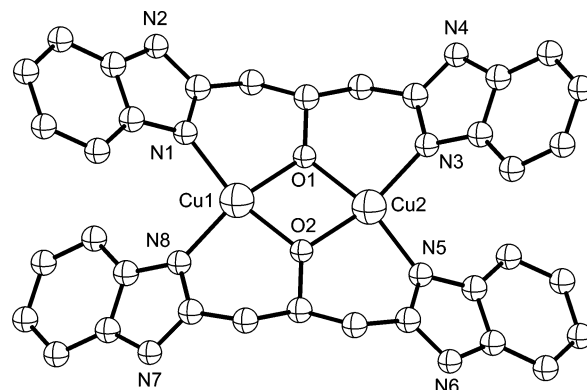
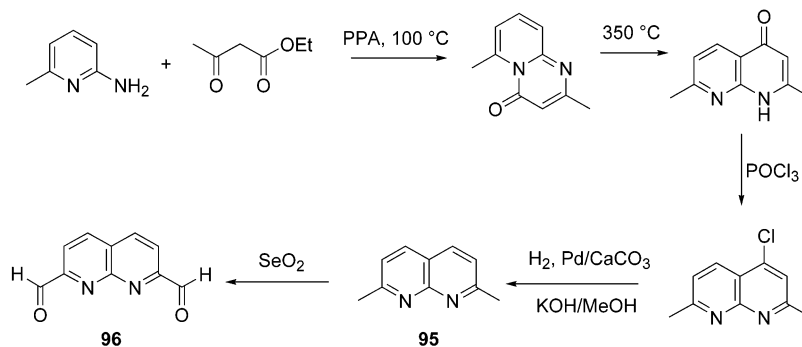
The preparation of the ligands **90–93** relies on the formation of the 2,7-dialdehyde **96** by the methods outlined in Scheme 8.<sup>121</sup> The scheme follows known procedures. With the two aldehyde groups incorporated, multidentate amine arms can be attached by reductive amination procedures,<sup>121</sup> eq 7.



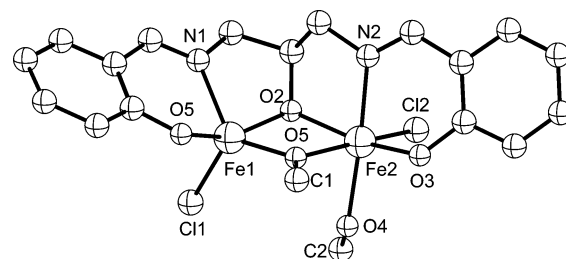
## 3.9. Alkoxide Bridging Ligands

There is extensive literature on binucleating ligands with alkoxide bridges and their bimetallic complexes. Many of these studies explore the structures and physical properties of the bimetallic complexes, but others, in addition, are concerned with stoichiometric

### Scheme 8



**Figure 27.** Crystal structure of  $[\text{Cu}_2(\mathbf{97})_2]^{2+}$ . (Adapted from ref 122. Copyright American Chemical Society.)



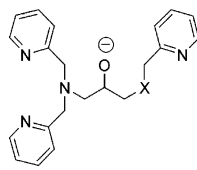
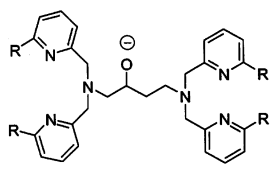
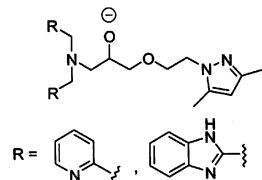
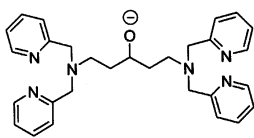
**Figure 28.** Crystal structure of  $[\text{Fe}_2(\mu\text{-OCH}_3)(\mathbf{103})\text{Cl}_2(\text{CH}_3\text{OH})]$ . (Reprinted with permission from ref 127. Copyright 1991 The Royal Society of Chemistry.)

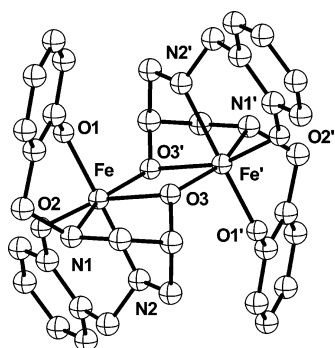
and catalytic transformations and dioxygen reactivity. Table 10 provides a list of some of these ligands and the bimetallic complexes that have been prepared. The structures of the bimetallic complexes formed with alkoxide bridging ligands are generally unexceptional. Usually, the metal–metal separation is about 3 Å. A typical structure is exemplified by the bis-ligand–di- $\text{Cu}^{2+}$  complex  $[\text{Cu}_2^{2+}(\mathbf{97})_2](\text{ClO}_4)_2 \cdot 2\text{CH}_3\text{OH}$ , Figure 27,<sup>122</sup> where the two  $\text{Cu}^{2+}$  ions are in a square planar geometry. The ligand **103** forms a di- $\text{Fe}^{3+}$  complex  $[\text{Fe}_2^{3+}(\mu\text{-OCH}_3)(\mathbf{103})(\text{Cl})_2(\text{CH}_3\text{OH})]$ , the structure of which in the solid state is shown in Figure 28.<sup>127</sup> One  $\text{Fe}^{3+}$  (Fe(1)) is five-coordinate, and the other is six-coordinate, the  $\text{Fe}\cdots\text{Fe}$  distance is 3.140 Å, and two alkoxide bridges are present, one is from the ligand alkoxide and the other is from an exogenous methoxide group. The di- $\text{Fe}^{3+}$  complex of the ligand **104** forms two structurally different bis-ligand complexes.<sup>128–130</sup> One of the structures is shown in Figure 29 and is precipitated from aqueous methanol to give the complex  $[\text{Fe}_2^{3+}(\mathbf{104})_2] \cdot 2\text{H}_2\text{O}$ . In this structure, the quinquidentate ligands bind to

**Table 10. Alkoxide Bringing Ligands**

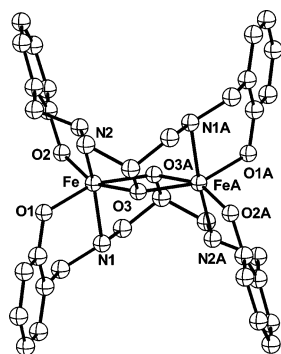
Ligand Number	Ligands	Metal Complex	Reference	Ligand Number	Ligands	Metal Complex	Reference
97		di-Cu <sup>2+</sup>	122	107		di-Fe <sup>3+</sup>	139
98		di-Cu <sup>2+</sup>	122	108		di-Cu <sup>2+</sup>	140
99		di-Cu <sup>2+</sup>	123	109		di-Fe <sup>3+</sup>	141
100		di-Cu <sup>2+</sup>	124	110		di-Fe <sup>2+</sup> , di-Cu <sup>2+</sup> , di-Fe <sup>3+</sup> , di-Mn <sup>2+</sup>	142- 151
101		di-Cu <sup>2+</sup> , di-Zn <sup>2+</sup>	125		R'' = H; R' = H, CH <sub>2</sub> CH <sub>3</sub> , CH <sub>2</sub> CH <sub>2</sub> OH R'' = CH <sub>3</sub> ; R' = H		
102		di-Cu <sup>2+</sup> , di-Ni <sup>2+</sup>	126	111		di-Cu <sup>2+</sup> , di-Fe <sup>2+</sup> ,	134, 135, 151
	R = CH <sub>3</sub> , C <sub>6</sub> H <sub>5</sub> , CF <sub>3</sub>				R = H, C <sub>6</sub> H <sub>5</sub>		
103		di-Fe <sup>3+</sup>	127	112		di-Zn <sup>2+</sup>	152
104		di-Fe <sup>3+</sup>	128- 130	113		di-Fe <sup>2+</sup>	153
105		di-Mn <sup>3+</sup>	131- 132		R = NHCOC(CH <sub>3</sub> ) <sub>3</sub>		
	X = H, Br			114		di-Cu <sup>2+</sup> , di-Fe <sup>2+</sup> , di-Fe <sup>3+</sup>	154- 157
106		di-Cu <sup>2+</sup> , di-Fe <sup>3+</sup> , di-Ni <sup>2+</sup> , di-Fe <sup>3+</sup> , di-Co <sup>2+</sup>	133- 138		R = H, CH <sub>3</sub>		
	R = H, CH <sub>3</sub>						

Table 10. (Continued)

Ligand Number	Ligands	Metal Complex	Reference	Ligand Number	Ligands	Metal Complex	Reference
115		di-Cu <sup>2+</sup> , di-Ni <sup>2+</sup> ,	158-159	117		Fe <sup>2+</sup> -Fe <sup>3+</sup> , di-Co <sup>3+</sup>	162, 163
116		di-Ni <sup>2+</sup>	160, 161	118		di-Co <sup>2+</sup> , di-Co <sup>3+</sup>	164



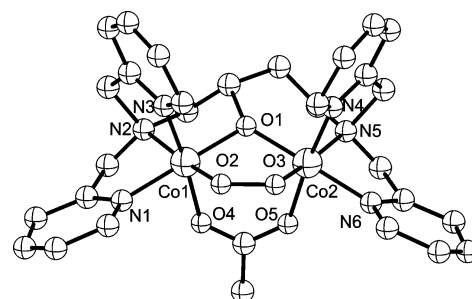
**Figure 29.** Crystal structure of one structural form of [Fe<sub>2</sub>(**104**)<sub>2</sub>]. (Reprinted with permission from ref 130. Copyright 2000 The Royal Society of Chemistry.)



**Figure 30.** Crystal structure of one structural form of [Fe<sub>2</sub>(**104**)<sub>2</sub>]. (Reprinted with permission from ref 129. Copyright 2002 Elsevier.)

each of the Fe<sup>3+</sup> ions and the alkoxide groups bridge the two iron atoms. The other structural form is obtained from DMF solution and crystallizes as [Fe<sub>2</sub><sup>3+</sup>(**104**)<sub>2</sub>] $\cdot$ 2DMF. The structure is shown in Figure 30. In this structural modification, the two ligands span both Fe<sup>3+</sup> ions with alkoxide bridges.

