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Coordination chemistry of bidentate medium ring ligands (mesocycles)

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CONTENTS

ABBREVIATIONS

acac	acetylacetone
BME-DACO	*N*,*N*′-bis(2-mercaptoethyl)-1,5-diazacyclooctane
bipy	2,2′-bipyridine
3-CH_2-1,5-DTCO	3-methylene-1,5-DTCO
cyclam	1,4,8,11-tetraazacyclotetradecane
DACHDA	1,4-diazacycloheptene-*N*,*N*′-diacetic acid
DACHDEA	1,4-diazacycloheptene-*N*,*N*′-(α-ethyl)acetic acid
DACHDEN	*N*,*N*′-bis(2-aminoethyl)-1,4-diazacycloheptane
DACHDMA	1,4-diazacycloheptane-*N*,*N*′-(α-methyl)acetic acid
DACHDPA	1,4-diazacycloheptane-*N*,*N*′-(α-propyl)acetic acid
DACHDPN	*N*,*N*′-bis(3-aminopropyl)-1,4-diazacycloheptane
1,5-DACO	1,5-diazacyclooctane
DACODA	1,5-diazacyclooctane-*N*,*N*′-diacetic acid
1,4-DACH	1,4-diazacycloheptane

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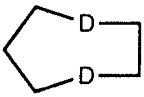
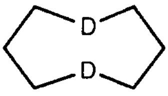
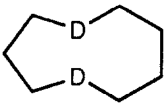
DMSO	dimethylsulfoxide
1,4-DTCH	1,4-dithiacycloheptane
1,5-DTCO	1,5-dithiacyclooctane
1,5-DTCO-O	1,5-dithiacyclooctane 1-oxide
EDDA	ethylenediaminediacetic acid
Me_2BME-DACO	*N*,*N′*-bis((2-methylmercapto)ethyl)-1,5-diazacyclooctane
EDTA	ethylenediaminetetraacetic acid
mnt^{2-}	maleonitriledithiolate
MPHZ	*N*-methyl-5,6,11,12-tetrahydro-2,8-dimethylphenhomazine
3-OCH_3-1,5-DTCO	3-methoxy-1,5-dithiacyclooctane
3-OH-1,5-DTCO	3-hydroxy-1,5-dithiacyclooctane
PHZ	5,6,11,12-tetrahydro-2,8-dimethylphenhomazine
8-PP	1,5-diphenyl-1,5-diphosphacyclooctane
8-PS	5-phenyl-1-thia-5-phosphacyclooctane
PYAZ	4,4-dimethyl-7-(5,5,7-trimethyl-1,4-diazepan-1-yl)-5-azaheptan-2-ol
TACO	5-methyl-1-thia-5-azacyclooctane
TMDZ	5,5,7-trimethyl-1,4-diazacycloheptane

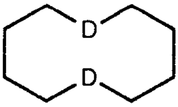
A. INTRODUCTION

Medium-sized rings (mesocycles) are molecules which contain seven- to ten-membered rings. The most symmetrical members of the series of saturated bidentate heterocyclic mesocycles with transannular donor atoms (D) are illustrated below. All are potential chelating agents; however, the coordination chemistry of only the first two members of this series, the 1,4-disubstituted cycloheptanes and 1,5-disubstituted cyclooctanes, and their derivatives has been studied. It is the purpose of this manuscript to review the coordination chemistry of these ligands and to describe some of the more important properties of their complexes. Mesocyclic tridentate and tetradentate ligands will not be discussed.





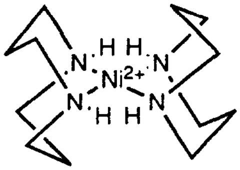


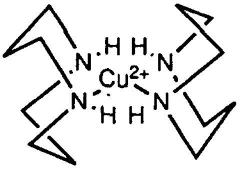


B. COORDINATION CHEMISTRY OF 1,5-DIAZACYCLOOCTANE (1,5-DACO), 1,4-DIAZACYCLOHEPTANE (1,4-DACH) AND THEIR DERIVATIVES

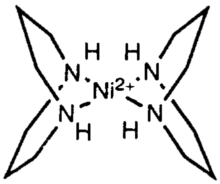
(i) Structure and spectra

In 1966, we reported that both $Ni(ClO_4)_2$ and $Cu(ClO_4)_2$ react with 1,5-diazacyclooctane (1,5-DACO) to give solid bis-complexes which appeared to be rigorously square planar [1]. Models showed that the planarity of the bis-complexes of 1,5-DACO is conferred by the geometry of the ligands. When both ligands are arranged in the boat–chair conformation, all intramolecular interactions are minimized and the methylene groups at the three and/or seven positions will effectively block the *z*-axis so that additional coordination is prevented.





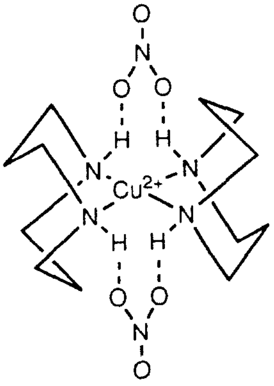
The first crystal structure of a mesocyclic complex, Ni(1,5-DACO)$_2$(ClO$_4$)$_2$·2H$_2$O, was carried out by Royer et al. in 1971 [2]. They reported that the nickel(II) atom was "strictly planar and square within experimental error". The most unexpected observation was that the trimethylene groups did not fold over the *z*-axis as predicted [1] but are arranged in a plane so that all the hydrogen atoms in the trimethylene groups are eclipsed. Although the axial positions are completely open, neither the perchlorate ions nor the water molecules are in a position in the lattice to interact with the metal along the *z*-axis. The Ni—N bond distance is 1.95(3) Å and the C—C bond distances vary from 1.47(4) to 1.52(4) Å.



An X-ray crystal structure of the same molecule, Ni(1,5-DACO)$_2$(ClO$_4$)$_2$·2H$_2$O, was reported later by Hussain et al. [3] who reconfirmed the structure found by Royer et al. [2]. The angles and distances were found to be slightly different, but the same eclipsing of the hydrogens was observed. They report that the Ni—N bond distances are 1.921(5) and 1.932(5) Å but the C—C bonds in the trimethylene groups are appreciably shorter (from 1.339(13) to 1.385(12) Å) than normal sp^3 hybrids (1.54 Å). They conclude by stating that Ni(II) forms planar complexes with mesocyclic diamines irrespective of their steric requirements [3]. However, low-temperature magnetic studies show that the conformation may change from square planar to octahedral or tetrahedral or simply undergo a long-range exchange interaction along the *z*-axis below 78 K [3].

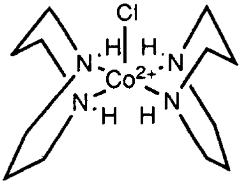
A third X-ray crystal structure of Ni(1,5-DACO)$_2$(ClO$_4$)$_2$·2H$_2$O was reported by Boeyens et al. [4]. In this report, molecular disorder in the structure was discovered by the use of empirical force field calculations, which indicated that the rings were in a boat–chair relationship as originally predicted [1]. This disorder was responsible for the apparent planarity of the trimethylene groups. By this analysis, the C—C bond distances are more normal (1.549 Å) and the average Ni—N bond distance is calculated to be 1.947 Å. Water molecules are hydrogen bonded to the N—H groups and act as bridges between cations. The crystal structure of a different salt, [Ni(1,5-DACO)$_2$]-(B(C$_6$H$_5$)$_4$)$_2$, also reveals that the eight-membered rings are in the boat–chair conformation [4].

The structure of the only Cu(II) complex of 1,5-DACO, Cu(1,5-DACO)$_2$(NO$_3$)$_2$, was determined only recently [5(a),(b)]. The molecule is planar with Cu—N bond distances of 1.997(1) and 2.034(1) Å. The 1,5-DACO ligands are in the boat–chair conformation and there is no disorder problem. The only unusual feature in the structure is that the four N—H bonds in each Cu(1,5-DACO)$_2^{2+}$ cation are hydrogen bonded to the two nitrate groups to give what the authors describe as a "macrocycle-like" ring system.

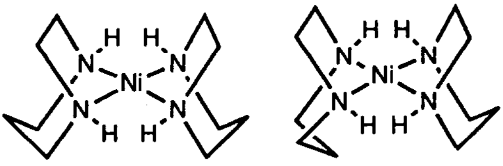


Although Ni(II) and Cu(II) only seem to form crystalline four-coordinated complexes with 1,5-DACO, CoCl$_2$ forms a five-coordinated complex, [Co(1,5-DACO)$_2$Cl]Cl [6]. The X-ray crystal structure was reported, but no structural data was given in the paper [7]. The Co(II) is in a square pyramidal environment formed by four nitrogen atoms and one chlorine. We initially thought that the increase in coordination number might be due to the slightly larger size of Co(II) relative to Ni(II) and Cu(II); however, the metal—nitrogen bond distances in the cobalt complex are similar. The Co—N bond distances are 1.97(1) and 1.91(1) Å. The Co—Cl bond distance is 2.49(1) Å. The cobalt atom lies 0.23(1) Å above the plane of the four nitrogen atoms. The two 1,5-DACO ligands are related to each other by a mirror plane imposed by the choice of space groups, Pnma vs. Pna2$_1$. Although this assumption has little effect on the coordination around cobalt, it can affect the conformation that is assigned to the two 1,5-DACO rings. The middle carbons of the trimethylene groups which lie on the same side of the basal plane as the coordinated chlorine, point away from the chlorine. The trimethylene groups which lie below the basal plane are arranged so that all the hydrogen atoms are eclipsed.

