

Synthesis and Complexes of Unsymmetrical Multidentate Ligands. Part III. Quadridentate Ligands

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Received October 27, 1979

The synthesis and characterization of some new highly unsymmetrical quadridentates and their metal complexes are reported. The ligands are obtained by the stepwise condensation of: (A) one molecule of phenylhydrazine with one molecule of glyoxal, followed by a molecule of *o*-phenylenediamine, and then a molecule of salicylaldehyde in the presence of Ni(II) ion; (B) one molecule of *o*-aminobenzaldehyde with one of 2-pyridylhydrazine, followed by a molecule of salicylaldehyde; (C) one molecule of *o*-aminobenzaldehyde with one of *o*-phenylenediamine, followed by one of salicylaldehyde in the presence of Ni(II) ions. Mass spectral analysis has been used to establish the existence of these highly unsymmetrical ligands.

Discussion

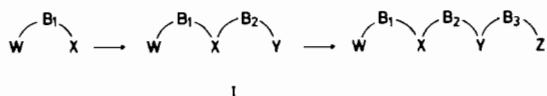
Previous papers have described the preparation and metal complexes of some unsymmetrical:

(i) bidentate ligands obtained, by a single Schiff base condensation [1], and

(ii) tridentates prepared by a further similar reaction upon such bidentate ligands [2].

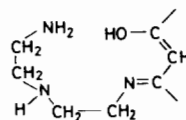
This paper is the first of a series dealing with the synthesis and chemistry of a number of unsymmetrical quadridentate ligands prepared by successive Schiff base reactions.

Much of the interest in linear quadridentates has centred upon ligands of structure (I), in which



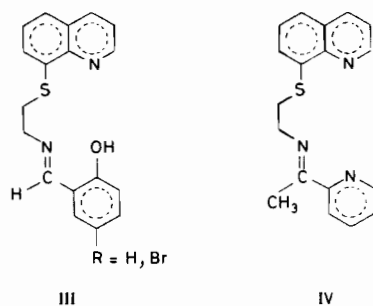
either $B_1 = B_2 = B_3$ or $B_1 = B_3 \neq B_2$ (where B_1 , B_2 and B_3 represents chains linking the donor atoms W, X, Y, and Z), and there appears to have been a lack of study of quadridentate ligands systematically built up where the bridging groups B_1 , B_2 , B_3 are different in character with the donor centres being either identical or different. However, Kuska and co-workers [3] have reported in a study of bonding in copper(II) complexes of low symmetry, the synthesis of copper(II) complexes of unsymmetrical ligands which fit structure (I) and which have $B_1 \neq B_2 \neq B_3$ and $W = Z$ and $X = Y$. The unsymmetrical ligands were not isolated as such, but rather their copper(II) complexes were separated from the product obtained when acetylacetonone, a copper(II) salt and ethylenediamine were reacted with salicylaldehyde, *o*-hydroxyacetophenone, *o*-hydroxypropionophenone and *o*-hydroxybutrophenone respectively.

Wallis and Cummins [4] in a study of unsymmetrical quadridentate Schiff base ligands have prepared nickel(II) and copper(II) complexes of ligands of type (II) either by direct synthesis from singly condensed Schiff base ligand salts or by metal ion induced, partial hydrolysis of doubly condensed quinquedentate Schiff base ligands.



Although few examples exist where unsymmetrical linear quadridentates have been synthesised from a stepwise sequence of Schiff base condensations of the type shown above to produce structure (I), Black and McLean [5] have reported the stepwise generation of quadridentate ligands such as (III) and (IV).

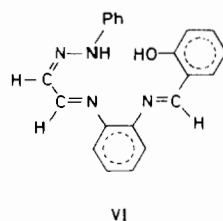
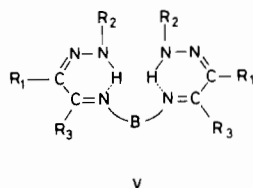
*Author to whom correspondence should be addressed. Unfortunately reprints are not available.



No complexes of (III) were isolated when the ligands were treated with ethanolic or aqueous solutions of Fe(II), Co(II) or Ni(II) chlorides or perchlorates, although a Cu(II) perchlorate compound was obtained.

In this work we report on the preparation of quadridentates derived from, firstly glyoxal mono-phenylhydrazone, and secondly *o*-aminobenzaldehyde.