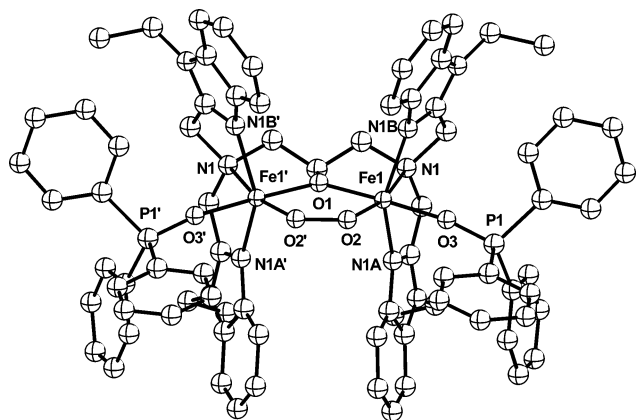
One of the most interesting properties of some of these bimetallic complexes is their ability to react with O<sub>2</sub>, sometimes reversibly. This work has been reviewed.<sup>134</sup> Bimetallic complexes of cobalt and iron have generated dioxygen complexes with some of these binucleating alkoxide bridging ligands. Reac-



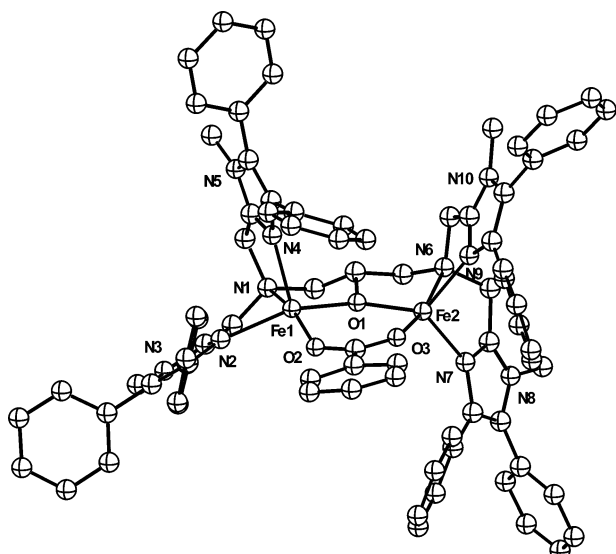
**Figure 31.** Crystal structure of [Co<sub>2</sub>( $\mu$ -O<sub>2</sub>)( $\mu$ -O<sub>2</sub>CCH<sub>3</sub>)(**117**, R = H)]<sup>2+</sup>. (Reprinted with permission from ref 163. Copyright 1994 The Chemical Society of Japan.)

tion of the ligands **106** (R = H), **117** (R = H), and **118** with Co<sup>2+</sup> acetate gives complexes believed to have the formula [Co<sub>2</sub><sup>2+</sup>( $\mu$ -acetate)(ligand)]<sup>2+</sup>, where the Co<sup>2+</sup> ions are five-coordinate. All of these complexes absorb O<sub>2</sub> to give stable dioxygen complexes. A crystal structure<sup>163</sup> of the dioxygen complex [Co<sub>2</sub><sup>2+</sup>( $\mu$ -O<sub>2</sub>)(**117**, R = H)( $\mu$ -O<sub>2</sub>CCH<sub>3</sub>)](PF<sub>6</sub>)<sub>2</sub> $\cdot$ CH<sub>3</sub>CN $\cdot$ 0.5H<sub>2</sub>O is shown in Figure 31, where the dioxygen ligand bridges the two Co<sup>3+</sup> ions in a normal way.

One di-iron dioxygen complex of a binucleating alkoxide bridging ligand has been reported.<sup>143</sup> The structure of the complex [Fe<sub>2</sub>( $\mu$ -O<sub>2</sub>)(**110**, R' = H; R' = CH<sub>2</sub>CH<sub>3</sub>)(Ph<sub>3</sub>PO)<sub>2</sub>](BF<sub>4</sub>)<sub>3</sub> $\cdot$ 3CH<sub>3</sub>CN is shown in Figure 32. The dioxygen complex is stable indefinitely at -40 °C or below but decomposes rapidly above 30 °C in CH<sub>3</sub>CN solutions. The dioxygen binding to this complex is irreversible, in contrast to a similar series of di-Fe<sup>2+</sup>- $\mu$ -carboxylate complexes, incorporating the ligands **111** (R = Ph) and **106** (R = H and CH<sub>3</sub>), for which at -20 °C in CH<sub>3</sub>CN or CH<sub>2</sub>Cl<sub>2</sub> solutions O<sub>2</sub> uptake is reversible over several cycles.<sup>134</sup> The crystal structure<sup>135</sup> of the complex [Fe<sub>2</sub><sup>2+</sup>( $\mu$ -O<sub>2</sub>CC<sub>6</sub>H<sub>5</sub>)(**111**, R = C<sub>6</sub>H<sub>5</sub>)(ClO<sub>4</sub>)<sub>2</sub>] $\cdot$ 2CH<sub>3</sub>CN $\cdot$ (CH<sub>3</sub>CH<sub>2</sub>)<sub>2</sub>O $\cdot$ H<sub>2</sub>O is shown in Figure 33, where it will be seen that the two Fe<sup>2+</sup> ions are five-coordinate. Presumably upon O<sub>2</sub> uptake, the iron atoms become six-coordinate and the structure of the dioxygen adduct may resemble that of the di-cobalt structure shown in Figure 31.

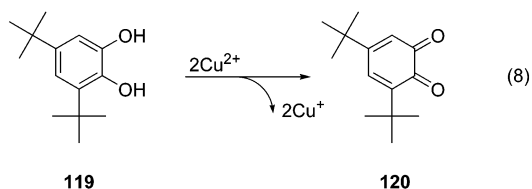


**Figure 32.** Crystal structure of  $[\text{Fe}_2(\mu\text{-O}_2)(\mathbf{110}, \text{R}' = \text{H}; \text{R}'' = \text{CH}_2\text{CH}_3)(\text{Ph}_3\text{PO})_2]^{3+}$ . (Reprinted with permission from ref 143. Copyright 1996 WILEY-VCH.)

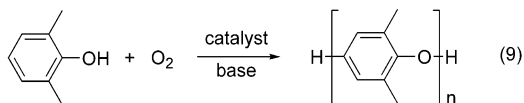


**Figure 33.** Crystal structure of  $[\text{Fe}_2(\mu\text{-O}_2\text{CC}_6\text{H}_5)(\mathbf{111}, \text{R} = \text{C}_6\text{H}_5)]^{2+}$ . (Reprinted with permission from ref 135. Copyright 1998 The Chemical Society of Japan.)

The complex ions  $[\text{Cu}_2^{2+}(\mathbf{97})_2]^{2+}$  and  $[\text{Cu}_2^{2+}(\mathbf{98})_2]^{2+}$  were examined for catecholase activity using 3,5-di-*tert*-butylcatechol, **119**, as a substrate. The first complex does not react with **119** but the second does to give the *o*-quinone **120** (eq 8).<sup>122</sup>

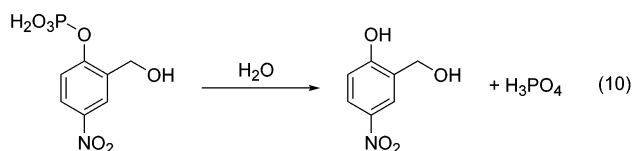


The difference in reactivity between the two complexes was ascribed to the greater chelate ring size provided by the ligand **98**, which will enhance the stability of the  $\text{Cu}^+$  state. The ion  $[\text{Cu}_2^{2+}(\mathbf{99})_2]^{2+}$  was found to polymerize 2,6-dimethylphenol as shown in eq 9.<sup>123</sup> A di- $\text{Cu}^{2+}$  complex of the ligand **100** is found

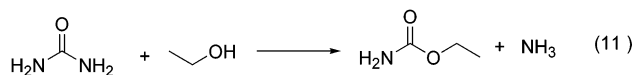


to promote the hydrolysis of phosphodiester bonds.<sup>124</sup>

Whereas it was established that two  $\text{Cu}^{2+}$  ions per ligand were required for this hydrolysis reaction, the structure of the active complex was not determined. Similarly,<sup>152</sup> the di- $\text{Zn}^{2+}$  complex of the ligand **112** promotes the hydrolysis of 2-hydroxypropyl-4-nitrophenyl phosphate (eq 10). The complex ion<sup>138</sup>  $[\text{Ni}_2(\mu\text{-O}_2\text{CCH}_3)(\mathbf{106}, \text{R} = \text{Me})(\text{ClO}_4)(\text{CH}_3\text{OH})]\text{ClO}_4$  when dissolved in ethanol solution at 80 °C acts as a catalyst for the ethanolysis of urea (eq 11).



$[\text{Ni}_2(\mu\text{-O}_2\text{CCH}_3)(\mathbf{106}, \text{R} = \text{Me})(\text{ClO}_4)(\text{CH}_3\text{OH})]\text{ClO}_4$  when dissolved in ethanol solution at 80 °C acts as a catalyst for the ethanolysis of urea (eq 11).



Overall, these binucleating ligands bearing alkoxide bridges have provided several interesting reactions which rely on the presence of contiguous metal ions. In particular, the reactions with  $\text{O}_2$  lead to bridging peroxide complexes which result from two-electron reduction, one electron being derived from each of the metals. The hydrolysis of various substrates is believed to be induced by substrate binding to both metals.

### 3.9.1. Ligand Synthesis

Several different approaches to the synthesis of binuclear multidentate alkoxide ligands have been reported. Some of the general procedures are outlined here. Reductive amination has been used on several occasions for attachment of various heterocyclic bases.<sup>133,162,163</sup> Such a reaction is illustrated in Scheme 9, which includes phthalimide displacement and epoxide ring opening to give the unsymmetrical ligand.<sup>133</sup> Epichlorohydrin, **121**, provides a route to unsymmetrical ligands, as shown in Scheme 9, but whether chloro substitution or epoxide ring opening occurs depends on the nucleophile and the conditions of reaction. The procedure outlined in Scheme 10 illustrates how, at low temperatures, an amine can open the epoxide ring. Displacement of the chloride by a similar nucleophile occurs at higher temperatures.<sup>160</sup>

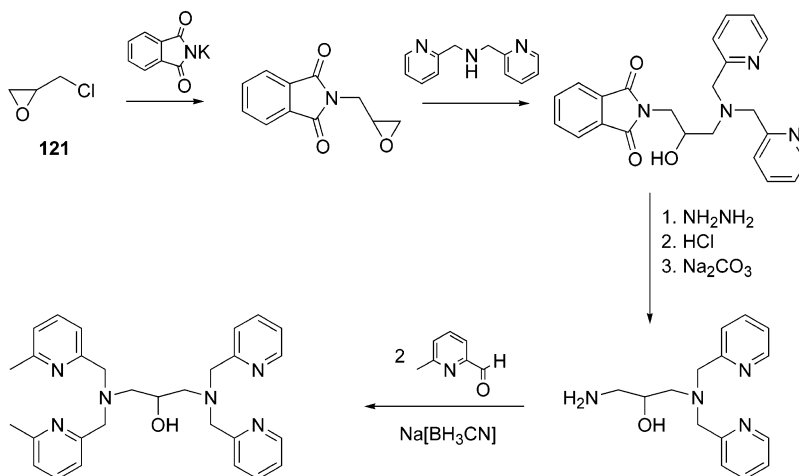
The formation of the tribenzimidazole product is achieved by heating an intimate mixture of the tricarboxylic acid and *o*-phenylenediamine at 180 °C. Formation of benzimidazoles from carboxylic acids and *o*-phenylenediamine by reaction of the two in hot aqueous hydrochloric acid is well-known.<sup>122</sup>

### 3.10. Phenoxide Bridging Ligands

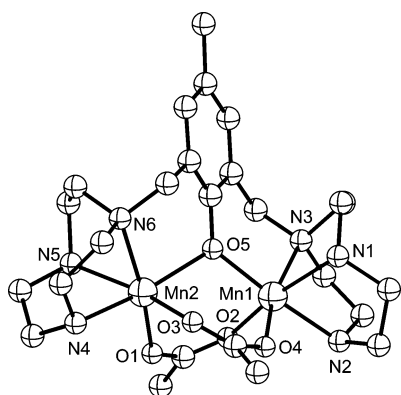
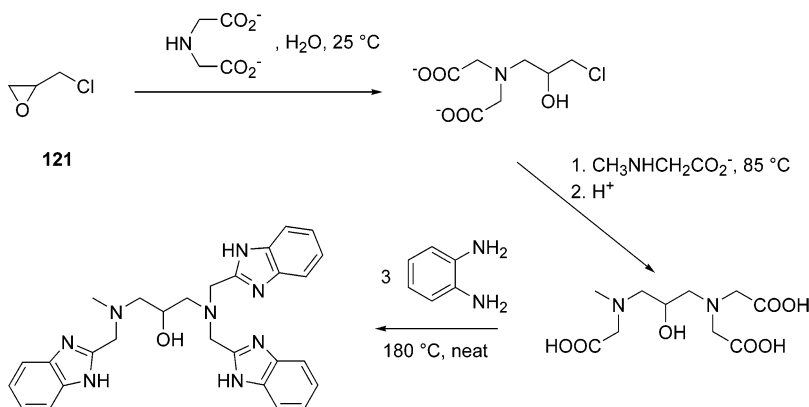
Multidentate phenoxide binucleating ligands and their complexes have been studied extensively, and several reviews summarize some of this chemistry.<sup>166–172</sup> The dioxygen chemistry associated with complexes of these ligands has also been reviewed.<sup>173</sup> Not all of the phenoxide binucleating ligands will be listed here; rather representatives of the various classes of these ligands will be considered.

