

latter two species, a greater distance exists between the metal ion and the carboxylate group in the "effective" ion pair leading to stable complex formation. Identical behavior has now been reported for the related ligands, glycyl-L-leucinate and L-leucylglycinate.⁴⁹

Although these authors did not attempt to analyze the underlying cause for the shift in kinetic behavior, the difference in reactivities in the two types of amino acids can be readily explained by the relative difficulty in closing the chelate ring *via* mechanism I. In line with our recent analysis of substituted diamine ligands,² much greater steric hindrance will be encountered in closing the chelate ring to the peptide nitrogen as compared to the primary amine nitrogen in glycine. In view of the noted lability of the metal-carboxylate bonds, the result is to slow down the ring closure process to the point where mechanism I becomes slower than mechanism II. The net result is that mechanism II then becomes the dominant reaction path as indicated by the close correlation between our predicted value of $k_{Ni}^L \leq 0.6 \times 10^4 M^{-1} sec^{-1}$ and the experimentally obtained value of $0.3 \times 10^4 M^{-1} sec^{-1}$ for Ni(II) reacting with glycylglycinate ion.³² In fact, for these larger amino acids, the predicted rate constant for attack at the primary (terminal) nitrogen

(49) R. F. Pasternack, L. Gipp, and H. Sigel, *J. Amer. Chem. Soc.*, 94, 8031 (1972).

donor atom is very close to the experimental value since the value of a' greatly exceeds 6.5 Å (attack at the peptide nitrogen being sterically unfavorable²).

Conclusion

The concept of *reactive encounters* in the formation of an outer-sphere complex preceding ligand-solvent exchange at a metal ion center implies a distinction between two distance parameters in the calculation of the outer-sphere equilibrium constant for bulky ligands: (i) the reactive site center-to-center distance, a , and (ii) the charge center-to-center distance, a' . The former distance is presumed to be relatively independent of the bulk ligand dimensions, whereas the latter value is a function of ligand structure including conformational variations. Values generated for the two constants in this work appear to be consistent with experimental kinetic data and permit decisions to be made with respect to competitive mechanistic pathways. It is suggested that a more precise value of a' may be generated by selecting a reaction system which can be studied at lower ionic strength where electrostatic interactions will be magnified.

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Registry No. Ni(H₂O)₆²⁺, 15365-79-4; tmen-Br-HCl, 2565-57-3.

Contribution from the Department of Chemistry,
Michigan State University, East Lansing, Michigan 48823

Reactivity of Coordinated Carbonyl Groups. Formation of Nickel(II) Complexes with Macrocyclic and Noncyclic Ligands Derived from Benzil Monohydrazone

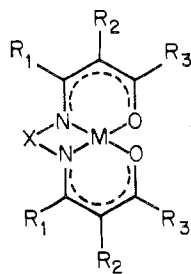
C. MICHAEL KERWIN and GORDON A. MELSON*

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Reactions between nickel(II) complexes containing a coordinated tetradentate "N₂O₂" ligand derived from benzil monohydrazone and various amines have been investigated. It has been shown that condensation reactions take place to produce both macrocyclic and noncyclic ligands. These new compounds have been characterized by a variety of physical techniques.

Introduction

The formation of Schiff base complexes by the condensation of amines with coordinated aldehydes or ketones is well known.¹ Recently, several authors have reported attempts to synthesize coordinated macrocyclic ligands by condensation reactions between diamines and the -CO group in complexes containing tetradentate ligands of type I. The re-



I, X = C₂H₄, C₃H₆, C₆H₄

(1) (a) L. F. Lindoy, *Quart. Rev., Chem. Soc.*, 25, 379 (1971); (b) J. P. Candlin, K. A. Taylor, and D. T. Thompson, "Reactions of Transition Metal Complexes," Elsevier, Amsterdam, 1968, p 83; (c) R. H. Holm, G. W. Everett, and A. Chakravorty, *Progr. Inorg. Chem.*, 7, 83 (1968).

