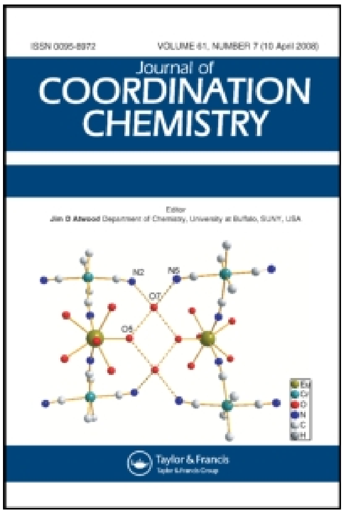

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

NICKEL(II) COMPLEXES OF DIBENZOYLMETHANE AND N-BENZYLETHYLENEDIAMINE, AND THEIR SCHIFF MONOBASE

J. A. Gutiérrez[a]; M. C. Zárraga[a]; G. Mendoza[a]
[a] Departmento de Postgrado en Química Inorgánica, Facultad de Química, Universidad de Guanajuato, México

To cite this Article Gutiérrez, J. A. , Zárraga, M. C. and Mendoza, G.(1993) 'NICKEL(II) COMPLEXES OF DIBENZOYLMETHANE AND N-BENZYLETHYLENEDIAMINE, AND THEIR SCHIFF MONOBASE', Journal of Coordination Chemistry, 28: 3, 305 — 312
To link to this Article: DOI: 10.1080/00958979308037111
URL: http://dx.doi.org/10.1080/00958979308037111

J. Coord. Chem. 1993, Vol. 28, pp. 305–312
Reprints available directly from the publisher
Photocopying permitted by license only

NICKEL(II) COMPLEXES OF DIBENZOYLMETHANE AND *N*-BENZYLETHYLENEDIAMINE, AND THEIR SCHIFF MONOBASE

J. A. GUTIÉRREZ,* M. C. ZÁRRAGA and G. MENDOZA

Departmento de Postgrado en Química Inorgánica, Facultad de Química, Universidad de Guanajuato, Noria Alta s/n, Guanajuato, Gto., 36050 México

(Received 10 July 1991; in final form 1 October 1992)

N-Benzylethylenediamine and dibenzoylmethane (1,3-diphenyl-1,3-propanedione) condense in stoichiometric ratio 1:1 by direct reaction giving the corresponding Schiff monobase; however, this reaction takes place in a significant yield only under very specific conditions due to the low reactivity of dibenzoylmethane (assigned to electronic and steric factors). The neutral bis-chelate of Ni(II) with the deprotonated ligand can readily be prepared in aqueous methanol. Condensation between the diamine and the β-diketone has also been attempted by template reaction assisted by the same metal ion yielding only new mixed complexes of these ligands but without Schiff base condensation. As in the case of direct reaction of the amine with the β-diketone, it seems that template formation of the Schiff base is made difficult by electronic and steric limitations of dibenzoylmethane.

KEY WORDS: Schiff base, template, mixed complexes, nickel(II), 4,7-diaza-1,3,8-triphenyl-2-octen-1-one.

INTRODUCTION

The α,ω-alkanediamines condense with β-polyketones and analogous ligands in the stoichiometric ratio 1:2, respectively, giving Schiff bases that act as acyclic, polydentate O- and N-donors towards metal ions.[1,2] Alternatively, new ligands of this type may be prepared by *N*-substituting the diamine, leaving only one group as primary amine and thus being the only one able to condense yielding the imino group; a variety of this type of ligand may be obtained by condensing *N*-substituted diamines with β-diketones, β,δ-triketones, β-ketoesters or β-hidroxiketones and analogous aldehydic compounds.

The synthesis of Schiff bases uses two general strategies, direct reaction, or adding a metal ion to assist condensation. It is well known that the first method is easy for aldehydes, whereas for ketones it sometimes requires special reaction conditions.[3] In some cases, difficulties may be obviated by the second method; a metal ion could template the condensation of the diamine with the β-diketone.[4] In order to evaluate these two possibilities for a ligand of interest, we here report attempts to condensing 1,3-diphenyl-1,3-propanedione (dibenzoylmethane: dbmH) with *N*-benzylethylenediamine (bzen) both by direct reaction and by template reaction with nickel(II) salts.