Table 11 lists a representative collection of binucleating monophenoxide ligands. Ligands bearing single binding site arms such as **122** form bisligand bime-

## Scheme 9



## Scheme 10

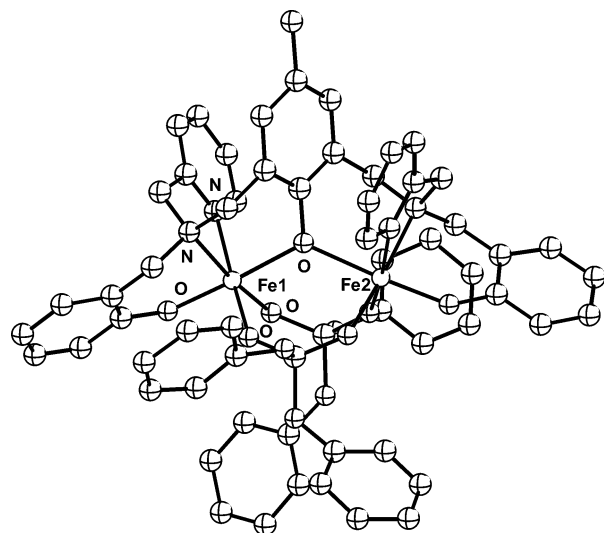


**Figure 34.** Crystal structure of  $[\text{Mn}_2(\mu\text{-O}_2\text{CCH}_3)_2(\mathbf{133})]^{2+}$ . (Adapted from ref 186. Copyright American Chemical Society.)

tallic complexes.<sup>174</sup> The ligands with two or more binding site arms form monoligand bimetallic complexes, usually with exogenous bridges. Generally, the metal–metal separations are about 3.0 Å for a one-atom exogenous bridge. Larger metal–metal separations are observed when the two- or three-atom exogenous bridges are present.

Several interesting bimetallic structures of the ligands listed in Table 11 have been reported. The ligand **133** forms a mixed-valent  $\text{Mn}^{3+}\text{-Mn}^{2+}$  complex having the formula  $[\text{Mn}_2(\mu\text{-O}_2\text{CCH}_3)_2(\mathbf{133})](\text{ClO}_4)_2 \cdot \text{CH}_2\text{Cl}_2$ .<sup>186</sup> The crystal structure is shown in Figure 34. In this structure the (valence-trapped)  $\text{Mn}^{3+}$  is Mn(2), which displays a Jahn–Teller distortion

along the N(5)–Mn(2)–O(3) direction. Both manganese ions are in (distorted) octahedral geometries. The bimetallic non-heme iron protein purple acid phosphatase catalyzes the hydrolysis of phosphate esters. A number of “analogues” of the binding site of this protein have been reported, including the complex<sup>190</sup>  $[\text{Fe}_2^{3+}(\mu\text{-O}_2\text{P}(\text{O}(\text{Ph})_2)_2)(\mathbf{136})]\text{BPh}_4 \cdot \text{CHCl}_3 \cdot \text{CH}_3\text{OH}$ . The structure<sup>190</sup> of this complex is shown in Figure 35. This structure has two diphenylphosphate

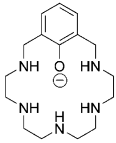
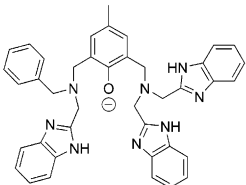
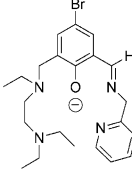
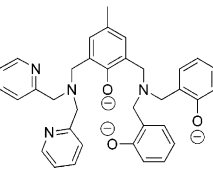
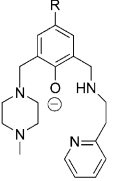
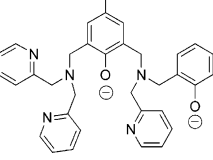
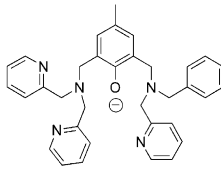
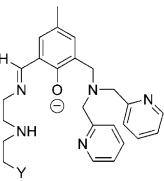


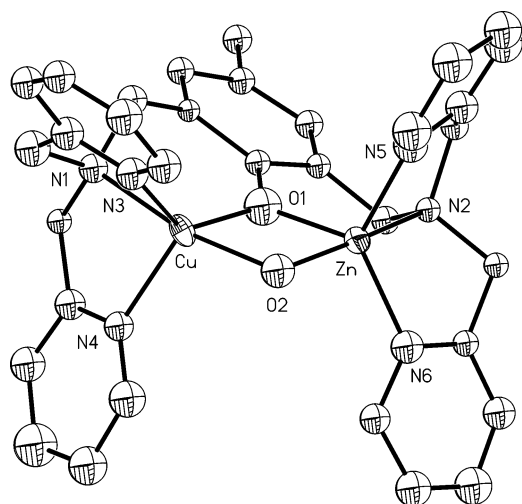
**Figure 35.** Crystal structure of  $[\text{Fe}_2(\mu\text{-O}_2\text{P}(\text{OPh})_2)_2(\mathbf{136})]^+$ . (Adapted from ref 190. Copyright American Chemical Society.)

**Table 11. Binucleating Monophenoxide Ligands**

Ligand Number	Ligands	Metal Complex	Reference	Ligand Number	Ligands	Metal Complex	Reference
122		di-Cu <sup>2+</sup>	174	131		di-Cu <sup>2+</sup>	183
123		di-Zn <sup>2+</sup>	175	132		di-Cu <sup>2+</sup> , di-Zn <sup>2+</sup>	184, 185
124		di-Cu <sup>2+</sup>	176	133		Mn <sup>2+</sup> - Mn <sup>3+</sup>	186
125		di-Mn <sup>2+</sup>	177	134		Fe <sup>2+</sup> -Fe <sup>3+</sup>	187
126		di-Cu <sup>2+</sup>	176	135		di-Fe <sup>3+</sup>	188
127		di-Zn <sup>2+</sup>	178, 179	136		di-In <sup>3+</sup> , di-Fe <sup>3+</sup>	189, 190
128		di-Cu <sup>2+</sup>	176, 180	137		R = H, di-Cu <sup>+</sup> R = CH <sub>3</sub> , di-Fe <sup>2+</sup> , di-Co <sup>2+</sup> , Cu <sup>2+</sup> -Zn <sup>2+</sup> , Zn <sup>2+</sup> -Fe <sup>3+</sup> , Fe <sup>2+</sup> -Fe <sup>3+</sup> R = F, Cu <sup>2+</sup> - Zn <sup>2+</sup>	191- 195
129		di-Cu <sup>2+</sup>	181	138		di-Ni <sup>2+</sup> , di- Co <sup>3+</sup> , di-Fe <sup>3+</sup>	196, 197
130		di-Cu <sup>2+</sup>	182	139		di-Fe <sup>3+</sup>	198, 199

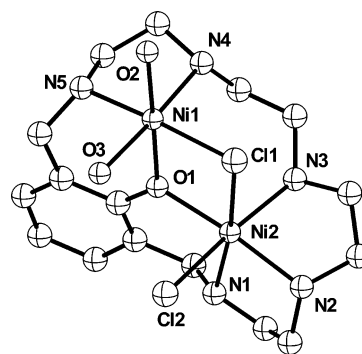
**Table 11. (Continued)**

Ligand Number	Ligands	Metal Complex	Reference	Ligand Number	Ligands	Metal Complex	Reference
140		di-Ni <sup>2+</sup>	200	144		di-Cu <sup>2+</sup>	205
141		di-Cu <sup>2+</sup>	201	145		di-Fe <sup>3+</sup> , Zn <sup>2+</sup> -Fe <sup>3+</sup> , Fe <sup>2+</sup> -Fe <sup>3+</sup>	206, 207
142		di-Cu <sup>2+</sup>	201, 202	146		Mn <sup>2+</sup> -Mn <sup>3+</sup> , Fe <sup>3+</sup> -Mn <sup>2+</sup> , Zn <sup>2+</sup> -Fe <sup>3+</sup> , Fe <sup>2+</sup> -Fe <sup>3+</sup>	208- 211
143		Fe <sup>2+</sup> -Fe <sup>3+</sup> , di-Mn <sup>2+</sup> , Mn <sup>2+</sup> -Mn <sup>3+</sup>	203, 204	147		di-Ni <sup>2+</sup>	212
	R = H, Br				Y = OH, NH <sub>2</sub>		



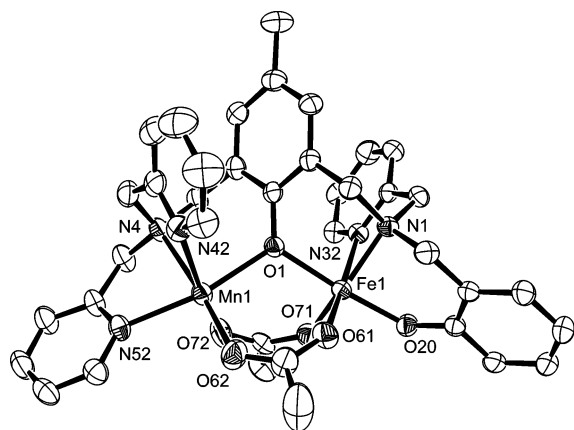
**Figure 36.** Crystal structure of [CuZn( $\mu$ -OH)(**137**, R = CH<sub>3</sub>)]<sup>2+</sup>. (Reprinted with permission from ref 195. Copyright 2002 Elsevier.)

bridging ligands, the iron atoms have roughly octahedral geometries, and the Fe $\cdots$ Fe distance is 3.549(3) Å. The ligand **137**, R = CH<sub>3</sub> or F, forms heterobimetallic Cu<sup>2+</sup>-Zn<sup>2+</sup> complexes with exogenous OH bridges.<sup>195</sup> The structure<sup>195</sup> of the complex [Cu<sup>2+</sup>Zn<sup>2+</sup>( $\mu$ -OH)(**137**, R = CH<sub>3</sub>)](ClO<sub>4</sub>)<sub>2</sub> is shown in Figure 36. It is interesting that both the Cu<sup>2+</sup> and Zn<sup>2+</sup> ions are in roughly trigonal bipyramidal geometries. The Cu $\cdots$ Zn distance is 3.028(6) Å. The macrocyclic ligand

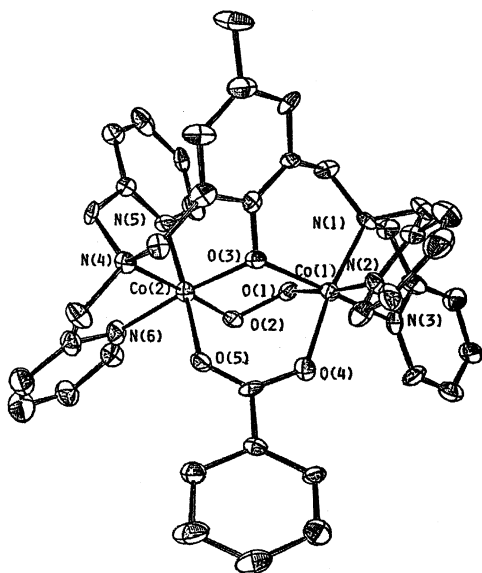


**Figure 37.** Crystal structure of [Ni<sub>2</sub>( $\mu$ -Cl)(**140**)(H<sub>2</sub>O)<sub>2</sub>Cl]<sup>+</sup>. (Adapted from ref 200. Copyright American Chemical Society.)

