

Kinetics and Mechanism of Metal Substitution and the Irving–Williams Series: Anion-Catalyzed Substitution of Nickel for Copper in Cu(amben) [= (N,N'-Ethylenebis(2-aminobenzaldiminato))copper(II)]

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Visible spectrophotometry was used to study the kinetics of metal substitution in the system Cu(amben)/Ni(DMF)₆(ClO₄)₂/R₄NX in DMF at 298 K and I = 0.2 M (Bu₄NPF₆) (H₂amben = N,N'-ethylenebis(2-aminobenzaldimine); X = Br⁻, SCN⁻, Cl⁻; DMF = N,N-dimethylformamide). The rate of nickel for copper substitution is markedly affected by the nature of the anion X, the order of reactivity being ClO₄⁻ < Br⁻ < SCN⁻ ≪ Cl⁻. For X = Cl⁻ and under excess conditions [(Cu(amben)) ≪ [Ni(DMF)₆(ClO₄)₂], [BzEt₃NCl]], the overall process is triphasic and multiwavelength analysis in the range 350–900 nm yields the experimental rate constants *k*_{obsd}(1), *k*_{obsd}(2), and *k*_{obsd}(3). Rate constant *k*_{obsd}(1) is nickel and chloride dependent, whereas *k*_{obsd}(2) and *k*_{obsd}(3) are not. For the rate of disappearance of Cu(amben), *v* = -d[Cu(amben)]/dt, it is found that *v* ∝ [Cl]_{tot}² at [Ni(DMF)₆(ClO₄)₂]₀ = constant and *v* ∝ [Ni]_{tot}³ at [nickel]:[chloride] = 1:2 ([Cl]_{tot} and [Ni]_{tot} refer to the total concentration of chloride and nickel, respectively). These dependencies suggest a second-order rate law, *v* = *k*₁[Cu(amben)][“NiCl₂”], for the first step, with *k*₁ = 64 ± 8 M⁻¹ s⁻¹ at 298 K. In view of the ligand properties of Cu(amben) it is concluded that the species “NiCl₂” is tetrahedral Ni(DMF)₂Cl₂ which reacts with Cu(amben) as ligand to form a binuclear adduct in the first step. It is suggested that the observed rate effects of the anions X are linked with their ability to favor the formation of nickel species with reduced coordination number, such as four-coordinate Ni(DMF)₂X₂. The mechanism of the overall process of nickel for copper substitution in Cu(amben) is discussed. The results of the analysis of the visible spectra of Cu(amben) and Ni(amben) and of MO calculations on the charge distribution in these complexes are reported.

Introduction

The Irving–Williams series states that copper(II) complexes are thermodynamically more stable than the corresponding nickel(II) complexes.¹ Complex formation with 1,2-diaminoethane (en) is the favorite textbook example to document this statement convincingly by quoting the corresponding data for *K*₁ (1:1 complexes) and *K*₂ (1:2 complexes).² In agreement with *K*(Cu) > *K*(Ni) it can be shown that, in solution, Cu²⁺ ions replace the nickel in Ni(en)₂²⁺ and Ni(en)₂²⁺ easily.

It is important to note that the Irving–Williams series refers to the formation of *six-coordinate octahedral* complex species. Moving to only *four-coordinate* Cu(II) and Ni(II) complexes with a planar arrangement of the four donor atoms changes the situation in the sense that the consideration of ligand field stabilization effects clearly predicts a higher stabilization for

3d⁸ (nickel) than for 3d⁹ (copper). A planar four-coordinate species Ni^{II}L₄ should therefore be thermodynamically more stable than the corresponding copper species Cu^{II}L₄. From the kinetic point of view, one would thus expect that there is a driving force to make Ni²⁺ ions replace the copper in a planar, strictly four-coordinate species CuL₄. To our knowledge, there is no example so far proving or disproving this expectation which, at first glance, seems to contradict the Irving–Williams series.

The well-known N₂O₂ ligand “Salen” has its N₄ counterpart in the less known ligand “Amben” (see Chart 1), first described by Pfeiffer et al. in 1937.³ In the reaction with divalent metals M(II), the ligand is doubly deprotonated and forms neutral complexes M(amben). The preparation and properties of the nickel(II) and copper(II) complex of Amben have been studied by various groups.^{3–12} Recently Brewer et al.¹³ carried out the X-ray structure analysis of Cu(amben) and Ni(amben) and found

(1) Irving, H.; Williams, R. J. P. *J. Chem. Soc.* **1953**, 3192.

(2) The Irving–Williams series is discussed in terms of electrostatic effects (variation of the ionic radius of the metal) and variations in LFSE. The fact that, for bidentate ligands such as en, *K*₁(Cu) > *K*₁(Ni) and *K*₂(Cu) > *K*₂(Ni) as well as the fact that *K*₃(Ni) > *K*₃(Cu) for the 1:3 complexes is finally ascribed to the Jahn–Teller effect (see: Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry-Principles of Structure and Reactivity*, 4th ed.; Harper Collins College Publishers: New York, 1993; Chapter 11).

(3) Pfeiffer, P.; Hesse, Th.; Pfitzner, H.; Scholl, W.; Thielert, H. *J. Prakt. Chem.* **1937**, 149, 217.

(4) Green, M.; Tasker, P. A. *J. Chem. Soc. A* **1970**, 2531.

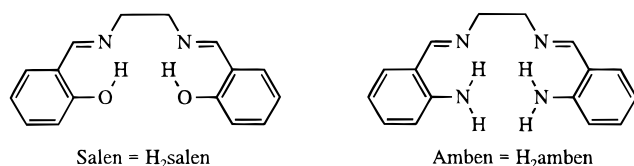
(5) Green, M.; Tasker, P. A. *J. Chem. Soc. A* **1970**, 3105.

(6) Green, M.; Smith, J.; Tasker, P. A. *Inorg. Chim. Acta* **1971**, 5 (1), 17.

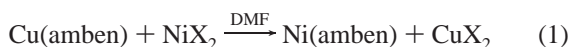
(7) Green, M.; Tasker, P. A. *Inorg. Chim. Acta* **1971**, 5 (1), 65.

(8) Higson, B. M.; McKenzie, E. D. *J. Chem. Soc., Dalton Trans.* **1972**, 269.

