Condensation Reactions of Some Monohydrazones in the Presence of Nickel(II) Ions

DOUGLAS B. BONFOEY and GORDON A. MELSON*

The reaction between acetone and 2,3-butanedione monohydrazone, I, or 3,3-dimethyl-1,2-butanedione monohydrazone, II, in the presence of nickel(II) ions has been shown to result in the formation of complexes containing tetradentate ligands in which two monohydrazone residues are linked by a single carbon atom from the ketone. Proton magnetic resonance (pmr) spectroscopy has been used to determine the mode of coordination of the ligands. Reaction of the complex obtained from I with diamines results in the formation of a coordinated macrocyclic ligand, although the complex derived from II does not react with amines under a variety of conditions. This difference in reactivity is correlated with a possible mechanism of macrocycle formation in these and similar systems.

Introduction

During the past few years there has been considerable interest in metal ion controlled condensation reactions which give rise to complexes containing new ligand systems, some of which are macrocyclic and contain four nitrogen donor atoms coordinated to the metal ion.[1-3]

In a previous publication, we[4] reported that condensation reactions between benzil monohydrazone and some ketones R^1R^2CO in the presence of nickel(II) ions give rise to complexes containing ligands of type III, R = C_6H_5. Later,

III
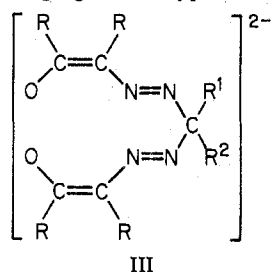
we[5] studied the reactivity of the coordinated cis-oriented CO groups in the nickel(II) complex with $R^1 = R^2 = CH_3$ toward some diamines. Complexes containing 13-membered macrocyclic ligands, IV, R = C_6H_5, R^3 = H, CH_3, were isolated

IV
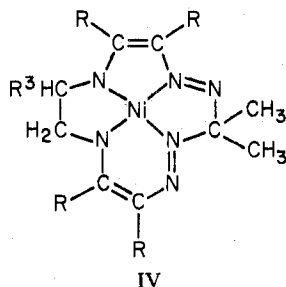
and the modes of coordination of the ligands were established.[6]

We have now extended these studies to include reactions involving 2,3-butanedione monohydrazone and 3,3-dimethyl-1,2-butanedione monohydrazone. It was anticipated that from these investigations we should be able to (1) determine the generality of the metal ion controlled condensation reaction between monohydrazones and ketones, (2) establish the mode of coordination of type III and IV ligands in the new complexes obtained, and (3) determine the influence of the R group in III on condensation reactions with diamines.

Experimental Section

Materials. 2,3-Butanedione (Aldrich) was used as supplied. 3,3-Dimethyl-1,2-butanedione was prepared from 3,3-dimethyl-2-butanone (Aldrich) by the method of Taylor, *et al.*[7] The melting point was similar to that reported by these authors. Diamines were distilled from sodium hydroxide under nitrogen before use. All other chemicals were of reagent grade or equivalent.

Preparation of Complexes. [3,3'-Isopropylidenebis[azo]di-2-buten-2-olato]nickel(II) [NiDMK]. To a hot, stirred solution of 1.75 ml (0.02 mol) of 2,3-butanedione in 100 ml of absolute ethanol was added 1.2 ml (0.02 mol) of hydrazine hydrate (85% solution). The solution was refluxed for 1 hr and then a hot solution of nickel acetate tetrahydrate (2.5 g, 0.01 mol) in 100 ml of 95% ethanol and 7.4 ml (0.1 mol) of acetone were added. An intense red solution was formed upon addition of the first few drops of the nickel acetate solution. After addition of all the nickel acetate, the solution was brown and appeared to be a suspension of very small particles. The resulting mixture was stirred and refluxed for 6 days. The hot solution was then filtered by suction, and the filtrate allowed to stand in air at room temperature until the volume was reduced to approximately 50 ml. Small golden crystals and an amorphous black solid were obtained and removed by filtration. Recrystallization of the crystals from ethanol and 1-butanol afforded golden-brown crystals of the product which was dried under vacuum at room temperature; yield 0.6 g. Purification of the product may also be achieved by sublimation at 110–120° under reduced pressure.