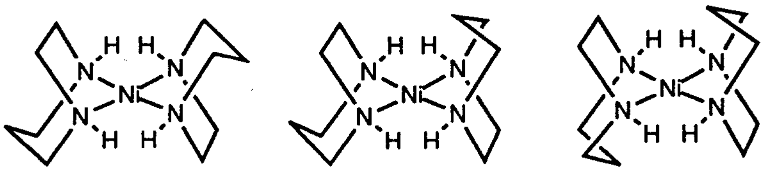
However, the C—C bond distances in this trimethylene group are unusual for C—C single bonds and they have rather large temperature factors. This may be related to a disorder problem or it may have been imposed on the structure by the choice of the space group. The normal tests for a non-centrosymmetric space group was carried out but a centrosymmetric space group always seemed to fit the data better [7]. If the ligands are disordered, the disorder may not be the same as that found in Ni(1,5-DACO)$_2^{2+}$, but may be an interconversion of twist conformations that are proposed in the interconversion of the two chair forms of cyclohexane. This twisting would minimize the eclipsing of the methylene groups while not increasing the interaction between the middle methylene groups.



Since 1,4-diazacycloheptane (1,4-DACH) has both a dimethylene and trimethylene group spanning the two nitrogen atoms, several stable arrangements of the 1,4-DACH ligands about a metal can be envisioned. If one focuses on just the two 1,4-DACH ligands themselves, the cis form has the two dimethylene groups on the same side of the basal plane, which includes the metal with the two rings in either a boat–boat or a boat–chair conformation. There are three possible trans forms depending on the folding of the rings (boat–boat, boat–chair and chair–chair).



Cis forms

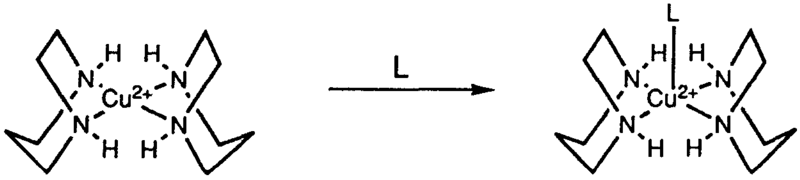


Trans forms

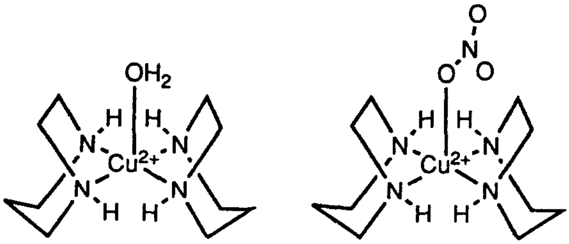
The crystal structure of the NiCl$_2$ complex, Ni(1,4-DACH)$_2$Cl$_2$, shows that the Ni(II) is planar with Ni—N bond distances of 1.917(5) and 1.921(6) Å and with the two 1,4-DACH ligands in the trans boat–boat conformation [8]. Although the

z-axis is not blocked as effectively by 1,4-DACH as by 1,5-DACO, there is still a sufficient steric effect to prevent additional coordination by the chloride ions. Some interaction between the chloride and the metal can be seen from an analysis of the magnetic properties of the complex [9].

Planar Cu(1,4-DACH)$_2^{2+}$ complexes are obtained only in the presence of very weakly coordinating anions and solvents but one additional ligand can be coordinated easily to give a series of pentacovalent complexes having square pyramidal geometry [10,11].



The crystal structure of Cu(1,4-DACH)$_2$(NO$_3$)$_2\cdot\frac{1}{2}$H$_2$O was found to have two different cations in the unit cell, Cu(1,4-DACH)$_2$(NO$_3$)$^+$ and Cu(1,4-DACH)$_2$(H$_2$O)$^+$ [12]. The 1,4-DACH ligands in both complexes adopt the cis boat–boat conformation. The Cu–N and Cu–O bond distances are 2.011(9) and 2.355(8) Å, respectively, in the nitrate complex and 2.007(9) and 2.322(9) Å in the aqua complex.



Since the local environment around the metal ion due to the coordination of 1,5-DACO or 1,4-DACH is almost identical, differences in physical and spectral properties can often be attributed to the additional ligand occupying the fifth (apical) position. Because there are no π bonding ligands present, this may be the best series of compounds to use to study the change from four-coordination to five-coordination. For example, the spectrum of both [Cu(1,4-DACH)$_2$](ClO$_4$)$_2$ and [Cu(1,5-DACO)$_2$](ClO$_4$)$_2$ show maxima near 20 000 cm^{-1}. By the use of a single crystal polarized spectrum of [Cu(1,5-DACO)$_2$](ClO$_4$)$_2$, Royer [2] concluded that the order of the d-orbital energies are $d_{x^2-y^2} > d_{xy} > d_{xz} > d_{yz} > d_{z^2}$.

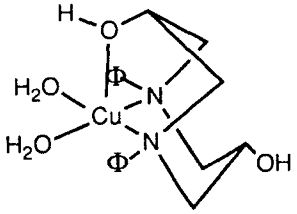
Both of these light red solid complexes, when dissolved in nitromethane, give maroon solutions with absorption maxima at a wavelength which is similar to the solid samples. Therefore, nitromethane is not coordinated to the metal ion and the structure of the complexes in the solid state and in solution is almost identical [10]. When coordination occurs, the spectrum shifts to lower energy. In Cu(1,4-

DACH)$_2$(NO$_3$)$_2$, where the nitrate ion is coordinated, the maximum occurs at 18 850 cm^{-1} in the solid state. The spectrum of [Cu(1,4-DACH)$_2$Cl]ClO$_4$ shows a maximum at 17 200 cm^{-1} and [Cu(1,4-DACH)$_2$Br]ClO$_4$ shows a maximum at 17 300 cm^{-1}, indicating that the halide ions are coordinated to the copper. A spectrochemical series can be established based on the shift of the absorption maxima to lower energy as various ligands are added to the apical position: $ClO_4^- \sim CH_3NO_2 < (CH_3)_2CO < CH_3CN < DMSO < NO_3^- < H_2O < HCONH_2 \ll SCN^- \sim Br^- \sim Cl^-$ [10]. This order appears anomalous because of the position of the neutral ligands (DMSO, H$_2$O, and HCONH$_2$) relative to the halides. This phenomenon is usually attributed to a variation in the displacement of the Cu(II) from the four "in-plane" ligands [13]. Thus, the Cu(II) atom in the aqua complex would lie closer to the plane than in the halide complexes [13].

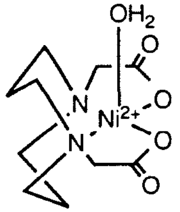
Pentacoordinated complexes are not normally observed in Cu(1,5-DACO)$_2^{2+}$ complexes in the solid state or in solution [10]. The absorption maximum remains in the same region of the spectrum regardless of the anion or the solvent. However, it has recently been shown that [Cu(1,5-DACO)$_2$](NO$_3$)$_2$ undergoes a color change from orange to violet during a phase transition on heating from 25 to 90°C [5]. One possibility is that one of the nitrates may be coordinated to the copper at the higher temperature. This possibility was rejected in favor of a dynamic process in which the nitrate anions which are hydrogen bonded to the N—H bonds cause an appreciable distortion of the planar coordination of Cu(II) as the temperature is raised.

Low-temperature specific heat and magnetization studies [14(a),(b)] on polycrystalline samples of [Cu(1,4-DACH)$_2$Br]ClO$_4$ indicate the existence of a bromide-bridged Cu(1,4-DACH)$_2^{2+}$ dimer. Measurements on the dibromide, Cu(1,4-DACH)$_2$Br$_2$, reveal the formation of one-dimensional linear chains. EPR studies of [Cu(1,4-DACH)$_2$](ClO$_4$)$_2$,[Cu(1,4-DACH)$_2$Br]ClO$_4$ and Cu(1,4-DACH)$_2$Br$_2$ also reveal the interaction between the bromide ion and the Cu(II) as the coordination changes from four to five to six. Variation of the *g*-value and the hyperfine coupling constant in the EPR spectra also reveals an interaction between the solvent and the metal in certain complexes. These results confirm the prediction that the position of the neutral ligands (DMSO, H$_2$O, and HCONH$_2$) relative to the halides in the spectrochemical series is due to a variation of the displacement of the Cu(II) from the "in-plane" ligands. Low-temperature specific heat and magnetization studies [9] of Ni(1,4-DACH)$_2$(ClO$_4$)$_2$ and Ni(1,4-DACH)$_2$Cl$_2$ reveal that the perchlorate salt remains diamagnetic down to 44 K whereas the chloride becomes paramagnetic at 77 K. This result suggests that superexchange interactions in the chloride complex are appreciably greater than in the perchlorate complex [9].

