

Amine Exchange Reactions of Bis(isonitroso- β -ketoimino) Nickel(II) Complexes with Polyamines and Thiosemicarbazide

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Amine-exchange reactions on Ni(II) complexes of bidentate oximino- β -ketoimines are investigated. With diethylene triamine and tetraethylene pentamine, both the —NH_2 ends of polyamines undergo amine-exchange with the imine —NH protons of the parent complexes. In the case of thiosemicarbazide, it is found that only the imine —NH proton of 5-membered ring undergoes amine exchange. The structures of the amine exchange reaction products have been discussed based on the spectroscopic results.

Key Words: Amine exchange, Nickel(II) oximino- β -ketoimine.

INTRODUCTION

The reactions of coordinated ligands find certain applications as models to understand and explore certain biochemical processes such as amination, *trans*-amination or deamination etc., to mention a few. Interaction of coordinated imine ligands like β -ketoimines and oximino- β -keto alkylamine, etc., with a primary amine can produce either an amine product or exchange the substituent R (= R, alkyl or aryl) of the $>\text{C}=\text{(NR)—}$ moiety by the added amine, R—NH_2 ^{1–6}. The latter reaction was employed for the first time by Schiff⁷ to prepare new coordination compounds. *Trans*-esterification and amidation reaction were performed on bis(salicyaldimine) copper(II)^{8–10}. The amine exchange reactions of ethylenediamine and *o*-phenylenediamine on Mn(III) (salicyaldimine), OAC¹¹ to a lesser extent on bis(β -ketoiminato) copper(II) complexes have also been studied. Similar amine exchange reactions were also conducted on bis(isonitroso- β -ketoimino) nickel(II) and palladium(II) complexes^{12–14}. Investigations on the reactions of the coordinated imine group with primary amine are important from the point of view of their synthetic utility and also because of their relevance in the biological processes like *trans*-amination and *trans*-esterification. Although

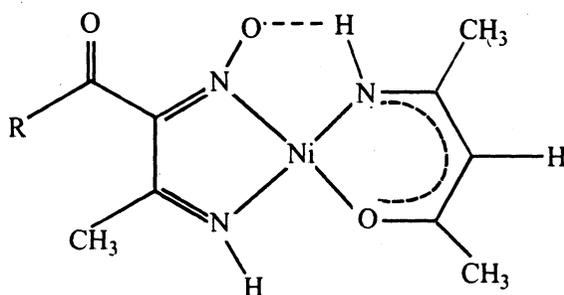
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several reports are available in literature¹²⁻¹⁶ concerning these studies, factors attending these reactions are not yet understood clearly. In most of the previous studies conducted in our laboratory on the amine exchange reaction of bis(isonitroso- β -ketoimino) nickel(II) complexes with simple aliphatic mono- and di-amines, only the roles of basicity and steric factors in the reactions have been emphasized^{13, 17}. The present work on the other hand deals with the reactions of bis(isonitroso- β -ketoimino) nickel(II) complexes with long chain polyamines like diethylene triamine (DET), tetraethylene pentamine (TEP) and thiosemicarbazide (TSC). This is done with a view to exploring the possible factors like basicity, chelating effect, concentration, etc., based on their spectrochemical investigations and also to propose a probable mechanism of the same.

EXPERIMENTAL

All the bis(isonitroso- β -ketoimino) nickel(II) parent complexes, on which the a-e reactions are carried out, were prepared by the known methods¹³.



Structure 1

Parent complex	R	Abbreviation*
1	CH ₃	Ni(IAI)(IAI')
2	OCH ₃	Ni(IMI)(IMI')
3	OC ₂ H ₅	Ni(IEI)(IEI')

*IAI, IMI and IEI Isonitroso N-bonded ligand moieties.
IAI', IMI' and IEI' Isonitroso O-bonded ligand moieties.

Preparation of the complexes: Amino-exchange reactions of all the above listed parent complexes were carried out by the following general typical procedure.

A solution of the mixture of bis(isonitroso- β -ketoimino) nickel(II) parent complex (R = CH₃ or OCH₃ or OC₂H₅; 0.01 mol) and the diethylenetriamine/tetraethylene pentamine/thiosemi-carbazide (0.01 mol) in chloroform (50 mL) was refluxed over a water bath for a period of above 6 h when coloured crystalline solids were obtained. They were filtered, washed with chloroform followed by ethanol and dried over conc. H₂SO₄. The yields of the complexes ranged from 60-75% (Table-1).