Anal. Calcd for $C_{11}H_{18}N_4O_2Ni$: C, 44.44; H, 6.06; N, 18.85. Found: C, 44.64; H, 5.85; N, 19.03.

[1,1'-Isopropylidenebis(azo)bis(3,3-dimethyl-1-buten-2-olato)]nickel(II) (NiTBK). To a hot, stirred solution of 2.5 g. (0.02 mol) of 3,3-dimethyl-1,2-butanedione in 100 ml absolute ethanol was added 1.2 ml (0.02 mol) of hydrazine hydrate (85% solution). The solution was heated for 30 min. during which time the solution slowly turned yellow. A hot solution of nickel acetate tetrahydrate (2.5 g., 0.01 mol) in 100 ml of 95% ethanol and 7.4 ml (0.1 mol) of acetone were added. The initial drops of the nickel solution produced a red precipitate and a cherry red solution. After addition of all the nickel acetate solution the mixture was dark red. The resulting mixture was stirred and refluxed for 6 days. The hot solution was then filtered by suction and the filtrate allowed to stand in air at room temperature. A brown solid was obtained. Recrystallization from ethanol afforded dark red crystals of the product, which were dried under vacuum at room temperature; yield 0.9 g.

Anal. Calcd for $C_{15}H_{26}N_4O_2Ni$: C, 50.99; H, 7.36; N, 15.86. Found: C, 51.23; H, 7.40; N, 16.02.

[3,3,6,7,12,13-Hexamethyl-1,2,4,5,8,11-hexaazacyclotrideca-1,-4,6,12-tetraenato]nickel(II) (NiDMM). To 5 ml of anhydrous ethylenediamine under dry N_2 was added 0.103 g (0.45 mmol) of [3,3'-isopropylidenebis(azo)di-2-buten-2-olato]nickel(II). The reaction mixture was heated to a temperature just below the boiling point and stirred. After approximately 10 min, red-orange crystals appeared. After 30 min, the flask and contents were allowed to cool and the crystals removed by filtration. A second batch of product was obtained from the filtrate by evaporation of the ethylenediamine. The two batches were combined and recrystallized from acetone. The product was obtained as small red-orange crystals which were dried under vacuum at room temperature; yield 0.10 g.

Anal. Calcd for $C_{13}H_{22}N_6Ni$: C, 48.59; H, 6.85; N, 26.17. Found: C, 48.34; H, 6.82; N, 26.54.

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. Mass spectra were obtained with a Hitachi Perkin-Elmer RMU-60 mass spectrometer. Proton magnetic resonance spectra were obtained by using

Table I. Proton Magnetic Resonance Spectra[a]

Compd	δ,[b] ppm	Rel intens	Assignment
NiDMK	1.50	6	*gem*-CH₃
	1.85	3	
	1.99	3	–CH₃
	2.07	3	
	2.26	3	
NiDMM	1.57	6	*gem*-CH₃
	1.95	3	
	1.99	3	–CH₃
	2.10	3	
	2.38	3	
	3.63	4	–CH₂CH₂–
	4.10		
NiTBK	1.52	6	*gem*-CH₃
	1.21	9	–C(CH₃)₃
	1.23	9	
	6.56	1	–H
	7.26	1	

[a] 100-MHz spectra in CDCl₃ at ambient temperature. [b] Chemical shift in parts per million downfield from an internal TMS standard.

a Varian HA-100 spectrometer in chloroform-*d* using TMS as an internal standard. Elemental analyses were performed by Chemalytics, Tempe, Ariz.