The only example of a complex containing a tridentate 1,5-DACO derivative was reported by Jensen et al. in 1972 [15]. They prepared the Cu(II) and Fe(III) complexes of *cis*-3,7-dihydroxy-1,5-diphenyl-1,5-diazacyclooctane and, based on a continuous variation study which showed the formation of a 1 : 1 complex, they proposed that the Cu(II) was five-coordinated to one hydroxyl group and two amine groups of the mesocycle and two water molecules. The Fe(III) complex was not discussed. They also reported that they could not make complexes of Ni(II), Co(II), Co(III), Mn(II), Cr(III) or V(III).

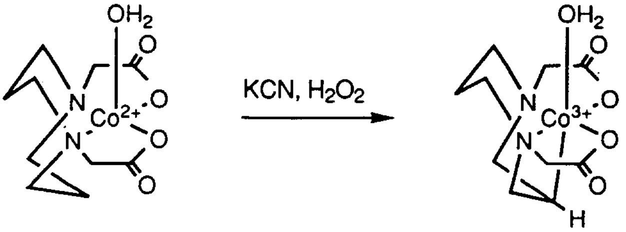


A number of derivatives of 1,5-DACO and 1,4-DACH have been prepared by substituting the hydrogen on the amine group with alkyl substituents having pendant arms containing functional groups such as carboxylic acids, amines and thiols. The first reported example of one of these derivatives is 1,5-diazacyclooctane-*N*,*N*-diacetic acid, DACODA [16,17]. Complexes of Co(II), Ni(II), Cu(II) and Zn(II) were prepared. The crystal structure of the Ni(II) complex showed that the nickel is square pyramidal with a water molecule occupying the fifth site with a Ni—O (water) bond distance of 2.011(7) Å [18]. The Ni—N bond distances are 2.025(7) and 2.030(7) Å and the Ni—O (carboxylate) bond distances are 1.997(7) and 1.983(6) Å. The eight-membered ring adopts a boat–chair conformation with one of the methylene groups blocking the sixth position.

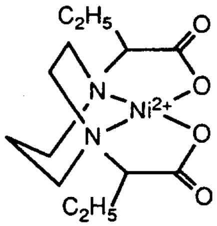


The Co(II) and Zn(II) complexes are isomorphous with the Ni(II) complex and are considered to be square pyramidal. The Co(II) complex is unusual in that it is stable to oxidation. Neither air nor hydrogen peroxide oxidizes the Co(II) to Co(III), in contrast to the behavior of ethylenediaminediacetic acid (EDDA) complexes of Co(II). Although the Cu(II) complex is not isomorphous with the Ni(II) complex, it still has all the characteristics of a five-coordinated complex. Detailed spectral and magnetic data are reported for these complexes [17].

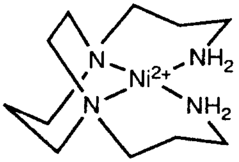
In a later report on DACODA complexes, it was shown that the unactivated C—H bond which folds over the *z*-axis in Co(DACODA(H_2O)) could be activated by oxidation with hydrogen peroxide but only in the presence of a strong field ligand like KCN [19]. The strong field ligand is required for the production of the Co(III) species. The crystal structure of the dark red Co(III) complex has a very short Co—C bond (Co—C bond distance = 1.941(4) Å). Thus the 1,5-DACO framework is severely strained. However, the molecule is quite stable in boiling water for three hours. When sulfite is used as the strong field ligand, an isolable Co(III) agostic intermediate having a (Co–agostic H) bond distance of 2.26(5) Å is formed. Treatment of the Co(III) sulfite complex with base causes deprotonation to occur along with the formation of the Co—C bond.



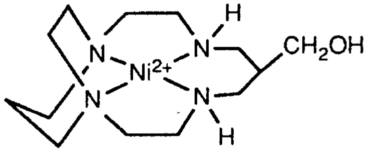
Fukuda et al. [20] have synthesized a series of analogous carboxylic acid derivatives of 1,4-DACH where a methylene group, placed between the nitrogen in the ring and the carboxylic acid group is unsubstituted (DACHDA) or dialkylated (DACHDMA (methyl), DACHDEA (ethyl) and DACHDPA (propyl)). The crystal structure of the nickel complex of DACHDEA reveals that the molecule is planar and the DACH ligand is in the boat form. In aqueous solution the spectrum of Ni(DACHDA) corresponds to an diaqua complex so the structure in solution is octahedral. However, the spectra of Ni(II) complexes with the dialkylated derivatives reveal an equilibrium between planar and five-coordinated species in solution.



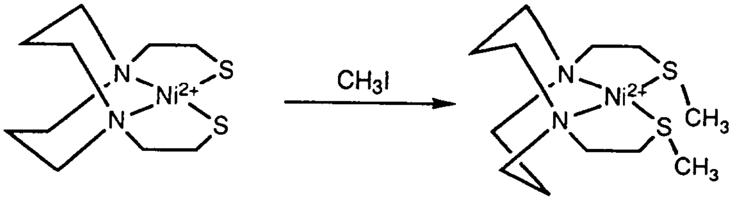
Phillip prepared derivatives of 1,4-DACH in which the pendant arms were substituted with two aminoethyl groups (DACHDEN) to give planar Cu(II), Ni(II) and Pd(II) complexes [21]. Billo [22(a)] prepared related derivatives in which the pendant arms are substituted with one ethylamine group (DACHEN) and two propylamine groups (DACHDPN). Co(II), Ni(II), Cu(II) and Zn(II) complexes of DACHDEN were prepared and their stability constants were determined [22(b)]. Only the Ni(II) and Cu(II) complexes of DACHEN were sufficiently stable for titration studies [22(b)]. The Cu(II) complex appears to be planar with a water molecule occupying the fourth site. The Ni(II) complex is octahedral with three coordinated water molecules but is converted to Ni(DACHEN)OH$^+$ at a pH of about 8.8, a value which is extremely low for the hydrolysis of a water molecule. Zn(II) and Co(II) complexes of DACHDEN are believed to be five coordinate by spectral and equilibrium measurements, whereas the Ni(II) complex is square planar. When DACHDPN is used as the ligand, the complex is predominantly square planar in aqueous solution (91%) but is in equilibrium with a five coordinated complex [22(a)]. The addition of an inert electrolyte such as $NaClO_4$ shifts the equilibrium more toward the planar form [22(a)]. The crystal structure of $Ni(DACHDPN)^{2+}$ was recently carried out and shows $Ni{-}NRH_2$ bond distances of 1.912(5) and 1.930(5) Å and $Ni{-}R_3$ bond distances of 1.919(5) and 1.938(5) Å [23].

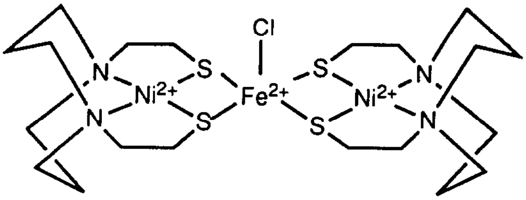


The incorporation of a 1,4-DACH ligand into several macrocycles has been carried out by Hancock et al. [24]. The structure of a representative Ni(II) complex is illustrated below. The 1,4-DACH ring is in the boat conformation with $Ni{-}NR_2H$ bond distances of 1.880(8) and 1.923(7) Å and $Ni{-}NR_3$ bond distances of 1.902(7) and 1.870(8) Å. Spectrally, it has been observed that the macrocycle with the primary amine substituent instead of a hydroxymethyl group exerts the highest ligand field known for any complex of Ni(II) with saturated rings. Thus, the presence of secondary and teriary amines in a complex with a low steric strain appears to lead to ligands having the highest ligand field strengths.