Chart 1



both complexes to have an approximately planar coordination core. Our interest in these complexes arose from the fact that the Lewis acidity of the metal is nearly zero, which follows from practically identical visible absorption spectra of Cu(amben) and Ni(amben), respectively, in toluene, DMF (*N,N*-dimethylformamide), and even in toluene/pyridine mixtures. This means that, in DMF, one is dealing with planar, strictly four-coordinate compounds. Reaction 1 describes therefore a



system which should be suitable for the study of the argument raised above, namely, that nickel should replace the copper. The results of the kinetic investigation of (1) with different anions X are reported together with an analysis of the visible spectra of Cu(amben) and Ni(amben) and calculations concerning the charge distribution in these complexes.

Experimental Section

Chemicals. BzEt₃NCl (=benzyltriethylammonium chloride), Bu₄NPF₆ (=tetrabutylammonium hexafluorophosphate), Bu₄N(SCN) (=tetrabutylammonium thiocyanate), Et₄NBr (tetraethylammonium bromide), and the solvent DMF (=N,N-dimethylformamide) were purchased in reagent grade quality and used without further purification.

Ligand and Complexes. Amben,^{3,4} Ni(amben),⁴ Cu(amben),¹³ and Ni(DMF)₆(ClO₄)₂¹⁴ were prepared according to published procedures. (**WARNING!** *Perchlorate salts and organic solutions of such salts are potentially explosive. They should be handled in small quantities and with caution.*)

UV/Vis Spectra. The spectra were recorded with a diode array spectrophotometer (Zeiss, Specord S10) in two-chamber quartz cells ($d = 2 \times 0.439$ cm).

Kinetic Measurements. Reaction 1 with X = Cl was followed spectrophotometrically in DMF at 298 K, $I = 0.2$ M (Bu₄NPF₆), and [Cu(amben)] = 5×10^{-5} M with a variable excess of nickel and chloride, respectively. The procedure was such that, at $t = 0$, the solution of Cu(amben) was mixed with equilibrated solutions containing Ni(DMF)₆(ClO₄)₂ and BzEt₃NCl at the desired molar ratio (for the sake of brevity, the notation [Ni]_{tot} = [Ni(DMF)₆(ClO₄)₂]₀ and [Cl]_{tot} = [BzEt₃NCl]₀ will be used below). The A, t data, resulting from the observed change in absorbance A with time in the wavelength range 350–900 nm, were computer-fitted with eq 2 (irreversible first-order

$$A = a_1 \exp[-k_{\text{obsd}}(1)t] + A_{\infty} \quad (2)$$

$$A = a_1 \exp[-k_{\text{obsd}}(1)t] + a_2 \exp[-k_{\text{obsd}}(2)t] + A_{\infty} \quad (3)$$

$$A = a_1 \exp[-k_{\text{obsd}}(1)t] + a_2 \exp[-k_{\text{obsd}}(2)t] + a_3 \exp[-k_{\text{obsd}}(3)t] + A_{\infty} \quad (4)$$

reaction), eq 3 (biphasic reaction), or eq 4 (triphasic reaction) to find

(9) McKenzie, E. D.; Moore, R. D.; Worthington, J. M. *Inorg. Chim. Acta* **1975**, *14*, 37.

(10) McKenzie, E. D.; Worthington, J. M. *Inorg. Chim. Acta* **1976**, *16*, 9.

(11) Fischer, J.; Elias, H. *Inorg. Nucl. Chem. Lett.* **1975**, *11*, 239.

(12) Bowmaker, G. A.; Waters, T. N.; Wright, P. E. *J. Chem. Soc., Dalton Trans.* **1975**, 867.

(13) Brewer, G.; Jasinski, J.; Mahany, W.; May, L.; Prytkov, S. *Inorg. Chim. Acta* **1995**, 183.

Table 1. Visible Absorption Data for Cu(amben) and Ni(amben)

solvent	λ_{max} , nm (ϵ_{max} , M ⁻¹ cm ⁻¹)			
	Cu(amben)		Ni(amben)	
toluene	419 (12 500)	689 (170)	366 (5560)	488 (4200)
chloroform	417 (12 500)	687 (180)	361 (6800)	482 (5030)
acetone	415 (11 900)	676 (200)	361 (6170)	480 (4850)
DMF	416 (13 500)	670 (210)	362 (6880)	484 (5170)
toluene/py ^a	420 (12 700)	689 (180)	366 (5810)	490 (4320)

^a Toluene with 1 M pyridine.

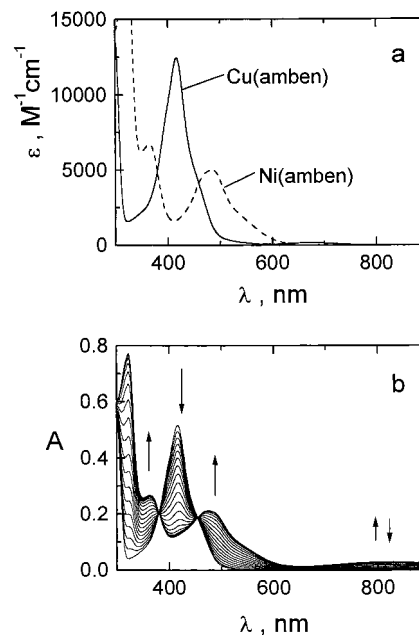


Figure 1. Visible spectra of Cu(amben) and Ni(amben) in DMF at 298 K (a) and spectral changes as recorded for the reaction of Cu(amben) (5×10^{-5} M) with nickel ions ($[\text{Ni}(\text{DMF})_6(\text{ClO}_4)_2] = 5 \times 10^{-5}$ M) in the presence of chloride ions ($[\text{BzEt}_3\text{NCl}] = 5 \times 10^{-3}$ M) in DMF within 30 min at 318 K (b).

the best fit and the experimental rate constants k_{obsd} (a = amplitude). The programs used were based on the least-squares method.

Analysis of the Electron Spectra and Molecular Orbital Calculations. The theoretical methods used for the analysis of the spectra and for the MO calculations are provided as Supporting Information.

Results and Discussion

Visible Absorption in Various Solvents. As pointed out above, the visible absorption spectra of Cu(amben) and Ni(amben), respectively, in coordinating and noncoordinating solvents are practically identical. Table 1 summarizes the data for DMF, chloroform, acetone, toluene, and toluene with an admixture of pyridine. One can conclude, therefore, that coordination of polar solvents such as DMF in the axial positions of Cu(amben) and Ni(amben) does not occur to a considerable extent. It follows from the visible spectra of Cu(amben) and Ni(amben) in DMF (Figure 1a) that it should be easy to follow the substitution of nickel for copper according to reaction 1 spectrophotometrically.