activity of these systems toward diamines is dependent on the nature of the substituent in the R₂ (meso) position. When R₂ = -COR or -COOR, cyclization readily occurs with aliphatic diamines,² although no reaction is observed between ethylenediamine and complexes that do not have either of these substituents in the R₂ position.³ Cyclization does occur however when compounds with X = C₆H₄ and R₂ = H or -COR are heated in molten *o*-phenylenediamine.⁴ When R₂ and R₃ are part of a cyclohexane ring and X = C₆H₄, cyclization will not take place with either aliphatic or aromatic diamines.⁵ If the cyclohexane ring contains a -C=O group, cyclization does not take place with *o*-phenylenediamine, but with ethylenediamine cyclization is observed, accompanied by amine exchange. The reactivity of the coordinated -CO group in complexes of type I is thus dependent on the nature of the ligand "backbone" and the amine used.

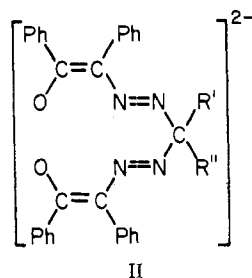
(2) E. G. Jager, *Z. Chem.*, 8, 30, 392, 470 (1968).

(3) (a) T. J. Truex and R. H. Holm, *J. Amer. Chem. Soc.*, 94, 4529 (1972); (b) D. St. C. Black and M. J. Lane, *Aust. J. Chem.*, 23, 2039 (1970).

(4) E. Jager, *Z. Chem.*, 4, 437 (1964); *Z. Anorg. Allg. Chem.*, 364, 177 (1969).

(5) P. Bamfield, *J. Chem. Soc. A*, 2021 (1969).

We⁶ have reported that reaction between benzil monohydrazone and some ketones R'R''CO in the presence of nickel(II) ions results in the formation of complexes containing tetradentate ligands in which two benzil monohydrazone residues are linked by a single carbon atom from the ketone, II. In view of the varied reactivity of the coordinated



-CO group in complexes of type I and the fact that compounds derived from type II ligands also contain coordinated -CO groups but with a completely different backbone, the reactivity of the latter compounds toward amines has been investigated. It was anticipated that condensation reactions with diamines should produce new macrocyclic ligand systems of varying ring size.

We report here reactions between various amines and one of the complexes of type II, *viz.*, R' = R'' = Me, abbreviated NiMMK throughout.

Experimental Section

Materials. [α' , α'']-[Isopropylidenebis(azo)]di- α -stilbenolato]-nickel(II), NiMMK, was prepared as previously described.⁶ Diamines were distilled from sodium hydroxide under nitrogen before use. All other chemicals were of reagent grade or equivalent.

Reactions of NiMMK with Amines. [3,3-Dimethyl-6,7,12,13-tetraphenyl-1,2,4,5,8,11-hexaazacyclotrideca-1,4,6,12-tetraenato]-nickel(II) (NiHcyclo-13). To 10 ml of anhydrous ethylenediamine under dry N₂ was added 0.54 g (0.001 mol) of NiMMK. The reaction mixture was heated to a temperature just below the boiling point and stirred for 30 min. The dark red solution was allowed to cool to room temperature. The bright red powder obtained was 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 a bright red powder. *Anal.* Calcd for C₃₃H₃₀N₆Ni: C, 69.60; H, 5.32; N, 14.76. Found: C, 69.22; H, 5.28; N, 14.71.

The same product can be isolated by stirring NiMMK with anhydrous ethylenediamine at room temperature for 48 hr.

[3,3,9-Trimethyl-6,7,12,13-tetraphenyl-1,2,4,5,8,11-hexaazacyclotrideca-1,4,6,12-tetraenato]-nickel(II) (NiMcylo-13). This compound is obtained as a red powder by procedures similar to those described above, using NiMMK and anhydrous *rac*-1,2-diaminopropane. *Anal.* Calcd for C₃₄H₃₂N₆Ni: C, 69.99; H, 5.54; N, 14.41. Found: C, 69.28; H, 5.54; N, 14.36.