TABLE-1
CHARACTERISTIC IR FREQUENCIES (IN cm^{-1}) OF POLYAMINE (DET/TEP)
RELATED PRODUCTS IN NUJOL MULL

Complex	5-Membered ring structure			6-Membered ring structure			v(NH) (DET/TEP)
	v(CO) (Non- bonded)	v(NO) (N- bonded)	v(NH)	v(CO) (Non- bonded)	v(NO) (N- bonded)	v(NH)	
Ni(IAI)(IAI')	1650 s	1210 m	3230 b	1700 s	1150 m	3258 b	—
Ni(IAI-DET-IAI')	1640 s	1210 m	—	1710 s	1130 m	—	3310 (m,b)
Ni(IAI-TEP-IAI')	1650 s	1205 m	—	1700 s	1145 m	—	3310 (m,b)
Ni(IMI)(IMI')	1690 s	1202 m	3330 b	1729 s	1102 m	3171 b	—
Ni(IMI-DET-IMI')	1704 s	1200 m	—	1729 s	1100 m	—	3300 (m,b)
Ni(IMI-TEP-IMI')	1685 s	1200 m	—	1730 s	1100 m	—	—
Ni(IEI)(IEI')	1700 s	1198 m	3375 b	1720 s	1100 m	3220 b	—
Ni(IEI-DET-IEI')	1690 s	1200 m	—	1720 s	1110 m	—	3300 (m,b)
Ni(IEI-TEP-IEI')	1695 s	1200 m	—	1720 s	1110 m	—	3310 (m,b)

IAI/IMI/IEI = Isonitroso-N-bonded moiety; IAI'/IMI'/IEI' Isonitroso-*o*-bonded moiety.

RESULTS AND DISCUSSION

The principal IR bands of the products formed by amino-exchange of the nickel(II) complexes and their probable assignments are given in Tables 2 and 3. Owing to the insoluble nature of the complexes, NMR spectral studies could not be carried out.

TABLE-2
CHARACTERISTIC IR FREQUENCIES (IN cm^{-1}) OF Ni (TSC-IAI/IMI/IEI)
(IAI'/IMI'/IEI') COMPLEXES IN NUJOL MULL

Complex	5-membered ring structure						6-membered ring structure		
	v(CO) (Non- bonded)	v(NO) (N- bonded)	v(NH)	v(NH) (TSC)	asym. v(NH ₂)	sym. v(NH ₂)	v(CO) (Non- bonded)	v(NO) (N- bonded)	v(NH)
Ni(TSC-IAI)(IAI')	1655 s	1190 m	—	3330 M	3440 b	3140 b	1698 s	1140 m	3260 b
Ni(TSC-IMI)(IMI')	1635 s	1190 m	—	3280 M	3400 b	3150 b	1700 s	1140 m	3175 b
Ni(TSC-IEI)(IEI')	1710 s	1198 m	—	3410 M	3430 b	3330 b	1730 s	1098 m	3220 b

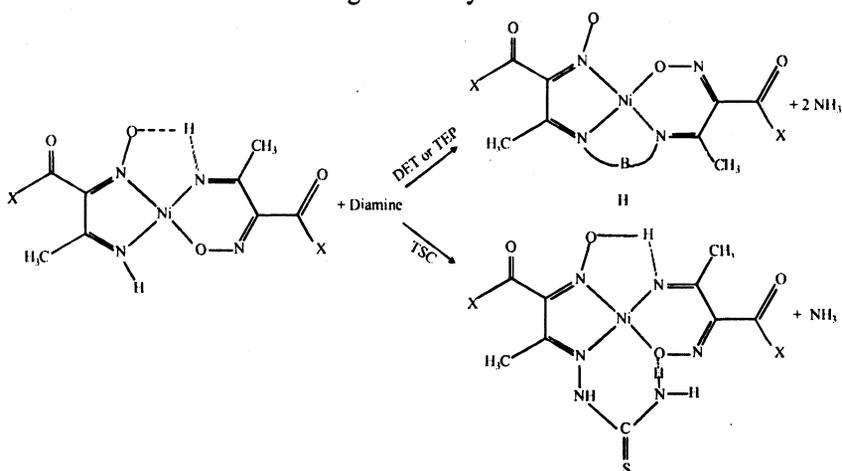
All the brightly coloured a-e reaction products obtained by reacting the parent nickel(II) complex with DET/TEP/TSC in the mole ratio of 1 : 1 (Table-1) are stable in air but melt with decomposition above 200°C. They are all almost insoluble in majority of the common organic solvents. This is rather indicative of some sort of polymeric or large molecular weight complexes. Further, the nickel(II) complexes are all diamagnetic indicating square-planar geometry around nickel(II). Their electronic absorption spectra, as nujol mull smear, display a shoulder around 23,300 cm^{-1} , probably due to the d-d transition expected for the square-planar nickel(II) complexes¹³. Thus, these suggest a gross square-planar stereochemistry around nickel(II) for the complexes.