Results and Discussion

Reactions between 2,3-butanedione monohydrazone, I, and acetone and between 3,3-dimethyl-1,2-butanedione mono-hydrazone, II, and acetone in the presence of nickel(II) ions give rise to red-brown microcrystalline products, abbreviated NiDMK and NiTBK, respectively. The monohydrazones used in the metal ion controlled condensation reactions can be prepared by the reaction of the diketone with hydrazine hydrate in a 1:1 molar ratio in ethanol for approximately 1 hr at reflux temperature and isolated from the resultant solution. The monohydrazones must be freshly prepared since they undergo self-condensation producing polymeric species, even in the solid state. We reduced the possibility of self-condensation occurring during the metal ion controlled condensation reactions by preparing the monohydrazones *in situ* and then adding the nickel acetate and acetone to the resultant solution (see Experimental Section). The condensation products NiDMK and NiTBK are identical whether the monohydrazones are freshly prepared or prepared *in situ*.

The analytical data for NiDMK and NiTBK indicate that in each case, the complex is neutral and contains a ligand formed by the condensation of one molecule of acetone with two monohydrazone residues as in III. Thus the reactions reported produce similar products to those obtained from the nickel(II) ion controlled condensation reactions between benzil monohydrazone and ketones[4] and verify the generality of this type of reaction.

The nature of the ligands and their mode of coordination to the nickel(II) ion in NiDMK and NiTBK have been confirmed from infrared, proton magnetic resonance, and mass spectral measurements. The infrared spectra of the complexes do not show any absorptions which may be associated with ν(NH₂), δ(NH₂), or ν(C=O) as found in the monohydrazones themselves. The strongest absorptions in the spectrum of NiDMK are at 1322 and 1150 cm⁻¹ (1340 and 1180 cm⁻¹ in NiTBK) and are associated with ν(C–O) and ν(C–N) vibrations. The observed changes are consistent with the NH₂ groups of the monohydrazones having undergone condensation with the acetone.

Proton magnetic resonance spectra confirm the ligand structures and their mode of coordination to the nickel(II) ion in the complexes. Table I records the chemical shifts, relative intensities, and assignments made for NiDMK and NiTBK. For NiDMK, five singlets are observed, one of these having twice the intensity of the other four (see Figure 1). The singlet
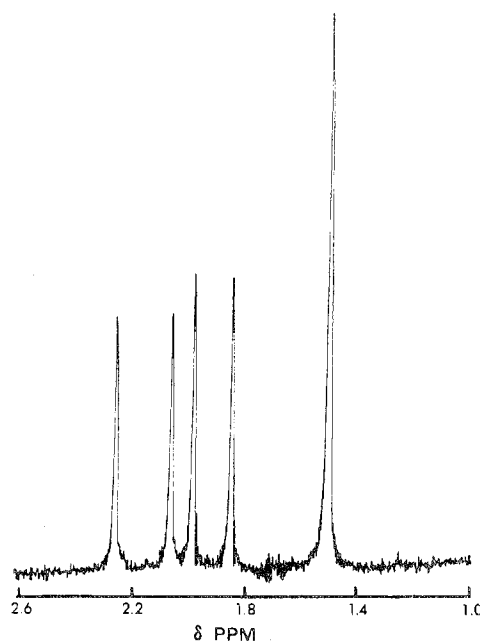
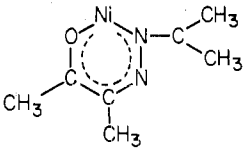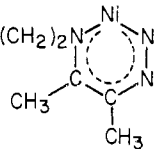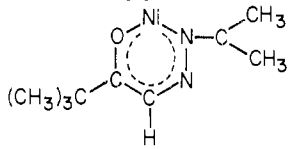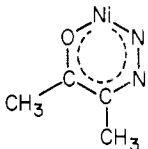**Figure 1.** The 100 MHz proton magnetic resonance spectrum of NiDMK.
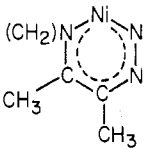
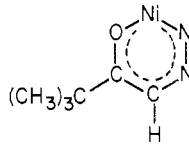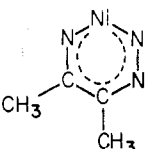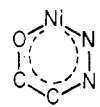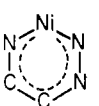with a relative intensity of 6 is assigned to the hydrogens of the geminal methyls of the ligand. The four singlets, each with relative intensity 3, correspond to the methyl hydrogens from the 2,3-butanedione monohydrazone residues of the ligand. The observed spectrum is consistent with the ligand being coordinated to the nickel(II) ion as in V, with the nitrogen

