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REACTIVITY OF OXIDIZED NICKEL(II) PnAO* QUASI-AROMATIC COMPLEXES

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ABSTRACT

The chemical and physical properties of a neutral nickel(II) complex ion containing a Ni,2N,3C quasi-aromatic ring are presented. Electrophilic substitution at the C12 position of the ring readily occurs producing highly stable compounds whose identity has been determined by single crystal X-ray diffraction. The ring is capable of conjugation with aromatic molecules giving substances with very high visible light absorption. The platinum(II) analogue has been prepared and shows similar reactivity.

A. INTRODUCTION

The reactivity toward electrophiles of several macrocyclic nickel(II) complexes having charge-delocalized six membered (Ni,2N,3C) chelate rings has been reported on several occasions [1-4]. In 1967 it was reported[5] that the (2,2,3,9,10,10-hexamethyl-5,7-dioxa-6-hydra-1,4,8,11-tetraazacyclotetradeca-3,8-diene)nickel(II) ion,[Ni(PnAO)-H)]$^{+}$,was easily oxidized in basic media to [Ni((PnAO)-6H)]^{o} a quasi-aromatic system of quite unusual properties. The uncharged (2,2,3,9,10,10-hexamethyl-5,7-dioxa-6-hydra-1,4,8,11-tetraazacyclotetradeca-3,8,11,13-tetraene) nickel(II),[Ni((PnAO)-6H]^{o} was easily prepared,highly stable and reacted with electrophiles predominately at the C-12 position[6]. Early on it was not found possible to obtain single crystals of the parent complex and thus X-ray crystal structures were conducted on the -NO [7] and -NO_2

*PnAO = [3,3'-(1,3-propanediamino)*bis*-(3-methyl-2-butanoneoxime)]

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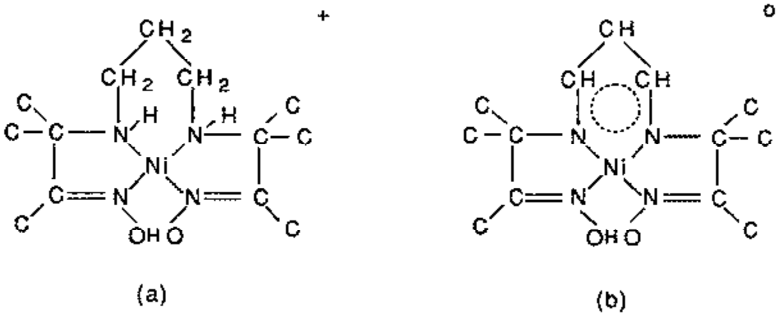
[8] derivatives. This established the planar nature of the ring and the extent and position of unsaturation. Studies have continued with emphasis on the reactivity of this electron rich benzene-like ring which has a high electron density on the C-12 position. Thus the ring behaves like that of phenol or an aromatic amine while the rest of the molecule is remarkably unreactive. Similar reactivity has been suggested for some other complexes and this property has been used for attachment of functional groups[9].

The purpose of this manuscript is to describe the present status of our studies on this molecule and to try to answer some of the questions which naturally arise about its reactivity,its potential usefulness and the generality of the concepts developed. It is intended to present mostly structural results on solid single crystals because of the conclusive nature of the findings and because at this stage of the study little thermodynamic,kinetic or mechanistic results are available. Most of the crystal structures which will be presented have not been published and thus are not generally available. It is hoped that these brief X-ray structural descriptions of structure solutions carried out at Missouri will provide an insight into potential applications of these molecules and stimulate interest in this general area of research.

The ligands are generally prepared by the reaction of an amine or diamine (1,3-diaminopropane) with a chlorooxime (3-chloro-3-methyl-2-butanoneoxime) in acetonitrile. At least three crystal structures have been completed AO,EnAO,PnAO [10,11,12]. The bond distances and angles are all normal in these stable well characterized ligands.

The ligands form thermodynamically stable planar and octahedral complexes with a variety of metal ions utilizing the amine and oxime nitrogens for bonding. Often in basic media both oxime nitrogen and oxygen are strongly coordinated leading to multinuclear ions. Nickel(II) with bi- or tetradentate α-amineoxime ligands invariably gives four-coordinate,singly charged,yellow,planar,diamagnetic ions containing a strong intramolecular hydrogen bond formed by the ionization of an oxime hydrogen (Figure 1a). The O-H-O grouping is generally unreactive in the pH region 3-11. The O-O bond distance is about 2.4 Å with the H atom often centered unless perturbed by unsymmetric intermolecular interactions and the OHO bond angle is about 175°. The nickel and four nitrogen atoms form a nearly perfect plane and there is very little tendency to add a fifth or sixth ligand. These complexes, utilizing aliphatic ligands, are moderately labile and, for instance, dissociate slowly in acidic media.

Oxidation of $[Ni(PnAO)-H]^{+1}$ (Figure 1a) in 1.0 M NaOH solution with a variety of agents (O_2 or $NaIO_3$ are best) gives one product, $[Ni(PnAO)-6H]^{\circ}$, in high yield with no discernible intermediates (Figure 1b). It has the same basic structure as the aliphatic complex but is zero charged and has the quasi-aromatic Ni,3C,2N ring. This ring is coplanar with the Ni,N_4 plane and in fact in most examples all non-hydrogen atoms in the molecule are basically coplanar except the *gem*-dimethyl carbons which lie above and below the plane. It has an orange color, is diamagnetic , is kinetically and thermodynamically more stable than the starting complex, contains a strong intramolecular hydrogen bond with essentially the same bond distances and angles as the parent and has almost no tendency to add additional ligands to the apex positions. The complex does not dissociate in acidic media but is reversibly protonated below pH=3 at the oxygens. Over long periods of time hydrolysis of the ligand takes place leading to condensation reactions. No reaction occurs with cyanide ion, even on boiling for one hour in an ethanol-water solution which points out the kinetic and/or thermodynamic stability of this species[6]. $[Ni(PnAO)-6H]^{\circ}$, (NioylH), exists in several crystal modifications depending on subtle modifications in crystallizing conditions (3 different structures have been observed[13]) and all give essentially the same molecular dimensions. Figure 2 gives a PLUTO drawing with the numbering system and the important bond distances and angles. Table 1 contains the distance of each atom from the average plane of the atoms listed. Clearly, except for the *gem*-dimethyl carbons, the molecule is exceptionally planar. The bond distances in the quasi-aromatic ring are shorter than the corresponding distances



(a) (b)

Figure 1

in the parent molecule indicating aromatic type character.