Structural features of the DET/TEP exchange reaction products of Ni(IAI) (IAI')

The reported IR spectrum of the parent complex, Ni(IAI)(IAI')¹² has shown the presence of two vibrational bands for NH stretch; one for the six-membered chelate ring at 3230 cm^{-1} and the other for the five-membered chelate ring at 3258 cm^{-1} . Besides, two more bands for the uncoordinated CO at 1650 cm^{-1} for the O-coordinated (6-membered ring CO), IAI' ligand and two NO stretching frequencies at 1210 cm^{-1} for the N-coordinated IAI and at 1150 cm^{-1} for the O-coordinated IAI' have also been reported¹².

On the other hand, the metal chelated product produced in the present study on the reaction of the parent complex with the polyamines DET/TEP manifests the complete absence of both the NH bands in their IR spectra, indicating clearly the formation of polyamine bridges mixed ligand bis(isonitroso- β -ketoimino) nickel(II) complexes of the type II (Scheme-1). Contrary to this observation, the IR spectrum of the reacted product with the thiosemicarbazide (TSC) shows the absence of only one of the imine NH bands of the parent complex at 3258 cm^{-1} . Since the presence of the broad NH band at 3210 cm^{-1} is quite in harmony with that of the six-membered NH of the Ni(IAI)(IAI') complex, it is quite clear that the amine-exchange has occurred at the 5-membered ring NH group of the parent complex. It may also be mentioned that even under forcing conditions like the large excess of TSC, Ni(TSC-IAI)(IAI'), there appear four additional frequencies in the NH regions, namely, 3440, 3330, 3140 and 825 cm^{-1} . The former two (3440 and 3140 cm^{-1}) could be attributed to asym NH_2 and sym NH_2 respectively, while the latter two could be due to $-\text{C}-\text{NH}-$ (3330 cm^{-1}) and CS (825 cm^{-1}), respectively, of the thiosemicarbazide moiety. The presence of a weak shoulder in the region 3310 cm^{-1} in all probability could be assigned to the NH hydrogen bonded with the protruding oxygen of the N-bonded NO *cis* to it. Comparing the spectrum^{18, 19} of the free thiosemicarbazide, the frequency due to NH_2 (sym 3180, asym 3365) which is adjoining to $-\text{NH}$ of TSC, is missing in the spectra of TSC exchanged products. This can be taken as an experimental evidence to show that during a-e reaction, only the NH_2 adjoining to $-\text{NH}$ of TSC ($\text{NH}_2-\text{NH}-\text{CS}-$) undergoes amine-exchange. The lowering of N-O stretch of the O-bonded

IAI' moiety, and the broad NH_2 of TSC moiety present in the product suggest the presence of hydrogen bonded between one of the NH of NH_2 of the TSC and O of the coordinated NO of IAI' ligand moiety.



Scheme 1

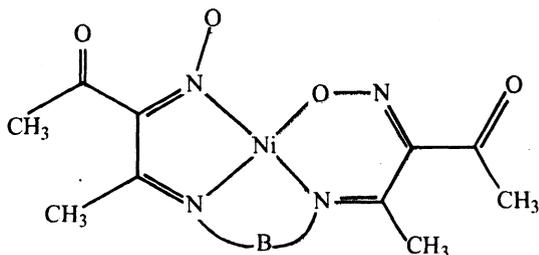
X = CH_3OCH_3 or OC_2H_5 , Amine = ET, TEP or TSC,
 B = $-(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2$ or $-(\text{CH}_2\text{CH}_2)_4(\text{NH})_3$

Thus with the prominent changes in the IR imine NH frequencies of the reaction products of DET, TEP and TSC with respect to the parent reactant complex and the remaining and rest of the two carbonyl and two NO frequencies the same (with minor difference of $5\text{--}15\text{ cm}^{-1}$), it can be inferred that the present set of reaction products continues to have the same gross structural features as that of $\text{Ni}(\text{IAI})(\text{IAI}')$.