V
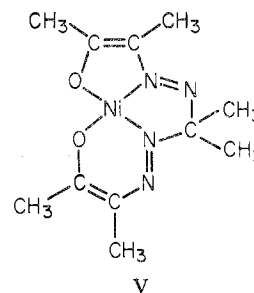
atoms of the hydrazone residues comprising parts of five-membered monoaza and triaza chelate rings and a six-membered diaza chelate ring. Alternate modes of coordination of the ligand as a tetradentate with an N₂O₂ donor set would give rise to diaza and tetraaza rings only, although these modes are not consistent with the observed pmr spectrum. Baldwin, *et al.*,[8] and Goedken and Peng[9] have recently reported some complexes containing macrocyclic ligands derived from di-hydrazones. These ligands are coordinated such that a maximum number of triaza rings, rather than tetraaza rings, are produced.

For NiTBK, five singlets are observed in the pmr spectrum (see Table I and Figure 2). The singlet of relative intensity 6 is assigned to the hydrogens of the geminal methyls of the ligand. The two singlets each of relative intensity 9 and the singlets of relative intensity 1 arise from hydrogens of the 3,3-dimethyl-1,2-butanedione monohydrazone residues of the ligand. No evidence for isomerization of NiTBK (or for 3,3-dimethyl-1,2-butanedione monohydrazone) was observed. We thus conclude that the initial condensation reaction between the diketone and hydrazine occurs exclusively at one carbonyl group. We further conclude that this condensation takes place at the carbonyl group with the hydrogen substituent, since Newman and Kahle[10] have noted the low reactivity toward hydrazine of a carbonyl with a *tert*-butyl substituent. The observed pmr spectrum of NiTBK is consistent with the ligand

Table II. Major Peaks in Mass Spectra of Compounds

NiDMK		NiDMM		NiTBK	
m/e^a	Assignment^b	m/e^a	Assignment^b	m/e^a	Assignment^b
296	Parent	320	Parent	352	Parent
281	P – CH$_3$	305	P – CH$_3$	337	P – CH$_3$
268	P – N$_2$	292	P – N$_2$	324	P – N$_2$
		236	P – NNC(CH$_3$)$_2$N	267	P – OCC(CH$_3$)$_3$
				240	P – OCC(CH$_3$)$_3$CHN
198	[structure]	182	[structure]	226	[structure]
156	[structure]	168	[structure]	184	[structure]
140	NiNNC(CH$_3$)C(CH$_3$)	154	[structure]	170	NiOC(CH$_3$)$_3$CHN
128	NiOC(CH$_3$)C(CH$_3$)	138	CH$_3$CNC(CH$_3$)NNC(CH$_3$)$_2$	126	[structure]
		124	[structure]	115	NiC(CH$_3$)$_3$

^{a} For nickel-containing species, the value for ^{58}Ni is given. These species were identified by the isotope pattern. ^{b} All fragments assumed to be positively charged.
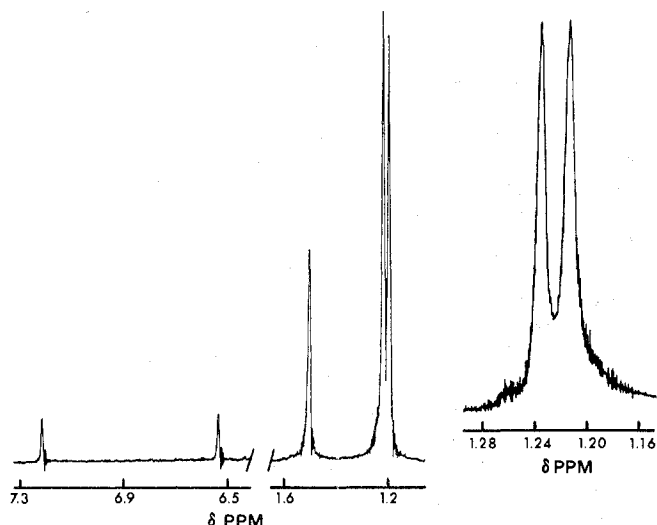

**Figure 2.** The 100 MHz proton magnetic resonance spectrum of NiTBK.

structure and the mode of coordination as in VI, t-Bu = C(CH$_3$)$_3$.