---

* Author for correspondence.

EXPERIMENTAL SECTION

Measurements

Melting points are uncorrected and were determined using a Fisher-Johns apparatus. Carbon, hydrogen and nitrogen analysis were performed by Desert Analytics (Tucson, U.S.A.); nickel was determined by EDTA titrations of solutions of digested complexes. IR spectra were recorded on a Perkin Elmer 567 spectrometer. ^1H NMR spectra were recorded on a 60 MHz Varian EM 360 NMR spectrometer. Electronic spectra were obtained with a Perkin Elmer Lambda 4B spectrophotometer. Mass spectra were recorded on a Hewlett-Packard 5985 B mass spectrometer.

Reagents

All reagents were used as such from commercial sources (reagent grade) without further treatment, except where mentioned.

N-Benzylethylenediamine

Under a dry N_2 atmosphere, 0.09 mol of benzyl chloride (Aldrich Chemical Co.) was slowly added to 1.20 mol of anhydrous, freshly distilled and vigorously stirred ethylenediamine (J.T. Baker) in a flask in an ice bath; the addition was completed within one hour. The flask was heated in a boiling water bath for one hour and then two thirds of the volume eliminated on a rotatory evaporator. Some 6 g of KOH pellets were added to the residue and the flask was placed in the boiling water bath for two more hours. The mixture was filtered, the precipitate washed with diethyl ether, and the liquids distilled, with collection of the fraction that boiled between 133 and 136°C at 11 mmHg. Yield 76%.

Schiff Monobase (4,7-diaza-1,3,8-triphenyl-2-octen-1-one:dbmbzenH)*

This new ligand was prepared by modification of the method reported for bis-(dibenzoylmethane)ethylendiimine.[1] Bzen (10 mmol) was added with stirring to 10 mmol of dbmH (Aldrich Chemical Co.) dissolved in 15 cm^3 of isopropanol. The apparent pH was adjusted to 6.0 with glacial acetic acid; the solution was refluxed one hour and then allowed to cool and stand for four hours. The solid formed was vacuum filtered and 5 cm^3 of bzen were added to the filtrate, adjusting the pH to 6.0 and refluxing in the same way; the filtered solid from this step was combined with the first precipitate, washed with cold isopropanol and recrystallized from toluene. The white solid obtained (60% yield respect to dbmH) was the acetic acid salt of the Schiff monobase, dbmbzenH.CH_3COOH, and could be converted to dbmbzenH (acetic acid free) by dissolving it in CH_2Cl_2 and treating it with an equimolar amount of $NaHCO_3$ in water. When the organic solvent was eliminated the product was obtained as a pale yellow, dense oil. From a reaction that yielded mainly the complex $[Ni(dbm)(bzen)_2]NO_3$ (see below) the white crystalline compound dbmbzenH.HNO_3 was isolated; this compound could also be easily prepared by rapidly mixing ethanolic solutions of equimolar amounts of dbmbzenH and HNO_3 to form a voluminous precipitate that was crystallized from the same solvent.

---

* Keto-amine tautomer (Figure 1).

[*Ni(dbmbzen)*$_2$]

Nickel(II) chloride (1 mmol) dissolved in 1 cm^3 of water was added drop wise to a solution of dbmbzenH (2 mmol) in 12 cm^3 of MeOH-H_2O (5:1, v/v). After stirring for 15 minutes, 15 cm^3 of water was added all at once to form a yellow precipitate. The mixture was stirred for two hours, when the colour of the solid changed to pale green. It was filtered off, wahsed with the MeOH-H_2O mixture and recrystallized from CH_2Cl_2-MeOH-H_2O (8:4:1, v/v/v) giving green crystals. Yield 80%. This compound could also be prepared by using dbmbzenH.CH_3COOH instead of dbmbzenH but adjusting the mixture to pH 6.0 to neutralize the acetic acid.

[*Ni(dbm)*$_2$*(bzen)*]

A solution of dbmH (2 mmol) and KOH (2 mmol) in 10 cm^3 of ethanol was added to a solution of bzen (1 mmol) and nickel(II) nitrate (1 mmol) in 10 cm^3 of EtOH-H_2O (1:1, v/v). The green solution was stirred for 30 minutes, concentrated to half its volume and cooled in an ice bath to form a green precipitate. The solid was filtered off, washed with water and EtOH and recrystallized from CH_2Cl_2 giving dark green crystals. Yield 80%.