[α' -[1-[2-[(3-Aminopropyl)amino]-1,2-diphenylvinyl]azo]-1-methylethyl]azo]- α -stilbenolato]-nickel(II) (NiApSo). To 10 ml of anhydrous 1,3-propanediamine under dry N₂ was added 0.54 g (0.001 mol) of NiMMK. The reaction mixture was stirred at room temperature for 48 hr. The solution was filtered and the bright red residue isolated. The amine was removed from the filtrate by distillation under vacuum. A bright red powder remained. The two batches of red solid obtained were combined and recrystallized from methanol (or ethanol). The product was obtained as bright red crystals. *Anal.* Calcd for C₃₄H₃₄N₆ONi: C, 67.89; H, 5.71; N, 13.98. Found: C, 67.54; H, 5.93; N, 14.75.

[α' -[1-[2-(Ethylamino)-1,2-diphenylvinyl]azo]-1-methylethyl]azo]- α -stilbenolato]-nickel(II) (NiESo). Fifteen milliliters of ethylamine was added to 0.54 g (0.001 mol) of NiMMK in a pressure tube. The tube and contents were cooled to liquid N₂ temperature and then connected to a vacuum pump for 15 min. The tube was sealed, allowed to warm to room temperature, and then heated in an oil bath at ~110° for 3 hr. After cooling to liquid N₂ temperature,

the tube was opened and warmed until all the ethylamine evaporated. The red solid obtained was purified by chromatography on a neutral alumina column using a benzene-diethyl ether mixture as eluent. The product was obtained as a red solid. Satisfactory analyses could not be obtained for this compound although a parent ion peak of *m/e* 571 (based on 58 for Ni) was observed.

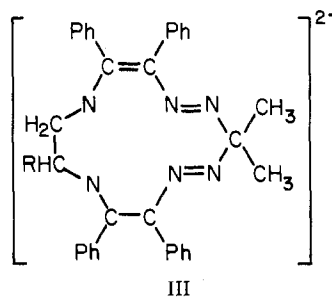
Physical Measurements. Infrared spectra were obtained on a Perkin-Elmer Model 457 spectrophotometer using Nujol and Fluorolube mull techniques. Visible and ultraviolet spectra were obtained with a Unicam SP 800B spectrophotometer. Mass spectra were determined with Hitachi Perkin-Elmer RMU-60 and CEC21-110B double-focusing mass spectrometers. Accurate masses were measured with a Nier-type peak matching unit attached to the latter instrument (accuracy ~4 ppm). Elemental analyses were performed by Chemalytics, Tempe, Ariz.

Results and Discussion

Reactions with Ethylenediamine and 1,2-Propanediamine.

When NiMMK is stirred with ethylenediamine or 1,2-diaminopropane at room temperature or 110°, the color of the solution slowly changes from orange-red to dark red. Standard work-up procedures result in the isolation of dark red microcrystalline nickel(II) complexes from these reaction media. The structures of the new ligand systems produced have been deduced from the infrared and mass spectra of these complexes.

The infrared spectra of both complexes are complicated in that many absorptions are observed. However, they bear close resemblance to the spectrum of NiMMK but with significant differences. The very strong composite band centered at 1280 cm⁻¹ in NiMMK and assigned to a combination of ν (C-N) and ν (C-O) is modified after reaction with the diamines. Two new very strong bands are now observed at 1295 and 1270 cm⁻¹ and are assigned to ν (C-N). Additional bands in the region of 700 cm⁻¹ are assigned to vibrations characteristic of CH₂ groups, which must be present in the new complexes. The strong band at 1530 cm⁻¹ in NiMMK is shifted to 1490 cm⁻¹ in the new complexes. It is thus concluded that condensation reactions between the amines and NiMMK must have taken place. Confirmation of the structures of the ligands is provided from a study of the mass spectra and fragmentation patterns of the complexes. For both complexes, the highest mass peak observed corresponds to the parent ion. The distribution of masses expected from isotopes of nickel, carbon, and nitrogen is observed. Table I lists the fragmentation patterns for the complexes; for nickel-containing species the mass corresponding to ⁵⁸Ni is given. One of the characteristic features of the observed patterns is the considerable stability associated with a five-membered chelate ring containing the nickel ion, as also noted in our previous paper on the nickel ketazines.⁶ The observed fragmentation patterns can be readily explained assuming structure III for the new macrocyclic ligand. Thus,



R = H, NiHcyclo-13 from ethylenediamine
R = Me, NiMcylo-13 from 1,2-diaminopropane

in the above reactions, condensations have taken place between the -CO groups of the coordinated ligand in NiMMK

(6) C. M. Kerwin and G. A. Melson, *Inorg. Chem.*, 11, 726 (1972).

