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Nickel(II) Complexes Containing Tetradentate Ligands Formed by the Condensation of Ketones with Benzil Monohydrazone in the Presence of Nickel(II) Ions

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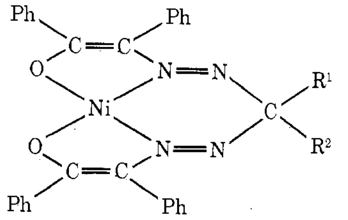
The reaction between some ketones R^1R^2CO and benzil monohydrazone in the presence of nickel(II) ions has been shown to result in the formation of complexes containing tetradentate ligands in which two benzil monohydrazone residues are linked by a single carbon atom from the ketone (R^1 = Me, R^2 = Me, Et, *n*-Pr, *n*-Bu, or Ph; R^1 = Et, R^2 = Et). The complexes have been characterized by infrared, visible, and ^1H nmr spectroscopy, mass spectral analysis, and magnetic susceptibility measurements. The dinegatively charged ligands are coordinated about the nickel(II) ion in a square-planar configuration.

Introduction

In recent years there have been reported a number of condensation reactions involving metal–amine complexes and carbonyl compounds. The resultant complexes have been shown to contain either cyclic or noncyclic ligands depending on the amine employed and the type of condensation that takes place.[1] In one type, a coordinated amine group is converted to a Schiff base, whereas the characteristic feature of a second type is the linking of two coordinated amine groups by a three-carbon bridge.

In 1939, Taylor, Callow, and Francis[2] isolated a small quantity of red needles when the nickel complex of benzil monohydrazone was prepared in boiling acetone. Although these authors were uncertain of the structure of this new complex, they did suggest that a condensation reaction had taken place.

We report here a study of reactions between some ketones, R^1R^2CO, and benzil monohydrazone in the presence of nickel(II) ions. A third type of condensation reaction has been characterized in which the carbon atom from the carbonyl group of a ketone forms the sole bridge between terminal nitrogen atoms of two coordinated benzil monohydrazone residues. The resultant dinegatively charged tetradentate ligands are coordinated as shown in structure I. A preliminary account of some of this work has been published earlier.[3]



I

Experimental Section

Materials.—Benzil monohydrazone (Aldrich) was used as supplied. All other chemicals employed were of reagent grade or equivalent.

Preparation of Complexes. 1,2,8,9-Tetraphenyl-3,4,6,7-tetraaza-5,5-dimethylnona-1,3,6,8-tetraen-1,9-dioxynickel(II) (NiMMK).—To a hot solution of 4.5 g (0.02 mol) of benzil monohydrazone in 125 ml of 95% ethanol was added 7.4 ml (0.1 mol) of acetone and then was added a hot solution of 2.5 g (0.01 mol) of nickel acetate tetrahydrate in 85 ml of 95% ethanol. A dark red-brown precipitate was formed immediately on addition of the nickel acetate solution. The resulting mixture was stirred and refluxed for 7 days. During this time, the solution turned orange-red and an orange-red precipitate was formed. The hot solution was filtered by suction. Cooling the filtrate resulted in the production of orange-red needles which were removed by filtration. Further batches of crystalline product were obtained by concentration of this filtrate and also by extraction with benzene of the residue from the initial filtration followed by concentration and cooling of the solution obtained. The batches were combined and recrystallized from 1-butanol. The product was obtained as fine orange-red needles and was dried under vacuum at room temperature.

Reactions involving methyl ethyl ketone, MEK, diethyl ketone, EEK, methyl *n*-propyl ketone, MPrK, methyl *n*-butyl ketone, MBuK, and methyl phenyl ketone, MPhK, were carried out using a similar procedure. All products were obtained as orange-red crystals. Analytical data are recorded in Table I, together with percentage yields.

When benzophenone (diphenyl ketone) was used, a dark-red brown crystalline product was obtained on initial mixing of the reactants which did not change with prolonged refluxing as was the case with the other reactions. This compound was removed by suction filtration, washed with ethanol, and dried under vacuum at room temperature. *Anal.* Calcd for $C_{42}H_{32}N_6O_2Ni_2$: C, 64.16; H, 4.11; N, 10.69; Ni, 14.93. Found: C, 63.98; H, 4.05; N, 10.60; Ni, 14.67.