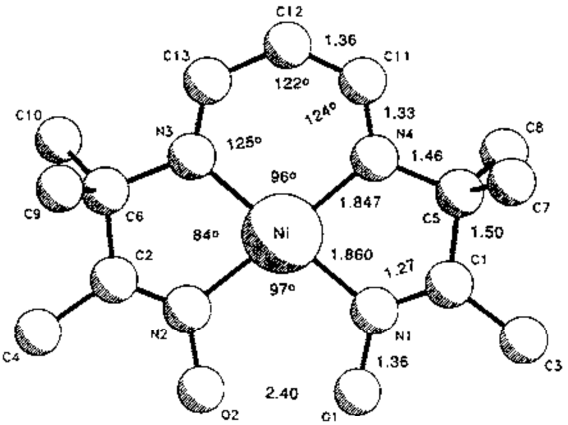


Figure 2. NioylH: distances in Å, angles in °.

Table 1. Least-squares planes in [Ni(PnAO)-6H]°

Plane 1	Ni	N1	N2	N3	N4	O1	O2
(deviation)	.009	-.044	.028	.013	.017	-.050	.028 Å

Other atoms C1,C2,C5,C6 (.066,-.017,.145,-.030)

Plane 2	Ni	N1	N2	C11	C12	C13
(deviation)	.134	.032	.057	-.086	-.032	-.106 Å

Dihedral angle plane 1/plane 2 =3.5°

Proton and ^{13}C NMR results on [Ni(PnAO)-6H]° are given in Table 2 where clearly the C12 and the attached hydrogens are in the ethylenic region whereas the C11 carbon and its protons are in the benzene region. The C11 protons give a doublet and the C12 a 1-2-1 triplet NMR signal as expected.

Table 2. NMR Chemical Shifts of NioylH(in D-DMSO/tms)

^{13}C/ppm	C1,2=161.4	C3,4=11.5	C5,6=69.4	C7,9=26.6
	C8,10=26.6	C11=147.7	C12=93.3	
^{1}H/ppm	C3,4=1.98s	C7,8,9,10=1.33s	C11=7.04d (J=6Hz)	C12= 5.07t (J=6Hz)
	Oxime H 19.10s			

The hydrogen in the intramolecular hydrogen bond is a sharp singlet shifted far downfield in the region of 18-19 ppm/tms in $CDCl_3$ or D_6-DMSO. Whereas the oxime-N to Ni bond is always shorter than the amine-N in the aliphatic complex, in the aromatic complex the amine-N to Ni bond changes and becomes the shorter of the two reflecting the partial multiple bond character of the metal ion-amine bond in the aromatic ring.

All nickel(II) complexes of aliphatic and aromatic PnAO ligands show one visible absorption band in the region of 4000Å with an ε of about 1-200 characteristic of the diamagnetic planar geometry and resulting from the $^1A_{1g} \rightarrow {}^1A_{2g}$ transition. When the quasi-aromatic ring is conjugated to another group, new intense bands appear in the lower visible energy region and the extinction coeffients often are in the region of 10^4.

EHMO computations have been performed on the quasi-aromatic ring in NioylH ([Ni(PnAO)-6H]^{o})[14]. They show a high charge density at C12 in agreement with the NMR carbon and hydrogen chemical shifts (Table 2) and with the C12 nucleophilic reactivity. The orbital overlap with the metal involves N-2p:Ni-4p mostly and N-2p:Ni-3dxz,dyz orbitals.

NET CHARGE C11 +0.115 C12 -0.239

As will be shown later the reaction characteristics of the C12 position depend on having the C11 positions unsubstituted and it is also important that the *gem*-dimethyl groups be present in the ligand.

B. REACTIONS OF [Ni(PnAO)-6H]^{o}

Rapid reaction occurs between a halogen (Cl_2,Br_2,I_2) in methanol to give [Ni(PnAO)-7H(X)]^{o} (Nioyl-X) by electrophilic substitution at C12 [6]. Catalytic amounts of $FeCl_3$ facilitate the reaction. The crystal structure of the chloro derivative shows it to be isomorphous with one form of the parent but with a slightly larger volume.

Nioyl-Cl:[[$NiClO_2N_4C_{13}H_{21}$: $P2_1/c$, 12.001(2),10.308(2)14.268 (3)Å, ß=114.3(3)°, Z=4, V=1608(1)Å^3 R=0.035, R_w=0.050]]

Reaction with nitrous acid either in methanol-water solutions or in biphasic CCl_4-water mixtures produces the green nitroso derivative (Nioyl-NO) in nearly quantitative yield. The nitroso group is nearly in the plane of the complex ion and bent making the C11 carbons and protons unequivalent and suggesting C_s symmetry[6]. The C12-N distance is short, 1.298Å as is the N-O distance, 1,245Å indicating multiple bonding and the C12-N-O angle is 117.9(2)°.

Nioyl-NO: [[$NiO_3N_5C_{13}H_{21}$: P2_1/c, 10.160(3),11.305(3), 14.053(3)Å, ß=107.9°, V=1536.3(3)Å^3, Z=4, R=0.039]]

Reaction with concentrated nitric acid in CCl_4 gives the nitro complex (Nioyl-NO_2) which is very similar in color and properties to the nitroso derivative[6]. The C12-NO_2 bond distance is 1.430(4) and the two identical N-O distances are 1.221(3) suggesting minimal multiple bonding of -NO_2 to the ring.

Nioyl-NO_2: [[$NiO_4N_5C_{13}H_{21}$: P2_1/a, 14.118(7),10.669(4), 10.542(4)Å,ß=103.70°(2),Z=4,V=1547.1(5)Å^3,R=0.063,R_w= 0.082]]

In acidic media the visible spectrum of NioylH reversibly shifts to lower energy as the molecule protonates. The crystal structure of the protonated perchlorate salt[15] shows that the intramolecular hydrogen bond is protonated but only weakening, not breaking, the existing hydrogen bond.

Nioyl-$HClO_4$: [[$NiClO_6N_4C_{13}H_{23}$: P2_1/c, 10.268(1),15.880(3), 11.452(2)Å, ß=96.55(1)°,Z=4,V=1855.2(9)Å^3,R=0.035, R_w=0.051]]

Over a longer period of time or at elevated temperatures a deep purple complex is quantitatively and irreversibly formed which can be isolated as crystalline salts with various anions including NO_3^- and ClO_4^-[15]. It has a strong visible absorption band at 5480 Å ; ε=5X10^4. From the crystal structure of the nitrate salt it has been found to be unexpectedly dimeric being coupled at the C12 position by a $(-CH-)_3$ grouping.