The Kinetic Effect of the Anion X. The study of reaction 1 with different anions X¹⁵ revealed that the substitution of nickel for copper does take place indeed but is strongly

(14) Fee, W. W.; McElholum, D. E.; McPherson, A. J.; Runde, D. L. *Aust. J. Chem.* **1973**, *26*, 1207.

(15) The nickel salts NiCl₂, NiBr₂, and Ni(SCN)₂ were prepared in situ by equilibrating Ni(DMF)₆(ClO₄)₂ with BzEt₃NCl, Et₄NBr, and Bu₄N(SCN), respectively, in DMF.

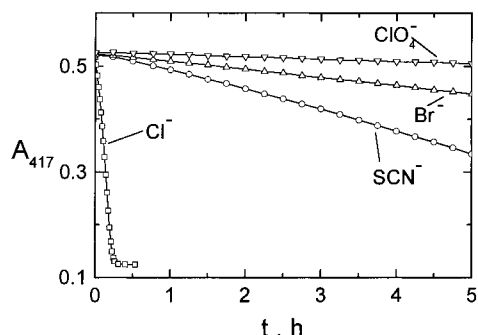


Figure 2. Decrease in absorbance at 417 nm with time for reaction 1 as studied with different anions X in DMF at 318 K ($[\text{Cu}(\text{amben})]_0 = [\text{Ni}(\text{DMF})_6(\text{ClO}_4)_2]_0 = 5 \times 10^{-5} \text{ M}$, $[\text{X}^-] = 2 \times 10^{-3} \text{ M}$).

depending on the nature of X. As shown in Figure 2, for X = chloride the substitution is much faster than for X = perchlorate. The anion effect on the initial rate of metal substitution at 45 °C follows the order $\text{ClO}_4^-:\text{Br}^-:\text{SCN}^-:\text{Cl}^- = 1:4:9:470$. The more detailed kinetic investigation of reaction 1 was therefore carried out with X = Cl. As an example, Figure 1b shows a series of consecutive spectra, recorded at 45 °C within ca. 30 min, which document the conversion of Cu(amben) into Ni(amben). One should note that at ca. 800 nm there is a small intermediate increase and decrease in absorbance (see below).

It is important to point out that, even for the 1:1 condition, $[\text{Cu}(\text{amben})]_0 = [\text{Ni}(\text{DMF})_6(\text{ClO}_4)_2]_0$, the copper complex is completely converted into the nickel complex (see spectra shown in Figure 1b). The rate of this conversion obviously depends on the concentration of chloride ions present. One can therefore conclude that (i) in DMF Ni(amben) is thermodynamically more stable than Cu(amben) and (ii) chloride ions catalyze the substitution of nickel for copper in Cu(amben). In agreement with the first conclusion, the reverse reaction of (1), i.e. the copper for nickel substitution at $[\text{Ni}(\text{amben})]_0 = [\text{Cu}(\text{DMF})_6(\text{ClO}_4)_2]_0 = 5 \times 10^{-5} \text{ M}$ and $[\text{Cl}^-]_0 = 1 \times 10^{-3} \text{ M}$ does not take place within 24 h at 318 K. Support for the second conclusion, i.e., for the catalytic role of chloride ions, comes from the fact that the final spectrum shown in Figure 1b can be synthetically reproduced by mixing corresponding amounts of Ni(amben), Cu(DMF)₆(ClO₄)₂, and BzEt₃NCl.

For comparison, the corresponding reaction of Cu(salen) with Ni(DMF)₆(ClO₄)₂ in the presence of BzEt₃NCl was studied under the same conditions. It was found that the Salen complex of copper(II) is analogously converted into Ni(salen), but this conversion is slower, by a factor of approximately 30, than in the case of Cu(amben).

The System Ni²⁺/Cl⁻/DMF. In principle, the catalytic effect of chloride ions on reaction 1 could be due to their interaction with either Cu(amben) or with the species Ni(DMF)₆²⁺. Spectrophotometrically, adduct formation between chloride ions and Cu(amben) was not to be observed. On the other hand, the spectrum of Ni(DMF)₆(ClO₄)₂ in DMF changes drastically with increasing [BzEt₃NCl] (see Figure S1 provided as Supporting Information). The growth of intense absorption bands in the range 550–750 nm indicates the formation of tetrahedral species.¹⁶ Ishiguro et al.¹⁷ studied the formation of chloro complexes of nickel(II) in DMF by titrating Ni(DMF)₆(ClO₄)₂ with Et₄NCl. This calorimetric and spectrophotometric study showed that stepwise coordination of one, two, three, and finally four Cl⁻ ions to the nickel takes place, the overall formation

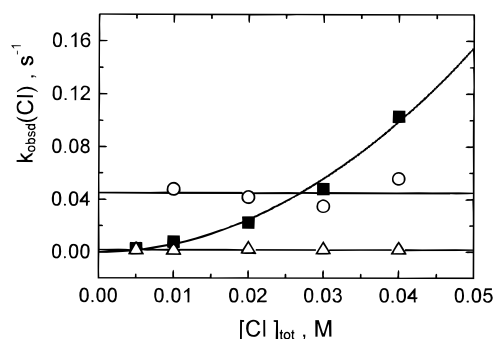


Figure 3. Plot of the experimental rate constants $k_{\text{obsd}}(1,\text{Cl})$ (■), $k_{\text{obsd}}(2,\text{Cl})$ (○), and $k_{\text{obsd}}(3,\text{Cl})$ (△)¹⁸ vs $[\text{Cl}]_{\text{tot}}$ ($=[\text{BzEt}_3\text{NCl}]_0$) for reaction 7 ($[\text{Cu}(\text{amben})]_0 = 5 \times 10^{-5} \text{ M}$; $[\text{Ni}(\text{DMF})_6(\text{ClO}_4)_2]_0 = 5 \times 10^{-3} \text{ M}$; $I = 0.2 \text{ M Bu}_4\text{NPF}_6$; 298 K).

constants being $\log \beta_1 = 2.85$, $\log \beta_2 = 3.76$, $\log \beta_3 = 5.53$, and $\log \beta_4 = 7.40$ (298 K; $I = 0.4 \text{ M Et}_4\text{NClO}_4$). With regard to coordination number and coordination geometry, the authors suggest the formation of the species Ni(DMF)₅Cl⁺ (octahedral), Ni(DMF)Cl₃⁻ (tetrahedral), and NiCl₄²⁻ (tetrahedral). In the case of the thermodynamically less favored dichloro species Ni(DMF)_xCl₂ the spectral analysis and assignment turned out to be less safe with respect to the size of x and the coordination geometry. The spectral data obtained were tentatively interpreted to indicate a largely distorted six-coordinate or even a five-coordinate structure.