Symmetrical ligands of type (V)

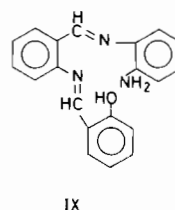
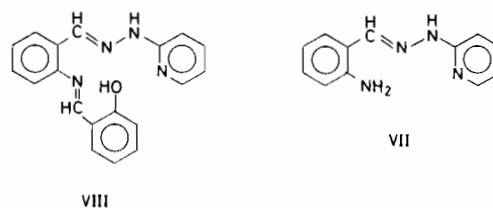


$R_1 = \text{Ac}; \text{Bz}; \text{CN}$
 $R_2 = \text{Aryl}$
 $R_3 = \text{Me}; \text{Ph}$
 $B = -(\text{CH}_2)_n-$; $n = 2, 3, 4, 5, 6$.

have been prepared by Hirsch and coworkers by the action of diazonium salts on bis-imines containing an active methylene group. We have prepared quadridentates of this type in which $B = -(\text{CH}_2)_n-$ ($n = 2$ or 3); $B = o$ -subst. benzene ring; $B = 1, 2$ -subst. cyclohexane ring, by the alternative method of the condensation of two molecules of glyoxalmono-phenylhydrazone and one molecule of the required diamine. Some Ni(II) and Cu(II) complexes of the ligands were prepared analytically pure and found to possess the general formula $[\text{M}(\text{L} - 2\text{H})]$ (where $\text{L} - 2\text{H} =$ doubly deprotonated quadridentate). The copper complexes possess normal magnetic moments.

while the nickel compounds are diamagnetic, and have been shown by an X-ray crystallographic study to have a distorted square planar arrangement of the four nitrogen donor atoms. The actual donors used are the iminic nitrogen atoms from each hydrazine residue and the azomethine nitrogens provided by the bridging system of the ligands.

The unsymmetrical quadridentate of structure (VI), developed from glyoxal mono-phenylhydrazone by condensation with *o*-phenylenediamine followed by further reaction of the product with salicylaldehyde, has been isolated only in the form of its nickel(II) complex. As described earlier [2], attempts to condense glyoxal-(2-aminophenyl)-anil-(1)-phenylhydrazone-(2) with further carbonyl containing compounds led to a breakdown of the ligand system to yield symmetrical quadridentates. The presence of the nickel atom appears to stabilise the highly unsymmetrical ligand, which decomposes upon attempts to remove the metal.



o-aminobenzaldehyde has proved an excellent starting material for the preparation of unsymmetrical quadridentate ligands. As previously noted [2], the condensation product of this material with 2-pyridylhydrazone yields the tridentate (VII), which can be further condensed with a molecule of salicylaldehyde to give the quadridentate ligand (VIII). A similar quadridentate, (IX) has also been obtained as its nickel(II) complex. This latter ligand has the 2-pyridylhydrazone of (VIII) replaced by *o*-phenylenediamine, and possesses a primary amine capable of further condensation to yield a quinque-dentate ligand [9].

The infrared spectrum of (VII) exhibits two bands in the region $3200-3400 \text{ cm}^{-1}$, at 3360 cm^{-1} sharp and intense, and at 3260 cm^{-1} , a much weaker band. These two bands are assigned to the primary amine stretches, on the basis that they are absent in the spectrum of (VIII) where the amine group has been lost due to the condensation with salicylaldehyde.

TABLE I. ^1H n.m.r. of Ligands (VII) and (VIII).*

Compound	Solvent	-CH=N-	-NH ₂ **	-NH-	-OH
(VII)	(CD ₃) ₂ SO	8.22(SI)	6.62(S)	10.60(SI)	-
(VII)	(CD ₃) ₂ SO + D ₂ O	8.22(S)			-
(VIII)	(CD ₃) ₂ SO	8.44(SI)	-	10.84(SI)	12.24(SI)
		8.84(SI)			
(VIII)	(CD ₃) ₂ SO + D ₂ O	8.44(SI)	-		
		8.84(SI)			

*TMS internal reference [δ values]. The figure given in parentheses after the multiplicity is the relative intensity of the resonance.

**Due to the proximity of this resonance to the aromatic region (δ 8-6) no reliable integrated intensity data are available.