Nioyl-$(CH)_3$-Nioyl$^+$ $NO_3^-\cdot 2H_2O$: [[$Ni_2O_9N_9C_{29}H_{49}$: C2/c, 22.374(5), 11.459(2),14.573(6)Å, ß=101.25(3)°,Z=4, V=3664(3)Å^3,R=0.026, R_w=0.034]]

Each Nioyl- group is conjugated through the unsaturated three carbon chain to the other and all are in the same plane. The unsaturated C_3 chain arises from condensation of the two Nioyl groups with malondialdehyde in a two stage reaction. The dialdehyde was shown to be formed by an initial hydrolysis of a portion of the NioylH complex. The stages of the reaction as well as some kinetic values were determined with separately prepared malondialdehyde and with 2-methyl-malondialdehyde. The first stage of the reaction,and the slowest step is the first order hydrolysis leading to malondialdehyde. Both additions to the aldehyde follow second order kinetics and the first reaction is about ten times faster than the second. An ORTEP drawing of the +1 ion is given in Figure 3 with some bond angles and distances. The least-squares plane of the Ni,N1,N2,C11, C12,C13 atoms shows a deviation of any atom of less than 0.03Å and the dihedral angle between it and the related aromatic ring is 2.6°. The dihedral angle between the quasi· aromatic ring and the $-C_3$-bridging group plane is 8.4°. The bond distances in the bridging group are 1.411 and 1.388Å, which are shorter than single bonds(1.49 and 1.51), reflecting the conjugation between the complexes through the $-C_3-$ chain.

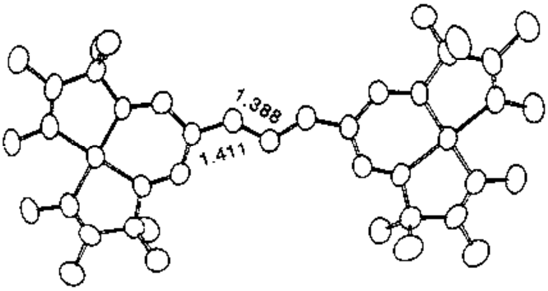


Figure 3. $[\text{Nioyl-(CH)}_3\text{-Nioyl}]^+ \ NO_3^-$: Å

The reaction of NioylH with the stoichiometric amount of formaldehyde [16] is also a two step reaction forming $(\text{Nioyl})_2CH_2$. The intermediate can be isolated in pure form but does not crystallize and is presumed to be a monomeric alcohol, $(\text{Nioyl})CH_2(OH)$ on the basis of IR, ^{1}H-NMR and mass spectroscopy. In 1/3 v/v $MeOH-H_2O$ the rates of both reactions were of second order, first order in NioylH and first order in either CH_2O or the intermediate. The rate constants at 25° were 0.055 and 8.52 $dm^3mol^{-1}s^{-1}$. Thus the reaction with the intermediate is about 150 times faster than with formaldehyde. With excess formaldehyde the intermediate is formed by reaction with $(Nioyl)_2CH_2$ with a second order rate constant of 0.025 $dm^3mol^{-1}s^{-1}$, comparable to the rate constant for the first step. The crystal structure of $(Nioyl)_2CH_2$ is in a preliminary report also containing ^1H and ^{13}C NMR values [17]. The complex subunits are highly planar with the dihedral angle between them being 77° while the Nioyl-CH_2-Nioyl bond angle is 113.5°. There is no evidence from the bond distances or angles of electronic interaction between the quasi-aromatic rings.

$(Nioyl)_2CH_2 \cdot CH_3CN$:[[$Ni_2O_4N_9C_{29}H_{47}$: $P2_12_12_1$, 8.241(3), 17.456(6),23.919(7)Å, Z=4, V=3441(2)$Å^3$,R=0.035,R_w=0.037]]

NioylH reacts rapidly with aromatic aldehydes in acidic acetonitrile-water solutions giving the analogous product to that with formaldehyde, $(Nioyl)_2CH(C_6H_5)$. Electronegative or positive substituents on the ring seem to have little effect (p-nitrobenzaldehyde derivative given, Figure 4.).

$(Nioyl)_2CH(p\text{-}(NO_2)C_6H_4)$: [{$Ni_2O_6N_9C_{33}H_{47}$:$P2_1/c$, 17.467(3), 11.670(8), 21.788(4)Å, ß=113.27(9)Å, Z= 4,V= 4075.(1)$Å^3$, R= 0.039, R_w=0.052}]

The structures always contain a tetrahedral central carbon with the metal-containing rings and the benzene ring staggered to reduce their interaction. These substances can be oxidized by a variety of agents including air by either one or two electrons per molecule as is discussed later.

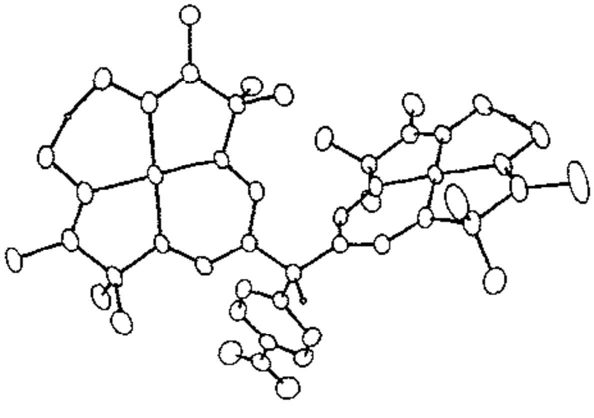


Figure 4. $(Nioyl)_2CH(p\text{-}NO_2\text{-}C_6H_4)$:

Reaction of NioylH with aromatic diazonium salts in acidic media results in attachment at the C12 position. This seems to be a very general reaction with nearly quantitative yields. The crystal structure of the derivative from nitrosated sulfanilic acid has been completed and an ORTEP drawing of the molecule is given in Figure 5.