Kinetics of Metal Substitution According to Reaction 1 for X = Cl. The substitution of nickel for copper according to (1), when followed in the wavelength range 350–900 nm under excess conditions ($[\text{Cu}(\text{amben})]_0 \ll [\text{Ni}]_{\text{tot}}$, $[\text{Cl}]_{\text{tot}}$), turned out to be described best as a three-step process (see Figure S2 provided as Supporting Information). Multiwavelength analysis in the range 350–900 nm according to eq 4 led to rate constants $k_{\text{obsd}}(1)$, $k_{\text{obsd}}(2)$, and $k_{\text{obsd}}(3)$, the dependence of which on the excess concentration of chloride and nickel ions was studied systematically.

The effect of the variation of $[\text{Cl}]_{\text{tot}}$ on the experimental rate constants $k_{\text{obsd}}(1,\text{Cl})$, $k_{\text{obsd}}(2,\text{Cl})$, and $k_{\text{obsd}}(3,\text{Cl})$ ¹⁸ is shown in Figure 3. One learns that the dependence $k_{\text{obsd}}(1,\text{Cl}) = f([\text{Cl}]_{\text{tot}})$ can be satisfyingly described by relationship (5) with $k_1(\text{Cl}) =$

$$k_{\text{obsd}}(1,\text{Cl}) = k_1(\text{Cl})[\text{Cl}]_{\text{tot}}^2 \quad (5)$$

$62 \pm 4 \text{ M}^{-2} \text{ s}^{-1}$. Rate constants $k_{\text{obsd}}(2,\text{Cl})$ and $k_{\text{obsd}}(3,\text{Cl})$ appear to be independent of $[\text{Cl}]_{\text{tot}}$ and averaging leads to $k_2(\text{Cl}) = 4.5 \times 10^{-2} \text{ s}^{-1}$ and $k_3(\text{Cl}) = 1.7 \times 10^{-3} \text{ s}^{-1}$ (see Table 2).¹⁹ One has to point out however that $k_2(\text{Cl})$ and $k_3(\text{Cl})$ originate from a fitting procedure based on small absorbance differences, which raises the limits of uncertainty of the data obtained.

The effect of the variation of $[\text{Ni}]_{\text{tot}}$ (in the presence of 2 equiv of chloride)²⁰ on the experimental rate constants $k_{\text{obsd}}(1,\text{Ni})$, $k_{\text{obsd}}(2,\text{Ni})$, and $k_{\text{obsd}}(3,\text{Ni})$ ¹⁸ is shown in Figure 4. The size of $k_{\text{obsd}}(1,\text{Ni})$ grows strongly with $[\text{Ni}]_{\text{tot}}$, and this dependence can be reasonably well fitted with relationship (6), which

$$k_{\text{obsd}}(1,\text{Ni}) = k_1(\text{Ni})[\text{Ni}]_{\text{tot}}^3 \quad (6)$$

leads to $k_1(\text{Ni}) = (6.4 \pm 0.3) \times 10^4 \text{ M}^{-3} \text{ s}^{-1}$. As in the case of

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(18) Rate constants $k_{\text{obsd}}(1,\text{Cl})$, $k_{\text{obsd}}(2,\text{Cl})$, and $k_{\text{obsd}}(3,\text{Cl})$ are those obtained at variable $[\text{Cl}]_{\text{tot}}$ ($[\text{Ni}]_{\text{tot}} = \text{constant}$); rate constants $k_{\text{obsd}}(1,\text{Ni})$, $k_{\text{obsd}}(2,\text{Ni})$, and $k_{\text{obsd}}(3,\text{Ni})$ are those obtained at variable $[\text{Ni}]_{\text{tot}}$ (at $[\text{nickel}]:[\text{chloride}] = 1:2$).

Table 2. Summary of Rate Data for the Reaction of Cu(amben) with Divalent Nickel in the Presence of Chloride Ions According to (7)^a

Variation of [Cl] _{tot} (Excess) at [Ni] _{tot} = 5 × 10 ⁻³ M ([Cu(amben)] = 5 × 10 ⁻⁵ M)		
$k_{\text{obsd}}(1, \text{Cl}) = k_1(\text{Cl})[\text{Cl}]_{\text{tot}}^2$	$k_{\text{obsd}}(2, \text{Cl}) \neq f([\text{Cl}]_{\text{tot}})^b$	$k_{\text{obsd}}(3, \text{Cl}) \neq f([\text{Cl}]_{\text{tot}})^b$
$k_1(\text{Cl}) = (62 \pm 4) \text{ M}^{-2} \text{ s}^{-1}$	$k_2(\text{Cl})^c = (4.5 \pm 1.0) \times 10^{-2} \text{ s}^{-1}$	$k_3(\text{Cl})^c = (1.7 \pm 0.2) \times 10^{-3} \text{ s}^{-1}$
Variation of [Ni] _{tot} (Excess) at [Cl] _{tot} = 2[Ni] _{tot} ([Cu(amben)] = 5 × 10 ⁻⁵ M)		
$k_{\text{obsd}}(1, \text{Ni}) = k_1(\text{Ni})[\text{Ni}]_{\text{tot}}^3$	$k_{\text{obsd}}(2, \text{Ni}) \neq f([\text{Ni}]_{\text{tot}})^d$	$k_{\text{obsd}}(3, \text{Ni}) \neq f([\text{Ni}]_{\text{tot}})^d$
$k_1(\text{Ni}) = (6.4 \pm 0.3) \times 10^4 \text{ M}^{-3} \text{ s}^{-1}$	$k_2(\text{Ni})^e = (4.3 \pm 0.1) \times 10^{-2} \text{ s}^{-1}$	$k_3(\text{Ni})^e = (5.3 \pm 0.2) \times 10^{-3} \text{ s}^{-1}$

^a Solvent DMF, $T = 298 \text{ K}$, $I = 0.2 \text{ M}$ Bu₄NPF₆. ^b See Figure 3. ^c See ref 19. ^d See Figure 4. ^e See ref 21.