A relatively intense band at 3190 cm^{-1} in the spectrum of (VII), and at 3200 cm^{-1} in the spectrum of (VIII) is assigned to the amine stretch of the hydrazone residue, on the basis that no band exists in this region for the metal complexes where it is proposed, on the basis of ^1H n.m.r. evidence principally, that deprotonation of this group occurs upon complexation. By similar reasoning a band at 1629 cm^{-1} in the spectrum of (VII) and absent in that of (VIII) is assigned to the amine group of (VII). The 1600 cm^{-1} region however, is far more complicated than that above 3200 cm^{-1} , being overlapped by ring vibrations and C=C vibrations, making band assignment tentative. An intense sharp band at 1600 cm^{-1} in the spectrum of (VII), and a broad intense band at 1602 cm^{-1} in the spectrum of (VIII) are tentatively assigned to azomethine vibrations.

The lack of a band due to the free -OH stretching vibrations in the spectrum of (VIII) is consistent with the findings of Kovacic [10] that intramolecular hydrogen bonding results in formation of a stable 6-membered ring for the condensation product of salicylaldehyde and aniline.

The principal peaks of the ^1H n.m.r. spectra of ligands (VII) and (VIII) are listed in Table I.

Due to the complexity of the aromatic region (δ 8-6), no band assignments have been made for the aromatic protons. The signals at δ 10.60 and δ 6.62 in the spectrum of (VII) are assigned to the -NH- and -NH₂ groups, on the observation of rapid loss of these signals when D₂O is added to the solution. In particular, the signal at δ 10.60 is assigned to the -NH- group, on the observation of a similar signal at δ 10.84 in the spectrum of (VIII) being lost upon addition of D₂O to the solution. The only group common to both (VII) and (VIII) expected to show such behaviour is the -NH- group. Higson and McKenzie [11] in a study of ligands of somewhat similar type have reported the azomethine resonance (-CH=N-) in the region δ 7-9. A singlet at δ 8.22 in the spectrum of (VII) is assigned to the azomethine resonance, while the

spectrum of (VIII) shows two singlets at δ 8.84 which is expected, since this ligand contains two non-equivalent azomethine groups. Due to the similarity in the chemical shifts of signals at δ 8.22 in the spectra of (VII) and at δ 8.44 in the spectra of (VIII), the signal at δ 8.44 is further assigned to the azomethine resonance of the hydrazone residue, whereas the signal at δ 8.84 is assigned to the azomethine resonance of the salicylaldehyde residue. On the observation of rapid loss of the signal at δ 12.24 in the spectrum of (VIII), upon addition of D₂O to the solution, this signal is assigned to the -OH group.

Initial attempts at preparation of metal complexes of (VIII) involved reaction of the ligand in ethanol with Ni(II) and Cu(II) salts, usually the acetate. On the basis of analytical figures these preparations yielded compounds other than those sought and these were not further characterised. The Ni(II) and Cu(II) complexes with the ligand (VIII) acting in a dibasic mode were obtained by firstly treating the ligand with sodium ethoxide to facilitate deprotonation of the ligand, followed by addition of the appropriate metal acetate. The analytical data indicate an empirical stoichiometry compatible with one doubly deprotonated ligand per metal ion, while the mass spectra of complexes show parent peaks at 373 and 378 respectively, which indicate the correct composition of the complexes.

The ^1H n.m.r. spectrum of the [Ni ligand (VIII)] complex in (CD₃)₂SO solution has peaks at δ 8.13 and δ 8.93, which are assigned to the azomethine resonance of the hydrazone and the azomethine resonance of the salicylaldehyde residues respectively, on the basis of a similar chemical shift for the azomethine resonances in the ligand spectra.

The lack of bands above 3200 cm^{-1} in the infrared spectra of the metal complexes provides clear evidence for the loss of imine protons. A band at 3190 cm^{-1} in the spectrum of (VII) and at 3200 cm^{-1} in the spectrum of (VIII) was assigned to the imine vibration of the hydrazone residue, and the

disappearance of this band in the spectra of the complexes provides further evidence of deprotonation of this group upon complexation.