**140** forms a structurally interesting di-Ni<sup>2+</sup> complex<sup>200</sup> [Ni<sub>2</sub>( $\mu$ -Cl)(**140**)(H<sub>2</sub>O)<sub>2</sub>Cl]Cl·H<sub>2</sub>O·CH<sub>3</sub>OH. The structure of the cation is shown in Figure 37. The two Ni<sup>2+</sup> ions are chemically distinct, one (Ni(2)) is coordinated to three nitrogen atoms, a chloro and phenoxide bridge, and to a terminal chloro group. The other (Ni(1)) is bound to the phenoxide bridge, two nitrogen atoms, two aquo ligands, and the chloro bridge. The unsymmetrical ligand **146** forms a number of mixed-valence and heterobimetallic complexes.<sup>208-211</sup> The crystal structure<sup>209</sup> of [Mn<sup>2+</sup>-Fe<sup>3+</sup>( $\mu$ -O<sub>2</sub>CCH<sub>3</sub>)<sub>2</sub>(**146**)]ClO<sub>4</sub>·0.5H<sub>2</sub>O is shown in Figure 38. The Mn<sup>2+</sup> ion lies in the bispyridyl site, while the Fe<sup>3+</sup> ion is in the other compartment. Both metals are in roughly octahedral environments and are



**Figure 38.** Crystal structure of  $[\text{Mn}^{2+}\text{Fe}^{3+}(\mu\text{-O}_2\text{CCH}_3)_2]^{2+}$  (**146**)<sup>+</sup>. (Adapted from ref 209. Copyright American Chemical Society.)



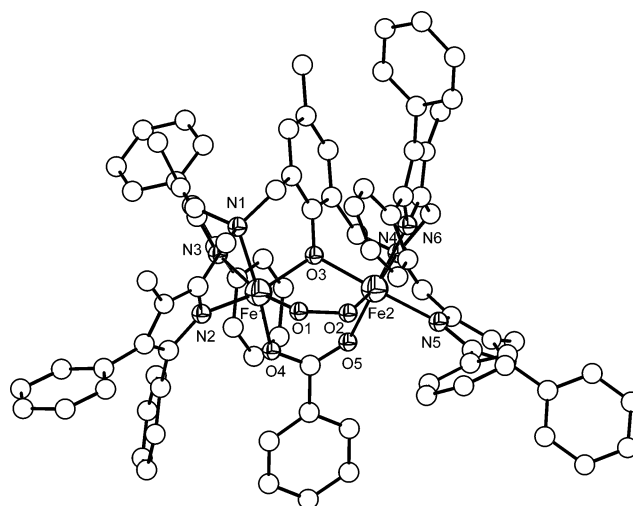
**Figure 39.** Crystal structure of  $[\text{Co}_2(\mu\text{-O}_2)(\mu\text{-O}_2\text{CC}_6\text{H}_5)_2]^{2+}$  (**137**,  $\text{R} = \text{CH}_3$ )<sup>2+</sup>. (Reprinted with permission from ref 213. Copyright 1983 The Chemical Society of Japan.)

bridged by two carboxylate groups and the phenoxide ligand. The  $\text{Fe}\cdots\text{Mn}$  distance is 3.510(9) Å.

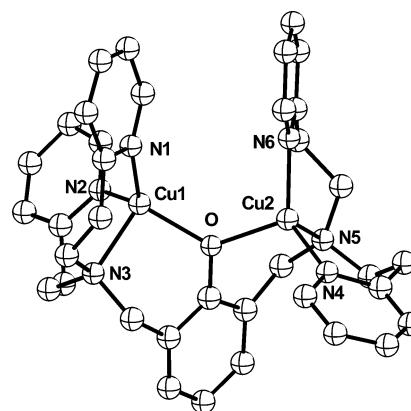
### 3.10.1. Dioxygen Complexes

Some of the monophenolate ligand complexes form stable dioxygen adducts. In some cases, the  $\text{O}_2$  uptake is reversible.<sup>173</sup>

The ligand **137** forms di- $\text{Co}^{2+}$  complexes of the type,  $[\text{Co}_2^{2+}(\mu\text{-O}_2\text{CR}')(\mathbf{137}, \text{R} = \text{CH}_3)]^{2+}$  and  $[\text{Co}_2^{2+}(\mu\text{-O}_2\text{CR}')_2(\mathbf{137}, \text{R} = \text{CH}_3)]^+$ ,  $\text{R}' = \text{CH}_3, \text{C}_6\text{H}_5$ .<sup>194</sup> In the former, the metals are five-coordinate, whereas in the latter six-coordination is obtained. Dioxygen reacts reversibly with the former, and the latter only becomes reactive with  $\text{O}_2$  upon dissociation of one of the carboxylate bridges. The crystal structure of  $[\text{Co}_2^{3+}(\mu\text{-benzoate})(\mathbf{137}, \text{R} = \text{CH}_3)(\mu\text{-O}_2)](\text{BF}_4)_2 \cdot 2\text{H}_2\text{O}$  is shown in Figure 39.<sup>213</sup> The  $\text{Co}^{3+}$  ions are octahedrally coordinated, and the dioxygen (peroxide) ligand bridges the two metals with a torsion angle ( $\text{Co}-\text{O}-\text{O}-\text{Co}$ ) of 51°. The di- $\text{Fe}^{2+}$  complex formed from the ligand **135** of the composition  $[\text{Fe}_2^{2+}(\mu\text{-O}_2\text{CPh})(\mathbf{135})]^{2+}$  reacts reversibly with  $\text{O}_2$  at room temperature in  $\text{CH}_3\text{CN}$  solution.<sup>188</sup> The unusual stability of the



**Figure 40.** Crystal structure of  $[\text{Fe}_2(\mu\text{-O}_2)(\mu\text{-O}_2\text{CC}_6\text{H}_5)_2]^{2+}$  (**135**)<sup>2+</sup>. (Adapted from ref 188. Copyright American Chemical Society.)



**Figure 41.** Crystal structure of  $[\text{Cu}_2(\mathbf{137}, \text{R} = \text{H})]^+$ . (Adapted from ref 191. Copyright American Chemical Society.)

dioxygen adduct of the di-iron system is ascribed to the steric protection provided by the phenyl substituents of the ligand. The crystal structure<sup>188</sup> of the dioxygen adduct  $[\text{Fe}_2^{3+}(\mu\text{-O}_2\text{CPh})(\mathbf{135})(\mu\text{-O}_2)](\text{BF}_4)_2 \cdot 2\text{CH}_3\text{CN} \cdot (\text{C}_2\text{H}_5)_2\text{O} \cdot \text{H}_2\text{O}$  is shown in Figure 40. The overall structure is very similar to that of the analogous cobalt complex shown in Figure 39. The  $\text{O}-\text{O}$  bond length of 1.426(6) Å is consistent with a peroxide formulation.

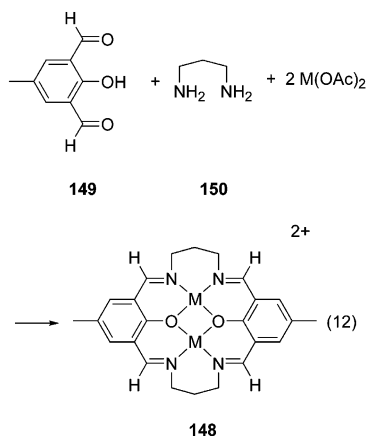
The ligand **137** forms a di- $\text{Cu}^+$  complex of composition  $[\text{Cu}_2^+(\mathbf{137})]\text{PF}_6$ .<sup>191</sup> The crystal structure<sup>191</sup> is shown in Figure 41. Each of the  $\text{Cu}^+$  ions is in a distorted tetrahedral geometry, and they are separated by about 3.6 Å. When a  $\text{CH}_2\text{Cl}_2$  solution of this di- $\text{Cu}^+$  complex is exposed to  $\text{O}_2$  at temperatures below  $-50^\circ\text{C}$ , a di- $\text{Cu}^{2+}-\text{O}_2^{2-}$  complex is formed reversibly. This dioxygen adduct is unstable at room temperature. The interest in these di-copper dioxygen adducts is related to the non-heme di-copper respiratory protein hemocyanin.<sup>214</sup>

## 3.11. Diphenoxide Ligands

The first binucleating diphenoxide ligand was reported by Robson,<sup>215,216</sup> who found that the bimetallic macrocyclic complex of the type **148** was formed



by reaction of the dialdehyde **149** with the diamine **150** in the presence of the metal acetate, eq 12. This



reaction proceeds well with propylenediamine, **150**, but not with ethylenediamine, most probably because the analogous ethylenediamine macrocyclic bimetallic system is very strained. After Robson's report, the area of macrocyclic and non-macrocyclic diphenoxide bimetallic complexes developed rapidly. This work has been reviewed<sup>165–169</sup> extensively, and only a few examples will be given here. Table 12 lists a representative set of diphenoxide binucleating ligands.

The homo- and heterobimetallic complexes of the macrocyclic ligands **151** have been described and reviewed.<sup>165</sup> Complexes of these ligands are generally inert to oxidation. For example, the di-Fe<sup>2+</sup> complex of ligand **151** ( $n = m = 1$ ) is stable to O<sub>2</sub> oxidation. This aspect of these complexes will be discussed presently.

The ligand **152** was prepared by sequential template reactions to give either Ni<sup>2+</sup>–Pb<sup>2+</sup> or Cu<sup>2+</sup>–Pb<sup>2+</sup> complexes<sup>226</sup> from which the heterobimetallic complexes of the type Ni<sup>2+</sup>–M<sup>2+</sup> or Cu<sup>2+</sup>–M<sup>2+</sup>, respectively, could be derived. The crystal structure<sup>226</sup> of [Cu<sup>2+</sup>Mn<sup>2+</sup>(μ-O<sub>2</sub>CCH<sub>3</sub>)(**152**)]BPh<sub>4</sub> is shown in Figure 42. In this structure, the Mn<sup>2+</sup> ion is six-coordinate and the Cu<sup>2+</sup> ion is five-coordinate. An acetate bridge spans the two metals.