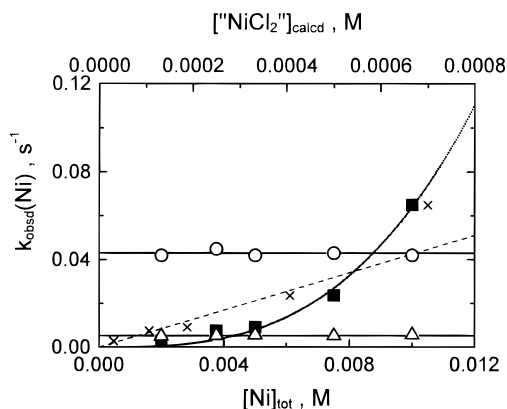
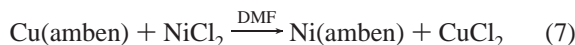


Figure 4. Plot of the experimental rate constants $k_{\text{obsd}}(1, \text{Ni})$ (■), $k_{\text{obsd}}(2, \text{Ni})$ (○), and $k_{\text{obsd}}(3, \text{Ni})$ (△)¹⁸ vs $[\text{Ni}]_{\text{tot}}$ ($=[\text{Ni}(\text{DMF})_6(\text{ClO}_4)_2]_0$) for reaction 7 in the presence of chloride ions at the ratio [nickel]:[chloride] = 1:2 ($[\text{Cu}(\text{amben})]_0 = 5 \times 10^{-5} \text{ M}$; $I = 0.2 \text{ M}$ Bu₄NPF₆; 298 K). The dashed line with the slope $k_1 = 64 \pm 8 \text{ M}^{-1} \text{ s}^{-1}$ is the linear fit of the data points (symbol ×) representing the dependence $k_{\text{obsd}}(1, \text{Ni}) = f([\text{NiCl}_2]_{\text{calcd}})$.

the variation of $[\text{Cl}]_{\text{tot}}$, rate constants $k_{\text{obsd}}(2, \text{Ni})$ and $k_{\text{obsd}}(3, \text{Ni})$ appear to be independent of $[\text{Ni}]_{\text{tot}}$ and one obtains $k_2(\text{Ni}) = 4.3 \times 10^{-2} \text{ s}^{-1}$ and $k_3(\text{Ni}) = 5.3 \times 10^{-3} \text{ s}^{-1}$ (see Table 2).²¹ It is thus found that, despite the inherent uncertainties concerning their origin, rate constants $k_2(\text{Cl})$ and $k_2(\text{Ni})$ agree surprisingly well and rate constants $k_3(\text{Cl})$ and $k_3(\text{Ni})$ are of the same order.

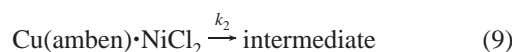
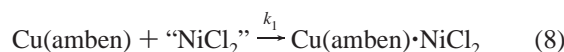
Mechanism of Metal Substitution. The substitution of nickel for copper in Cu(amben) according to (7) is found to be



a three-step process, as described by the experimental rate constants $k_{\text{obsd}}(1)$, $k_{\text{obsd}}(2)$, and $k_{\text{obsd}}(3)$. One of these rate constants, $k_{\text{obsd}}(1)$, depends on the excess concentration of chloride ions, $[\text{Cl}]_{\text{tot}}$, and nickel ions, $[\text{Ni}]_{\text{tot}}$, according to (5) and (6), respectively. The size of the two remaining first-order rate constants, $k_{\text{obsd}}(2)$ and $k_{\text{obsd}}(3)$, is not significantly affected by the excess concentration of chloride or nickel (see Table 2). It is reasonable to assume that the concentration-dependent $k_{\text{obsd}}(1)$ step is the first step in a series of three consecutive steps, in which the slowest $k_{\text{obsd}}(3)$ step is, most probably, the last one.

One can conclude from the quadratic chloride dependence (5), obtained at $[\text{Ni}]_{\text{tot}} = \text{constant}$, that two chloride ions are involved in the formation of the transition state of the first step. The observed nickel dependence (6), $k_{\text{obsd}}(1, \text{Ni}) \propto [\text{Ni}]_{\text{tot}}^3$, as obtained at [nickel]:[chloride] = 1:2, is formally equivalent to

$k_{\text{obsd}}(1, \text{Ni}) \propto [\text{Ni}]_{\text{tot}}[\text{Cl}]_{\text{tot}}^2$. Spectrophotometrically, adduct formation between Cu(amben) and chloride ions was not to be observed. It appears to be reasonable therefore to suggest that in the initial step of metal substitution a nickel dichloro species “NiCl₂”, carrying two chloride ions (and, additionally, several DMF molecules), reacts with Cu(amben). A possible reaction scheme for copper substitution according to (7) would thus be given by eqs 8–10.



It follows from (8), that rate constant $k_{\text{obsd}}(1, \text{Ni})$ should increase linearly with “NiCl₂” according to $k_{\text{obsd}}(1, \text{Ni}) = k_1[\text{“NiCl}_2\text{”}]$. Since $[\text{Ni}]_{\text{tot}} = [\text{Ni}] + [\text{NiCl}] + [\text{NiCl}_2] + [\text{NiCl}_3] + [\text{NiCl}_4]$ (charges omitted for clarity), the calculation of “NiCl₂” at variable $[\text{Ni}]_{\text{tot}}$ and $[\text{Cl}]_{\text{tot}}$ should consider all of the possible nickel chloro species; i.e., it should be based on complex formation constants β_1 – β_4 .¹⁷ The nickel dependence (6), $k_{\text{obsd}}(1, \text{Ni}) \propto [\text{Ni}]_{\text{tot}}^3$, follows from experiments carried out at the constant concentration ratio [nickel]:[chloride] = 1:2. This means that, in these experiments, NiCl⁺ and NiCl₂ (coordinated solvent omitted) were the dominating species. As an approximation, the size of “NiCl₂” was therefore calculated by considering merely the equilibrium $\text{NiCl}^+ + \text{Cl}^- \rightleftharpoons \text{NiCl}_2$, governed by $K_2 = \beta_2/\beta_1 = 8.13 \text{ M}^{-1}$.¹⁷ The plot of $k_{\text{obsd}}(1, \text{Ni})$ vs “NiCl₂”_{calcd}, as shown in Figure 4, is indeed linear up to $[\text{Ni}]_{\text{tot}} = 6 \times 10^{-3} \text{ M}$ and leads to second-order rate constant $k_1 = 64 \pm 8 \text{ M}^{-1} \text{ s}^{-1}$. The value obtained for rate constant $k_{\text{obsd}}(1, \text{Ni})$ at the highest nickel concentration however deviates from linearity. To really prove the linear dependence of $k_{\text{obsd}}(1, \text{Ni})$ on “NiCl₂” according to (8), all of the equilibria in the system Ni²⁺/Cl⁻/DMF should be considered in the calculation of “NiCl₂” and more kinetic data in the concentration range $[\text{Ni}]_{\text{tot}} = 6 \times 10^{-3}$ – $12 \times 10^{-3} \text{ M}$ should be collected.