Reaction of Benzil Monohydrazone with Acetone in the Absence of Nickel(II) Ions.—To a hot solution of 2.25 g (0.01 mol) of benzil monohydrazone in 100 ml 95% ethanol was added 3.7 ml (0.05 mol) of acetone. This solution was stirred and refluxed for 7 days, and the resulting pale yellow solution was reduced in volume to approximately 40 ml and allowed to cool overnight. Thick hexagonal yellow crystals were obtained, removed by filtration, and recrystallized from methanol; mp 77°. The compound was characterized as benzilacetone azine $C_6H_5C(=O)C(C_6H_5)=NN=C(CH_3)_2$. *Anal.* Calcd for $C_{17}H_{16}N_2O$: C, 77.23; H, 6.11; N, 10.60. Found: C, 77.05; H, 6.06; N, 10.50.

Physical Measurements.—Infrared spectra were obtained on a Perkin-Elmer Model 457 spectrophotometer using Nujol and Fluorolube mull techniques. Visible and ultraviolet spectra were obtained with a Unicam SP 800 B spectrophotometer. The reported proton magnetic resonance spectra were determined using a Varian HA 100 nmr spectrometer by a repetitive scanning technique. H_2SO_4 was used as an external reference and the instrument "locked on" to this during the scanning. Chemical shifts were determined by introduction of TMS as an internal reference. This procedure was necessitated by the low solubilities of the complexes in suitable solvents. Mass spectra were determined with Hitachi Perkin-Elmer RMU-60 and CEC21-110B double-focusing mass spectrometers. Accurate masses were measured with a Nier type peak matching unit attached to the latter spectrometer (accuracy ~4 ppm). Elemental analyses were performed by Spang Microanalytical Laboratories, Ann

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[1] N. F. Curtis, *Coord. Chem. Rev.*, **3**, 3 (1968).

[2] T. W. J. Taylor, N. H. Callow, and C. R. W. Frances, *J. Chem. Soc.*, 257 (1939).

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TABLE I
ANALYTICAL DATA FOR THE COMPLEXES

Compd	Ketone used	% yield[a]	% calcd C	% calcd H	% calcd N	% found C	% found H	% found N
NiMMK	Acetone	78.5	68.27	4.82	10.28	68.16	4.89	10.30
NiMEK	Methyl ethyl ketone	60.9	68.71	5.06	10.02	68.91	5.25	10.22
NiEEK	Diethyl ketone	39.4	69.12	5.28	9.77	69.19	5.33	9.87
NiMPrK	Methyl *n*-propyl ketone	58.2	69.12	5.28	9.77	68.76	5.35	9.70
NiMBuK	Methyl *n*-butyl ketone	60.3	69.52	5.50	9.54	69.32	5.32	9.44
NiMPhK	Methyl phenyl ketone	14.5	71.18	4.66	9.23	71.05	4.76	9.14

[a] Based on nickel(II).

Arbor, Mich., and by Galbraith Laboratories, Inc., Knoxville, Tenn.

Results and Discussion

Reaction between benzil monohydrazone and a ketone R^1R^2CO in the presence of nickel(II) ions yields in each case a neutral complex containing a ligand formed by condensation between the ketone and two benzil monohydrazone residues. The analytical data for the complexes are presented in Table I. All the complexes may be formulated as being derived from 1,2,8,9-tetraphenyl-3,4,6,7-tetraza-5-R^1-5-R^2-nona-1,3,-6,8-tetraen-1,9-dioxynickel(II) (R^1 = Me, R^2 = Me, Et, *n*-Pr, *n*-Bu, or Ph; R^1 = Et, R^2 = Et). These complexes are referred to as nickel ketazines[4] and the abbreviations used in the table and throughout the text are related to the ketone used in the condensation reaction, NiMMK corresponding to the nickel ketazine obtained by the use of methyl methyl ketone (acetone).

The structures of the ligands have been deduced from the infrared, ^1H nmr, and mass spectra of their complexes. The infrared spectra of the nickel ketazines are similar to one another but show significant differences compared with that of benzil monohydrazone. Strong absorption bands at 3390, 3275, and 3180 cm^{-1} assigned to $\nu(NH_2)$ and a strong, broad band at 1620 cm^{-1} assigned to $\delta(NH_2)$ and $\nu(C{=}O)$ of benzil monohydrazone are absent in the spectra of the nickel ketazines. A strong composite band centered at 1280 cm^{-1} in the nickel ketazines (but absent in benzil monohydrazone) is assigned to $\nu(C{-}N)$ and $\nu(C{-}O)$. The strong complex band centered around 1530 cm^{-1} in benzil monohydrazone ($\nu(C{=}C)$ from the phenyl rings and $\nu(C{=}N)$) is simplified in the nickel ketazines to a single medium-strong band at 1530 cm^{-1} assigned to $\nu(C{=}C)$ of the phenyl rings only. These changes are consistent with the NH_2 groups of benzil monohydrazone having undergone condensation with the ketones.