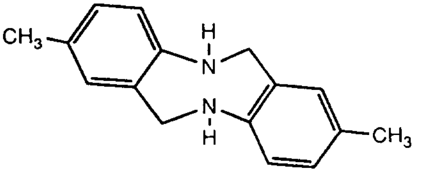


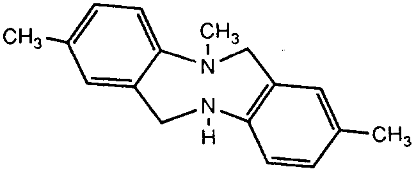
Recently, 1,5-DACO has been alkylated with ethylene sulfide to give a derivative with two pendant mercaptoethyl groups (BME-DACO) and then coordinated to Ni(II) [25]. These Ni(II) complexes may be prototypes for the active site in nickel-containing hydrogenases. The 1,5-DACO ring is predominantly in the unusual boat–boat conformation (75%) but there is some disorder to the chair–chair conformation (25%). Ni(BME-DACO) can be alkylated with methyl iodide to give the dithioether, $Ni(Me_2BME\text{-}DACO)I_2$. The structure of this derivative reveals that the 1,5-DACO rings are in the boat–chair conformation. Both methyl groups are on the same side of the nickel. In acetonitrile, conductance measurements suggest that the iodide is coordinated to the open face of the nickel. Treatment of Ni(BME-DACO) with $FeCl_2$ in acetonitrile gives a tetranuclear complex in which two Ni(BME-DACO) complexes are bonded to a square pyramidal iron(II) via chloride bridges [26]. Another unusual complex is formed when BME-DACO is treated with $Fe(acac)_3$ in toluene. The stoichiometry is $[(BME\text{-}DACO)Fe]_2$. The crystal structure shows that the iron is coordinated to the two nitrogens and the two sulfurs of the BME-DACO molecule and the fifth position is taken up by a sulfur atom of an adjacent molecule to give an Fe_2S_2 four-membered ring [26].



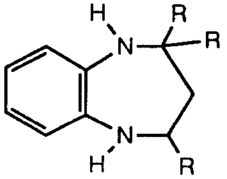


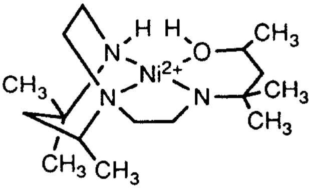
There are only a few other reported structures of complexes containing mesocyclic diamines. 5,6,11,12-Tetrahydro-2,8-dimethylphenhomazine(PHZ) is an eight-membered ring diamine in which two carbon atoms are part of a benzenoid ring system. *N*-Methyl-5,6,11,12-tetrahydro-2,8-dimethylphenhomazine(MPHZ) is its monomethyl derivative [27]. Complexes of Cu(II), Ni(II), and Zn(II), Pt(II) and Pt(IV) with both ligands have been prepared. In general, the stoichiometry of the PHZ complexes is $M(PHZ)_2X_2$ whereas the stoichiometry the MPHZ complexes is $M(MPHZ)X_2$ [28]. Cu(II) forms both mono and bis complexes with PHZ. $Cu(PHZ)_2^{2+}$ complexes are octahedral when nitrate or chloride are the anions but pentacoordinated when sulfate is the anion. Surprisingly, bis-complexes of MPHZ with the first row transition metals could not be prepared [28]. The crystal structure of $Ni(PHZ)_2(ClO_4)_2$ shows that it is planar with little apparent screening of the *z*-axis. However, no octahedral nickel(II) complexes were obtained, substantiating the suggestion that Ni(II) bis-complexes of mesocyclic diamines will be square planar [3].





Ni(II) and Cu(II) complexes of a 1,4-DACH derivative (1,5-benzodiazepine), have been prepared. Here, the dimethylene bridge is replaced by a benzene ring and some of the hydrogen atoms on the trimethylene group have been methylated [29]. The nickel bromide, iodide and perchlorate complexes are square planar, but the chloride complexes are pentacoordinated. The copper perchlorate salt of the trimethyl derivative is also planar but derivatives with fewer methyl substituents are five-coordinated. A more highly substituted derivative of 1,4-DACH has been prepared (4,4-dimethyl-7-(5,5,7-trimethyl-1,4-diazepan-1-yl)-5-azaheptan-2-ol(PYAZ)) and treated with nickel(II) perchlorate [30]. The complex is planar with three nitrogen atoms and one oxygen atom attached to the nickel. The 1,4-DACH ring adopts a boat conformation and the axial positions are not blocked.





(ii) Thermodynamics and kinetics

The stability constant of $[Ni(1,5\text{-}DACO)_2](ClO_4)_2$ was initially reported to be higher (pK = 18.7) [1] than the closely related bis-complexes of ethylenediamine (pK = 14.1), but a recent redetermination [23] of the constant (pK = 13.1) shows that it is slightly lower. The stability constant for $[Cu(1,5\text{-}DACO)_2](ClO_4)_2$ was found to be slightly lower than the corresponding complexes of ethylenediamine [1]. However, the absorption maximum of $[Cu(1,5\text{-}DACO)_2](ClO_4)_2$ is at a higher energy and intensity than ethylenediamine complexes, suggesting a very stable species. The stability constants of the corresponding 1,4-DACH complexes are lower than the 1,5-DACO complexes [10].

One of the first studies of the kinetics of substitution reactions of square planar Ni(II) was the reaction of the square planar $Ni(1,5\text{-}DACO)_2^{2+}$ complex with cyanide [31]. The reaction is relatively fast and there are few side reactions. The kinetics of the substitution reveal that the reaction with cyanide proceeds by an associative process to give an unstable ionic intermediate, $Ni(1,5\text{-}DACO)_2(CN)^+$, in the first step followed by the addition of a second cyanide to give an octahedral complex. Loss of one molecule of 1,5-DACO then gives a stable square planar intermediate, $Ni(1,5\text{-}DACO)(CN)_2$, which shows no tendency to disproportionate. Subsequent addition of cyanide finally gives $Ni(CN)_4^{2-}$. It should be emphasized that, even though the two 1,5-DACO molecules sterically block the z-axis in the solid state, reactions in solution proceed by an associative path.

The base-catalyzed hydrolysis of $Ni(1,5\text{-}DACO)_2^{2+}$ follows an associative path to give an unstable intermediate $Ni(1,5\text{-}DACO)_2OH^+$, which then collapses by loss of two 1,5-DACO molecules to give a hydroxo Ni(II) complex [32]. The rate of solvolysis of $Ni(1,5\text{-}DACO)_2^{2+}$ in acid solution is extremely slow and, in dilute acid, is independent of the acid concentration [31]. The reaction involves a weakening of a Ni—N bond followed by protonation and aquation which ultimately leads to cleavage of diprotonated 1,5-DACO.

Studies of the kinetics of the acid dissociation of $Cu(1,5\text{-}DACO)_2^{2+}$ also show that the rate is independent of the acid concentration but dependent on the concentration of $Cu(1,5\text{-}DACO)_2^{2+}$ [33]. At intermediate pH, the reaction proceeds as expected, by loss of one 1,5-DACO ligand and replacement by two water molecules to give the mono complex, $Cu(1,5\text{-}DACO)(H_2O)_2^+$. $Cu(1,5\text{-}DACO)_2^{2+}$ hydrolyzes at a rate which is about 5×10^4 faster than the Ni(II) complex. The difference in rate is attributed to the tetragonal distortion of the Cu(II) complex. The mono-complex, $Cu(1,5\text{-}DACO)^{2+}$, hydrolyzes about 7 times slower than the bis-complex. There also seems to be a specific carboxylate- and phosphate-catalyzed cleavage path which facilitates Cu—N bond cleavage. EDTA, as its carboxylate anion, also facilitates decomposition. The overall conclusion is that there are two independent paths; (1) a first-order, solvent-assisted dissociation of the complex and (2) a facilitation of the dissociation by added nucleophiles. Billo [31] also indicated an acetate dependence on the rate of the acid dissociation of the $Ni(1,5\text{-}DACO)_2^{2+}$ complex.

The kinetics of the acid hydrolysis of Ni(II) and Cu(II) complexes of 1,5-DACO, 1,4-DACH and a 1,4-DACH derivative, 5,5,7-trimethyl-1,4-diazacycloheptane (TMDZ), were re-examined and compared [34,35]. The relative reactivity is: $Ni(1,4\text{-}DACH)_2^{2+} > Ni(1,4\text{-}DACO)_2^{2+} \gg Ni(TMDZ)^{2+}$. The hydrolysis has both acid-independent and acid-dependent paths [32]. The Cu(II) complexes react faster than the Ni(II) complexes by a factor of 10^5, once again with the 1,4-DACH complex reacting the fastest. For Ni(II) the rate-determining step is the reaction of the bis-complex, while for Cu(II) the rate-determining step is the reaction of the mono-complex. Thus, both mono- and bis-complexes are seen with Cu(II), in contrast to Ni(II) where only the bis-complexes are observed. Although the rates for the meso-cyclic complexes are slow, they are faster than tetradentate macrocycles such as cyclam. The similarities in rates are attributed to the constrained nature of the ligand, which requires a concerted conformational change to cause cleavage of the Ni—N bond. The acid-independent rate occurs because this conformational change is rate-determining unless the acid concentration is very low. The conformational change is made more difficult to accomplish in TMDZ than in 1,4-DACH because of the extra methyl groups [34].