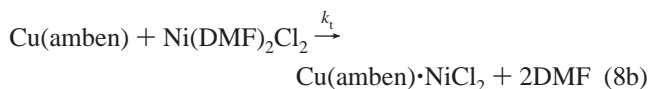
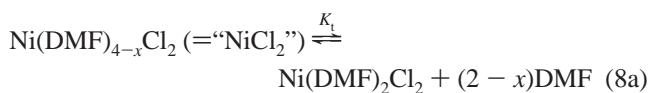
The postulate of the formation of the adduct Cu(amben)·NiCl₂ in (8) is in line with a number of studies on the ligand properties of Salen complexes. The work carried out by Sinn et al.^{22–31} proved that the lone pairs on the phenolic oxygen atoms of neutral complexes M(salen) make these compounds interesting bidentate oxygen donor ligands. It was shown that M(salen) (M = Cu, for example) interacts with metal salts M'X₂ to form

- (19) Rate constants $k_2(\text{Cl})$ and $k_3(\text{Cl})$ are the mean of the experimentally obtained data for $k_{\text{obsd}}(2, \text{Cl})$ and $k_{\text{obsd}}(3, \text{Cl})$, respectively, which are independent of the chloride concentration (see Figure 3).
 (20) The experiments with variable concentration of nickel were carried out with solutions in which the ratio [nickel]:[chloride], as adjusted by mixing Ni(DMF)₆(ClO₄)₂ and BzEt₃NCl, was kept to 1:2.
 (21) Rate constants $k_2(\text{Ni})$ and $k_3(\text{Ni})$ are the mean of the experimentally obtained data for $k_{\text{obsd}}(2, \text{Ni})$ and $k_{\text{obsd}}(3, \text{Ni})$, respectively, which are independent of the nickel concentration (see Figure 4).

- (22) Gruber, S. J.; Harris, C. M.; Sinn, E. *J. Inorg. Nucl. Chem.* **1968**, *30*, 1805.
 (23) Sinn, E.; Harris, C. M. *Coord. Chem. Rev.* **1969**, *4*, 391.
 (24) Gruber, S. J.; Harris, C. M.; Sinn, E. *Inorg. Chem.* **1968**, *7* (2), 268.
 (25) Harris, C. M.; Patil, H. R. H.; Sinn, E. *Inorg. Chem.* **1967**, *6*, 1102.
 (26) Gruber, S. J.; Harris, C. M.; Sinn, E. *Inorg. Nucl. Chem. Lett.* **1967**, *3*, 495.
 (27) Gruber, S. J.; Harris, C. M.; Sinn, E. *Inorg. Nucl. Chem. Lett.* **1968**, *4*, 107.
 (28) Harris, C. M.; Sinn, E. *J. Inorg. Nucl. Chem.* **1968**, *30*, 2723.
 (29) Coles, R. B.; Harris, C. M.; Sinn, E. *Inorg. Chem.* **1969**, *8*, 2607.

binuclear complexes $[M(\text{salen})M'X_2]$ for $X = \text{halide}$ and trinuclear complexes $[M(\text{salen})_2M']X_2$ for $X = \text{perchlorate}$. For steric reasons, the external metal M' in binuclear complexes $[\text{Cu}(\text{salen})M'\text{Cl}_2]$ has to adopt a (distorted) tetrahedral O_2Cl_2 coordination geometry,²³ which was confirmed by the X-ray structure analysis of the complex $[\text{Cu}(\text{Me-salen})\text{CuCl}_2]$.^{31,32} We were able to develop the corresponding coordination chemistry with the bidentate N_2 donor ligand $\text{Cu}(\text{amben})$ and confirmed that with metal *halides* $M'X_2$ binuclear complexes $[\text{Cu}(\text{amben})M'X_2]$ are formed and with metal *perchlorates* trinuclear complexes $[(\text{Cu}(\text{amben}))_2M'](\text{ClO}_4)_2$ are formed.³³ (For an example, see Figure S3 provided as Supporting Information.) The ligand properties of $\text{Cu}(\text{amben})$ thus provide a reasonable basis to postulate the formation of the adduct $\text{Cu}(\text{amben})\cdot\text{NiCl}_2$ according to (8) as the initial step of metal substitution. The published work on the behavior of $\text{Cu}(\text{salen})$ as ligand suggests strongly that the nickel in $\text{Cu}(\text{amben})\cdot\text{NiCl}_2$ is coordinated in a (distorted) tetrahedral fashion.