Nioyl-N=N-($C_6H_4SO_3H$): [[$Ni_1S_1O_5N_6C_{19}H_{26}$: $P2_1/c$, 12.76(1), 10.76(1),16.60(1)Å, ß =92.48°(9)' Z=4, V=2281.(1)$Å^3$, R=0.036, R_W=0.040]]

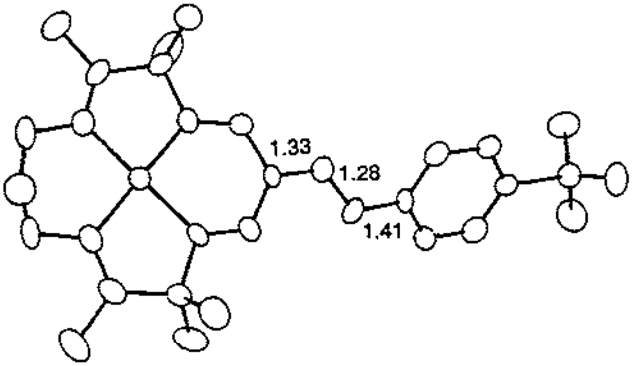


Figure 5. Nioyl-N=N-($C_6H_4SO_3H$): Å

The rings as well as the aza-nitrogens are in a single plane and from the shortening in the bond distances there appears to be conjugation between the two aromatic rings.

Reaction at room temperature with phenylisothiocyanate in CCl_4 yields the expected thioamide shown in [Figure 6].

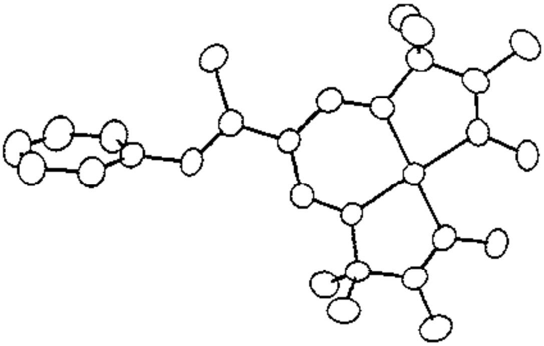


Figure 6. Nioyl-C(=S)-NH(C_6H_5):

Nioyl-C(=S)-NH(C_6H_5): [[$Ni_1S_1O_2N_5C_{20}H_{27}$: Pbca, 16.320(8) 16.150(9), 16.350(14)Å, Z=8, V=4309.(8)Å^3, R=0.030,R_w=0.037]]

Acetic anhydride in the presence of anhydrous $AlCl_3$ substitutes at the C12 position and gives the acetyl derivative. This has been characterized by ^{1}H-NMR and IR analyses [18] but crystalline material has yet to be obtained. The highly acidic catalyst causes some side reactions and makes purification more difficult than usual but it is noteworthy that the complex ion,with its hydrogen bond is able to survive this drastic treatment. The preparation of the benzoyl derivative has been accomplished in a less drastic oxidation reaction. (Nioyl)$_2$CH(C_6H_5) in acetonitrile was oxidized by dioxygen over a period of three weeks. The yellow-brown product(25% yield) was shown to be the C12-benzoyl derivative by X-ray diffraction analysis.

Nioyl-C(=O)(C_6H_5): [[$Ni_1O_3N_4C_{20}H_{26}$: Pca2$_1$, 14.81(3),15.28(2), 18.27(4)Å, Z=8, V=4124.(3)Å^3, R=0.057, R_w=0.087]]

It is likely that the reaction actually involves oxidation of the hydroxy intermediate Nioyl-C(OH)H(C_6H_5) formed reversibly by the hydrolysis of (Nioyl)$_2$CH(C_6H_5)

Attaching a benzene ring directly to the C12 position of Nioyl can be accomplished using an activated fluorobenzene. Thus reaction of 2,4-dinitrofluorobenzene with NioylH in nitromethane results in the loss of HF and attachment of the benzene ring to the C12 carbon. The benzene ring is nearly in the same plane as the Nioyl group and the deviation from planarity is likely due to the steric interference of the o-nitro group.

Nioyl-C_6H_3-2,4-(NO_2)$_2$: [[$Ni_1O_6N_6C_{19}H_{24}$: P1, 11.355(2), 11.988(4), 11.091(4)Å, 112.00(5), 108.02(5), 62.34(4)^o, Z=2, V=1222.9(12)Å^3, R=0.031, R_W=0.038]]

Numerous examples of charge-transfer complexes exist between aromatic hydrocarbons and planar *sym*-trinitro benzene or tetracyanoethylene. In an effort to see if such interaction exists with NioylH studies were conducted in the solvents CCl_4, $CHCl_3$ and CH_3CN. In all cases TNB,even in dilute (.01M) solution,produced a dramatic increase in light absorption in the visible region due presumably to the formation of complexes. Upon concentration, the complex crystallized and an X-ray structural determination showed the existence of an alternating array of planar molecules.

We expected the TNB to lie directly over the Nioyl aromatic ring but that was not quite the case. The drawing,Figure 7. shows that a nitro-oxygen actually is over the ring and we decided that perhaps this was due to the steric interaction of the *gem*-dimethyl groups of two adjacent Nioyl molecules. The distance between planes is 3.35Å. Thus efforts, given later, were made to produce the quasi-aromatic molecule without some or all of these methyl groups.

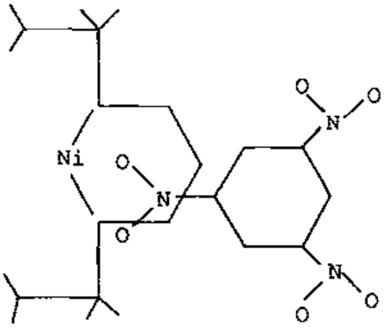


Figure 7. Nioyl·Trinitrobenzene

Nioyl·TNB: [[$Ni_1O_8N_7C_{19}H_{25}$: Pnam: 17.373(3), 20.192(5),6.702 (5)Å,Z=4,V=2351.(2)Å^3,R=0.042,R_w=0.047]]

With tetracyanoethylene Figure 8, a rapid charge-transfer color change occurs rapidly followed by a second reaction which produces the C12-substituted derivative shown in the equation. From this information it appears that the planar ring in NioylH is capable of pi-complexing and further more quantitative studies are warranted.