The major peaks observed in the mass spectra of NiDMK and NiTBK are listed in Table II. In each case, a series of highest mass peaks is observed with the most intense peak of the series corresponding to the parent ion containing ^{58}Ni. Less intense peaks of the series at higher mass numbers arise from other isotopes, (nickel, carbon, nitrogen, etc). The fragmentation patterns of the complexes are similar and can readily

Table III. Electronic Absorption Spectra^a

Compd	λ, nm	$10^{-3}\epsilon_M$, M^{-1} cm^{-1}	Compd	λ, nm	$10^{-3}\epsilon_M$, M^{-1} cm^{-1}
NiDMK	312	9.3	NiDMM	290	5.1
	364	8.8		337	5.6
	454	4.5		410	6.2
NiTBK	312	13.4		490 sh	3.2
	358	9.5	NiHcyclo13^c	350	17.5
	450	4.6		459	12.2
NiMMK^b	344	15.7			
	390	17.9			
	460 sh	8.8			
	495	7.7			

^{a} Spectra obtained in acetonitrile. ^{b} From ref 4. ^{c} From ref 5.

VI
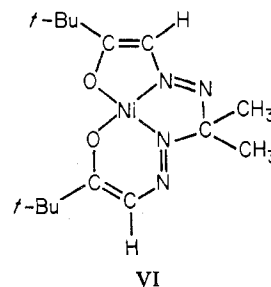
be accounted for on the basis of the proposed structures. Fragments containing six-membered diaza chelate rings are predominant, illustrating their presence in the complexes and the considerable stability of such electron-delocalized rings.

The ultraviolet and visible spectra for NiDMK and NiTBK are reported in Table III. The absorption band with a
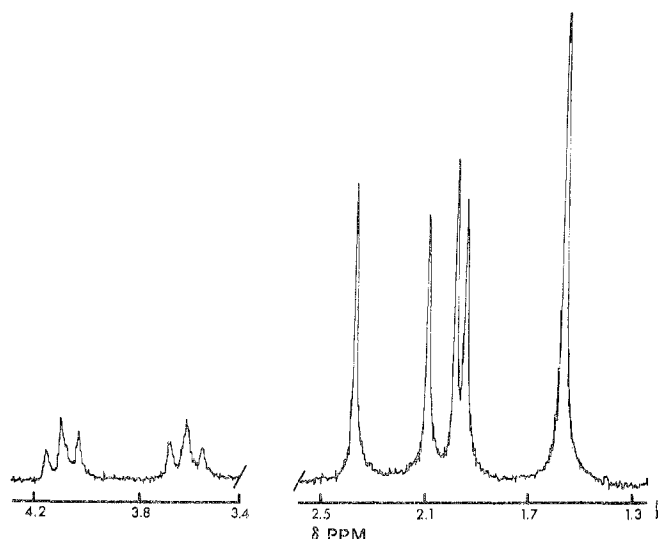
Figure 3. The 100 MHz proton magnetic resonance spectrum of NiDMM.

Figure 4. Proton magnetic resonance spectrum for NiDMM between 3.5 and 4.2 ppm: upper curve, experimental; lower curve, computer simulated.

maximum at about 450 nm is assigned to the $^1A_1 \rightarrow {}^1B_1$ transition for nickel(II) in a *cis*-NiO$_2$N$_2$ planar environment,[11,12] which is required by the nature of the ligands. These absorption bands are found at slightly higher energies than the corresponding band in NiMMK.[4] Other absorption bands in NiDMK and NiTBK are assigned as charge-transfer or ligand bands. Both complexes are diamagnetic in agreement with the proposed singlet ground state for the nickel(II) ion.