[*Ni(dbm)(bzen)*$_2$]*X(X* = *Cl*$^{-1}$, *NO*$_3^{1-}$*)*

Bzen (2 mmol) in 5 cm^3 of EtOH was added slowly to the blue suspension formed by mixing $NiX_2.6H_2O$ (1 mmol) and ammonia (6 mmol) in 5 cm^3 of the same solvent; a precipitate persisted but its colour changed to a bluish-pink. Dbmh (1 mmol) dissolved in 10 cm^3 of EtOH was then slowly added to the mixture during 30 minutes, changing the colour of the precipitate to brown and finally yellow. Good stirring was maintained for two hours and then the yellow solid was filtered off, washed with EtOH and recrystallized from CH_2Cl_2-EtOH giving brown crystals. Yield 82%.

The complexes [Ni(dbm)$_2$(H_2O)$_2$] and [Ni(bzen)$_2$$X_2$] (X = Cl^{-1}, NO$_3^{1-}$) were prepared according to literature methods[6,7] and dried *in vacuo*.

RESULTS

N-Benzylethylenediamine

Bzen was characterized by comparing its IR and ^1H NMR spectra with those reported in the literature.[7]

Schiff Monobase

Several attempts to obtain the product of mono- or di-condensation between bzen and dbmH by direct reaction (no metal ion present) in anhydrous EtOH, MeOH, $CHCl_3$, CCl_4, benzene and without a solvent, as well as with a Dean-Stark trap to eliminate water as an azeotrope, failed. From these media only starting substances were isolated together with reddish orange, oily or semi-solid mixtures that apparently are products of decomposition and polycondensation of the two reactants. According to the literature, the condensation of dbmH with ethylenediamine failed in ethanol but it takes place in isopropanol;[1] the method described in the experimental section in order to obtain the Schiff monobase is a modification of that technique and doubling the quantity of bzen led to the product of mono-condensation. Schiff dibase formation was not observed.

When [Ni(dbm)(bzen)$_2$]NO$_3$ was prepared by mixing Ni(NO$_3$)$_2$.6H$_2$O, dbmH and bzen in benzene, and after refluxing overnight, a small amount (yield 3%) of the compound dbmbzenH.HNO$_3$ was recovered; however, it was not possible to increase the yield of the Schiff monobase by this method.

Table 1 shows ^{1}H NMR data for the Schiff monobase and its acid salts; accordingly, these compounds are in the keto-amine tautomeric form (see Figure 1) and no evidence of the keto-amine and enol-imine were detected, in accordance with behaviour found for similar Schiff bases.[8,9] From these spectra it can also be inferred that the proton of the associated acid for dbmbzenH.CH$_3$COOH and dbmbzenH.HNO$_3$ is on the amino group bound to the benzyl group.

Table 2 gives elemental analysis for dbmbzenH.HNO$_3$. In addition, the four last peaks of the mass spectrum of this substance could be assigned as follows: [dbmbzenH − H$_2$O]$^+$ (0.1%), [dbmbzenH]$^+$ (0.8%), [dbmbzenH + H]$^+$ (0.6%), and [dbmbzenH + 2H]$^+$ (0.2%). Abundances are given in parentheses with respect to the base peak.

The IR spectra of the Schiff monobase and derivatives are quite similar in the range 1600–500 cm^{-1}, the main differences being the presence of the typically broad and intense absorption of the nitrate ion (1370 cm^{-1}) in the case of dbmbzenH.HNO$_3$, and the strong and broad absorption of the carboxylate group (1550 cm^{-1}) for

Table 1 ^{1}H NMR data for the three forms of the ligand

Assignment[b]	A	B[c]	C	D	E	F[d,e]	G[c,d]	Anion
dbmbzen (CDCl$_3$)	2.85 $J_{AB}=6$	3.40 $J_{AB}=6$ $J_{BG}=6$	3.87	5.99	7.36 to 8.37	1.95	11.82 broad $J_{BG}=6$	
dbmbzenH.CH$_3$COOH (CDCl$_3$)	2.86 $J_{AB}=6$	3.45 $J_{AB}=6$ $J_{BG}=6$	3.87	5.98	7.30 to 8.10	5.29[f]	11.60 broad $J_{BG}=6$	2.08 CH$_3$COO$^-$
dbmbzenH.HNO$_3$ [(CD$_3$)$_2$SO]	3.23 $J_{AB}=6$	3.49 $J_{AB}=6$ $J_{BG}=6$	4.20	5.88	7.40 to 8.15	8.95[f] broad	11.35 broad $J_{BG}=6$	no signal NO$_3^-$