The ^1H nmr spectra of the nickel ketazines are summarized in Table II. Due to the low solubility of the complexes in suitable solvents and also in CCl_4 for which the spectra were finally obtained, the spectra were obtained using a repetitive scanning technique. The resolution of some of the more complex regions of the spectra was still not very good even under these conditions. The spectra consist of two regions, an alkyl region, δ 0.9–2.2, and a region due to the phenyl resonances in the vicinity of δ 7, both downfield from TMS. The spectrum of NiMEK is shown in Figure 1. There was no indication of any –NH bands in the spectrum. The relative areas under the peaks are in ratios consistent with the assignments given (coupling constants, J_{H-H}, are calculated to be 7.0–7.7 cps from spectra exhibiting triplets and quartets). All the complexes containing R^1 = Me, except when R^2 = Ph, show a sharp singlet close to 1.65 ppm. When R^2 = Ph, however, *i.e.*, in NiMPhK, the methyl singlet peak is found at 2.06 ppm, the downfield shift indicating the methyl group is deshielded by the phenyl group. The ^1H nmr spectra suggest the formulation of the tetradentate ligands produced by the condensation reaction to be as shown in I.

TABLE II
PROTON MAGNETIC RESONANCE SPECTRA
OF NICKEL KETAZINES

Compd	Chem shift[a]	Type	Assignment
NiMMK	1.68	Singlet	$-CH_3$
	7.06–7.47	Multiplet	$-C_6H_5$
NiMEK	0.96[b]	Triplet	$-CH_2\mathit{CH_3}$
	1.65	Singlet	$-CH_3$
	2.17[c]	Quartet	$-\mathit{CH_2}CH_3$
	7.06–7.44	Multiplet	$-C_6H_5$
NiEEK	0.92[b]	Triplet	$-CH_2\mathit{CH_3}$
	2.20[c]	Quartet	$-\mathit{CH_2}CH_3$
	7.05–7.40	Multiplet	$-C_6H_5$
NiMPrK	0.91[b]	Triplet	$-CH_2CH_2\mathit{CH_3}$
	~1.40	Multiplet	$-CH_2\mathit{CH_2}CH_3$
	1.65	Singlet	$-CH_3$
	2.12[b]	Triplet	$-\mathit{CH_2}CH_2CH_3$
	7.06–7.39	Multiplet	$-C_6H_5$
NiMBuK	0.92[b]	Triplet	$-CH_2CH_2CH_2\mathit{CH_3}$
	1.22–1.43	Multiplet	$-CH_2\mathit{CH_2}\mathit{CH_2}CH_3$
	1.64	Singlet	$-CH_3$
	2.15[b]	Triplet	$-\mathit{CH_2}CH_2CH_2CH_3$
	6.94–7.49	Multiplet	$-C_6H_5$
NiMPhK	2.06	Singlet	$-CH_3$
	7.11–7.30	Multiplet	$-C_6H_5$

[a] Ppm downfield from tetramethylsilane. [b] Center of triplet. [c] Center of quartet.

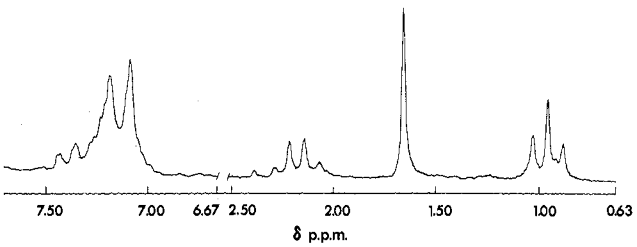

Figure 1.—The 100-MHz ^1H nmr spectrum of nickel methyl ethyl ketazine (NiMEK).

Models based on this structure for NiMPhK show the methyl group to be in the expected position relative to the phenyl group for the observed deshielding of the methyl to occur.