On the basis of all the evidence presented and the conclusion drawn that the mode of coordination of the ligands in NiDMK and NiTBK is similar, we assume that in NiMMK, which is derived from benzil monohydrazone, the ligand is also coordinated in a similar manner. Due to the complex nature of the pmr spectrum of NiMMK in the phenyl hydrogen region,[4] no differences in environment of the phenyl groups were detected and no *definite* conclusions concerning the mode of coordination of the ligand could be drawn at that time.

In an earlier paper,[5] we reported that reactions between NiMMK and some amines give rise to complexes containing macrocyclic ligands with N$_4$ donor sets, IV. As part of our overall program which is concerned with the determination of factors involved in metal ion controlled condensation reactions the compounds NiDMK and NiTBK provide an opportunity to determine the influence of the substituent at the cis-oriented coordinated CO groups on condensation reactions with amines. When NiDMK is heated with ethylenediamine at a temperature just below the boiling point for 30 min, a red-orange microcrystalline product (abbreviated NiDMM) is obtained. The analytical data suggest that NiDMM is a neutral nickel complex containing a ligand formed by a condensation reaction between ethylenediamine and the two coordinated CO groups of NiDMK. The infrared spectrum of NiDMM differs significantly from that of NiDMK. The absorption at 1322 cm^{-1} in the spectrum of NiDMK, assigned to ν(C–O), is absent in the NiDMM spectrum. However, the absorption at 1150 cm^{-1} in NiDMK, ν(C–N), is still present in NiDMM together with a new band at 1170 cm^{-1} (also assigned to ν(C–N)). These changes are consistent with the condensation reaction proposed above. Thus, the complex obtained contains a dinegatively charged 13-membered macrocyclic ligand, similar to that obtained from the reaction of ethylenediamine with NiMMK.

The pmr spectrum of NiDMM is shown in Figure 3, with the chemical shifts, relative intensities and assignments recorded in Table I. The spectrum is similar to that of NiDMK, with the methyl hydrogens from the 2,3-butanedione residue
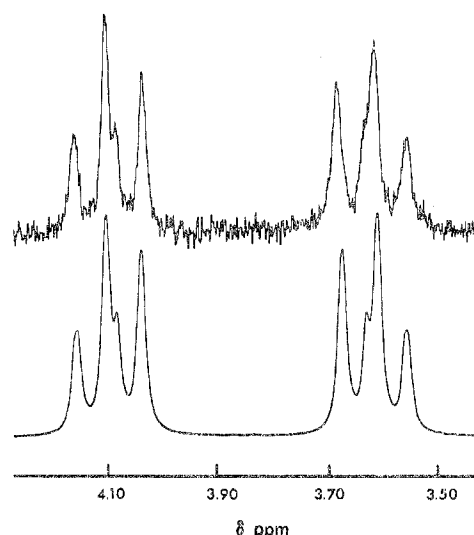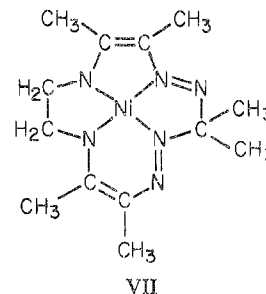
being in different chemical environments and the geminal methyl hydrogens occurring as a singlet (relative intensity 6). The methylene hydrogens of the new chelate ring appear as two "triplets," centered at δ 3.63 and 4.10 ppm. The pmr data are consistent with NiDMM having structure VII.

VII

The major peaks observed in the mass spectrum of NiDMM are listed in Table II. The parent ion and the fragmentation pattern are both consistent with structure VII. The stability of the six-membered chelate ring is again apparent. The uv–visible spectrum of NiDMM is similar to that of NiDMK although the major peaks are shifted toward higher energy (see Table III).

The absorption band at 410 nm is assigned to the $^1A_{1g} \rightarrow {}^1B_{1g}$ transition in this environment. The higher energy bands are assigned to charge-transfer or ligand transitions.