The effect that complexation has on the vibrational spectrum of azomethine groups is at this time unresolved. Kovacic [10], in a study of salicylidene anilines and their copper chelates, claims a shift to lower frequency of the C=N stretching vibration upon complexation. This he claims indicates less double-bond character in the C=N bond. However, Busch and Bailar [12] in a study of pyridinalmethylimine complexes claim that complexation of the N atom of the azomethine group leads to a shift to higher frequency. They explain their findings on the assumption that complexation has led to increased location of electrons in the aromatic ligand. Bands at 1600 and 1602 cm^{-1} in the spectra of (VII) and (VIII) respectively, were tentatively assigned to azomethine vibrations. There appears to be a shift to higher frequency for the azomethine band in going from the ligand (VIII) to the complexes of some 6–8 cm^{-1} . Because the assignment of the azomethine band in the free ligand was tentative to begin with, this latter observation is even more so. The findings tend to verify those of Busch and Bailar for the particular systems under study, but are far from conclusive. The effect of complexation upon the azomethine vibration may not be a general phenomenon but rather a specific effect dependent upon the particular system under study. That this perhaps is the case is shown [12] by the divergent behaviour on the part of aromatic and α -diimine ligands upon complexation; α -diimine systems appear to show a shift to lower frequency for the azomethine band upon complexation.

That both complexes are neutral species is confirmed by molar conductivity values of 0.19 and 0.54 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ for Ni(II) and Cu(II) respectively in nitromethane. These values clearly indicate the formation in nitromethane of non-electrolyte species. The nickel(II) complex is diamagnetic, indicating a square planar or distorted square planar structure. This is normal behaviour for nickel(II) with Schiff base ligands containing nitrogen and oxygen donors. The copper(II) complex also has a normal magnetic moment, $\mu_{\text{eff}} = 1.84 \text{ B.M.}$

Attempts to prepare the tridentate, derived from the condensation of *o*-aminobenzaldehyde and *o*-phenylenediamine, as a precursor to the unsymmetrical quadridentate ligand (IX), always yielded two products (i) the required tridentate, and (ii) the symmetrical quadridentate derived from the reaction of two molecules of *o*-aminobenzaldehyde per *o*-phenylenediamine molecule. Extensive attempts at separation of the two compounds by recrystallization and column chromatography proved unsuccessful. In an attempt to obtain a nickel(II) complex of either ligand, the reaction mixture was

treated with salicylaldehyde, followed by nickel acetate. Upon standing for several days a black crystalline product was obtained for which analytical data indicated the empirical stoichiometry consistent with the compound [Ni(ligand IX)]. The mass spectrum of this compound has a large parent peak at 372 which confirms the formulation $\text{C}_{20}\text{H}_{15}\text{N}_3\text{ONi}$, rather than the alternative possibility $\text{C}_{20}\text{H}_{16}\text{N}_4\text{Ni}$ ($M = 371$) for the Ni(II) complex of the symmetrical quadridentate (ii) above, the spectrum having no peak at 371. The two possible compounds of course would have very different nitrogen analyses (see Experimental).

Since the complex is diamagnetic it is concluded that the stereochemistry is square planar or distorted square planar. A molar conductivity value of 1.58 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ in nitromethane is indicative of a non-electrolyte species. The electronic spectrum has a peak at 365 nm ($\Sigma = 9.600$), and it would appear that both bands are ligand electronic transitions. Unfortunately no ^1H n.m.r. were able to be recorded due to the poor solubility of the complex in common solvents. Its infrared spectrum shows a band at 3340 cm^{-1} which is assigned to the $-\text{NH}-$ group and an unsymmetrical broad band at 1620 cm^{-1} is tentatively assigned to the azomethine vibrations.

The synthesis of [Ni(ligand IX)] in this manner, provides an excellent example of a metal ion in a templating role, in-so-far as no mass spectral evidence is found for the formation of a nickel(II) complex derived from the symmetrical quadridentate. Very little work has been done to elucidate the mechanisms where metal ions are involved in template reactions. One such system which has been studied [13] is the stepwise formation of nickel phthalocyanine from nickel(II) chloride and 1,3-diiminoisindoline. The reaction proceeds by way of an initial complexation of 1,3-diiminoisindoline (2 mol) with nickel chloride (1 mol). Condensation with 2 additional moles of 1,3-diiminoisindoline then occurs, followed by reaction with amyl alcohol to yield finally a bisalkoxyiminoisindoline complex which upon heating readily converts to nickel phthalocyanine. Clearly, ring closure proceeds by a template process.

The ligand is proposed as structure (IX) rather than the alternative chemically indistinguishable isomer, in which double condensation on the *o*-phenylenediamine residue has occurred. Attempts to obtain the ligand (IX) free of nickel were unsuccessful.