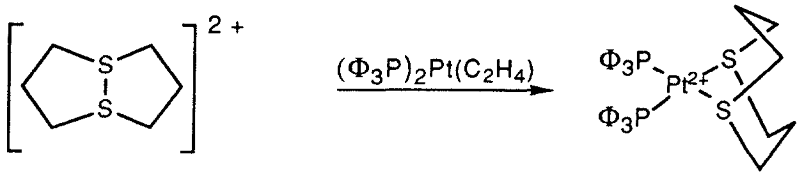
The stability constants for Ni(II) and Co(II) complexes of DACODA reveal that they are less stable than those of EDDA by 2–3 log units [36]. The rate law for the formation of the complexes is first order in DACODA, first order in metal ion and inverse first order in acid, which suggests that the reactive species may be

MOH^+ and $HDACODA^-$. The mechanism of the complexation reaction proceeds by a stepwise process in which the carboxylate first binds to the metal in a fast step followed by a slower step involving coordination of the nitrogen. The second-order rate constants are higher for DACODA than for other amine carboxylic acids. This is attributed to the fact that the amine group in DACODA is a stronger base than the amine group in EDDA [36]. The acid dissociation of DACODA complexes proceeds by both acid-independent and acid-dependent paths.

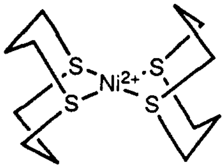
C. COORDINATION CHEMISTRY OF 1,4-DITHIACYCLOHEPTANE (1,4-DTCH), 1,5-DITHIACYCLOOCTANE (1,5-DTCO) AND THEIR DERIVATIVES

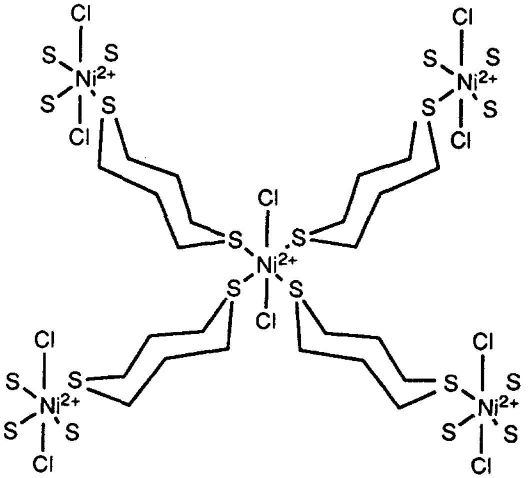
Although metal complexes of mesocyclic diamines and their derivatives have been examined most extensively, numerous studies have been carried out on the corresponding mesocyclic dithioethers 1,4-dithiacycloheptane (1,4-DTCH) and 1,5-dithiacyclooctane (1,5-DTCO).

Undoubtedly the most versatile of all the mesocyclic molecules is 1,5-DTCO. In addition to its use as a ligand, it can be oxidized to a cation radical and a dication having transannular sulfur–sulfur bonds [37]. I will not discuss the chemistry of these ions in detail, but it should be noted that the dication, $1,5\text{-DTCO}^{2+}$, undergoes an oxidative addition reaction [38] with ethylene-bis(triphenylphosphine)platinum (0) to give $Pt(\Phi_3P)_2(1,5\text{-DTCO})^{2+}$.



The following complexes of Ni(II) with 1,4-DTCH and 1,5-DTCO have been isolated and characterized fully: $[Ni(1,4\text{-DTCH})_2](BF_4)_2$, $[Ni(1,5\text{-DTCO})_2](BF_4)_2$, $[Ni(1,5\text{-DTCH})_2](ClO_4)_2$, $[Ni(1,5\text{-DTCO})_2](ClO_4)_2$ and $Ni(1,5\text{-DTCO})_2Cl_2$ [39]. The nickel complexes containing tetrafluoroborate and perchlorate anions are square planar whereas the crystal structure of $Ni(1,5\text{-DTCO})_2Cl_2$ shows that it is polymeric with bridging 1,5-DTCO molecules in the horizontal plane and the two chlorides perpendicular to the plane [40]. This is the only confirmed example of a complex where the mesocycle is bridging. The square planar complexes slowly dissociate in nitromethane as evidenced by a change in the spectra. The 1,4-DTCH complexes dissociate more rapidly than the 1,5-DTCO complexes. Bromides and iodides were also prepared, but it is difficult to assign exact structures to them based on analytical, spectral and magnetic data [39]. For example, the stoichiometry of the bromides is $Ni_2(\text{dithioether})_3\ Br_4$, so numerous structures could be formulated. Spectral data reveal that the bromides dissociate in nitromethane to give tetrahedral complexes with one coordinated dithioether and two bromines atoms. Three different iodide complexes were prepared ($Ni(1,4\text{-}DTCH)_2I_2$, $Ni(1,5\text{-}DTCO)I_2$ and $Ni(1,5\text{-}DTCO)_2I_2$), but no crystallographic information was obtained [39].

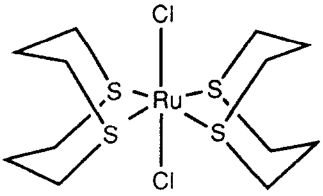




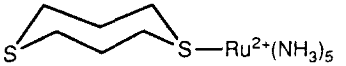
When 1,4-DTCH or 1,5-DTCO is treated with either $Cu(ClO_4)_2$ or $Cu(BF_4)_2$ in methanol, the Cu(II) is rapidly reduced and only the Cu(I) complexes, $[Cu(1,5\text{-}DTCO)_2]BF_4$, and $[Cu(1,4\text{-}DTCH)_2]BF_4$ are isolated [41]. No Cu(II) complexes could be prepared because they always underwent a rapid reduction to Cu(I) complexes. Further studies revealed that all dithioethers with either three or four methylene groups between the thioether sulfur atoms cause a rapid reduction of Cu(II) to Cu(I) when perchlorate of tetrafluoroborate salts are used [41]. The fate of the dithioether was not determined, but it is felt that it undergoes a one-electron oxidation to the cation radical which is destroyed by the solvent. Conversely, the reaction of $CuCl_2$ with 1,5-DTCO gives a chloride-bridged Cu(II) dimer and oxidation can be achieved only if the complex is refluxed in methanol. The product of this reaction is 1,5-DTCO sulfoxide [41]. Thus, the reaction of $CuCl_2$ with thioethers is thought to proceed by a direct two-electron oxidation.

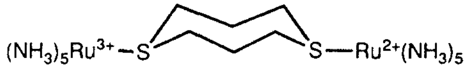
Co(II) and Rh(III) complexes of 1,5-DTCO have been prepared in acetonitrile [42]. Spectral and analytical evidence suggests that $[Co(1,5\text{-}DTCO)_2 \cdot CH_3CN](BF_4)_2$ is square pyramidal with one mole of acetonitrile bound to an axial position. Thus, the structure may resemble the $[Co(1,5\text{-}DACO)_2Cl]^+$ complex. $CoCl_2$ reacts with 1,5-DTCO to form a pentacoordinated complex with the empirical formula, $Co(1,5\text{-}DTCO)_2Cl_2$, which dissolves in nitromethane to give tetrahedral $Co(1,5\text{-}DTCO)Cl_2$. With larger metal ions, the axial positions are not as effectively blocked and additional ligands are easily coordinated to the metal. Thus, $RhCl_3$ reacts with 1,5-DTCO to give trans octahedral complexes with stoichiometry, $[Rh(1,5\text{-}DTCO)_2Cl_2]Cl$ [42].

An X-ray crystal structure confirmed the formation of an octahedral complex of 1,5-DTCO with $RuCl_2$ [43]. The four thioether groups lie in a plane with the two chlorine atoms perpendicular to the plane. The Ru–S bond distances are 2.352(1) and 2.345(1) Å and the Ru–Cl bond distance is 2.445(1) Å. The 1,5-DTCO molecule adopts the unusual boat–boat conformation to minimize interactions with the trans chlorides.

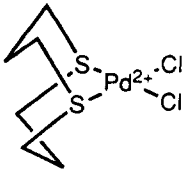


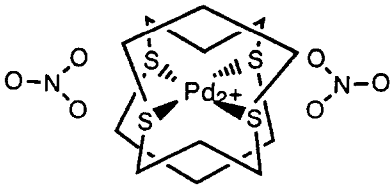
A monodentate 1,5-DTCO complex, $[(NH_3)_5Ru(1,5\text{-DTCO})]^{2+,3+}$ was prepared by Stein and Taube [44]. The redox characteristics of the Ru(II) complex and the spectral properties of the Ru(III) complex reveal an intramolecular interaction between the electron pair of the non-coordinated thioether and the coordinated thioether. The mixed valence bis-complex, $[(NH_3)_5Ru(1,5\text{-DTCO})Ru(NH_3)_5]^{5+}$, was also prepared and shows an intervalence transition between the two metal ions that is facilitated by the bridging thioether [44].