Confirmation of the structures of these nickel ketazines was obtained by a study of their mass spectra and fragmentation patterns. In each case a series of highest mass peaks is observed, corresponding to the singly charged parent ion. The most intense peak of the series corresponds to the ion containing ^{58}Ni with less intense peaks at higher mass numbers from other iso-

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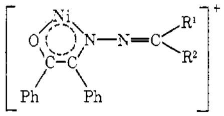
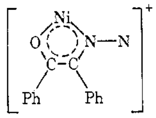
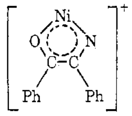
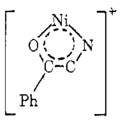
(4) W. J. Stratton, *Inorg. Chem.*, **9**, 517 (1970).

topes (nickel, carbon, nitrogen). The fragmentation patterns of the complexes are similar and can readily be accounted for on the basis of the proposed structures (see Table III). For each complex, the next highest mass peaks down from the parent ion, P^+, correspond to $[P - 28\text{ amu}]^+$ and $[P - 56\text{ amu}]^+$. It is possible that these complexes could lose either CO or N_2 in the mass spectrometer. Since both of these molecules have the same nominal mass, high-resolution mass spectrometry was used to differentiate between these two possible fragmentation routes. Exact mass measurement on the $[P - 28\text{ amu}]^+$ peak for NiMMK showed that this corresponds to the loss of an N_2 molecule from the parent ion (theoretical 516.1348, measured 516.1343). For the $[P - 56\text{ amu}]^+$ peak, this was found to correspond to the loss of a CO molecule from the $[P - 28\text{ amu}]^+$ fragment (theoretical 488.1399, measured 488.1375). Measurement of metastable ions by the defocusing technique indicated the loss of these molecules was a consecutive rather than a concurrent process. The initial elimination of a nitrogen molecule from the parent ion suggests the presence of a nitrogen–nitrogen double bond in the nickel ketazines as shown in I. A study of the mass spectra of some triazinones, containing –C=O and –N=N– groups also showed that the initial loss of 28 mass units corresponded to N_2 elimination.[5] In benzilacetone azine, however, the mass spectrum showed the loss of 28 mass units, corresponding to elimination of a CO molecule. For the nickel ketazines, several common peaks are observed which are tentatively assigned to the residues in Table III. One feature of these residues is the stability of the five-membered chelate ring containing nickel(II), probably stabilized by electron delocalization. Cummings and Sievers[6] noted unusual stability of a six-membered chelate ring in the mass spectra of two macrocyclic nickel(II) complexes.

TABLE III
MASS SPECTRA OF NICKEL KETAZINES

m/e^a	Assignment
P	[Parent ion]$^+$
P − 28	$[P - N_2]^+$
P − 56	$[(P - N_2) - CO]^+$
P − 222	
280	
266	
240	$[NiOC(Ph)_2]^+$
238	$[NiNC(Ph)_2]^+$
224	$[NiC(Ph)_2]^+$
203	
192	[PhCC(N)Ph]$^+$
178	[PhCCPh]$^+$
166	$[C(Ph)_2]^+$
135	?
117	[PhCCO]$^+$ or $[PhCN_2]^+$
105	[PhCO]$^+$
99	?
91	[PhN]$^+$
77	[Ph]$^+$

[a] For nickel-containing species, the value for ^{58}Ni is given.

All the nickel ketazines are obtained as orange-red crystalline solids which are diamagnetic ($\mu_{\text{eff}} \leqslant 0.5$ BM) when pure. On initial preparation, small amounts of ferromagnetic impurities are sometimes present, but these are readily removed by repeated recrystallizations. The ultraviolet and visible spectra of the complexes are reported in Table IV. The spectra are very similar to one another suggesting the nickel(II) ion is in a similar environment in all the complexes. The absorption band found about 495 nm is assigned to the $^1A_1 \rightarrow {}^1B_1$ transition for nickel(II) in a *cis*-NiO_2N_2 planar environment,[7,8] which is required by the nature of the tetradentate ligand. If this assignment is made, then the other bands in the spectrum are assigned as charge-transfer and ligand bands. The position and molar extinction coefficients of the low-energy bands are probably influenced by the strong ligand bands at 390 and ~340 nm.

The coordination of the tetradentate ligands to the nickel(II) ion in the nickel ketazines is proposed to be as shown in I, with the nitrogen atoms not linked by the bridging carbon atom being coordinated to the nickel(II) ion. This results in the formation of a six-membered chelate ring containing the bridging carbon atom and models based on this conclusion show very little strain present in the overall structure. The alternate mode of coordination in which the nitrogen atoms bridged by the carbon atom are coordinated involves much greater strain in the structure and it seems doubtful if the carbon atom would be able to bridge these coordinated nitrogen atoms as a four-membered ring would be produced. In previously reported reactions between coordinated amines and ketones, the ketone undergoes an aldol condensation and reaction with the amines produces a new six-membered chelate ring.[1] No examples have been reported in which the ketone bridges coordinated nitrogen atoms by a single carbon atom only.