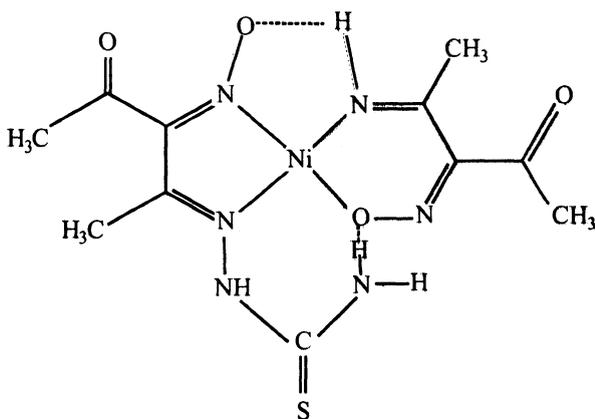
This means: (i) in $\text{Ni}(\text{IAI-DET/TEP-IAI}')$, the ligand IAI is coordinated to the nickel through the two nitrogens of isonitroso NO and diamine $\text{N}-\text{B}-$, while that of IAI' is coordinated to O- of NO and N of diamine $\text{N}-\text{B}-\text{N}$; and (ii) in $\text{Ni}(\text{TSC-IAI})(\text{IAI}')$, TSC-IAI is coordinated through the two nitrogens of isonitroso NO and of N-TSC while IAI' is coordinated through O- of isonitroso NO and N- of imine NH.

It may further be added that the IR spectra of the present set of complexes are in good agreement with that of the $\text{N,N}'$ -ethylene-bis(isonitrosoacetyl-acetoneimino) nickel(II)¹⁷, for which single crystal X-ray structural studies have shown the presence of two *cis* NO bands ($-\text{N}$ -coordinated $\text{M}-\text{NO}$ and $-\text{O}$ -coordinated) $\text{M}-\text{On}$ ¹⁷. Thus, the metal-donor ligational environment of the type (II) and type (III) (3a and 3b structures) could be proposed for these a-e reaction products.

Finally, it may also be added that the construction of molecular models lends additional conformational evidence towards the proposed sterically stable *cis* configuration (Type II). The work of Schlessinger²⁰ on polymethylene bis (imino acid) copper(II) chelates also supports this view.

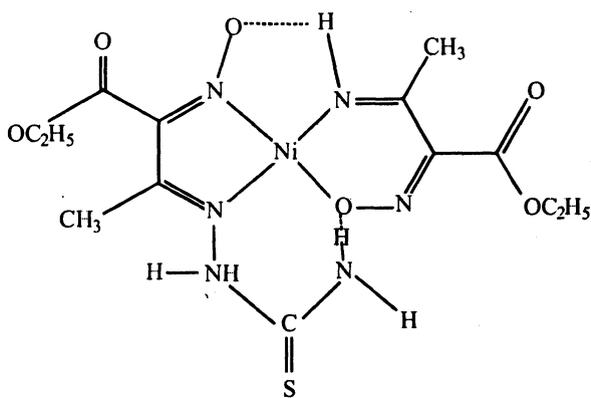


Type II Ni(IAI-DFT/TEPIAI') complexes
Structure 3a



Type III Ni(TSC-IAI)(IAI') complex
Structure 3b

Similar results we also obtained for polyamine-exchange reaction products on Ni(IMI)(IMI') and on Ni(ICI)(IEI').



Ni(TSC-IEI)(IEI')

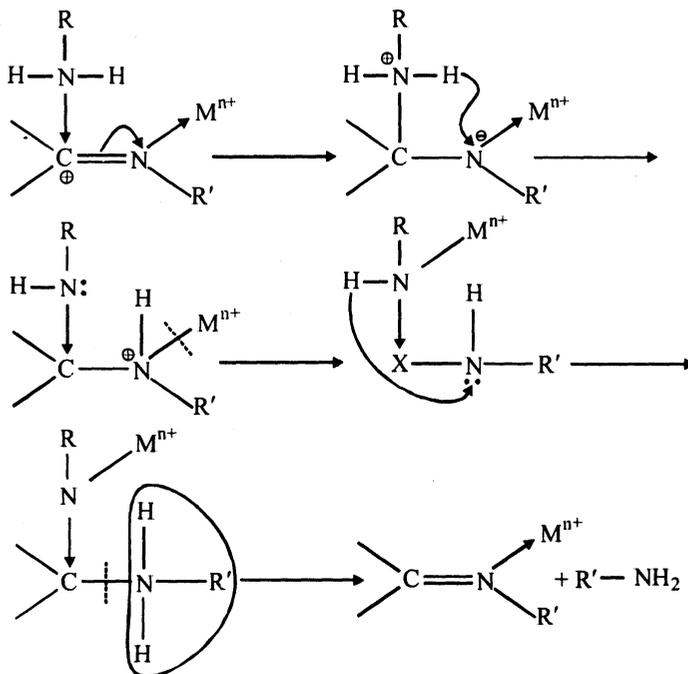
Interestingly enough one may note that the only difference between the above two types of amine condensation products' structures in the presence of NH—C—NH₂ end of the TSC moiety.