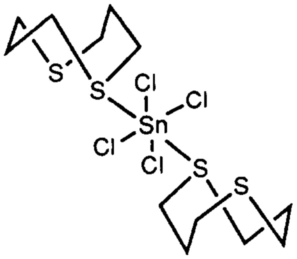


Recently, several Pd(II) and Pt(II) complexes of 1,5-DTCO have been prepared. The crystal structures of $Pd(1,5\text{-DTCO})Cl_2$ and $Pd(1,5\text{-DTCO})_2(NO_3)_2$ were determined, and the kinetics of ligand substitution reactions by 2,2′-bipyridine (bipy) and maleonitriledithiolate (mnt^{2-}) were investigated [45]. The mono complex of $PdCl_2$ with 1,5-DTCO is square planar with 1,5-DTCO in the boat–chair conformation. The Pd–S bond distances are 2.267(1) and 2.264(1) Å. In $Pd(1,5\text{-DTCO})_2(NO_3)_2$, 1,5-DTCO is in the boat–chair conformation, which is similar to that found in $Ni(1,5\text{-DACO})_2^{2+}$ and $Pd(TACO)_2^{2+}$ (TACO = 5-methyl-1-thia-5-azacyclooctane). However, the planes of the two nitrate ions are oriented perpendicular to the PdS_4 plane. The Pd–S bond distance is 2.321(1) Å and the Pd–O (nitrate) distance is 3.687(2) Å. The rate of the reaction of $Pd(1,5\text{-DTCO})_2^{2+}$ with bipy is second order overall and corresponds to an associative pathway. The negative entropy of activation (-32.2 cal K^{-1} mol^{-1}) supports this conclusion. The proposed mechanism involves an approach of the ligand toward the metal perpendicular to the PdS_4 plane to give a "pseudo-octahedral" activated complex which resembles the interaction of the nitrate ion with the Pd(II) in the crystal structure. The 1,5-DTCO molecule then leaves to give a stable mixed ligand complex, $Pd(1,5\text{-DTCO})(bipy)^{2+}$. The mixed ligand complex is stable because $Pd(bipy)_2^{2+}$ cannot assume a planar structure. The reaction of $Pd(1,5\text{-DTCO})_2^{2+}$ with mnt^{2-} is four orders of magnitude faster than with bipy and the reaction goes to completion to give $Pd(mnt)_2^{2-}$ [45].



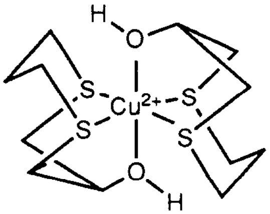


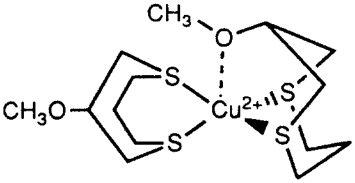
The only molecule which exhibits a non-bridging, monodentate 1,5-DTCO ligand is an octahedral tin(IV) complex with the stoichiometry $SnCl_4(1,5\text{-DTCO})_2$ [46]. The four chlorine atoms lie in a plane and the monodentate 1,5-DTCO molecules lie perpendicular to the plane. The mesocycle exists in the boat–chair form with an apparent interaction between the remote sulfur and the coordinated sulfur. The S···S distance is 3.271(3) Å and the Sn–S···S angle is 171.5(1)°. The crystal structure of a bis iodine complex of 1,5-DTCO has also been reported. There are two different molecules in the asymmetric unit; in one, the 1,5-DTCO molecule is in the chair–chair conformation while in the other is in the boat–chair conformation. The intramolecular S···S distances are 3.443(8) and 3.227(8) Å, respectively [46].



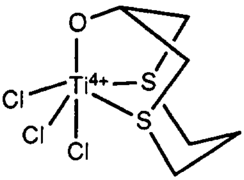
(i) 1,5-DTCO derivatives

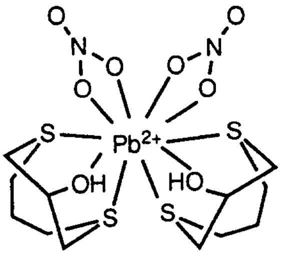
Since Jensen et al. [15] found that a substituent at the 3-position in 1,5-DACO gives a tridentate ligand that coordinates to Cu(II) in a facial manner, we decided to examine the coordination chemistry of 3-hydroxy-1,5-dithiacyclooctane (3-OH-1,5-DTCO) [41]. The results with $Cu(ClO_4)_2$ were most surprising because we were able to prepare a Cu(II) complex, $Cu(3\text{-OH-}1,5\text{-DTCO})_2(ClO_4)_2$, without any reduction to the Cu(I) complex [41]. As mentioned previously, we were unable to prepare Cu(II) complexes of 1,5-DTCO itself in the presence of perchlorate or tetrafluoroborate [41]. The crystal structure shows that the copper is coordinated to two tridentate 3-OH-1,5-DTCO ligands with the hydroxyl groups in trans positions. The Cu–S bond distances are 2.333(1) and 2.335(1) Å and the Cu–O bond distance is 2.350(1) Å. The OH groups are tilted 13.6° from the perpendicular to the $Cu–S_4$ plane and the rings are in the boat–chair conformation. A Cu(II) complex with only one coordinated 3-OH-1,5-DTCO molecule was observed in solution by the method of continuous variations. To account for the lack of reduction of the 3-OH-1,5-DTCO complexes, it was proposed that the mechanism for a one-electron reduction of Cu(II) requires a linear orientation of Cu—S···S bonds so that a dithioether cation radical can be formed. The coordination of the OH group to the Cu(II) prevents this alignment and therefore prevents reduction. When the OH group is converted to a methoxy group, reduction occurs more readily and both Cu(II) and Cu(I) complexes are obtained [47]. The structure of the Cu(II) complex of 3-OCH_3-1,5-DTCO is almost identical to the hydroxy complex with the OCH_3 group 10.5° off the perpendicular to the CuS_4 plane. The Cu(I) complex has a distorted-tetrahedral arrangement of the four sulfur atoms with an unusual long-range interaction between the oxygen of the methoxy group and the Cu(I). Although the oxygen atom could easily have folded away from the Cu(I), it folded toward it through one of the tetrahedral faces at a distance of 3.069(5) Å. The Cu—S bond distance trans to the oxygen is 0.04 Å longer than any of the other Cu—S bond distances. If the oxygen atom is included in the geometry, the Cu(I) is trigonal bipyramidal.



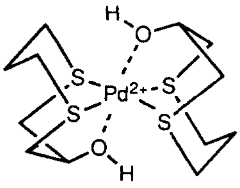


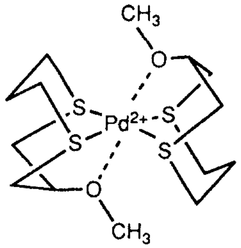
The crystal structures of complexes of Ni(II) and Fe(II) with 3-OH-1,5-DTCO all show that two molecules of the ligand are coordinated to the metal and the geometry of the complexes is quite similar to the Cu(II) complex [48]. In the Ni(II) complex, the Ni—S bond distances are 2.398(1) and 2.396(1) Å and the Ni—O distance is 2.046(3) Å. In the Fe(II) complex, the Fe—S bond distances are 2.565(1) and 2.514(1) Å and the Fe—O distance is 2.062(3) Å. 1,5-DTCO itself does not form complexes with the hard metals, Ti(IV) or Pb(II). However, when $TiCl_4$ and $Pb(NO_3)_2$ were treated with 3-OH-1,5-DTCO, a mono-complex is formed with $TiCl_4$ and a bis-complex with $Pb(NO_3)_2$ [49]. The titanium complex has the stoichiometry Ti(3-O-1,5-DTCO)Cl_3 where the OH proton has been lost. The complex is highly distorted from octahedral symmetry and is the first example of a crystal structure of a molecule having a Ti—thioether bond. The Ti—O bond is short (1.791(4) Å) and the Ti—S bonds are 2.595(1) and 2.607(2) Å, suggesting that the thioether group only reluctantly binds to the Ti(IV) atom. As expected, if one proceeds from right to left across the first row of transition metals, the length of the metal–oxygen bond decreases (Cu–O = 2.350(1) Å; Ti–O = 1.791(4) Å), while the length of the metal–thioether bond increases (Cu–S = 2.333(1) and 2.335(1) Å; Ti–S = 2.595(1) and 2.607(2) Å). The lead complex has the stoichiometry $Pb(3\text{-}OH\text{-}1,5\text{-}DTCO)_2(NO_3)_2$. Each 3-OH-1,5-DTCO is tridentate and each nitrate ion is bidentate, giving a ten-coordinated Pb(II) complex. Therefore, it appears that only the presence of the hard OH group causes the soft thioether groups to bind these hard metals.