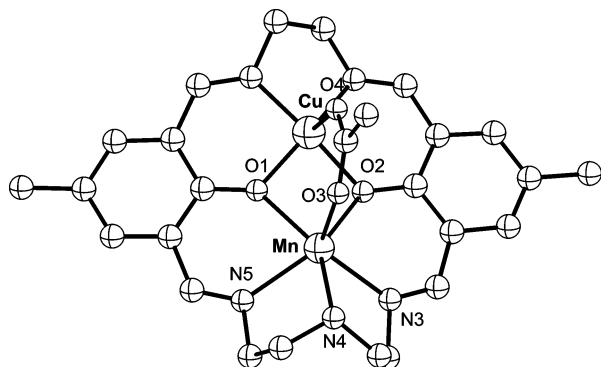
The ligand **154** has been extensively investigated.<sup>227</sup> Notable is the ready preparation of site-specific heterobimetallic complexes.<sup>228</sup> The complex [Cu<sup>2+</sup>(**154**,  $n = 0$ )Fe<sup>3+</sup>(Cl)(CH<sub>3</sub>OH)] exhibits antiferromagnetic coupling, whereas in [Cu<sup>2+</sup>(**154**,  $n = 0$ )-Cr<sup>3+</sup>(H<sub>2</sub>O)<sub>2</sub>]<sup>+</sup> ferromagnetic interaction occurs because of the orthogonality of the magnetic orbitals in the latter.<sup>228</sup>

The ligands **155** form homobimetallic complexes with Cu<sup>2+</sup> and Ni<sup>2+</sup>, but with other first-row transition metals oligomeric species are formed.<sup>217</sup> The six-coordinate site of these ligands requires the formation of seven-membered chelate rings, and this may be connected with their tendency toward oligomer formation.

Several aspects of the ligands **156** and **157** are of interest.<sup>218</sup> One is related to the preparation of site-specific heterobimetallic complexes that are derived from the monometallic dialdehyde **158**. Reaction of **158** with a diamine gives **159**, a protonated complex which allows for the formation of the heterobimetallic

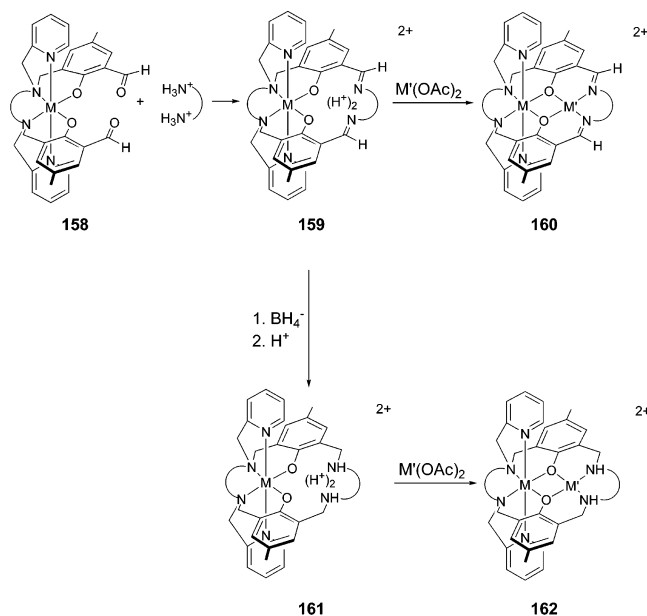
**Table 12. Binucleating Diphenoxide Ligands**

Ligand Number	Ligands	Metal Complex	Reference
151	 $n = 0, 1; m = 0, 1$	di-Cu <sup>2+</sup> , di-Ni <sup>2+</sup> , di-Mn <sup>2+</sup> , di-Fe <sup>2+</sup> , di-Co <sup>2+</sup> , di-Zn <sup>2+</sup>	165
152		Cu <sup>2+</sup> -Mn <sup>2+</sup> , Cu <sup>2+</sup> -Fe <sup>2+</sup> , Cu <sup>2+</sup> -Co <sup>2+</sup> , di-Cu <sup>2+</sup>	167
153		Ni <sup>2+</sup> VO <sup>2+</sup>	168
154	 $n = 0, 1$	di-Cu <sup>2+</sup> , di-Ni <sup>2+</sup> , di-Co <sup>2+</sup> , Cu <sup>2+</sup> -Ni <sup>2+</sup> , Ni <sup>2+</sup> -Co <sup>2+</sup> , Zn <sup>2+</sup> -Mn <sup>2+</sup>	169
155	 $n = 0, 1$	di-Cu <sup>2+</sup> di-Ni <sup>2+</sup>	217
156	 $n = 0, 1; m = 0, 1$	di-Co <sup>2+</sup> , di-Mn <sup>2+</sup> , di-Ni <sup>2+</sup> , Cu <sup>2+</sup> -Zn <sup>2+</sup> , Co <sup>3+</sup> -Co <sup>2+</sup> , Co <sup>3+</sup> -Mn <sup>2+</sup>	218- 223
157	 $n = 0, 1; m = 0, 1$	di-Fe <sup>2+</sup> , di-Zn <sup>2+</sup> , di-Co <sup>2+</sup>	218, 224, 225

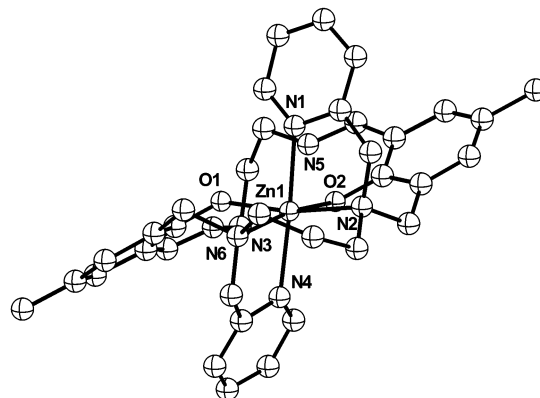
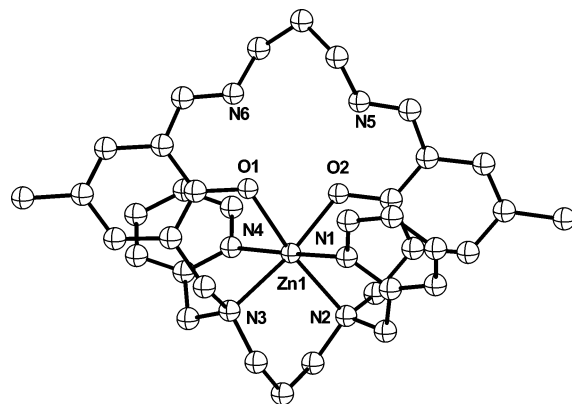


**Figure 42.** Crystal structure of  $[\text{CuMn}(\mu\text{-O}_2\text{CCH}_3)(\mathbf{152})]^+$ . (Adapted from ref 226. Copyright American Chemical Society.)

complex **160** under mild conditions. The diimine complex **159** can be reduced to give **161**, which, in turn, allows for the mild formation of **162**.<sup>224</sup> The other aspect of interest with these systems is the variation of oxidation potential of the metals in the six-coordinate site. When either  $\text{Co}^{2+}$  or  $\text{Fe}^{2+}$  is present in the six-coordinate site of **158** or **161**, the metals are readily oxidized to the  $\text{M}^{3+}$  state, but when a second metal,  $\text{M}'$ , is incorporated as in **162** or **160**, the metal in the six-coordinate site becomes deactivated to oxidation.<sup>218</sup> The major cause of this oxidative deactivation is believed to be mechanical coupling,<sup>218</sup> a phenomenon that transmits structural changes at one metal site to the other by ligand conformational changes. In the case of the macrocyclic bimetallic complex **162**, oxidation of one of the metals causes changes in bond lengths that will induce conformation changes which will be transmitted to the other metal. In other words, the ligand structures about the two metals are coupled so that changes at one site cannot occur independently of changes at the other metal site. As a consequence, it was not possible to oxidize both metals in any of these systems and in some cases neither metal could be oxidized.

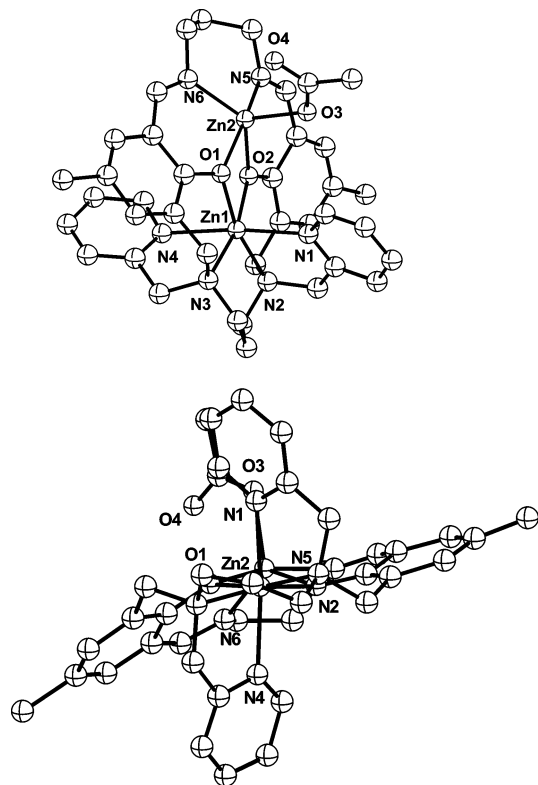


The structures of the complexes of the ligands **156** and **157** illustrate how the overall topology can be

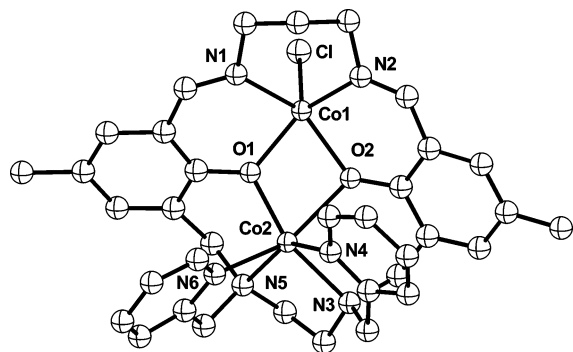


**Figure 43.** Crystal structure of  $[\text{Zn}(\mathbf{156}, n = m = 1)(\text{H}^+)_2]^{2+}$ . (Adapted from ref 222. Copyright American Chemical Society.)

controlled by chelate ring size and how mechanical coupling between metal sites can occur. The monometallic zinc complex  $[\text{Zn}(\mathbf{156}, n = m = 1)(\text{H}^+)_2]^{2+}$  that has the  $\text{Zn}^{2+}$  in the six-coordinate site and the two protons in the four-coordinate site is shown in Figure 43.<sup>222</sup> The structure is twisted, the topology of the ligand about the  $\text{Zn}^{2+}$  is as expected with *trans* disposed pyridine ligands, and presumably the two protons reside in the cavity formed by O(1), O(2), N(5), and N(6). When the protons are replaced by a second  $\text{Zn}^{2+}$  ion to form  $[\text{Zn}_2(\mathbf{156}, n = m = 1)(\text{O}_2\text{-CCH}_3)]^+$ , considerable conformational change occurs in the ligand, although the overall topology is the same as in the monometallic precursor. The bimetallic structure is shown in Figure 44.<sup>222</sup> In both the mono- and bimetallic structures the 1,3-diamino ring which carries the 2-picoyl ligands is in a skew conformation; the other 1,3-diamino ring is in a distorted chair conformation in both structures. When the chelate ring size is changed from  $n = 1$  to  $n = 0$  for either of the ligands **156** or **157**, the monometallic complexes of the type  $[\text{M}^{2+}(\text{Ligand})(\text{H}^+)_2]^{2+}$  have essentially the same topology as shown by the structure in Figure 43. Upon addition of a second metal, the topology of the complexes undergoes a significant rearrangement where the two pyridine groups are now *cis* disposed. An example of this topology is illustrated by the di- $\text{Co}^{2+}$  complex,  $[\text{Co}_2(\mathbf{157}, n = 0, m = 1)\text{Cl}]^+$ , the structure of which is shown in Figure 45.<sup>219</sup> The *cis*-pyridine topology is observed for all bimetallic complexes of ligands **156** and **157**, having  $n = 0$ , irrespective of the value of



**Figure 44.** Crystal structure of  $[\text{Zn}_2(\mathbf{156}, n = m = 1)(\text{O}_2\text{-CCH}_3)]^+$ . (Adapted from ref 222. Copyright American Chemical Society.)