Experimental

Bis(glyoxaliminephenylhydrazone) Ligands (V)

These ligands were prepared by the reaction of one mol of the appropriate diamine with two mol of

TABLE II. Complexes of Ligand (V)^a of Stereochemistry [M(L - 2H)].

Ligand	Metal	Analyses (%)					μ_{eff} (B.M.)
			C	H	N	M	
(GMPh) ₂ en	Ni	Found	57.11	4.89	21.70	15.12	—
		Calc.	57.34	4.78	22.30	15.58	
(GMPh) ₂ en	Cu	Found	56.59	4.87	21.80	16.30	1.88
		Calc.	56.62	4.72	22.02	16.64	
(GMPh) ₂ tn	Ni	Found	58.25	5.19	21.37	15.30	—
		Calc.	58.35	5.12	21.50	15.20	
(GMPh) ₂ tn	Cu	Found	57.48	5.18	21.15	16.30	1.87
		Calc.	57.65	5.06	21.24	16.06	
(GMPh) ₂ <i>o</i> -PD	Ni	Found	61.46	4.47	19.50	13.82	—
		Calc.	62.16	4.24	19.78	13.82	
(GMPh) ₂ ChD	Ni	Found	60.86	5.74	18.50	13.65	—
		Calc.	61.30	5.57	19.50	13.63	
(GMPh) ₂ ChD	Cu	Found	60.61	5.60	19.30	14.38	1.91
		Calc.	60.61	5.51	19.29	14.58	

^aen = ethylenediamine; tn = 1,3-diaminopropane; *o*-PD = *o*-phenylenediamine; ChD = 1,2-cyclohexanediamine; GMPh = glyoxalmonophenylhydrazone.

glyoxalmonophenylhydrazone dissolved in a minimum volume of warm ether. The bis-iminehydrazones which separated as yellow crystalline solids were recovered by filtration, washed with ether and air dried. The ligands were recrystallised from a minimum of hot methanol or ethanol. *Anal.*: (i) Ligand V, B = -(CH₂)₂-: Found: C, 67.6; H, 6.3; N, 26.1. Calc. for C₁₈H₂N₆, C, 67.5; H, 6.3; N, 26.2%. M.p. 147 °C. (ii) Ligand V, B = -(CH₂)₃-: Found: C, 67.9; H, 6.8; N, 25.0. Calc. for C₁₉H₂₂N₆: C, 68.2; H, 6.6; N, 25.1%. M.p. 165 °C.

Metal Complexes of Ligands V

Deprotonated nickel(II) and copper(II) complexes of these quadridentate ligands were prepared by either an *in situ* or a direct reaction procedure. In the *in situ* method, the appropriate diamine and the stoichiometric amount of glyoxalmonophenylhydrazone both in hot methanol were mixed and treated with a hot methanolic or aqueous methanolic solution of nickel(II) or copper(II) acetate. The required metal complex crystallised from the warm reaction mixture and was recovered by filtration, washed with a minimum of cold methanol and air dried.

For the direct reaction, the appropriate ligand dissolved in a minimum of hot methanol was reacted with nickel(II) or copper(II) acetate dissolved in hot methanol or aqueous methanol, the precipitated complex being recovered as for the *in situ* preparation described above. The metal complexes prepared are listed in Table II.

Preparation of [Ni(Ligand VI)]

5 mmol of glyoxal-(2-aminophenyl)-anil-(1)-phenylhydrazone-(2), prepared as previously described [2], dissolved in 5 ml warm ethanol was added slowly to a warm solution of 5 mmol salicylaldehyde and 5 mmol nickel(II) acetate in 10 ml ethanol. The green solution turned red-brown and deposited the red-brown nickel(II) complex. *Anal.*: Found: C, 62.6; H, 3.2; N, 13.9; Ni, 14.8. Calc. for C₂₀H₁₆N₄NiO: C, 63.2; H, 4.0; N, 14.0; Ni, 14.7%. A mass spectrum of the compound shown a major parent peak at the expected value of 387 a.m.u., although minor peaks are seen at 425 a.m.u. and at 373 a.m.u., which correspond to the Ni(II) complexes of *o*-phenylenediamine condensed with two molecules of glyoxalmonophenylhydrazone and salicylaldehyde respectively. (*o*-aminobenzaldehyde [14], 2-pyridylhydrazine [15], and 2-aminobenzaldehyde-2'-pyridylhydrazone(VII) [2] were prepared by published methods.