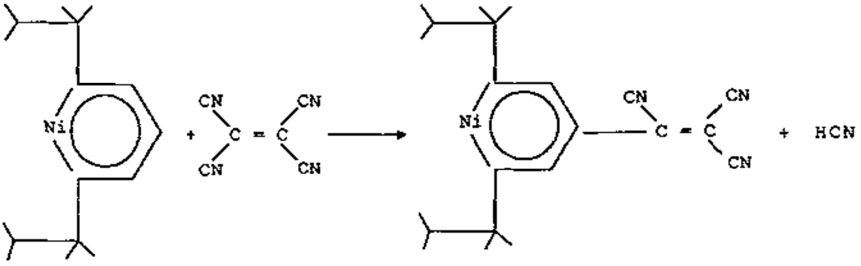


Figure 8. Reaction of tetracyanoethylene

Nioyl-C(CN)=C(CN)$_2$: [[$Ni_1O_2N_7C_{18}H_{21}$: Pna2$_1$, 7.646(4),12.458 (5), 20.352(6)Å, Z=4,V=1938.5(9)Å^3, R=0.035, R_w=0.044]]

Oxidation of NioylH in water solution either by air or electrochemically at a Pt electrode produces the dimer connected at the C12 positions. The yellow product has the usual Nioyl planar structure with no large changes in bond distances or angles from the parent. The planar groups are tilted (66.3°) to each other preventing conjugation.

(Nioyl)$_2$: [[$Ni_2O_4N_8C_{26}H_{42}$: P4$_2$2$_1$2, 12.205(5),12.205(4), 10.254(3)Å, Z=2 ,V=1527.(1)Å^3, R=0.024, R_w=0.029]]

While NioylH is stable in methanol-water solutions in the dark a slow reaction takes place in the presence of pyrex-filtered sunlight. Over a period of weeks a saturated 1-1 methanol-water solution of the complex deposits long needles of a new neutral complex. ^{1}H-NMR shows all of the peaks of NioylH except the triplet assigned to the C12 proton and there appears to be a very weak singlet in the aliphatic CH region. The X-ray crystal structure refined easily and gave for the molecular structure a trimeric complex, (Nioyl)$_3$CH. The same compound was obtained when ethyl or propyl alcohol water mixtures were used as the solvent. It is surprising that the carbon source can be varied without a change in the product. While this suggests certain possibilities for the sequence of reactions leading to the product nothing conclusive can be said at this time with the present state of knowledge. An ORTEP drawing is

(Nioyl)$_3$CH:[[$Ni_3O_6N_{12}C_{40}H_{64}$: P2$_1$/c, 20.540(4), 12.050(7), 23.164(5)Å, Z=4, V=5267(1)Å^3, R=0.061, R_w=0.058]]

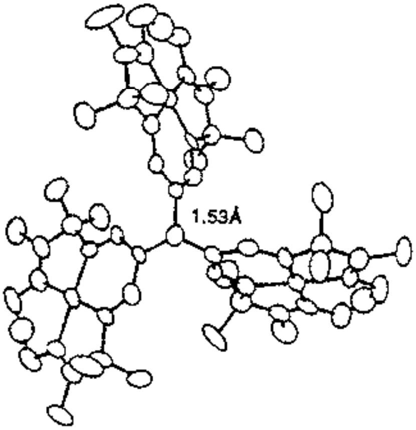


Figure 9. (Nioyl)$_3$CH:

given in Figure 9 which shows the essentially tetrahedral nature around the central carbon and the staggered arrangement of the three Nioyl groups. As expected from the normal planar nickel(II) spectra there is no significant interaction between the rings as verified by the normal single bond distances to the Nioyl groups.

C. REACTION OF DERIVATIVES

One aim of these studies was to prepare the C12 amine and carboxylic derivatives so they could be used in a variety of coupling reactions to give unique and potentially useful binuclear materials. It seemed reasonable to reduce either the nitro or nitroso derivative to the amine. Toward this end H_2 and activated Pd were used in methanol. Dihydrogen was taken up in roughly the correct amount by either the nitro or nitroso Nioyl and a faintly yellow solution was obtained which very quickly(few seconds) reacted completely with the oxygen in air to give an intensely purple salt. The same yellow intermediate and purple salt could be obtained using excess Zn and HCl solution for reduction. The purple salt was eventually crystallized from dilute perchloric acid solution and an X-ray crystal determination showed it to be a conjugated

$(\mathrm{Nioyl})_2N^+$ $ClO_4^-\cdot HClO_4\cdot 2.5CCl_4$: [[$Ni_2Cl_{12}O_{12}N_9C_{28.5}H_{43}$: C2/C,14.555(3), 26.283 (3), 25.728(3)Å, ß= 93.33(2)° ,Z=12, V=9826.(4)$Å^3$, R=0.052, R_w=0.059]]

dimer with a single nitrogen bridging the Nioyl groups. The other nitrogen appears in the products as ammonia or ammonium ion. Figure 10 gives an ORTEP drawing of this salt with some of the important bond angles and distances. The C12 to aza-nitrogen ,(N5) bond distance is relatively short at 1.33(1)(ave). The C12-N5-C12 angle is 124.6(1.2)°

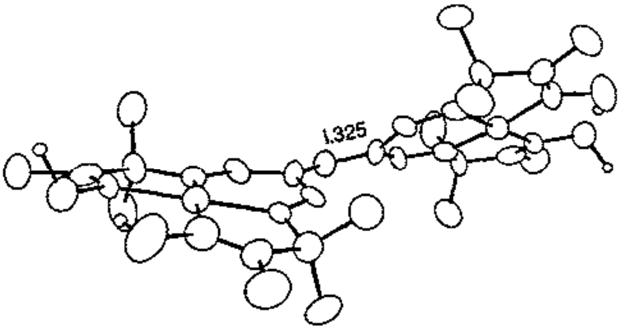


Figure 10. $(\mathrm{Nioyl})_2N^{+}$):Å

The purple binuclear aza complex can be reversibly reduced by 2 electrons in the absence of air using dithionite ion or electrochemically on a Pt electrode. The oxidation-reduction cycle can be repeated many times but there is a significant loss with each cycle. We have not been successful in isolating the reduced form of this dimer because of its extreme sensitivity to molecular oxygen. If the Nioyl-amine molecule ever is formed during the reduction of Nioyl-NO it condenses on itself or with an intermediate with the loss of one of the nitrogen atoms in forming the product. At this time we do not understand how or why this unexpected product is produced especially when the yield is almost theoretical.