The conformation of the five-membered chelate ring containing the dimethylene chain in NiDMM may be either eclipsed or staggered if rapid flexing of the ring is not taking place on an nmr time scale. If the conformation is eclipsed or if rapid flexing of the ring is taking place, an A$_2$B$_2$ pattern should be observed for the pmr spectrum of the methylene hydrogens. If the ring possesses a staggered conformation and ring flexing is slow, a more complex spectrum should be observed. Figure 4 shows the experimental pmr spectrum of the methylene hydrogens for NiDMM as the upper curve and the computer-simulated spectrum[13] as the lower curve. The experimental spectrum does not change up to ~55°, close to the boiling point for CHCl$_3$-d. Good agreement between the simulated and experimental spectra could not be obtained by assuming an A$_2$B$_2$ system, as found for the corresponding macrocycle derived from NiMMK.[6] Thus for NiDMM we can eliminate rapid flexing of the ring and an eclipsed conformation. Satisfactory agreement between experimental and simulated spectra is achieved, however, if an AA'BB' system

is assumed, with J_{AB}(gem) = –13 Hz, $J_{AA'}$(vic) = 4.7 Hz, and $J_{AB'}$(vic) = 7.1 Hz. This pattern is consistent with the mode of coordination of the macrocyclic ligand in VII and also indicates a staggered conformation for the dimethylene chain, with a small difference in environment between the axial and equatorial hydrogens. This difference is most probably due to the deshielding of the axial hydrogens by electrons in the d_{z^2} orbital of the nickel(II) ion as predicted by Buckingham and Stevens.[14] Warner, Rose, and Busch[15] have also noted the difference between axial and equatorial protons of a dimethylene chain in a nickel(II) complex containing a macrocyclic ligand.

When NiTBK is heated with ethylenediamine under similar or more forcing conditions to those used with NiDMK, no reaction takes place and NiTBK is recovered unchanged from the reaction medium. It is thus apparent that the reactivity of the coordinated CO groups in complexes containing ligands of type III is dependent on the attached R group. Since the nature of the R group will affect the electron density at the carbon atom of the CO group, the extent of nucleophilic attack at that carbon atom may also be affected. The C(CH3)3 group is both electron releasing and bulky and this results in the CO group of NiTBK being less susceptible to nucleophilic attack than the CO group in NiDMK or NiMMK with methyl and phenyl substituents, respectively. We may thus conclude that reactions with amines proceed *via* attack of the amine at the

carbon of the coordinated CO group, followed by elimination of a water molecule. This may be preceded by initial coordination of the amine as a unidentate ligand to the nickel. The role of the metal ion in condensations of this type is both that of an electron-withdrawing species and that of a template, holding the CO groups in cis orientation such that macrocyclic ligands may be produced by reaction with a suitable diamine.

References and Notes

(1) N. F. Curtis, *Coord. Chem. Rev.*, **3**, 3 (1968).
(2) D. H. Busch, *Advan. Chem. Ser.*, No. 100, 44 (1971).
(3) L. F. Lindoy and D. H. Busch, *Prep. Inorg. React.*, **6**, 1 (1971).
(4) C. M. Kerwin and G. A. Melson, *Inorg. Chem.*, **11**, 726 (1972).
(5) C. M. Kerwin and G. A. Melson, *Inorg. Chem.*, **12**, 2410 (1973).
(6) G. A. Melson, *Inorg. Chem.*, **13**, 994 (1974).
(7) T. W. J. Taylor, N. H. Callow, and C. R. W. Francis, *J. Chem. Soc.*, 257 (1939).
(8) J. E. Baldwin, R. H. Holm, R. W. Harper, J. Huff, S. Koch, and T. J. Truex, *Inorg. Nucl. Chem. Lett.*, **8**, 393 (1972).
(9) V. L. Goedken and S. M. Peng, *J. Chem. Soc., Chem. Commun.*, 62 (1973).
(10) M. S. Newman and G. R. Kahle, *J. Org. Chem.*, **23**, 666 (1958).
(11) G. Maki, *J. Chem. Phys.*, **29**, 1129 (1958).
(12) R. D. Archer, *Inorg. Chem.*, **2**, 292 (1963).
(13) Simulation achieved using NMRCAL, a nuclear magnetic resonance spectrum calculation program, Nicolet Instrument Corp., 1971.
(14) A. D. Buckingham and P. J. Stevens, *J. Chem. Soc.*, 4583 (1964).
(15) L. G. Warner, N. J. Rose, and D. H. Busch, *J. Amer. Chem. Soc.*, **90**, 6938 (1968).