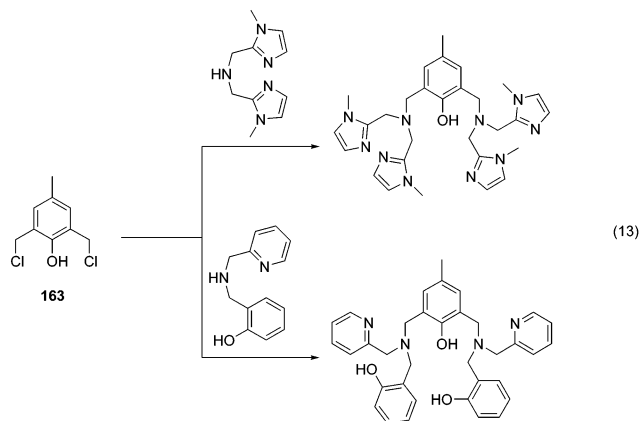
**Figure 45.** Crystal structure of  $[\text{Co}_2(\mathbf{157}, n = 0, m = 1)\text{-Cl}]^+$ . (Adapted from ref 219. Copyright American Chemical Society.)

*m*. These *cis*-pyridine structures embody strain and probably arise from the presence of one-atom bridging (i.e., O(1) and O(2) in Figure 45) and because the rigid phenolic groups are not flexible enough to relieve this strain. When the chelate ring is expanded to a six-membered ring ( $n = 1$ ), less strain exists and is relieved by considerable twisting of the structure (Figure 43). The tightly coupled conformational constraints imposed by the macrocyclic structures of the bimetallic complexes of the ligands **156** and **157** undoubtedly control the redox potentials of the metals. In some cases it is found that the mechanical coupling can amount to 1 eV.<sup>218</sup>

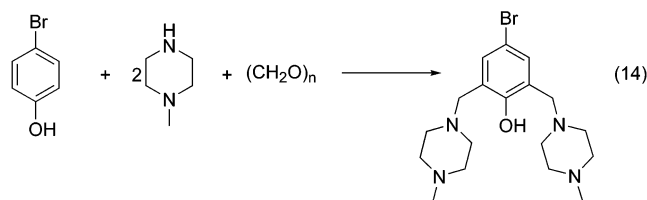
### 3.11.1. Ligand Synthesis

Some of the synthetic procedures are not especially general nor efficient and will not be discussed here. For the production of symmetrical monophenoxide

ligands, the precursor **163** has been coupled with a secondary amine as illustrated in eq 13.<sup>190</sup> In some

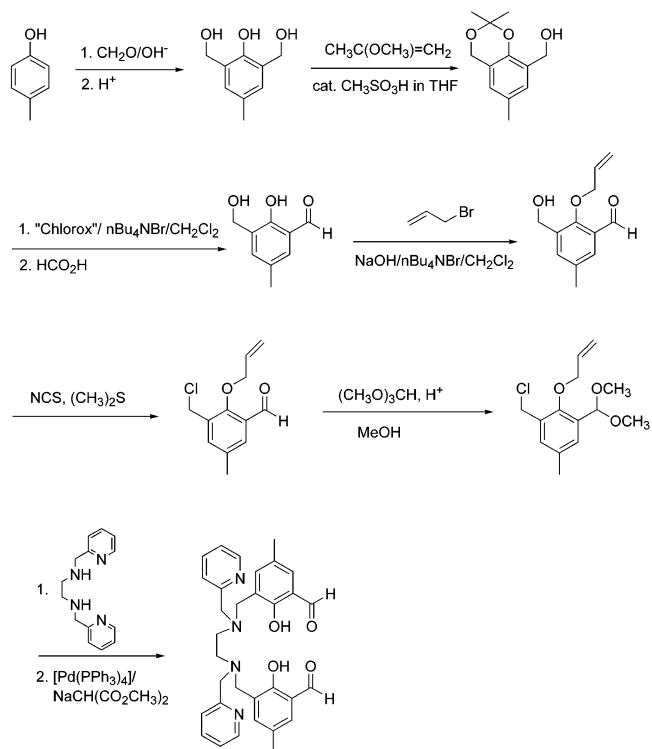


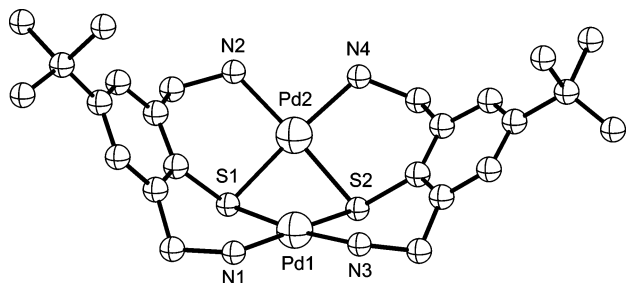
cases<sup>174</sup> the phenol group of **163** is protected with, for example, a benzyl group. An alternative and perhaps more efficient route to symmetrical monophenoxide binucleating ligands is the reaction of a 4-substituted phenol with formaldehyde and a secondary amine (Mannich base), as in the example<sup>176</sup> shown in eq 14.



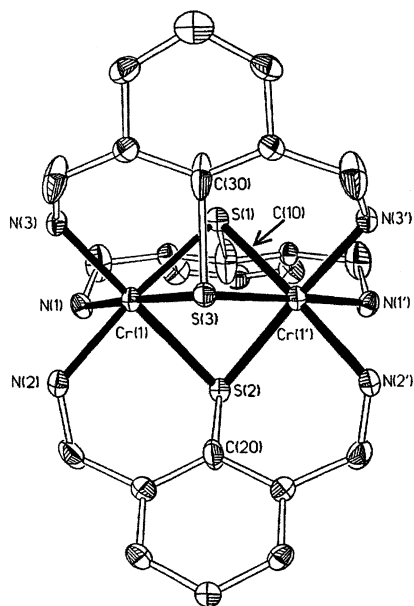
There are several published procedures for producing unsymmetrically substituted phenolates. Perhaps the most formal method is outlined in Scheme 11 for

### Scheme 11





**Figure 46.** Crystal structure of  $[\text{Pd}_2(\mathbf{165})_2]^{2+}$ . (Reprinted with permission from ref 229. Copyright 1998 Wiley-VCH.)



**Figure 47.** Crystal structure of  $[\text{Cr}_2(\mathbf{165})_3]^{3+}$ . *t*-Butyl groups are omitted for clarity (Adapted from ref 231. Copyright American Chemical Society.)

preparation of the dialdehyde **164**.<sup>219</sup> The steps in Scheme 11 are efficient, and it is clear that the unsymmetrically substituted intermediates can be used as precursors for the synthesis of other unsymmetrical binucleating ligands.

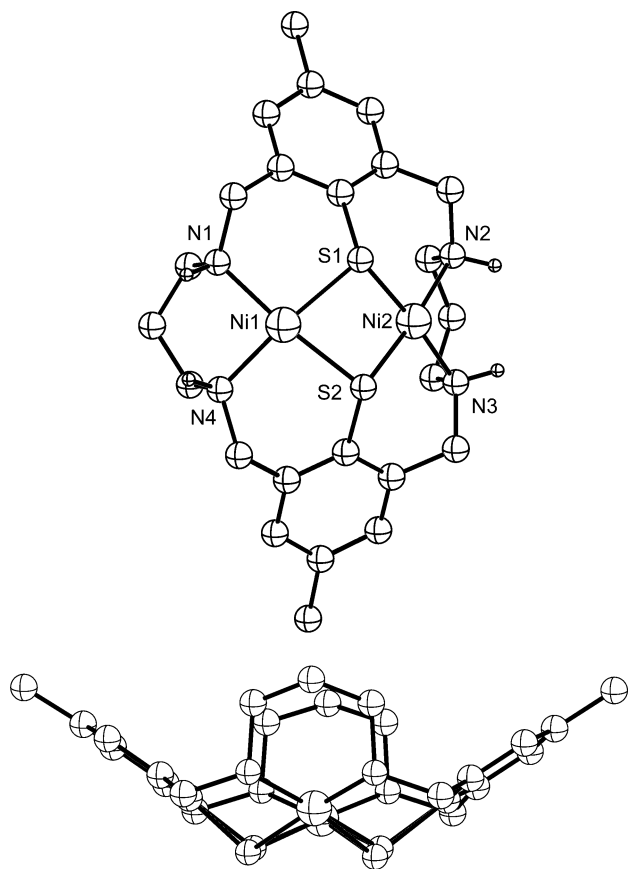
### 3.12. Thiolate Bridging Ligands

The chemistry of binucleating bridging thiolate ligands is much less extensive than that of the corresponding alkoxides and phenoxides. In part, this is because thiolates are subject to oxidation and the chemistry required to generate the ligands is less well-developed. Table 13 lists some binucleating thiophenoxide ligands that have been prepared. These have been reviewed recently.<sup>248</sup>

Compared to the phenoxide bridges, the thiophenoxide bridges form bimetallic complexes that are very distorted because of the larger size of the sulfur atom. This distortion is illustrated in the crystal structure of  $[\text{Pd}_2^{2+}(\mathbf{165})_2](\text{BPh}_4)_2$  shown in Figure 46.<sup>229</sup> As can be seen, the phenyl groups are buckled to form a bowl-like structure. When three sulfur bridges span two metals, as in the complex  $[\text{Cr}_2^{3+}(\mathbf{165})_3](\text{ClO}_4)_2\text{Cl}\cdot\text{H}_2\text{O}\cdot\text{CH}_3\text{OH}$ , the paddle-wheel structure shown in Figure 47 is observed.<sup>231</sup> Structures of bimetallic complexes of the macrocyclic ligands **167**,  $n = 1$  and 2, are also bowl-like<sup>234–239</sup> as are complexes

**Table 13. Binucleating Thiophenoxide Bridging Ligands**

Ligand Number	Ligands	Metal Complex	Reference
165		$\text{di-Ni}^{2+}$ , $\text{di-Pd}^{2+}$ $\text{di-Cr}^{3+}$	229-232
166		$\text{di-Ni}^{2+}$	233
167		$\text{di-Ni}^{2+}$ $\text{di-Cu}^{2+}$	234-239
168		$\text{di-Ni}^{2+}$	240
169		$\text{di-Co}^{3+}$ , $\text{Ni}^{2+}$ , $\text{Ni}^{3+}$ $\text{Fe}^{2+}$ , $\text{Fe}^{3+}$	241-242
170		$\text{di-Ni}^{2+}$ , $\text{di-Co}^{2+}$ , $\text{di-Co}^{3+}$ , $\text{Co}^{2+}$ , $\text{Co}^{3+}$	243-245
171		$\text{di-Ni}^{2+}$ $\text{di-Cu}^{2+}$	246
172		$\text{di-Ni}^{2+}$	247



**Figure 48.** Two views of the crystal structure of  $[\text{Ni}_2(\mathbf{168})]^{2+}$ . (Reprinted with permission from ref 240. Copyright 1998 The Royal Society of Chemistry.)

of the reduced analogue **168**. The crystal structure<sup>240</sup> of the ion  $[\text{Ni}_2^{2+}(\mathbf{168})]^{2+}$  is shown in Figure 48. It will be noted that the bowl-like structure is enforced by the N–H hydrogen atoms being disposed away from the concavity of the structure. Bimetallic complexes of the ligand **169**<sup>241,242</sup> have analogous structures to the trisligand (**165**) bimetallic complexes as illustrated in Figure 47.