In attempts to replace the nickel(II) ion in NioylH with copper(II) we equilibrated acetonitrile-water solutions of the parent with various copper salts and investigated the spectral changes. No significant changes occured over a period of several weeks. With all (Nioyl)$_2$CH(C_6H_4-X) complexes, new intensely red colored species were formed overnight and the ratio of Cu/complex varied between 1 and 2 depending on the nickel species used and on the conditions. Further investigation revealed that this reaction was not a metal ion replacement but rather an oxidation-reduction in which the Cu(II) was reduced to Cu(I) stabilized by complexation with acetonitrile. Further investigations using cyclic voltametry revealed the ease of oxidation of all (Nioyl)$_2$CH(C_6H_5-X) compounds that we have prepared. In Figure 11 three cyclic oxidations are shown in acetonitrile with a gold working electrode and tetrabutylammonium perchlorate electrolyte. It is clear that oxidation of NioylH and (Nioyl)$_2$CH$_2$ are not reversible. There is strong evidence that oxidation of NioylH by one electron leads predominately to Nioyl-Nioyl

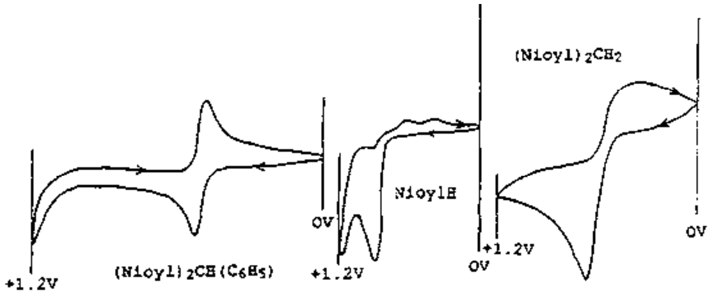


Figure 11. Cyclic Voltametry in Acetonitrile.

obtained previously by air oxidation. The product(s) of the second reaction is(are) not known. On the other hand a one electron oxidation of the third species is reversible at least over a short time span and thus may be isolatable. We were able to isolate and crystallize one example of this red oxidation product obtained by Cu(II) oxidation. The molecule is non-ionic,has both nickel's in the +2 oxidation state and is planar around the central carbon which attaches the three aromatic groups. It is a delocalized free radical stabilized by resonance in the rings. The hydrogen on that carbon has been removed. The bond distance to the Nioyl groups is shorter than expected for a single bond and there is conjugation between them but the bond to the substituted benzene ring is normal for a single bond.

$(\underline{\mathrm{Nioyl}})_2\underline{\mathrm{C}}(\underline{\mathrm{C}}_6\underline{\mathrm{H}}_5)$: [$\mathrm{Ni_2O_4N_8C_{33}H_{47}}$: $P\bar{1}$, 13.448(5), 13.595(4), 13.363(5)Å, 90.09(6), 97.42(6), 65.29(6)°, Z=4, V=2197.1(9)Å^3, R=0.095, R_w=0.127]]

In another example, an air oxidized sample of $(\mathrm{Nioyl})_2\mathrm{CH}(\mathrm{C_6H_4}(p\text{-}\mathrm{NO_2}))$ when treated with excess iodide ion gave a darkly colored salt which proved to be the two electron oxidation product of the parent molecule. In this case the I_3^- ion served as the counter ion formed by air oxidation of I^-. The three bonds around the central carbon atom are planar and the bond distances are very similar to those in the previous molecule. Resonance appears to occur between the two Nioyl groups with little interaction with

[$(\underline{\mathrm{Nioyl}})_2\underline{\mathrm{C}}(\underline{p\text{-}\mathrm{NO}}_2(\underline{\mathrm{C}}_6\underline{\mathrm{H}}_4)^+$] I_3^- :[[$\mathrm{Ni_2I_3O_6N_9C_{33}H_{46}}$: C2/c, 17.23(1), 18.34(2), 14.56(1)Å, ß =94.7(1)°, Z=4 ,V= 4589.(1)Å^3, R=.044, R_w=.047]]

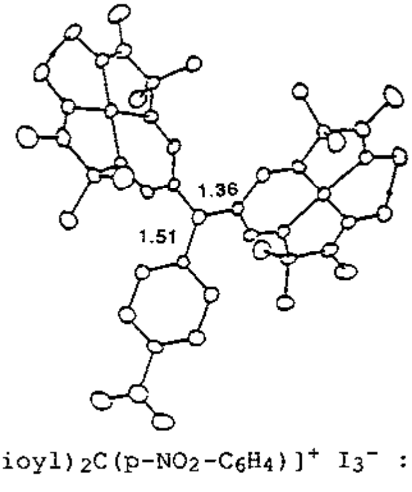


Figure 12. [$(\mathrm{Nioyl})_2\mathrm{C}(p\text{-}\mathrm{NO_2}\text{-}\mathrm{C_6H_4})]^+$ I_3^- : Å

the substituted benzene group. Figure 12 shows an ORTEP drawing of this ion.

We were interested in the bonding in the nitroso derivative of NioylH. In order to shed some light on this topic we investigated the protonation of the substituted complex. Crystals of the yellow perchlorate salt were not difficult to obtain from 1-4 M acid and analysis suggested strongly that they were singly protonated. A single crystal X-ray analysis established double protonation and the unit cell also contained a solvent water molecule. Washing of the solid before elemental analysis probably caused the loss of a molecule of the acid. The structure solution was well behaved and all the hydrogens were easily located by difference Fourier maps and their coordinates were included in the least-squares calculations. Protonation

(NioylNO)$\cdot$2(HClO$_4$)$_2\cdot$H$_2$O:[[Ni$_1$Cl$_2$O$_{12}$N$_5$C$_{13}$H$_{25}$: $\bar{P}1$, 7.30(1), 10.00(1),16.52(2)Å,95.53(4),91.04(3),106.32(3)$^{\circ}$,V=1156.(2) Å^3, Z=2, R=0.032, R$_w$=.045]]

took place on one of the oxime-oxygens which resulted in the original (hydrogen bond)-hydrogen being shifted toward the other oxygen but retaining its position between the two oxygens. This is exactly what was observed in the structure solutions for the protonated Nioyl$\cdot$HClO$_4$ and CH$_3$SO$_3$H salts. Thus the hydrogen bond is not broken by protonation but only distorted and weakened. The proton NMR no longer shows the far-downfield signal due to rapid exchange.

NioylH$\cdot$CH$_3$SO$_3$H: [[Ni$_1$S$_1$O$_5$N$_4$C$_{14}$H$_{26}$: Pbca, 10.98(2),16.77(6), 20.49(6)Å, Z=8,V=3787.(1)Å^3,R=.031, R$_w$=.052]]

Also as noted before the oxime O-N bond is lengthened (1.392 to 1.409Å) for the oxime group having the oxygen double-protonated.