Table I. Mass Spectra for Compounds

m/e^a	Assignment ^b	m/e^a	Assignment ^b
P	Parent ion	278	
P-15 ^c	P-CH ₃		
P-28	P-N ₂		
P-56	P-(NC(CH ₃) ₂)		
P-84	P-((N) ₂ C(N)(CH ₃) ₂)		
P-131 ^c	P-(PhC(N)(CH ₃) ₂)	264	
P-159	P-(PhC(N) ₂ C(CH ₃) ₂)		
P-187	P-(PhC(N) ₂ C(CH ₃) ₂ (N) ₂)		
P-276	P-(Ph(C) ₂ Ph(N) ₂ C(CH ₃) ₂)		
P-290	P-(PhC(N)CPh(N) ₂ C(CH ₃) ₂ N)	250	NiNCPhCPh
P-332	P-(CH ₂ NCPhCPh(N) ₂ C(CH ₃) ₂)	236	NiCPhCPh
306 ^c		201	
292 ^c	306-N	193	PhCNCPh
		178	PhCCPh
		166	CPh ₂
		147	NiCPh
		99	CPh
		77	Ph

^a For nickel-containing species, the value for ⁵⁸Ni is given. ^b All fragments assumed to be positively charged. ^c For macrocyclic compounds only.

and the diamines resulting in the formation of new macrocyclic ligand systems coordinated to nickel(II). These new dinegatively charged 13-membered macrocyclic ligands contain six potential donor nitrogen atoms but are assumed to coordinate as tetradentate ligands with the nitrogen atoms not linked by the bridging carbon atom being coordinated to the nickel(II) ion. A macrocyclic ligand containing a similar ring coordinated to nickel(II) has recently been shown to coordinate in this manner.⁷

The absorption spectra of NiHcyclo-13 and NiMyclo-13 are reported in Table II and in Figure 1. The spectra are typical of nickel(II) complexes with a singlet ground state in an N₄ square-planar environment,⁸ the lowest energy band in the region of 450 nm for both complexes being assigned to the ¹A_{1g} → ¹B_{1g} transition. The higher energy bands are assigned to ligand or charge-transfer transitions. Both complexes are diamagnetic ($\mu_{\text{eff}} \approx 0.5$ BM) in agreement with the proposed singlet ground state for the nickel(II) ion.

Molecular models indicate that the 13-membered macrocyclic ligands may be accommodated in a square-planar geometry about the nickel(II) ion in the proposed 6-5-5-5 arrangement. It is probable that a slight tetrahedral twisting of the ligand system takes place to reduce some apparent strain inherent in the purely planar configuration. This twisting is not sufficient however to result in removal of the singlet ground state for the nickel(II) ion. Tetrahedral distortions of this nature have been confirmed by structural characterization of nickel(II) complexes containing both 13-membered⁹ and 14-membered¹⁰⁻¹² macrocyclic ligands. Thirteen-membered macrocyclic ligands are the smallest known to coordinate in a roughly square-planar environment. Although it has been suggested⁹ that this is not the limiting

(7) N. W. Alcock and P. A. Tasker, *J. Chem. Soc., Chem. Commun.*, 1239 (1972).

(8) N. F. Curtis, *Coord. Chem. Rev.*, 3, 3 (1968).

(9) M. F. Richardson and R. E. Sievers, *J. Amer. Chem. Soc.*, 94, 4134 (1972).

(10) I. E. Maxwell and M. F. Bailey, *Chem. Commun.*, 883 (1966).

(11) B. T. Kilbourn, R. R. Ryan, and J. D. Dunitz, *J. Chem. Soc. A*, 2407 (1969).

(12) F. Hanic and D. Miklos, *J. Cryst. Mol. Struct.*, 2, 115 (1972).