[a] Solvent in brackets. Chemical shift (δ) in ppm from internal TMS. J values in Hz. [b] Refers to Figure. [c] J_{BG} decouples on D$_2$O addition. [d] Disappears on D$_2$O addition. [e] Variable chemical shift. [f] Integrates for 2 protons.

Table 2 Analyses for the ligand and complexes, together with other characteristic data

Compound	color[a]	mp[b]	Ni$_{calc}$[c]	Ni$_{exp}$[d]	C$_{calc}$	C$_{exp}$	H$_{calc}$	H$_{exp}$	N$_{calc}$	N$_{exp}$
dbmbzenH.HNO$_3$	white	180			68.72	68.38	6.00	5.82	10.02	10.20
[Ni(dbm)$_2$(bzen)]	green	225	8.95	8.76	71.46	71.26	5.53	5.35	4.27	4.25
[Ni(dbm)(bzen)$_2$]NO$_3$.H$_2$O[f]	brown	230	8.86	8.98	59.83	60.42	6.23	6.12	10.57	10.60
[Ni(dbm)(bzen)$_2$]Cl	brown	228	9.50	9.25	64.15	63.21	6.36	6.22	9.06	8.25
[Ni(dbmbzen)$_2$]	green	200	7.26	7.88	74.90	72.68	6.02	6.00	7.27	7.17

[a] Crystalline form. [b] Melting point in °C. [c] Calculated. [d] Experimental. [f] Water confirmed by TGA.

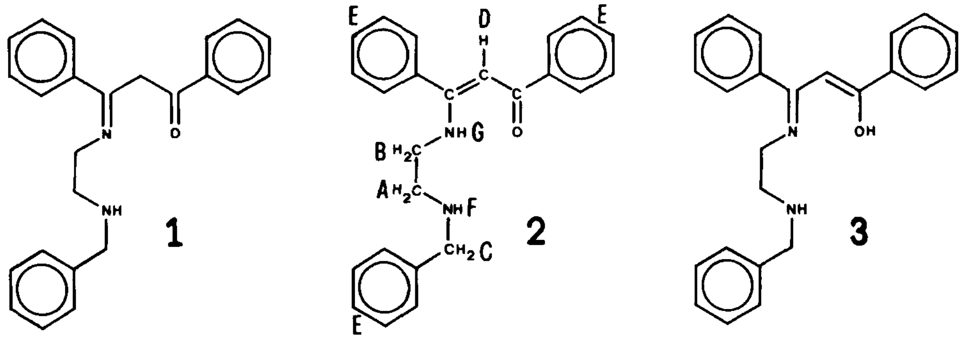

Figure 1 The three tautomers of the ligand dbmbzenH: keto-imine (1); keto-amine (2); enol-imine (3).

dbmbzenH.CH_3COOH. Moreover, both ionic derivatives have a broad absorption with maxima at 2750 and 2600 cm^{-1}, respectively, that can be assigned to the protonated secondary amino group. The pure Schiff monobase, dbmbzenH, has maxima at 1585, 1560 and 1540 cm^{-1} due to C---N, C---O and C---C.

Nickel Complexes

Attempts to condense bzen with dbmH assisted at nickel(II) salts in several solvents and under a wide variety of conditions invariably produced mixtures of Ni(II) complexes but not one with condensed diamine and β-diketone was observed. The new mixed complexes, $[Ni(dbm)_2(bzen)]$ and $[Ni(dbm)(bzen)_2]X$, were the predominant products obtained, while $[Ni(dbm)_2(H_2O)_2]$ and $[Ni(bzen)_2X_2]$ only formed in small amounts. The techniques described in the experimental section for the mixed complexes give good yields; the binary complexes were prepared and characterized some years ago,[5,6] and were prepared this time in order to identify their presence by comparing IR spectra. Table 2 gives elemental analyses for the newly prepared complexes as well as some physical properties.