The structures of bimetallic complexes of the three ligands **170**–**172** are largely predicted by the structures just discussed. The ligands **170** and **172** which have extra nitrogen atom donors form bimetallic complexes where these nitrogen atoms coordinate to the metal.

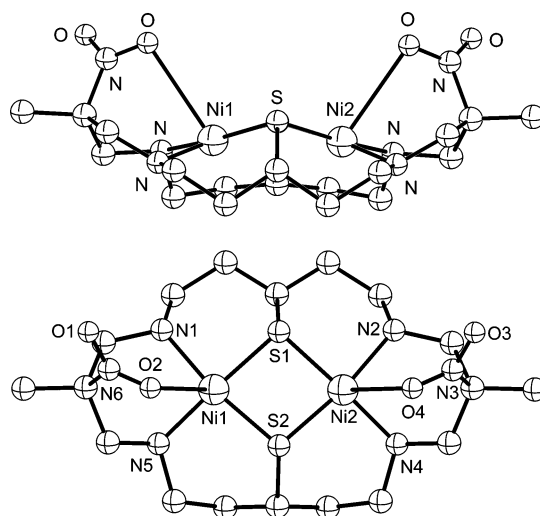
The few binucleating alkanethiolate ligands that have been studied are listed in Table 14. The ligand **173** forms bimetallic bisligand complexes with  $\text{Ni}^{2+}$  and  $\text{Pd}^{2+}$ , but the di- $\text{Co}^{3+}$  complex contains three ligands.<sup>251</sup> The ligand **174** forms bimetallic  $\text{Pd}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Cu}^{2+}$  complexes with a variety of exogenous bridges. Crystal structures of complexes of the ligands **173** and **174** have not been reported, but the crystal structure of the di- $\text{Ni}^{2+}$  complex of the macrocyclic ligand  $[\text{Ni}_2(\mathbf{175})]^{2+}$  is shown in Figure 49.<sup>251</sup> In this structure, the oxygen atoms of the nitro groups are coordinated and the sulfur bridges cause the central part of the ligand to form a bowl-like structure.

### 3.12.1. Ligand Synthesis

The preparation of binucleating thiophenolate ligands depends on finding methods of converting aryl

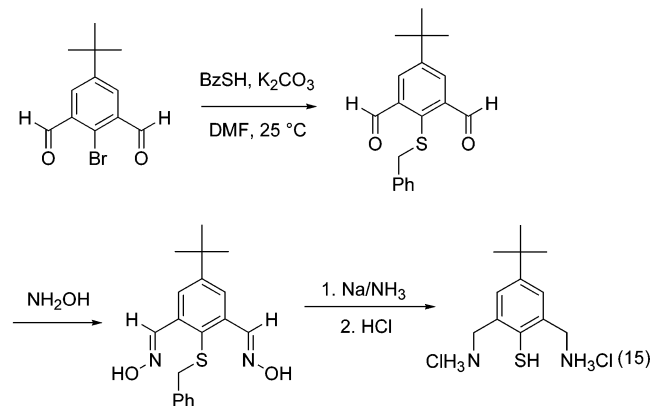
**Table 14. Binucleating Thiolate Bridging Ligands**

Ligand Number	Ligands	Metal Complex	Reference
173		di- $\text{Ni}^{2+}$ , di- $\text{Co}^{3+}$ , di- $\text{Pd}^{2+}$	249
174		di- $\text{Pd}^{2+}$ , di- $\text{Ni}^{2+}$ , di- $\text{Cu}^{2+}$	250
175		di- $\text{Ni}^{2+}$ , di- $\text{Pd}^{2+}$	251

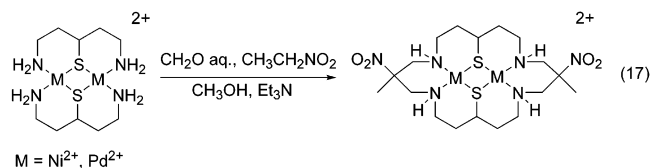
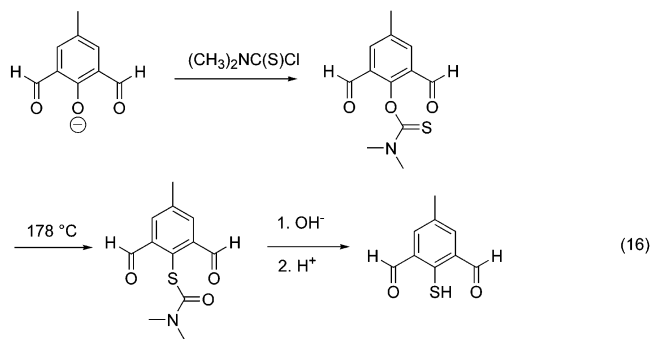


**Figure 49.** Two views of the crystal structure of  $[\text{Ni}_2(\mathbf{175})]^{2+}$ . (Reprinted with permission from ref 251. Copyright 1990 The Royal Society of Chemistry.)

halides or phenols to thiophenols. So far, two mild methods have been deployed. The first of these uses the powerful nucleophile benzylthiolate to displace an aryl bromide eq 15.<sup>229</sup> An alternative method of



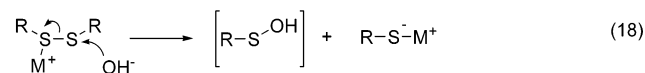
introducing a thiophenol group is by the sequence<sup>237</sup> shown in eq 16. Preparation of the macrocyclic ligand **175**, Table 14, is achieved by the procedure shown in eq 17.<sup>251</sup> The macrocyclic ligand is formed by metal templating. The product is the *syn* isomer.



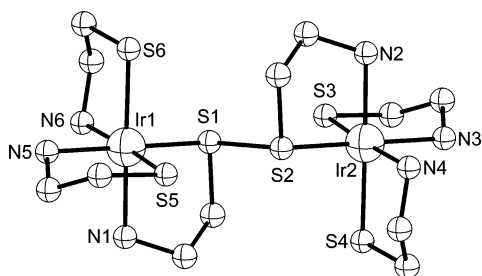
It should be noted that thiolates coordinated<sup>252</sup> or otherwise are subject to O<sub>2</sub> oxidation, and appropriate precautions are required.

### 3.13. Disulfide Bridging Ligands

There are a number of reports describing disulfide binucleating ligands that form bimetallic complexes where each metal binds to one of the sulfur atoms. It is known, however, that metal binding to a disulfide group can activate the S–S bond to nucleophilic attack leading, in the case of OH<sup>−</sup> reaction, to the formation of the (unstable) sulfenic acid and the metal sulfide,<sup>253–256</sup> eq 18. This cleavage can be retarded by providing steric hindrance about the disulfide bond.<sup>253</sup> The disulfide is also readily reduced, adding further to the complications that may ensue. Table 15 lists a number of binucleating disulfide ligands.



Most of these binucleating ligands were prepared by redox reactions of the metal-bound thiol ligands. Thus, the ligand **176** is derived from the complexes **180** by (Ce<sup>4+</sup>) oxidation<sup>257</sup> (eq 19). The crystal structure of **181** (M = Ir) is shown in Figure 50.<sup>257</sup> The



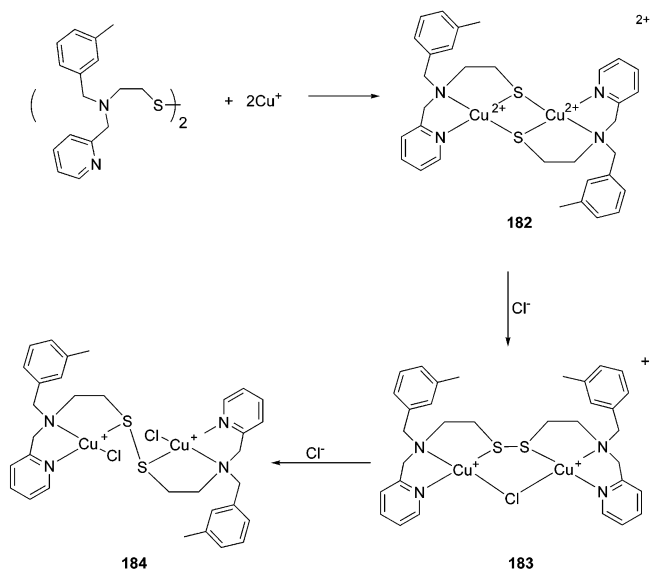
**Figure 50.** Crystal structure of [Ir(SCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>)<sub>2</sub>]<sub>2</sub><sup>2+</sup> (**176**)<sup>2+</sup>. (Reprinted with permission from ref 257. Copyright 1998 The Chemical Society of Japan.)

ligand **177** reacts with 2 equiv of Cu<sup>+</sup> to give a thiol-bridging di-Cu<sup>2+</sup> complex **182**, which upon addition of Cl<sup>−</sup> ions gives sequentially the two di-Cu<sup>+</sup> disulfide bridging complexes **183** and **184**, Scheme 12.<sup>258</sup>

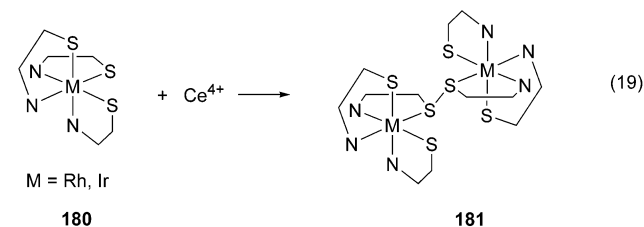
**Table 15. Binucleating Disulfide Ligands**