Table II. Electronic Absorption Spectra^a

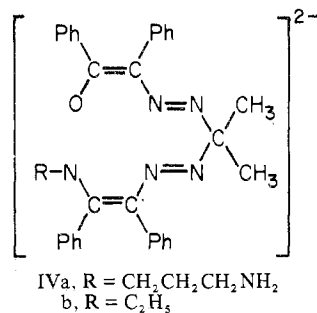
Compd	λ , nm	$10^{-3} \epsilon_{\text{cm}^{-1}}$		Compd	λ , nm	$10^{-3} \epsilon_{\text{cm}^{-1}}$	
		M^{-1}	cm^{-1}			M^{-1}	cm^{-1}
NiHcyclo-13	459	12.2		NiESo	510	7.5	
	350	17.5			464 sh	8.9	
NiMyclo-13	440	9.9			405	17.0	
	334	15.8			348	14.5	
NiApSo	440	12.2		NiMMK ^b	495	7.7	
	420 sh	12.0			460 sh	8.8	
	340	10.8			390	17.9	
					344	15.7	

^a All spectra obtained in benzene. ^b From ref 6.

ring size for square-planar coordination, nickel(II) and cobalt(III) complexes of 12-membered macrocycles contain the ligands in a folded conformation.^{13,14}

Reaction with 1,3-Propanediamine and Ethylamine. Reaction between NiMMK and 1,3-propanediamine at room temperature or $\sim 110^\circ$ results in the formation of a bright red complex, NiApSo. (At temperatures close to the boiling point of the amine, extensive decomposition takes place.) The bright red complex has been characterized by similar techniques to those used earlier. The infrared spectrum of NiApSo is very similar to that of NiMMK but shows some additional absorption bands in the region of 3100 and 1630 cm^{-1} assigned to $\nu(\text{NH}_2)$ and $\delta(\text{NH}_2)$, respectively. The 1280- cm^{-1} band in NiMMK is shifted slightly to 1270 cm^{-1} and new bands are observed around 700 cm^{-1} , as found for NiHcyclo-13 and NiMyclo-13. The strong band at 1530 cm^{-1} in NiMMK does not change position in NiApSo. The highest mass peak observed in the mass spectrum of NiApSo (600 for ⁵⁸Ni) corresponds to 18 mass units higher than that for the expected macrocycle. No mass peak at this lower value (582) was observed however. The fragmentation pattern shows some significant differences when compared with the patterns of the macrocyclic complexes (Table I).

From the infrared and mass spectral data, we conclude that although a condensation reaction has taken place between NiMMK and 1,3-propanediamine a closed macrocyclic ligand system has not been produced. Rather, condensation has taken place at one CO group of NiMMK only. The presence of an amine group in NiApSo was confirmed by the synthesis of a mono(*p*-toluenesulfonyl) derivative, identified by its infrared and mass spectra. We thus conclude that the ligand in NiApSo has the structure IVa. The new ligand is poten-



tially pentadentate and it is possible that the NH₂ group is coordinated to the nickel(II) ion. Such coordination would not necessarily inhibit the reactivity of the amine group toward *p*-toluenesulfonyl chloride since coordinated amine groups in nickel(II) compounds containing ornithine and

(13) G. A. Kalligeros and E. L. Blinn, *Inorg. Chem.*, 11, 1145 (1972).

(14) J. P. Collman and P. W. Schneider, *Inorg. Chem.*, 5, 1380 (1966).

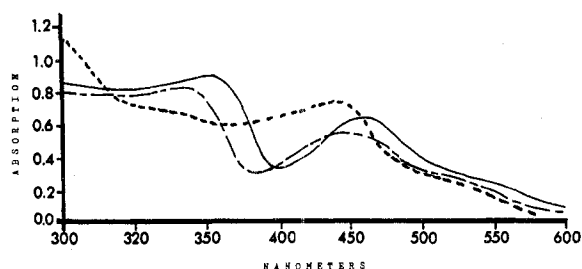


Figure 1. Absorption spectra $5 \times 10^{-5} M$ solutions in benzene: —, NiHcyclo-13; ---, NiMycyclo-13; - · -, NiApSo.