Reversible amine-exchange reactions

The *a-e* reaction products of Ni(IAI)(IAI'), Ni(IMI)(IMI) and Ni(IEI)(IEI') with DET, TEP and TSC were reacted with ammonia to find out the possibility of obtaining corresponding parent complexes by reversible *a-e* reaction process¹³. However, in all these cases, no reversible reaction took place, even under forcing experimental conditions like elevated reflux temperature (*i.e.*, use of comparatively high boiling solvent media), high concentration of ammonia, prolonged reflux time etc. (although reports are available on parallel systems)¹⁴.

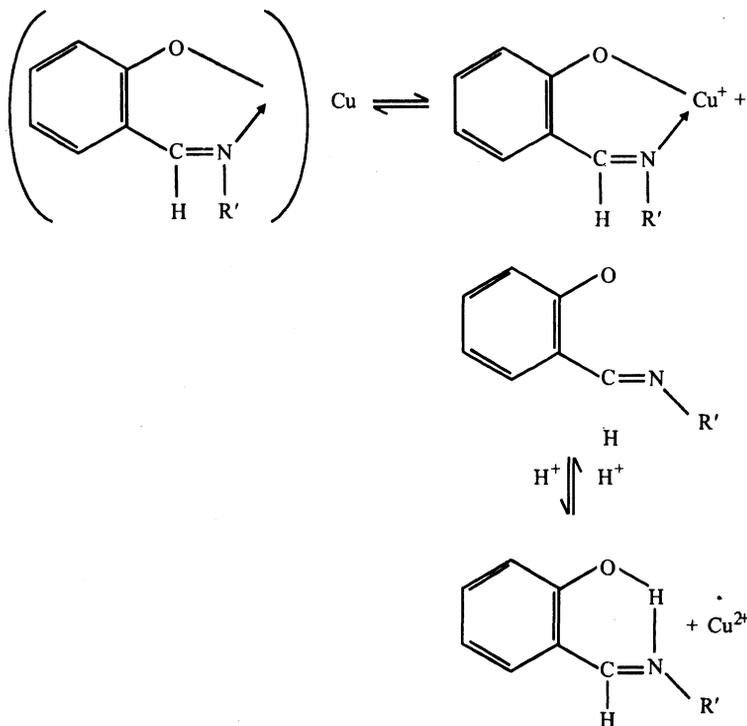
Mechanism of DET/TEP amine-exchange reaction

The total overall mechanistic picture involved in these DET/TEP polyamine exchange reactions, as depicted in **Scheme-2** clearly shows the involvement of the formation of two intermediates I and II. It may be pointed out that the formation of the intermediate I can very well be visualised by the nucleophilic attack of one of the amine groups of the incoming polyamine (DET/TEP) at the electron deficient azomethine carbon of the five-membered ring of the coordinated isonitroso- β -ketoimine ligand. This, in fact, is precisely the Verter-Frost mechanism⁵ which can be summarized as shown below (Str.).



It is, therefore, needless to stress that in this mechanism, the catalytic action of the metal ion coordination to the azomethine nitrogen has an important function to perform. It may also be pointed out that the formation of monoamine intermediate I can also be thought of by recourse to martin's mechanisms⁷. The

latter mechanism involves the formation of a Monochelated species as a consequence of the dissociation of the parent metal complex as depicted below.



Thereafter the exchanging polyamine (NH₂—B—NH₂) reacts with the monochelated species in a manner similar to that suggested in Verter-Frost mechanism. This indicates that the metal-nitrogen bond strength forms an important part in Martin's mechanism, meaning thereby the stronger the metal-donor bond in the starting complex, more difficult it is for amine-exchange to occur. In other words, stronger the metal-nitrogen bond, less likely is the elimination of the liberating amine or weaker the metal-nitrogen bond, more likely is the elimination of the R—N moiety.