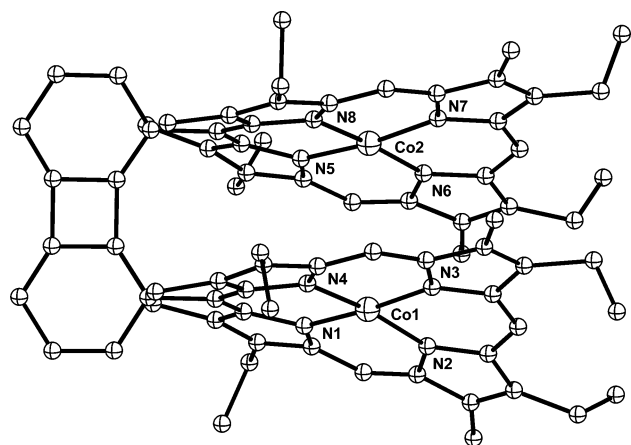
Ligand Number	Ligands	Metal Complex	Reference
176		di-Rh <sup>3+</sup> , di-Ir <sup>3+</sup>	257
177		di-Cu <sup>+</sup>	258
178		di-Ni <sup>2+</sup> , di-Cu <sup>2+</sup>	259
179		di-Ni <sup>2+</sup> di-Cu <sup>+</sup>	260 261

**Scheme 12**



Similar behavior is observed for the copper complexes of the ligand<sup>261</sup> **178**. This same ligand can be formed from the thiol–Ni<sup>2+</sup> complexes by O<sub>2</sub> oxidation.<sup>260</sup>





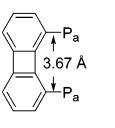
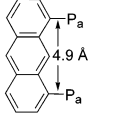
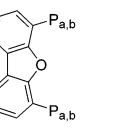
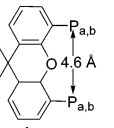
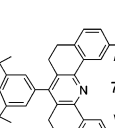
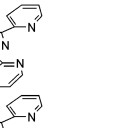
**Figure 51.** Crystal structure of  $[\text{Co}_2(\mathbf{185a})]$ . (Adapted from ref 264. Copyright American Chemical Society.)

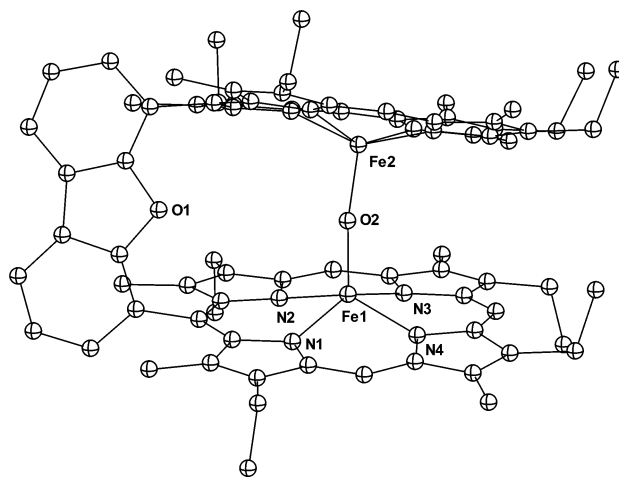
Bimetallic  $\text{Cu}^{2+}$  or  $\text{Ni}^{2+}$  complexes of the ligand **178** can be made either from the preformed bisdisulfide macrocycles or by  $\text{I}_2$  oxidation of the corresponding bishthio precursors.<sup>259</sup>

### 3.14. Face to Face Bimetallic Complexes

These bimetallic complexes are constructed without ligands bridging the two metals. Rather, two planar metal complexes are held apart by rigid molecular spacers. The two metals register with one another at a specific separation distance, which allows small molecules to bridge them. In other cases, the two face-to-face planar complexes can be used as molecular receptors for incarceration of molecular guests. A number of these face-to-face binucleating ligands are shown in Table 16. Only those ligands that rigidly enforce a face-to-face arrangement are included. Where the cofacial ligands are roughly parallel, the approximate maximum separations between the planar ligands are given in Table 16. The dibenzofuran spacer **186** disposes the porphyrins in a divergent array. Crystal structures of the bisporphyrin ligand complexes show that considerable distortion of the metalloporphyrin rings can be tolerated. The separation between the ligand planes, however, is flexible. By concerted rotation of the two chelators about the spacer, the interplanar ligand separation can be reduced from the maximum values shown in Table 16. None of the bisporphyrin systems **185** and **186** is capable of incarcerating an aromatic molecule within the molecular cleft, as is the case for the ligand **187**, because the "thickness" of an aromatic ring is about 3.45 Å. By coordinating bulky ligands on the outside faces of the metalloporphyrins, small substrates such as  $\text{O}_2$ ,  $\text{N}_2$ , and  $\text{H}_2$  can be induced to interact with the inside coordination positions of the metals.<sup>266</sup> In this way, for example,  $\text{O}_2$  can be induced to bridge between two cobalt atoms in the molecular cleft.<sup>264</sup> Similarly, the di-ruthenium systems absorb  $\text{H}_2$  and  $\text{N}_2$ .<sup>263</sup> Electrochemical reduction leads to interesting transformations of the substrates. Figure 51 shows the crystal structure of  $[\text{Co}_2^{2+}(\mathbf{185a})]$ .<sup>264</sup> This complex reacts with  $\text{O}_2$  upon addition of 1,5-diphenylimidazole, where the reduced  $\text{O}_2$  ligand probably bridges the two cobalt atoms. The mixed-valence complex  $[\text{Co}^{2+}\text{Co}^{3+}(\mathbf{185a})]^+$  absorbs  $\text{O}_2$  to give a superoxide complex. The dibenzofuran spacer bear-

**Table 16. Face-to-Face Planar Binucleating Ligands**

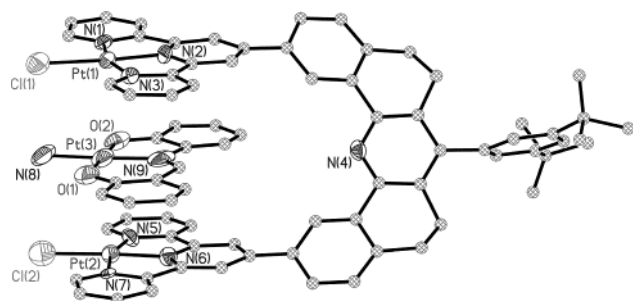
Ligand Number	Ligands	Metal Complex	Reference
185		di- $\text{Co}^{2+}$ , di- $\text{Ni}^{2+}$ , di- $\text{Cu}^{2+}$ , di- $\text{Ru}^{2+}$ , di- $\text{Os}^{2+}$	262-266
			
186		di- $\text{Mn}^{2+}$ , di- $\text{Fe}^{2+}$ , di- $\text{Cu}^{2+}$ , di- $\text{Fe}^{3+}$ , di- $\text{Ni}^{2+}$	267-270
			
187		di- $\text{Pd}^{2+}$ , di- $\text{Pt}^{2+}$	271-276
			



**Figure 52.** Crystal structure of  $[\text{Fe}_2(\mu\text{-O})(\mathbf{186aPa})]$ . (Adapted from ref 270. Copyright American Chemical Society.)

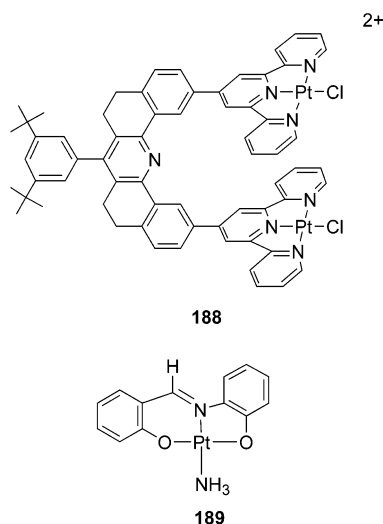
ing the porphyrin ( $\text{P}_a$ ) forms a di- $\text{Fe}^{2+}$  complex, which upon exposure to  $\text{O}_2$  and then alumina gives the  $\mu$ -oxo complex, the structure of which is shown in Figure 52.<sup>270</sup> The extensive distortion of the structure attests to the strength of the  $\text{Fe}^{3+}\text{-O-Fe}^{3+}$  bonds.

The di- $\text{Pd}^{2+}$  or di- $\text{Pt}^{2+}$  chloro complexes of the ligand **187** act as molecular receptors for large aromatic molecules and for planar  $\text{Pd}^{2+}$  and  $\text{Pt}^{2+}$  complexes bearing aromatic ligands.<sup>271-276</sup> Figure 53



**Figure 53.** Crystal structure of the 1:1 host-guest complex formed by **188** and **189**. (Adapted from ref 272. Copyright American Chemical Society.)

shows the crystal structure of the host-guest complex formed between **188** and **189**.<sup>272</sup> The host-guest complex shows Pt-Pt interaction, and it is this weak metal-metal bonding that enhances the molecular recognition. There are many supramolecular multi-metallic complexes that have been prepared by thermodynamically controlled self-assembly.<sup>277</sup> A survey of these systems is beyond the scope of this review.



#### 4. Possible Future Developments

This review has been concerned mainly with the design, preparation, and structures of bimetallic complexes bearing a variety of bridging ligands. The discussion given on the topologies of monometallic complexes was focused on those principles that can be transferred for the construction of binucleating ligands. During the presentation of the bimetallic complexes, less emphasis was placed on the physical properties such as magnetism and electronic spectra because, in most cases, these aspects are of less interest to the nonspecialist. Some of the unusual physical properties are discussed, however. It is the unique reactivities of bimetallic complexes that are of special interest, for they hint at the future development of the area.

In this regard, the chemical reactivity or redox property has to be peculiar to the bimetallic system. As noted at the beginning, there are surprisingly few reactions which can be regarded as transformations that require a bimetallic rather than a monometallic system. This is especially disconcerting when some of the remarkable reactions that are carried out by

bimetallic biological systems (Table 1) are considered. It is becoming clear that, in the biological cases, the reactivity of the bimetallic complexes depends on more than the metal coordination sphere. The way in which the surrounding protein superstructure modulates the properties of the metals appears to be crucial in most cases. The protein can serve a variety of functions, including protecting the metal site from the medium molecules, adjusting the geometry of the coordination sphere, and ordering the substrate in relation to the metals. These protein effects can alter the redox potentials of the metals and act to stabilize intermediates of reaction. Even "simple" protein electron-transfer reactions are finely tuned, as is the case of the copper protein azurin, where the protein provides an unusual geometry about the copper ion.<sup>278</sup> This imposed coordination allows for rapid electron transfer because of the greatly reduced reorganization energy.

It would seem, therefore, that more elaborate bimetallic systems are required in order to begin to emulate biological functions. The next major development in bimetallic complexes is likely to involve more elaborate complexes requiring increasingly more sophisticated binucleating ligands.

#### 5. Acknowledgement

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#### 6. Abbreviations

acac	acetylacetonate
bipy	2,2'-bipyridyl
bz	benzyl
DCC	dicyclohexyl carbodiimide
dhp	dihydropyran
DIBAH	diisobutylaluminum hydride
DME	1,2-dimethoxyethane
DMF	dimethylformamide
DMSO	dimethyl sulfoxide
im	imidazole
LAH	lithium aluminum hydride
NCS	<i>N</i> -chlorosuccinimide
OTf	Triflate
ph	phenyl
PPA	polyphosphoric acid
THF	tetrahydrofuran
THP	tetrahydropyran
TMEDA	<i>N,N,N,N</i> -tetramethylethylenediamine

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