Infrared spectroscopy

IR spectra of the ternary complexes resemble a superimposition of spectra of binary complexes, but in $[Ni(dbm)_2(bzen)]$ the signals of $[Ni(dbm)_2(H_2O)_2]$ predominate, while in $[Ni(dbm)(bzen)_2]X$ $[Ni(bzen)_2X_2]$ predominate (Figure 2). These data clearly suggest non-condensation. In the IR spectra some bands may be assigned as follows: strong bands at 3260 and 1590 cm^{-1} are due to the NH_2 group; a broad and strong band resolved into two peaks at 2920 and 2880 cm^{-1} is due to C-H vibrations of the ethyl group of bzen; a broad band resolved into several peaks in the region 1600 to 1400 cm^{-1} are due to C---C and C---O vibrations of the β-diketonate system plus those of the benzene ring. Some of these bands are superimposed in the mixed complexes and, depending on the predominant stoichiometric ligand, they are more or less intense. When $X = NO_3^-$ in cationic complexes, the IR spectra essentially differ from those corresponding to $X = Cl^-$, in the broad and very intense band at 1380 cm^{-1} due to the nitrate ion.

As it can also be seen in Figure 2, the IR spectrum of $[Ni(dbmbzen)_2]$ is quite

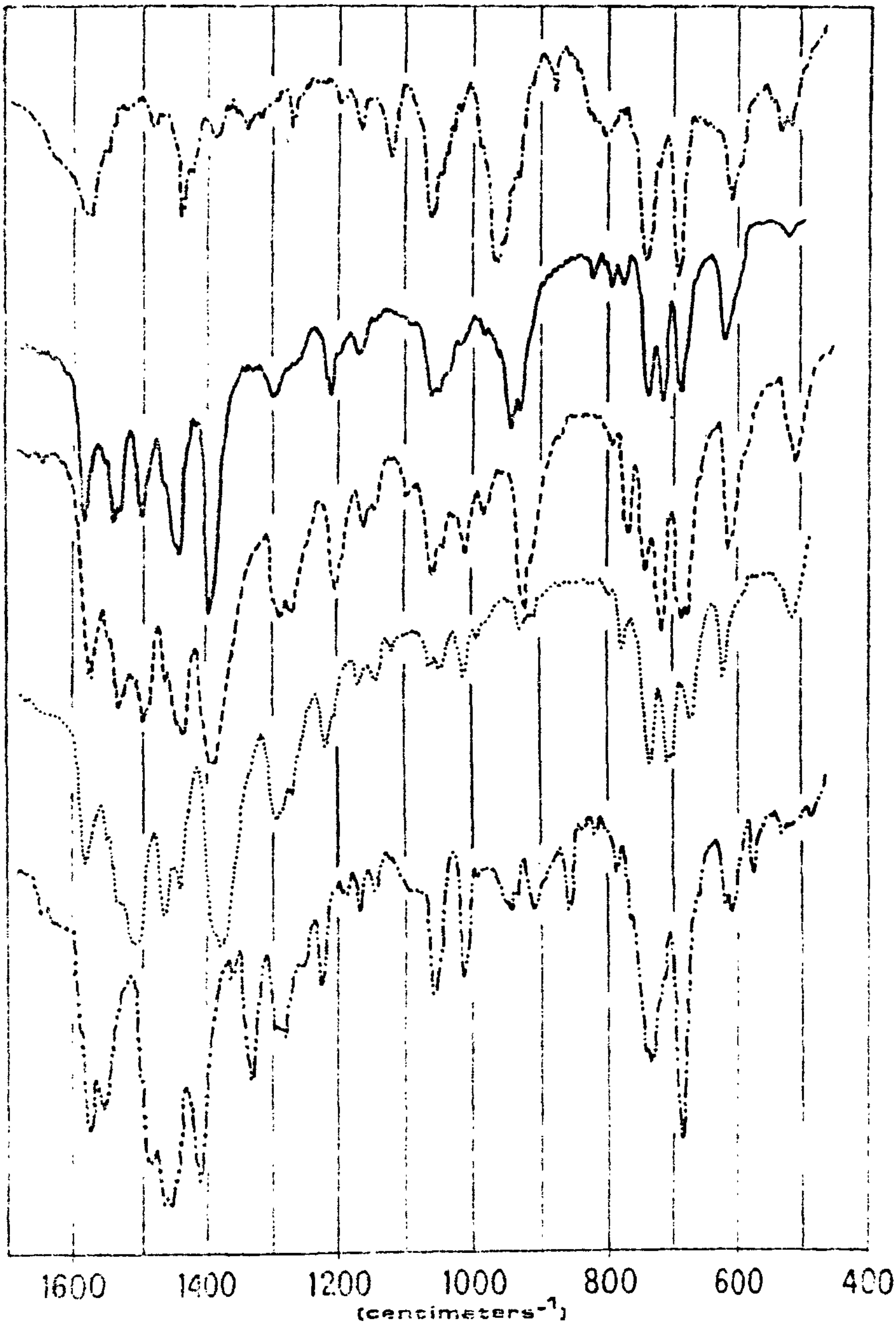

Figure 2 Infrared spectra of representative nickel complexes: $[Ni(bzen)_2Cl_2]$ (-.-.-.); $[Ni(dbm)(bzen)_2]Cl$ (——); $[Ni(dbm)_2(bzen)]$ (- - -); $[Ni(dbm)_2(H_2O)_2]$ (......); $[Ni(dbmbzen)_2]$ (-..-..-..).

different from those of the mixed complexes, due to new vibrations (mainly the stretching mode of the imino group of the β-ketoiminato system around 1550 cm^{-1}), and the lack of others (mainly the strong N-H absorptions of the primary amino group at 3200 and 1600 cm^{-1}). Other bands that must be present in all the compounds shift (those in the 800–600 cm^{-1} range, due to out-of-plane bending vibrations of phenyl groups, as well as those for C---C and C---O around 1600–1400 cm^{-1}).

Electronic spectroscopy

The ternary complexes have electronic spectra typical of nickel(II) in a pseudo-octaedral environment. They show a broad band with a maximum in the range 550–580 nm, and another around 900 nm; there is also a well defined shoulder near 790 nm. Very similar spectra are known for various mixed complexes of nickel(II) acetylacetonate with primary amines[10] that provide a similar environment around nickel(II).