lysine have been shown to form monobenzoyl derivatives under conditions similar to those employed by us.¹⁵ If coordination does take place, it is not sufficiently strong to remove the singlet ground state for the nickel(II) ion (NiApSo is diamagnetic). Assuming coordination in an axial position, the distortion will be small and the Ni-NH₂ bond distance significantly longer than the in-plane nickel-donor atom distance. Under these circumstances the level of the d_{z^2} orbital will be raised slightly in energy. If the d_{xy} orbital is still the highest filled orbital, then the transition $d_{xy} \rightarrow d_{x^2-y^2}$ will be the lowest in energy, just as in the case for a square-planar d^8 system. Since the energy difference between these two orbitals is independent of pentacoordination, it is thus not possible to use the position of the first transition in these spectra to differentiate between a square-planar environment and one with a weakly coordinated group in an axial position.¹⁶ The absorption spectrum for NiApSo (see Table II and Figure 1) is indeed very similar to those for complexes containing the macrocyclic ligands in a square-planar environment. Models indicate that coordination in the axial position could take place without the introduction of any substantial strain in the resultant chelate ring or ligand system.

The isolation of NiApSo is particularly interesting since the proposed structure is very similar to that suggested¹⁷ as a possible intermediate in a metal ion controlled condensation reaction involving a diamine and a diketone. A coordinated macrocyclic ligand is produced, the function of the metal ion being that of a template. We thus anticipated that it should be possible to produce a 14-membered macrocyclic ligand

(15) G. R. Brubaker and D. H. Busch, *Inorg. Chem.*, **5**, 2110 (1966).

(16) C. Furlani, *Coord. Chem. Rev.*, **3**, 141 (1968).

(17) M. Green, J. Smith, and P. A. Tasker, *Inorg. Chim. Acta*, **5**, 17 (1971).

either by carrying out the reaction between NiMMK and 1,3-propanediamine under more rigorous conditions or by ring closure of NiApSo. However, NiApSo was the only product isolated from condensation reactions run at higher temperatures in sealed tubes or for longer times than those described earlier. No macrocyclic product was obtained by heating NiApSo at 100° under vacuum over P₄O₁₀ for several days or by heating in a variety of solvents. When 1-butanol was used as solvent and the solution heated at the boiling point for 6 hr, a red product was obtained which displayed a parent ion peak of 596 in its mass spectrum, *i.e.*, 4 mass units less than NiApSo. From the infrared spectrum, we conclude this product has R = CH=CH-CH=NH in structure IV. Thus under the conditions used, NiApSo prefers to undergo dehydrogenation rather than elimination of a water molecule and ring closure. This behavior may be understood if the NH₂ group in NiApSo is coordinated sufficiently strongly to the nickel ion that reaction with the coordinated CO group will not take place. A contributing factor to the apparent reluctance of NiApSo to undergo ring closure may be that the "reactivity" of the second coordinated CO group appears to be reduced after the first has undergone condensation. The reaction of NiMMK with ethylamine at 110° in a sealed tube results in the formation of a red solid for which structure IVb (R = C₂H₅) is proposed. No disubstituted product is obtained even when longer reaction times or higher temperatures are employed. Since the reactions were carried out in the anhydrous amine, there is a very large excess of reactant present and one is led to conclude that the reactivity of one of the coordinated CO groups is less than that of the other.

How can we account for the difference in behavior of the diamines? Models indicate that very little strain is present in the ligand system of NiApSo when the NH₂ group is coordinated in the axial position. If a corresponding model is made using ethylenediamine or 1,2-propanediamine residues, considerable strain is present in the new chelate ring and the NH₂ group can be only weakly coordinated to the nickel ion. This difference in strength of coordination of the NH₂ group and the apparent difference in reactivity of the coordinated CO groups might determine whether further reaction takes place to give a macrocyclic ligand or not.

Registry No. NiHcyclo-13, 41267-48-5; NiMycyclo-13, 41184-55-8; NiApSo, 41184-56-9; NiESo, 41184-57-0; NiMMK, 41184-58-1; ethylenediamine, 107-15-3; 1,2-diaminopropane, 78-90-0; 1,3-propanediamine, 109-76-2; ethylamine, 75-04-7.