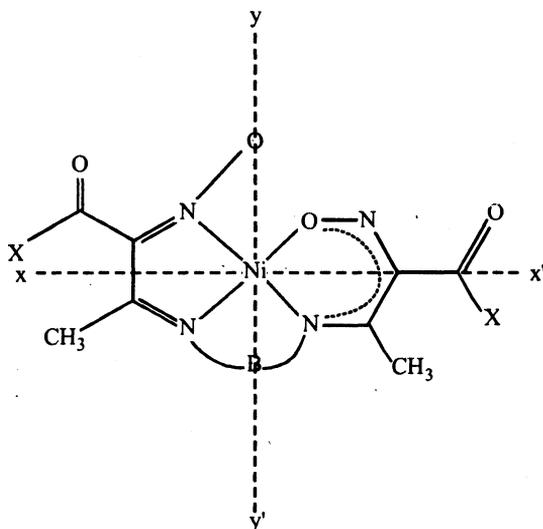
This clearly shows that whatever may be the mechanism (either Verter-Frost or Martin), the formation of the intermediate I (Scheme-2) does involve the activation of the electron deficient azomethine carbon atom of the five-membered ring by the coordinative effect of the metal ion towards the nucleophilic attack of one of the amine groups of the polyamines. The difference between the two mechanisms is, in fact, whether such an activation is brought about with or without the dissociation of the starting complex.

Another viewpoint for consideration of the end product formation could be as discussed below.

The formation of the monoaminated intermediate I (as explained earlier) introduces the bulky fragment, $C=N-B-NH_2$ in place of the $N-H$ group, releasing NH_3 . The $C=N-B-NH_2$ fragment has the possibility of coordination to the metal ion through its azomethine nitrogen. If, however, it is not coordinated, the other NH_2 can attack the azomethine carbon of the six-membered ring forming a bridge between the two azomethine groups and releasing ammonia. In this process, a rotation around $Ni-O$ bond may be expected to release the strain of the bridging group.

In the event of formation of a bond between the nitrogens of the azomethine group of $C=N-B-NH_2$ ($B = TEP/DET$) and the metal ion, the NH_2 of this group may not be in a position to attack the azomethine carbon of the six membered ring; but some disrupting the metal-nitrogen bond. Consequently, some rotation around the $Ni-O$ bond may be expected for rearrangement. In this process, one of the 'polyamine' molecules will be released and the other will form a bridge and get chelated. There could be some weak points in these arguments, but the ultimate complex formed shows that one or both of the view points may be operative.

It is known that the *trans* attack renders the $-Ni-N$ linkage in the six-membered ring weak, thereby making the carbon of $>C=N-$ group of the six-membered ring electron deficient¹⁹. So the amine group of polyamine can get attached to this carbon.



An important aspect regarding the stability of the end chelate product is worth mentioning. The stable configuration of the complex as proposed (Str. 8.8) can be visualised as arising from a bond rupture of $Ni-N$ and $Ni-O$ linkage in the six-membered ring followed by some kind of intramolecular rearrangement.

Alternatively, this stable form (str. 8) may be obtained by a partial or total intramolecular rotation of the six-membered ring (containing the N=N=H—N linkage) along the XX' axis. This kind of rotation or disruption of Ni—N and Ni—O linkages followed by intramolecular rearrangement can be expected to release the strain and instability caused in the molecule by the introduction of >N—B—N=< (first at the five- and the next in the six-membered ring) bridge to yield the stable form. An additional support to this kind of concept can be had in the works of Funke *et al.*¹⁶ and Bonfoey *et al.*¹⁷.

Factors influencing the amine-exchange reactions involving bis(oximino- β -ketoimino) nickel(II) complexes

The results of the present investigations show that the essential factors influencing the a-e reactions are:

- (i) the relative basicities and concentrations of the attacking amine and the amine(s) liberated,
- (ii) steric considerations,¹³
- (iii) chelate effect of the diamines, and
- (iv) the stability and solubility effects of reactant complexes, etc.

It may not be always possible to isolate the influence of a single factor alone to account for the a-e reactions. It can, therefore, imply that more than one factor can play the role in a-3 reactions at the same time.

A qualitative study in the present case reveals the order of a-3 with the their polyamines as follows:



Similar observations have also been made by Verter-Frost¹⁰ and Martin¹⁵, during their studies on a-e reactions of salicylaldehyde and β -ketoimine complexes of Cu(II). Further, in agreement with the same author's observations, the high concentration of the attacking amine often facilitates the reaction in the forward direction. The present a-3 reactions also confirm the same.

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