In NioylNO$\cdot$2HClO$_4\cdot$H$_2$O the C12-N5-O3 bond angle is 117.8°, very similar to that angle in the unprotonated complex; while the angles around C12 sum to nearly 360° and the plane of the Nioyl entity is within 3° of the C12-N5-O3 plane. These results suggest that the protonated NO group is multiply bonded to the Nioyl ring. Figure 13 makes a comparison between bond distances in NioylH, NioylNO, (NioylH$_2$)$^+$, and (NioylH(NOH))$^{2+}$. The slight lengthening,0.01Å of the metal-imine bond on NO protonation is probably significant and reflects the conjugation of the NO group to the quasi-aromatic ring.

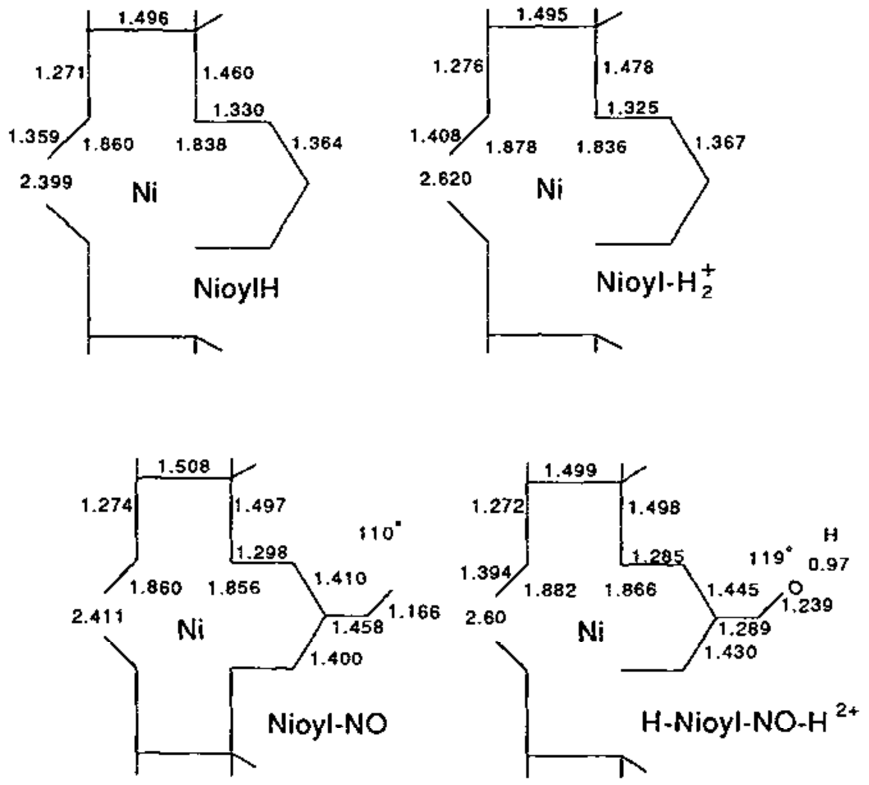


Figure 13. Bond Distances in Å.

We conclude that the protonation of Nioyl-NO at the oxime oxygen has little effect on the molecule except for predictable changes on the oxime O and N bond distances while protonation of the -NO group occurs on the oxygen and electron density is shifted from the electron-rich ring through C12 giving essentially double bond character to the C12-N5 bond,and more nearly single bond lengths from C12 to C11 and C13. A problem does arise however in that the NO bond remains quite short (1.239Å) and it would be expected to lengthen when the NO oxygen is protonated. AM1 calculations (19) using nitrosobenzene as a model result in bond distances and angles which are quite similar to those found in protonated Nioyl-NO. In reality after being protonated the nitroso derivative has bond distances and angles quite similar to a substituted hydroxylamine.

D. Other Metal Ions; Cu(II), Pd(II), Au(III), Pt(II).

From the beginning a major goal of this study has been to extend the potential uses of these substances by utilizing other metal ions. Obviously metal ions which usually assume planar or distorted planar configurations were the initial choice. While these studies are far from complete each of the methods has been tried usually on all of the metals listed above but with little success.

a. Direct replacement.

The extended (approx.2 months) reaction of NioylH in acetonitrile, acetonitrile-water mixtures or nitromethane with a soluble aquated-Cu(II), partially aquated $PdCl_4^{-2}$, $AuCl_4^-$, or partially aquated $PtCl_4^{-2}$ has produced no visible spectral changes or ^1H-NMR results which could be attributed to the substitution of one metal for the Ni in NioylH. This must be due to extemely slow rates of reaction because all of the metal ions listed are expected to have larger formation constants for the ligand than does Ni(II).

b. From free ligand.

We have not been successful in reacting 3-methyl,3-amino-2-butanone oxime with malondialdehyde to get the desired ligand. The dialdehyde appears to be too unstable for this condensation. Even in the presence of the metal ion in a template type reaction NioylH has not been produced. Attempts to free the ligand from Ni(II) with reagents such as CN^- have not met with success either because of lack of reaction with the replacement ligand or, at elevated temperatures, other reactions appear to take place.

c. Oxidation of the aliphatic complex.

Reaction of PnAO with Cu(II), $PdCl_4^{-2}$ or $PtCl_4^{-2}$ produces in good yield the corresponding aliphatic complex ion. In these three cases the complexes have been isolated and characterized by several methods and they have structures exactly analogous to $[Ni(PnAO)-H]^+$. The Au(III) complex is more difficult to prepare due to reduction by the ligand or by impurities present in it which gives Au(I) and ultimately the metal. However impure samples of $[Au(PnAO)-H]^{+2}$ are believed to have been prepared which have been subjected to oxidation. Only with platinum have we been able to prepare the quasi-aromatic complex. We have been extremely surprised that even after repeated trials it has not been possible to oxidize the palladium analogue with either dioxygen or sodium iodate. We have no explanation for this. Oxidation to PtoylH was recently accomplished in 1.0M NaOH solution with excess $NaIO_3$. The reaction is somewhat erratic in that it is usually rapid but other times slow and then may require heating. In spite of this abnormal behavior the product yield is good (>70%) and the purity high. The yellow complex is somewhat sensitive to light when in solution and even in the solid state darkens slowly with exposure to sunlight. This is not a serious problem however. The ^{1}H-NMR that given below is exactly analogous with NioylH except for the isotope splitting effect caused by 34% ^{195}Pt isotope. The X-ray structure has been completed and the molecule has almost identical structural parameters to NioylH with only a few slightly larger bond distances. Selected bond distances are compared in Figure 14.

<u>NMR: ^{1}H Chemical Shifts of PtoylH(in D-$CHCl_3$/tms) in ppm.</u>

C3/4=2.07s   C7/8/9/10=1.44s   C11/13=7.50d (J=6.6Hz)   C12=5.12t (J=6.5Hz)
Oxime-H=18.5s (Pt195 J=35.2Hz on C11/13 H's only).