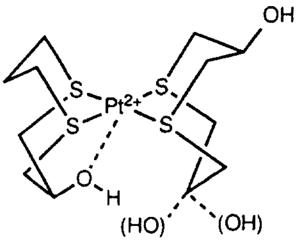




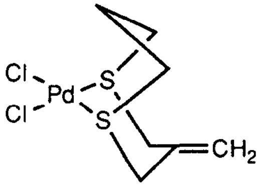
When 3-OH-1,5-DTCO is treated with *cis*-$Ru(DMSO)_4Cl_2$, an octahedral complex is formed with the stoichiometry $Ru(3\text{-}OH\text{-}1,5\text{-}DTCO)_2Cl_2$ [50]. The Ru–S bond distances are 2.339(1) and 2.336(1) Å and the Ru–O bond distance is 2.120(3) Å. The OH group lies about 8° from the perpendicular to the S_4 plane. When 3-OH-1,5-DTCO was treated with a d^8 metal, i.e. $PdCl_2$, we thought that a square planar complex would be formed with the OH group pointing away from the metal. However, when the crystal structure was determined, we discovered that the OH group had folded toward the Pd(II). Although the Pd–O distance is long (2.839(3) Å) and the Pd–O bond is 21° from the perpendicular to the S_4 plane, there appears to be some semi-coordination or electrostatic interaction which prevents the OH group from folding away from the Pd(II). Several additional complexes of Pd(II) and Pt(II) have now been prepared: the Pt(II) complex ($Pt(3\text{-}OH\text{-}1,5\text{-}DTCO)_2Cl_2$) and the methyl ethers ($Pd(3\text{-}OCH_3\text{-}1,5\text{-}DTCO)_2Cl_2$, and $Pd(3\text{-}OCH_3\text{-}1,5\text{-}DTCO)Cl_2$) [51]. In all these complexes at least one of the oxygen atoms folds over the axis. However, the oxygen atom in the methyl ethers is more displaced (about 30°) from the perpendicular than the oxygen atom in the alcohols. In the platinum complex, there is appreciable disorder in the OH groups. Although one OH group always folds over the axis, the OH group on the other 3-OH-1,5-DTCO molecule appears to have fractional occupancy in three of the four possible positions.



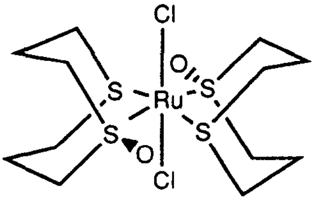




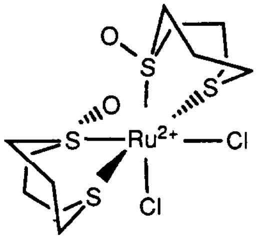
The only other reported example of a mesocyclic ligand having another functional group in the three position is 3-methylene-1,5-DTCO. The mesocycle was treated with $Pd(C_6H_5CN)_2Cl_2$ to give a product which has the stoichiometry, Pd(3-CH_2-1,5-DTCO)Cl_2. An X-ray crystal structure of this complex shows that the ring is in the boat–chair conformation with the methylene group pointing away from the palladium atom [52].



In bis-complexes of mesocyclic ligands, it was always observed that substituents on the four donor atoms lie in the plane of the metal and the four donor atoms. However, if only one of the heteroatoms in the mesocycle was substituted, the two substituents would rather occupy trans positions than cis positions so that they would not sterically interact with one another. This idea was the basis of the synthesis of an "all trans" octahedral Ru(II) complex in which thioether, sulfoxide and halide groups are all trans to each other [43]. It had been reported that this particular arrangement of donor atoms was the active species in the $RuCl_2$-catalyzed oxidation of thioethers to sulfoxides [53]. Although a number of ligands were tested prior to this work, none gave an "all trans" complex [53]. Thus, treatment of the monosubstituted dithioether (1,5-dithiacyclooctane 1-oxide (1,5-DTCO-O)) with *trans*-Ru(1,5-DTCO)$_2$Cl$_2$ gave *all trans*-Ru(1,5-DTCO-O)Cl$_2$ [2]. The "all trans" geometry was confirmed by an X-ray crystal structure. The bond distances are as follows: Ru—S = 2.359(4) Å, Ru—(SO) = 2.298(4) Å, and Ru—Cl = 2.413(4) Å. The rings are in the boat–boat conformation to minimize interactions with the axial chlorines. The complex dissociates in non-polar solvents so that it cannot be tested for catalytic activity. Another isomer was prepared by treatment of $RuCl_2$(tetrahydrothiophene)$_4$ with 1,5-DTCO-O. In this isomer, the two mesocyclic ligands did not lie in a plane but occupied cis positions: the thioether groups are trans and the chloride and sulfoxide groups are cis. The bond distances are as follows: Ru—S = 2.363(2) Å, Ru—(SO) = 2.239(3) Å, and Ru—Cl = 2.467(3) Å. The rings are in the boat–chair conformation. This is the first example of an octahedral complex where two mesocyclic ligands were found to occupy cis positions [43].



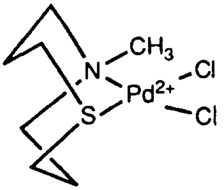
"all trans" isomer



cis isomer

D. COORDINATION CHEMISTRY OF 5-METHYL-1-THIA-5-AZACYCLOOCTANE (TACO)

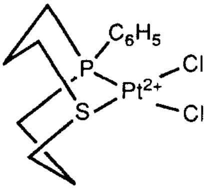
5-Methyl-1-thia-5-azacyclooctane (TACO) is not as readily synthesized as 1,5-DTCO and only palladium complexes have been prepared and characterized [54]. The crystal structure of Pd(TACO)Cl_2 reveals that TACO adopts a boat–chair conformation. The Pd—S bond distance is 2.268(1) Å and the Pd—N bond distance is 2.104(3) Å. Since the molecule is diamagnetic and does not dissociate in CH_2Cl_2, a detailed ^1H and ^{13}C NMR study was carried out. The 2DFT-J spectrum shows that the complex exhibits six coupled non-equivalent methylene hydrogens. The simulated spectrum confirmed the assignment of all the chemical shifts and the 15 coupling constants for the methylene protons. Based on these coupling constants, the conformation of Pd(TACO)Cl_2 in solution is consistent with an equilibrium between the two boat–chair conformers with little, if any, of the chair–chair form present. The crystal structure of the iodide complex is similar to the chloride. The Pd—S bond distance is 2.323(7) Å and the Pd—N bond distance is 2.14(2) Å.

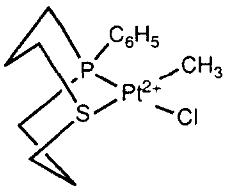


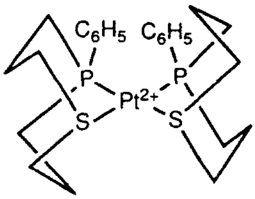
E. COORDINATION CHEMISTRY OF 5-PHENYL-1-THIA-5-PHOSPHACYCLOOCTANE (8-PS)

The eight-membered ring mesocycle with one sulfur and one phosphorus atom, 5-phenyl-1-thia-5-phosphacyclooctane (8-PS), has been prepared [55]. Four different

Pt(II) complexes of 8-PS were prepared and characterized by X-ray crystallography; the mono-complexes, Pt(8-PS)Cl_2 and Pt(8-PS)I_2, the bis-complex, *cis*-Pt(8-PS)$_2$(BF_4)$_2$, and a methylated complex, Pt(8-PS)(CH_3)Cl. The mono-methylation of the dichloride was carried out using Sn(CH_3)$_4$. No dimethylation was obtained even in the presence of excess Sn(CH_3)$_4$. The Pt—S bond distance trans to the methyl group (2.374(2) Å) is significantly lengthened relative to the Pt—S bond distances in Pt(8-PS)Cl_2 (2.258(2) Å) and Pt(8-PS)I_2 (2.280(8) Å). In the bis-complex, the phenyl groups on the phosphorus atoms of different ligands are oriented in a near parallel arrangement to each other and are about 3.36 Å apart. The mesocyclic rings are in the boat–chair conformation in all 8-PS complexes [55].



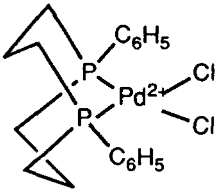


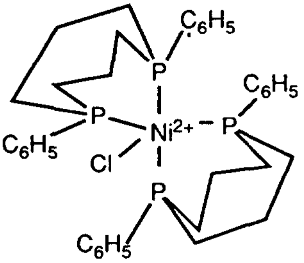


F. COORDINATION CHEMISTRY OF 1,5-DIPHENYL-1,5-DIPHOSPHACYCLOOCTANE (8-PP)

The cis and trans isomers of the mesocyclic diphosphine, 1,5-diphenyl-1,5-diphospha-cyclooctane (8-PP), were prepared and separated [56]. When the mixture of the isomers was treated with $PdCl_2(C_6H_5CN)_2$, only the cis form reacted to give a planar mono-complex, Pd(8-PP)Cl_2 [57]. The crystal structure shows that the rings are in the boat–chair conformation as usual but the middle carbon in the trimethylene group is disordered, indicating that there are two equivalent boat–chair conformers in the crystal lattice. The aromatic rings are essentially perpendicular to the P_2Cl_2 plane. The Pd—P bond distance is 2.234(4) Å and the Pd—Cl bond distance is 2.373(4) Å.