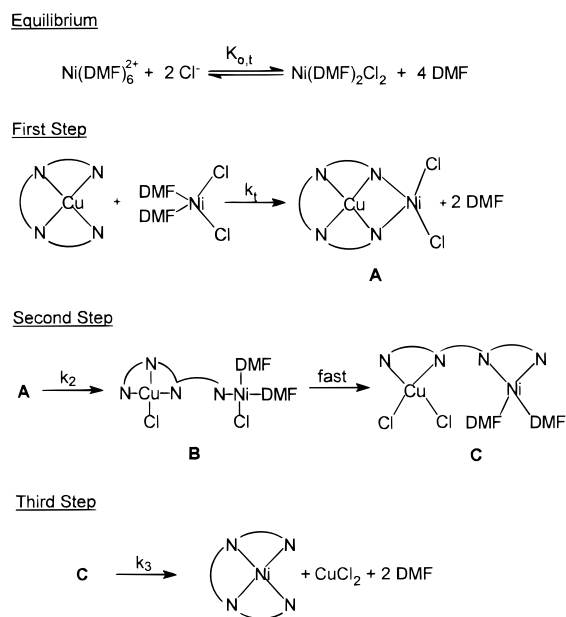
Reaction 8 can be classified as a complex formation reaction between the neutral nickel species “ NiCl_2 ” = $\text{Ni}(\text{DMF})_{4-x}\text{Cl}_2$ ($x = 0$ or 1 , according to Ishiguru et al.¹⁷) and the neutral planar ligand $\text{Cu}(\text{amben})$. Mechanistically, in this reaction two cis-orientated DMF molecules in $\text{Ni}(\text{DMF})_{4-x}\text{Cl}_2$ are replaced by the N donor atoms of the deprotonated amino groups of $\text{Cu}(\text{amben})$. Taking into account that the coordinated DMF molecules in $\text{Ni}(\text{DMF})_{4-x}\text{Cl}_2$ are expected to be very labile,^{34,35} the second-order rate constant $k_1 = 64 \pm 8 \text{ M}^{-1} \text{ s}^{-1}$ for reaction 8 (see Table 2) appears to be rather small. A possible explanation for the slowness of this reaction comes from the coordination geometry of the species formed. If the nickel in $\text{Cu}(\text{amben})\cdot\text{NiCl}_2$ is indeed tetrahedrally coordinated, it may well be that the formation of $\text{Cu}(\text{amben})\cdot\text{NiCl}_2$ occurs with (possibly distorted) tetrahedral $\text{Ni}(\text{DMF})_2\text{Cl}_2$ according to (8b).



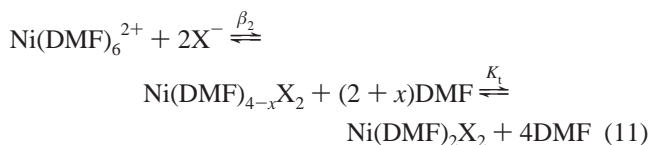
Four-coordinate $\text{Ni}(\text{DMF})_2\text{Cl}_2$ may be present at equilibrium concentration according to (8a) and, due to $K_1 < 1$, rate constant $k_1 = K_1 k_t$ would thus become smaller than expected for the reaction between $\text{Cu}(\text{amben})$ and six- or five-coordinate $\text{Ni}(\text{DMF})_{4-x}\text{Cl}_2 = \text{“NiCl}_2\text{”}$ according to (8).

This interpretation provides a very plausible basis for the understanding of the catalytic role of the anions X observed for the nickel for copper substitution according to (1) (see Figure 2). If the attacking nickel species has to be a tetrahedral one,

Scheme 1. Schematic Description of the Sequence of Steps Suggested for Reaction 7



its formation according to (11) should indeed be anion dependent.



For $X^- = \text{ClO}_4^-$ the equilibrium concentration of four-coordinate $\text{Ni}(\text{DMF})_2(\text{ClO}_4)_2$ (and also that of $\text{Ni}(\text{DMF})_4^{2+}$) is probably very small and the substitution is therefore very slow. The increase in substitution rate for $X^- = \text{Br}^-$ and SCN^- and the high rate for $X^- = \text{Cl}^-$ would then correspond to an increase in K_1 .

The mechanistic interpretation of the two consecutive first-order steps (9) and (10), associated with rate constants k_2 and k_3 , can only be speculative. As indicated in Scheme 1, the intermediate in (9) could be a species C with both copper and nickel sharing the ligand amben symmetrically. We suggest that rate control of the second step is associated with the reaction $\text{A} \rightarrow \text{B}$, in which internal Cu-N bond rupture and Ni-N bond formation as well as chloride transfer occurs. The reaction $\text{B} \rightarrow \text{C}$ is supposed to be fast compared to reaction $\text{A} \rightarrow \text{B}$. Liberation of the copper and full coordination of the nickel may then take place in the final k_3 step.

At first glance, the postulate of adduct and intermediate formation seems to contradict the experimental fact that, at 380 and 454 nm, two sharp isosbestic points are observed for reaction 7 (see Figure 1b). For the discussion of this apparent inconsistency it is important to note that (i) the isosbestic point at 380 nm remains sharp even at high $[\text{Cl}]_{\text{tot}}$ and high $[\text{Ni}]_{\text{tot}}$, whereas the one at 454 nm loses its sharpness with increasing $[\text{Cl}]_{\text{tot}}$ and high $[\text{Ni}]_{\text{tot}}$, and that (ii) as indicated in Figure 1b, in the range 700–900 nm there is a small intermediate increase and decrease of absorption. (The time dependence of the intermediate growth and decay of absorbance at 800 nm is shown in Figure S4 provided as Supporting Information.) The change in absorbance at 800 nm is small and becomes even smaller with decreasing $[\text{Ni}]_{\text{tot}}$. Since neither $\text{Cu}(\text{amben})$ nor $\text{Ni}(\text{amben})$ absorb at 800 nm, the minor spectral changes observed at this wavelength clearly prove the formation of

(30) Harris, C. M.; James, J. M.; Milham, P. J.; Sinn, E. *Inorg. Chim. Acta* **1969**, 3, 81.

(31) Sinn, E.; Robinson, W. T. *J. Chem. Soc., Chem. Commun.* **1972**, 359.

(32) The ligand R-salen, a Salen analogue, is obtained by the reaction of 1,2-diaminoethane with 2 equiv of 2-hydroxyacetophenone instead of salicylaldehyde.

(33) Fischer, J. Dissertation, Technische Hochschule Darmstadt, D 17, 1977.

(34) The rate of solvent exchange on the cation $\text{Ni}(\text{DMF})_6^{2+}$ is given by $k_{\text{ex}} = 3.8 \times 10^3 \text{ s}^{-1}$ (298 K).³⁵ One can extrapolate that in the neutral species $\text{Ni}(\text{DMF})_{4-x}\text{Cl}_2$ the DMF molecules are considerably more labile than in the cation $\text{Ni}(\text{DMF})_6^{2+}$.

(35) Meyer, F. K.; Newman, K. E.; Merbach, A. E. *Inorg. Chem.* **1979**, 18, 2142.