Preparation of Ligand (VIII)

9 mmol of salicylaldehyde in 5 ml of ethanol was added, dropwise, to a refluxing solution of 9 mmol of (VII) and 5 ml of glacial acetic acid in 100 ml of ethanol. After refluxing for 5 minutes the solution was allowed to cool. Upon cooling a bright yellow solid formed. The solid was filtered off on a sintered glass funnel, washed with ethanol and air-dried. Yields 80–85%; m.p. 196 °C. *Anal.*: Found: C, 72.2; H, 5.1; N, 18.1. Calc. for C₁₉H₁₆N₄O: C, 72.2; H,

5.1; N, 17.7%. The mass spectrum shows a large parent peak at 316 a.m.u.

Preparation of Complexes of VIII

Ni(II)Complex

2 mmol of (VIII) in 40 ml of absolute ethanol were treated with 4 mmol of sodium ethoxide solution. The mixture was refluxed until the ligand had completely dissolved. This solution was added, dropwise, to a refluxing solution of 2 mmol of anhydrous nickel(II) acetate dissolved in a minimum volume of methanol. A deep brown to black solution immediately formed, with precipitation of a fine, brown solid. The mixture was allowed to cool and the brown solid recovered by filtration, washed with cold ethanol and air-dried. The filtrate was allowed to stand in the refrigerator for several days, whereupon precipitation of a deep purple crystalline solid occurred. The crystals were filtered on a sintered glass funnel, washed with cold ethanol and air-dried. Infrared spectra show both products to be the same complex. Yields 60–70%; m.p. 240 °C. *Anal.*: Found: C, 61.5, H, 3.9; N, 14.9; Ni, 16.2. Calc. for $C_{19}H_{14}N_4NiO$: C, 61.2; H, 3.8; N, 15.0; Ni, 15.8%.

Cu(II) complex

The method of preparation was the same as for the Ni(II) compound, however there was no immediate formation of a solid. After several days standing, a deep blue crystalline solid precipitated out of solution. The product was filtered, washed with cold ethanol and air-dried. Yields 60–70%; m.p. 250 °C. *Anal.*: Found: C, 59.8; H, 4.0; N, 14.4; Cu, 16.4. Calc. for $C_{19}H_{14}N_4CuO$: C, 60.3; H, 3.7; N, 14.8; Cu, 16.8%.

Preparation of Ni(II) complex of Ligand (IX)

24 mmol of freshly prepared *o*-aminobenzaldehyde in a minimum volume of ethanol was added, dropwise, to a refluxing solution of 24 mmol of *o*-phenylenediamine in 100 ml of ethanol. Several drops of glacial acetic acid were added and the mixture brought to the boil and allowed to cool. Upon standing for a day in the refrigerator, a yellow solid formed. The solid was filtered, washed with cold ethanol and air-dried. Mass spectral data indicated the formation of a mixture of mono(*o*'-aminobenz-

aldehyde)-*o*-phenylenediamine, and bis(*o*'-aminobenzaldehyde)-*o*-phenylenediamine. Attempts to separate the mixture by recrystallisation and column chromatography were unsuccessful, and the required nickel(II) compound was obtained by adding 24 mmol of salicylaldehyde in 5 ml of ethanol over a period of 2 hr, to a refluxing solution of the foregoing mixed products in 200 ml of ethanol and 5 ml of glacial acetic acid. Refluxing was continued for a further 30 minutes after the last addition of salicylaldehyde resulting in a deep-orange solution. This mixture was added, dropwise, to a refluxing solution of 24 mmol of nickel(II) acetate dissolved in a minimum volume of methanol. The solution went deep brown to black, and was quickly filtered hot, to remove undissolved nickel acetate. Upon standing in the refrigerator for a day a black crystalline solid was formed. The solid was filtered, washed with cold ethanol and air-dried. Yields 30–40%. Decomposed 300 °C. *Anal.*: Found: C, 64.3; H, 4.1; N, 11.3; Ni, 15.8. Calc. for $C_{20}H_{15}N_3NiO$: C, 64.5; H, 4.0; N, 11.3; Ni, 15.9%.

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