<u>PtoylH</u> : [[$Pt_1O_2N_4C_{13}H_{22}$: $P2_1/c$, 21.975(10),9.665(5), 14.885(5)Å, ß=93.26(3)°, Z=4(2 molecules), V=3156.3(8)Å^3, R=0.029,R_w=0.039]]

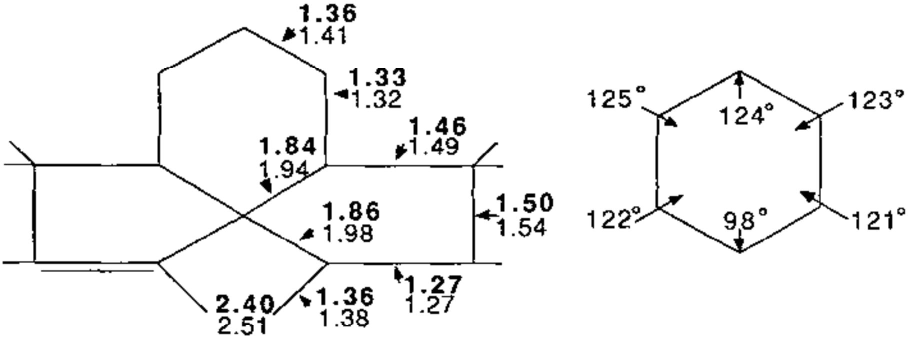


Figure 14. Bond distance and angle comparison NioylH (upper), PtoylH (lower)

d. Reactions of PtoylH.

At this point in the investigation only a few reactions of this macrocycle have been tried. In all cases it appears that the reactions give the same products as with the Ni(II) analogue. For instance, with I_2 in acetonitrile a deep green iodide is immediately formed which after treatment with ammonia to remove the acid formed turns yellow and gives a ^1H NMR almost exactly the same as the parent with the exception that the C12-proton signal is missing. This is expected for Ptoyl-I with substitution at the C12 position. The X-ray structure established that C12 substitution with iodine takes place.

Ptoyl-I: [[$Pt_1I_1O_2N_4C_{13}H_{21}$: $P2_1/c$, 12.025(5), 10.662(4), 14.487 (7)Å, ß=114.7(5)°, Z=4, V=1687.2(7)$Å^3$, R=0.057, R_w=0.087]]

Reactions with CH_2O and C_6H_5CHO give products which have the properties expected for those analogous to the NioylH reaction. The diazonium salt of sulfanilic acid produces a product with the properties expected and acid hydrolysis gives the same intensely purple colored substance which is also produced with malondialdehyde. While only one crystal structure on a derivative has been completed all indications are that PtoylH reacts in the same manner as NioylH and probably will have as rich a chemistry.

E. Aromatization With Related Ligands.

The *gem*-dimethyl groups in Nioyl always are above and below the plane of the molecule and interfere with close approach of another molecule on the plane face. Such was judged to be the problem with obtaining correct positioning of trinitrobenzene with Nioyl in the adduct as mentioned earlier. To partly alleviate this problem attempts have been made to oxidize the nickel(II) complex of PnAO which has one *gem*-methyl group on each side removed. The aliphatic complex of this ligand, $[Ni(PnAO-H)(-2CH_3)]^+$, is shown in Figure 15 and it has the *meso*-configuration.

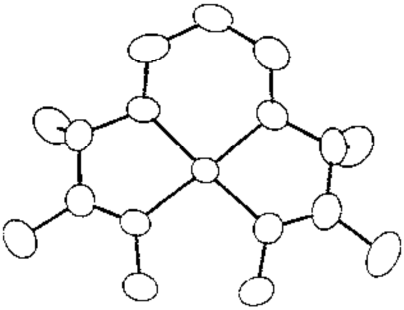


Figure 15. $[Ni(PnAO-H)(-2CH_3)]^+$

(2,3,9,10-tetramethyl-5,7-dioxa-6-hydra-1,4,8,11-tetraazacyclotetradeca-3,8-diene)nickel(II) perchlorate : [[$Ni_1Cl_1O_6N_4C_{11}H_{23}$: $P2_12_12_1$, 6.300(8),11.340(12), 22.01(15), Z=4, V=1655.3(8), R=0.036, R_w=0.052]]

All attempts to oxidize this complex with either dioxygen or $NaIO_3$ in basic solution have been unsuccessful. Other techniques are being tried but the results are disappointing and it appears that only certain molecules with special electronic characteristics give rise to stable quasi-aromatic metal containing rings.

F. Summary and Problems.

In this brief review we have attempted to present some of the properties of NioylH and a number of reactions which are characteristic of it. It does appear that it has some unique characteristics which may be used to design novel molecules. The two reactive sites are the intramolecular hydrogen bond which is sensitive to strong acids and bases but which appears in most cases to enter into reversible (over a short time) reactions and the C12 position which is highly electronegative and whose hydrogen is easily substituted for by a electrophilic reagent. Many of the reactions cited give the anticipated products but in nearly an equal number of cases the product obtained was unexpected and in these cases no reaction sequence can be defended. It has been established that at least one other metal ion, Pt(II) can generate a molecule of this type and that it has the same general reactivity as the parent. Thus there is added reason to believe that others exist and that this area is much broader than at first indicated.

Further study in this area of chemistry is necessary and to facilitate this a manuscript covering the preparation of the Quasi-aromatic complexes from easily available inexpensive reagents is being submited to Inorganic Synthesis.

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12. M.S.Hussain,MazHar-ul-Haque and Jamil Ahmad Acta Cryst.C40 (1984) 813.
13. In this paper brief X-ray structure descriptions are given enclosed in double brackets primarily for identification purposes.
    a. [[$NiO_2N_4C_{13}H_{22}$ $P2_1/c$ 10.659(3),10.097(4),15.018(5)Å, ß=101.96(2)^{o},V=1581(1)Å^3,Z=4,R=.040,R_w=.047]][Ref.15]
    b. [[$NiO_2N_4C_{13}H_{22}$; $P2_1/c$, 31.778(4),9.902(3),14.932(3)Å, ß=91.97(1)^{o}, Z=12,V=4695(1)Å^3 R=.078, R_w=.086]]
    c. [[$NiO_2N_4C_{13}H_{22}$: Pbcn, 9.892(4),14.920(4),31.507(25)Å, Z=12,V=4650.3(9)Å^3, R=.057, R_w=.085]]
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