Contribution from the Department of Chemistry and Biochemistry, Southern Illinois University, Carbondale, Illinois 62901

Molecular Charge-Transfer Complexes of Metalloporphyrins with Bis(*cis*-1,2-trifluoromethylethylene-1,2-dithiolato)nickel

GERALD M. SHKOLNIK and WILLIAM E. GEIGER, Jr.*

Zinc and cobalt tetraphenylporphyrins each form 1:1 molecular complexes with the strong acceptor Ni(S2C2(CF3)2)2, Ni(tfd)2. The optical absorption, infrared, and electron spin resonance spectra of these 1:1 complexes have been studied. Zn-(TPP)Ni(tfd)2 is a Mulliken-type donor–acceptor complex with a neutral ground state showing an intermolecular charge-transfer band at approximately 1900 nm (5.26 kK). Co(TPP)Ni(tfd)2 is a covalent compound having a Co–S bridging bond but nevertheless has a charge-transfer band (intramolecular) at 1370 nm (7.30 kK). The complexes disproportionate in solution, to an extent dependent on the solvent polarity. Solution thermodynamic data are presented.

Introduction

Metalloporphyrins have been studied widely in recent years because of the importance of these compounds as model systems involving photosynthesis, electron-transport, and other biologically important phenomena. Receiving perhaps the greatest attention have been the redox properties and the axial coordination tendencies of these compounds.[1–5] We were interested in the possibility of synthesizing donor–acceptor complexes of metalloporphyrins and chose to investigate reactions of the zinc and cobalt tetraphenylporphyrins with bis(*cis*-trifluoromethylethylene-1,2-dithiolato)nickel, Ni(tfd)2 (**1**), which had previously been shown to be a strong acceptor

1
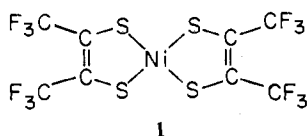
capable of forming donor–acceptor charge-transfer complexes in either neutral or ionic ground states.[6–8] The zinc and cobalt complexes were chosen on the basis of their published oxidation potentials, which suggested that they might act as donors when

* To whom correspondence should be addressed at the Department of Chemistry, University of Vermont, Burlington, Vt. 05401.

mixed with Ni(tfd)2.[9] A neutral ground-state donor–acceptor complex was formed between Ni(tfd)2 and the zinc complex, but a covalent compound was obtained from the reaction of the nickel and cobalt complexes. In spite of the formal difference in the two types of compounds formed, a near-infrared charge-transfer band was found in each case, indicating that relatively low-energy excited-state pathways for charge transfer exist in these compounds.

Experimental Section

Materials. α,β,γ,δ-tetraphenylporphine (TPP) was prepared by the method of Adler, *et al.*[10] It was washed numerous times with methanol and hot water, dried under vacuum at 56°, and purified by extraction with benzene,[11,12] followed by removal of benzene under vacuum. α,β,γ,δ-Tetraphenylporphinatozinc (Zn(TPP))[13] was prepared from zinc acetate (20-fold excess) and TPP in dimethylformamide and purified by twice eluting the red-violet band with benzene on alumina. Bis(*cis*-1,2-trifluoromethylethylene-1,2-dithiolato)nickel, Ni(tfd)2, was prepared by the method of Davison, *et al.*,[14] and purified by sublimation. Tetrabutylammonium bis-(*cis*-1,2-trifluoromethylethylene-1,2-dithiolato)nickelate, (Bu4N)-[Ni(tfd)2], was also synthesized by the literature method.[15] Spectroquality dichloromethane and toluene were dried before use, the former by refluxing over calcium hydride for 24 hr and the latter by distillation from sodium metal. Careful drying of these solvents was necessary if spurious reduction of neutral Ni(tfd)2 was to be avoided.