[Ni(dbmbzen)$_2$] has an electronic spectrum with substantial differences with respect to mixed complexes: a broad band at 871 nm and a shoulder around 815 nm; the complex has a charge-transfer band in the visible region ($\lambda = 402$ nm, $\varepsilon = 3650$) that could mask d-d absorptions in the 400–600 nm range. According to these data, the environment around nickel(II) must be quite different from that in the mixed complexes, a fact that arises from the terdentate chelating nature of the ligand dbmbzen^{1-}.

DISCUSSION

It is well known that *N*-substituted derivatives of ethylenediamine (including bzen) condense directly with derivatives of salycylaldehyde.[11] We observe that the condensation of bzen with salycylaldehyde, 2-hydroxy-1-naphthaldehyde, or 2-carboxybenzaldehyde occurs immediately after mixing their alcoholic solutions. The reason why dbmH does not react with bzen as salycylaldehyde derivatives do, may arise from keto-enol tautomerism in the β-diketones which should give rise to electronic differences and this to dissimilar reactivity patterns; in fact, it is well known that ketones are generally much less reactive than aldehydes in the formation of imines.[3] However, it is also known that sterically hindered ketones are particularly unreactive and that aromatics are less reactive than aliphatics;[3] the latter is due to different inductive effects.

Nucleophilic attack of the NH$_2$ group of uncoordinated bzen on a C---O group of nickel(II) dibenzoylmethanate could lead to Schiff base condensation (thermodynamic template effect)[4,12] but, as was indicated, this reaction only yields mixed complexes. This seems to be a particular case of more general behaviour that has been observed earlier. It has been pointed out that, while metal salycylaldehydates interact with primary amines to yield coordinated Schiff bases, metal β-diketonates often only form mixed complexes without undergoing Schiff base condensation; accordingly, it has been suggested that, again, this may be due to an electronic differences between the two chelating systems, as for metal salycylaldehydes there are certain bond resonance structures that cannot be formulated for metal β-diketonates.[10]

It could be thought that Schiff base condensation in the mixed complexes does not happen as a final step because there is no suitable intramolecular postioning of