Treatment of 8-PP with $NiCl_2 \cdot 6H_2O$ gives a pentacoordinated complex having the stoichiometry [Ni(8-PP)$_2$Cl]Cl [57]. This molecule exhibits a distorted trigonal bipyramidal geometry with chlorine occupying an equatorial position. The rings in the Ni(II) complex are in the boat–chair conformation and the phenyl groups on the phosphorus atoms of different ligands are oriented in a near parallel arrangement to each other. This arrangement is similar to that observed in *cis*-Pt(8-PS)$_2$(BF_4)$_2$. The Ni—P bond distances are 2.202(4), 2.215(1), 2.228(2) and 2.237(1) Å and the Ni—Cl bond distance is 2.410(1) Å. This is the first example of the structure of a five-coordinated Ni(II) complex with a mesocyclic ligand and may be an alternative model for the proposed square pyramidal structure of the five-coordinated intermediates, (Ni(1,5-DACO)$_2$CN]$^+$ and (Ni(1,5-DACO)$_2$OH]$^+$, that were proposed during the kinetic studies of the reactions of Ni(1,5-DACO)$^{2+}$ [31,32].





G. CONCLUSIONS

Mesocyclic ligands occupy an important place between acyclic and macrocyclic ligands. Their advantage over both these systems is that they often provide a steric effect along with a strong ligand field effect. Appropriately substituted mesocycles may enhance the preorganization of the ligand, thereby facilitating complexation [24].

ACKNOWLEDGEMENTS

I wish to express my thanks to my former students and my colleagues who have worked with mesocyclic ligands. Their contributions are mentioned in the manuscript and their names are listed in the references. I appreciate their dedication and perseverence during the time they spent in my laboratory. I also wish to thank the National Science Foundation, the Petroleum Research Fund and the University of California, Davis for supporting much of this research.

REFERENCES

1 W.K. Musker and M.S. Hussain, Inorg. Chem., 5 (1966) 1416.
2 D.J. Royer, V.H. Schievelbein, A.R. Kalyanaraman and J.A. Bertrand, Inorg. Chim. Acta, 6 (1972) 307.
3 M.S. Hussain, J. Ahmad, M. Haque and G.D. Khattak, Transition Met. Chem., 11 (1986) 155.
4 J.C.A. Boeyens, C.C. Fox and R.D. Hancock, Inorg. Chim. Acta, 87 (1984) 1.
5 (a) N. Hoshino, Y. Fukuda, K. Sone, K. Tanaka and F. Marumo, Bull. Chem. Soc. Jpn., 62 (1989) 1822.
(b) S. Yamaki, Y. Fukuda and K. Sone, Chem. Lett., (1982) 269.
6 W.K. Musker and E.D. Steffen, Inorg. Chem., 13 (1974) 1951.
7 E.D. Steffen and E.D. Stevens, Inorg. Nucl. Chem. Lett., 9 (1973) 1011.
8 M.S. Hussain, Inorg. Chim. Acta, 69 (1983) 227.
9 G.D. Khattak and M.S. Hussain, J. Magn. Magn. Mater., 69 (1987) 263.
10 W.K. Musker and M.S. Hussain, Inorg. Chem., 8 (1969) 528.
11 W.K. Musker and M.S. Hussain, Inorg. Nucl. Chem. Lett., 3 (1967) 271.
12 M.S. Hussain and H. Hope, Acta Crystallogr. Sect. B, 25 (1969) 1866.
13 J.S. Hwang and S. Hussain, Transition Met. Chem., 12 (1987) 214.

14 (a) G.D. Khattak, M.S. Hussain, P.H. Keesom and L.E. Wenger, J. Magn. Magn. Mater., 75 (1988) 407.
(b) G.D. Khattak, M.S. Hussain, G.W. Hunter and L.E. Wenger, Phys. Status Solidi B, 130 (1985) 587.
15 W.P. Jensen, J.J. Worman and O.D. Filbey, J. Heterocycl. Chem., 9 (1972) 145.
16 D.F. Averill, J.I. Legg and D.L. Smith, Inorg. Chem., 11 (1972) 2344.
17 J.I. Legg, D.O. Nielson, D.L. Smith and M.L. Larson, J. Am. Chem. Soc., 90 (1968) 5030.
18 D.O. Nielson, M.L. Larsen, R.D. Willett and J.I. Legg, J. Am. Chem. Soc., 93 (1971) 5079.
19 K. Kanamori, W.E. Broderick, R.F. Jordan, R.D. Willett and J.I. Legg, J. Am. Chem. Soc., 108 (1986) 7122.
20 Y. Fukuda, H. Miyamae, K. Yamagata and K. Sone, Chem. Lett., (1984) 1309.
21 A.T. Phillip, Aust. J. Chem., 22 (1969) 259.
22 (a) E.J. Billo, Inorg. Nucl. Chem. Lett., 14 (1978) 501.
(b) B.N. Patel and E.J. Billo, Inorg. Nucl. Chem. Lett., 13 (1977) 335.
23 R.D. Hancock, M.P. Ngwenya, A. Evers, P.W. Wade, J.C.A. Boeyens and S.M. Dobson, Inorg. Chem., 29 (1990) 264.
24 R.D. Hancock, M.P. Ngwenya, P.W. Wade, J.C.A. Boeyens and S.M. Dobson, Inorg. Chim. Acta, 164 (1989) 73.
25 D.K. Mills, J.H. Reibenspies and M.Y. Darensbourg, Inorg. Chem., 29 (1990) 4364.
26 D.K. Mills, Y.M. Hsiao, P.J. Farmer, E.V. Atnip, J.H. Reibenspies and M.Y. Darensbourg, J. Am. Chem. Soc., 113 (1991) 1421.
27 M.S. Hussain, J. Chem. Soc. Dalton Trans., (1982) 2545.
28 M.S. Hussain and S. Rehman, Inorg. Chim. Acta, 60 (1982) 231.
29 P.W.W. Hunter and G.A. Webb, J. Chem. Soc. Dalton Trans. (1973) 26.
30 K.R. Morgan, G.J. Gainsford and N.F. Curtis, Aust. J. Chem., 36 (1983) 1341.
31 E.J. Billo, Inorg. Chem., 12 (1973) 2783.
32 R.W. Hay, M.P. Pujari and R. Bembi, Inorg. Chim. Acta, 85 (1984) 191.
33 B. Fecher and H. Elias, Inorg. Chim. Acta, 168 (1990) 179.
34 W. Collier, L.S. Curtis and N.F. Curtis, Aust. J. Chem., 42 (1989) 1611.
35 N.F. Curtis, Aust. J. Chem., 39 (1986) 239.
36 C. Chatterjee and T.A. Kaden, Helv. Chim. Acta, 58 (1975) 1881.
37 W.K. Musker, Acc. Chem. Res., 13 (1980) 200.
38 A.S. Hirschon and W.K. Musker, Transition Met. Chem., 5 (1980) 191.
39 W.K. Musker and N.L. Hill, Inorg. Chem., 11 (1972) 710.
40 N. Hill and H. Hope, Inorg. Chem., 13 (1974) 2079.
41 W.K. Musker, M.M. Olmstead and R.M. Kessler, Inorg. Chem., 23 (1984) 1764.
42 T.L. Wolford and W.K. Musker, Inorg. Chim. Acta, 182 (1991) 19.
43 B.W. Arbuckle, P.K. Bharadwaj and W.K. Musker, Inorg. Chem., 30 (1991) 440.
44 C.A. Stein and H. Taube, J. Am. Chem. Soc., 100 (1978) 1635.
45 C. Drexler, H. Paulus and H. Elias, Inorg. Chem., 30 (1991) 1297.
46 M.M. Olmstead, K.A. Williams and W.K. Musker, J. Am. Chem. Soc., 104 (1982) 5567.
47 W.K. Musker, M.M. Olmstead and R.M. Kessler, Inorg. Chem., 23 (1984) 3266.
48 M.M. Olmstead, W.K. Musker and R.M. Kessler, Acta Crystallogr. Sect. C, 40 (1984) 1172.
49 M.M. Olmstead, R.M. Kessler, H. Hope, M.D. Yanuck and W.K. Musker, Acta Crystallogr. Sect. C, 43 (1987) 1890.
50 B.W. Arbuckle, Ph.D. Thesis, University of California, Davis, 1991.
51 W.K. Musker, unpublished results.
52 L. Love, M.S. Thesis, University of California, Davis, 1985.
53 D.P. Riley and J.D. Oliver, Inorg. Chem., 25 (1986) 1814, 1821, 1825.

54 A.S. Hirschon, W.K. Musker, M.M. Olmstead and J.L. Dallas, Inorg. Chem., 20 (1981) 1702.
55 S.D. Toto, M.M. Olmstead, B.W. Arbuckle, P.K. Bharadwaj and W.K. Musker, Inorg. Chem., 29 (1990) 691.
56 S.D. Toto, B.W. Arbuckle, P.K. Bharadwaj, J.T. Doi and W.K. Musker, Phosphorus, Sulfur, Silicon Relat. Elem., 56 (1991) 27.
57 B.W. Arbuckle and W.K. Musker, Polyhedron, 10 (1991) 415.