The formation of these ligands is dependent on the presence of the nickel(II) ion, and the reactions may best be described as template reactions.[9] In the absence of the nickel(II) ions, benzil monohydrazone and acetone undergo a Schiff's base condensation reaction to give benzilacetone azine, although Taylor, Callow, and Francis[2] reported this reaction did not take place. Nickel acetate reacts immediately with benzil monohydrazone in ethanol producing a dark red-brown precipitate. This same compound is obtained as the initial precipitate in the condensation reactions with ketones and in a crystalline form in the presence of benzophenone when no condensation reaction takes place.

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TABLE IV

ULTRAVIOLET AND VISIBLE SPECTRA OF NICKEL KETAZINES[a]

Compd	ν_1[b]	$10^{-3}\epsilon_M$	ν_2[b]	$10^{-3}\epsilon_M$	ν_3[b]	$10^{-3}\epsilon_M$	ν_4[b]	$10^{-3}\epsilon_M$
NiMMK	495	7.67	460 sh	8.80	390	17.9	344	15.7
NiMEK	498	7.85	460 sh	9.06	390	17.3	342	15.3
NiEEK	498	7.84	460 sh	8.88	390	17.3	342	15.2
NiMPrK	498	7.51	460 sh	8.64	390	16.7	342	14.8
NiMBuK	498	7.48	460 sh	8.75	390	16.8	342	14.8
NiMPhK	495	7.78	455 sh	9.14	390	16.7	336	14.8

[a] All spectra obtained in benzene. [b] In nm.

The early workers[2] in this area also reported the formation of a dark red solid for which varying analyses were obtained. We have characterized this compound as $Ni_2(L\text{-}H)_2(L\text{-}2H)$, where L-H and L-2H represent benzil monohydrazone minus one and two hydrogen atoms, respectively. As the condensation reactions proceed, this dark red-brown compound is slowly removed and orange-red crystals of the nickel ketazines are obtained. It is possible that the reaction proceeds *via* an equilibrium concentration of benzil monohydrazone, the nickel(II) ions coordinating the products or intermediates that are formed during the reaction.

Benzilacetone azine may be an intermediate in the formation of NiMMK since refluxing nickel acetate with this compound in the presence of benzil monohydrazone does result in the formation of a small amount of the condensation product. In the absence of the excess benzil monohydrazone, however, no reaction takes place.

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Thiocarbamate Complexes. I. Preparation and Properties of Nickel(II) Derivatives[1]

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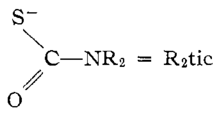
The syntheses of six *N,N*-dialkylthiocarbamate complexes of nickel(II) are reported. These new chelates have the empirical formula $Ni(OSCNR_2)_2$, where R is CH_3, C_2H_5, $n\text{-}C_3H_7$, $n\text{-}C_4H_9$, $-(CH_2)_4-$, and $-(CH_2)_5-$. Molecular weight measurements suggest that the complexes are low polymers, and electronic spectral measurements coupled with the observed paramagnetic moments of *ca.* 3.25 BM indicate that the nickel(II) ions are in octahedral environments. It is proposed that the complexes exist in the solid state as *cyclic* oligomers in which the oxygen atoms are coordinated and the sulfur atoms bridge between adjacent metal ions. Infrared spectral studies suggest that canonical forms involving appreciable multiple bonding in the (OS)C–N bond are important. The spin-allowed "d–d" electronic transitions have been assigned, and the ligands have been found to lie between fluoride and water in the spectrochemical series. The polymeric structure of the complexes is ruptured by treatment with pyridine and bis adducts are formed. The adducts have been characterized by spectroscopic and magnetic measurements. Structural similarities among thiocarbamate and other complexes having [Ni–O_4], [Ni–O_2S_2], and [Ni–S_4] donor atom sets are discussed.

Introduction

Complexes of ligands containing one or more sulfur donors have been of considerable recent interest. We have been particularly concerned with *N,N*-dialkyldithiocarbamate complexes,[2–5] which have long been known[6] but which continue to provide new and novel structures and reactions.[7,8]

Surprisingly, the ligational properties of analogous *N,N*-dialkylthiocarbamates (abbreviated R_2tic) remain



virtually unknown. To this time only derivatives of Cu(I) and Ag(I) are reasonably well characterized,[9,10] although complexes of several other similar sulfur–oxygen donors, such as monothiobenzoate, have been studied in some detail.[11–14] Comparative studies of

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[1] Presented in part at the Second Central Regional Meeting of the American Chemical Society, Columbus, Ohio, June 1970.

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