$C=O$ and NH_2 groups in the coordinated ligands; however, in any arrangement of bzen and dbmH around Ni(II) in the mixed complexes, at least one carbonyl group is *cis* to a primary amino group, a proper position for the condensation by the kinetic template reaction.[4] However, the coordinated primary amine group is unable to act as a nucleophilic, and this seems to be a necessary condition to initiate Schiff base condensation.[3,9]

Some metal ions (Ca^2, Ba^{2+}, Pb^{2+}, *etc.*) are usually employed as template metals because of their size and the ionicity of the coordination compounds (then being less restrictive to geometrical conditions necessary for the stability of the formed ligand). In the present case, although Ni(II) is relatively small and shows strong directionality in bonding, gives with the Schiff Base dbmbzenH the octahedral bis-chelate, $[Ni(dbmbzen)_2]$. This suggests that Ni(II) could be a suitable metal to template the condensation of bzen with dbmH and that this reaction does not take place due to the inherent low reactivity of the latter.

Acknowledgements

This work was partially supported by the Secretaría de Educación Pública (DGICSA, Grant No. 088-01-0154) and CONACYT (Programa de Fortalecimiento al Posgrado). We thank Dr. J. Gómez-Lara for his valuable comments and Mrs. E. Ramos and Miss V. Izumi-Shibata for their technical assistance. We also thank the Instituto de Química, U.N.A.M., for the mass spectra measurements.

References

1. D.F. Averill and R.F. Broman, *Inorg. Chem.*, **17**, 3389 (1978).
2. (a) D.E. Fenton, *Adv. Inorg. Bioinorg. Mechanisms*, **2**, 187 (1983); (b) M.J. Carter, D.P. Rillema and F. Basolo, *J. Am. Chem. Soc.*, **96**, 392 (1974); (c) U. Casellato, P.A. Vigato, D.E. Fenton and M. Vidalli, *Chem. Soc. Rev.*, **8**, 199 (1979).
3. R.L. Reeves, in *The Chemistry of the Carbonyl Group* edited by S. Patai (Interscience Publishers, Chichester, 1979), p. 608.
4. D.StC. Black, in *Comprehensive Coordination Chemistry*, edited by G. Wilkinson (Pergamon Press, Oxford, 1987), Vol. 1, p. 434.
5. R.L. Lintvedt, L.L. Borer, D.P. Murtha, J.M. Kuszaj and M.D. Glick, *Inorg. Chem.*, **13**, 18 (1974).
6. K.C. Patel and D.E. Goldberg, *J. Inorg. Nucl. Chem.*, **36**, 565 (1974).
7. (a) *The Sadtler Handbook of NMR Spectra*, edited by W.W. Simons (Sadtler Research Laboratories, Inc., Philadelphia, 1978), p. 542; (b) *The Sadtler Handbook of Infrared Spectra*, *ibid.*, p. 180.
8. R.H. Holm, G.W. Everett and A. Chakravorty, *Prog. Inorg. Chem.*, **7**, 83 (1966).
9. M. Calligaris and L. Randaccio, in *Comprehensive Coordination Chemistry*, edited by G. Wilkinson (Pergamon Press, Oxford, 1987), Vol. 2, p. 723 and 716.
10. J.T. Hashagen and J.P. Fackler, *J. Am. Chem. Soc.*, **87**, 2821 (1965).
11. (a) P.C. Chieh and G. Palenik, *Inorg. Chem.*, **11**, 816 (1972); (b) R.H. Petty, E.V. Dose, M.F. Tweedly and L.J. Wilson, *Inorg. Chem.*, **17**, 1064 (1978); (c) M.S. Haddad, M.W. Lynch, W.D. Federer and P.N. Hendrickson, *Inorg. Chem.*, **20**, 123 (1981); (d) *ibid.*, p. 131; (e) P.G. Simm, E. Sinn, R.H. Petty, C.L. Merril and L.J. Wilson, *Inorg. Chem.*, **20**, 1213 (1981); (f) M.D. Timken, D.N. Hendrickson and E. Sinn, *Inorg. Chem.*, **24**, 3947 (1985).
12. K.F. Purcell and J.C. Kotz, *Inorganic Chemistry* (W.B. Saunders Co., Philadelphia, 1977), p. 784.