Table 3. Results of the Gauss Analysis of the Visible Spectra of Cu(amben) and Ni(amben) (in Toluene) and of the Fitting Procedure

	[NiL]	[CuL]
Assigned Transition Energies (cm ⁻¹)		
$\Delta_1(d_{xy} \rightarrow d_{x^2-y^2})$	19 340	14 660
$\Delta_2(d_z^2 \rightarrow d_{x^2-y^2})$	20 014	21 550
$\Delta_3, \Delta_4(d_{xz}, d_{yz} \rightarrow d_{x^2-y^2})$	21 140, 21 520	23 810, 24 290
Calculated Orbital Energies (cm ⁻¹)		
	^a	^b
$\epsilon(d_{x^2-y^2})$	25 498	24 050
$\epsilon(d_{xy})$	3943	9390
$\epsilon(d_z^2)$	1267	2500
$\epsilon(d_{xz}, d_{yz})$	0	0
AOM Parameters (cm ⁻¹)		
e_σ	9814	11 147
e_π	1971	4695

^a Racah parameters fixed as $B = 800$ and $C = 3360$ cm⁻¹.

^b Calculated CFT parameters are $10Dq = 14\ 660$, $Ds = 4420$, and $Dt = 774$ cm⁻¹.

intermediate species. With regard to the spectral properties of the postulated adduct Cu(amben)·NiCl₂ and intermediate (see eqs 8–10), the results of the multiwavelength kinetic analysis in the range 350–900 nm can be summarized as follows: (i) The calculated spectrum of the intermediate suggested in eq 9 is rather similar to that of the product Ni(amben), and (ii) the calculated spectrum of the adduct Cu(amben)·NiCl₂ suggested in eq 8 is also close to that of Ni(amben) up to 700 nm but clearly different from it at 700–900 nm. This means that the formation and subsequent decay of the weak absorption at 700–900 nm can be assigned to the binuclear species Cu(amben)·NiCl₂. One should be aware of the fact however that the computer-assisted calculation of intermediate spectra, based on computational subtraction of the contribution of the excess partner and on a multiwavelength kinetic analysis of the overall spectra, is rather limited in precision. A further interpretation of the weak absorption at 700–900 nm was therefore not attempted.

As reviewed by Margerum et al.,³⁶ the kinetics of a chelate ligand such as EDTA exchanging between two metal ions in the medium water have been extensively studied. In such reactions, the general reaction pattern was found to be the stepwise “unwrapping” of the first metal accompanied by the stepwise coordination of the second, until the ligand is completely transferred. Each of these single steps involves the alternation of bond rupture with the first metal and bond formation with the attacking metal. This mechanistic pattern does not appear to be adequate when applied to the neutral complex Cu(amben) in the aprotic solvent DMF. Moreover, it does not provide an explanation for the accelerating effect of chloride ions. For Cu(amben), bond rupture of one of the terminal Cu–N bonds means charge separation according to $\text{CuN}_4 \rightarrow {}^+\text{CuN}_3\text{N}^-$. This process is facilitated in water by rapid protonation of the very basic N⁻ but not in DMF. Scheme 1, in which only neutral species are involved in the various steps suggested for reaction 7, is therefore more adequate.

Analysis of the Visible Spectra. The analysis of the spectra of Cu(amben) and Ni(amben) in toluene was undertaken to make sure that in solution the coordination geometry is square planar. The results of the analysis in the range 1.2×10^4 – 2.6×10^4 cm⁻¹ are summarized in Table 3.

Table 4. Calculated Charge Distribution in Cu(amben) and Ni(amben)

method	site	[NiL]	[CuL]	
QR-INDO/1	$d(\text{M})$	8.44	9.27	
	$Q(\text{M})$	-0.52	-0.42	
	$Q(\text{N}_\text{C})$	+0.07, 0.02	+0.04, -0.01	
	$Q(\text{N}_\text{H})$	-0.22, -0.16	-0.27, -0.19	
	$Q(\text{H}_\text{N})$	+0.14, +0.14	+0.14, +0.14	
ZINDO/1	$Q(\text{M})$	-0.16	-0.18	
	$Q(\text{N}_\text{C})$	-0.11, -0.10	-0.11, -0.10	
	$Q(\text{N}_\text{H})$	-0.29, -0.30	-0.29, -0.29	
	$Q(\text{H}_\text{N})$	+0.13, +0.13	+0.13, +0.13	
	$Q(\text{M})$	+0.03	+0.28	
ZINDO/S	$Q(\text{N}_\text{C})$	-0.24, -0.24	-0.33, -0.18	
	$Q(\text{N}_\text{H})$	-0.32, -0.29	-0.37, -0.36	
	$Q(\text{H}_\text{N})$	+0.13, +0.14	+0.13, +0.14	
	ab initio	Mulliken		
		$d(\text{M})$	8.19	9.99
$Q(\text{M})$		+1.38	+0.60	
$Q(\text{N}_\text{C})$		-0.77, -0.88	-0.80, -0.88	
$Q(\text{N}_\text{H})$		-0.89, -0.85	-0.64, -0.92	
SEN-n				
$Q(\text{M})$		+1.62	+0.25	
$Q(\text{N}_\text{C})$		-0.51, -0.62	-0.42, -0.51	
$Q(\text{N}_\text{H})$		-0.74, -0.67	-0.33, -0.58	

For Ni(amben), the ratio $e_\sigma/e_\pi = 9814/1971$ is obtained, and for Cu(amben) the ratio $e_\sigma/e_\pi = 11\ 147/4695$.³⁷ Consequently, the copper(II) complex becomes much less stabilized than the corresponding nickel(II) analogue. The data obtained for $e_\sigma/e_\pi(\text{Ni(amben)})$ and $e_\sigma/e_\pi(\text{Cu(amben)})$ are in line with those reported by Hitchman and Bremner for square planar Ni(daco)₂²⁺ and Cu(daco)₂²⁺ (daco = 1,8-diazacyclooctane);³⁹ namely, $e_\sigma/e_\pi(\text{Ni(daco)}_2^{2+}) = 10\ 870/1885$ and $e_\sigma/e_\pi(\text{Cu(daco)}_2^{2+}) = 7800/1971$.

The present interpretation of the visible spectra of Ni(amben) and Cu(amben) is somewhat different from that given by Bowmaker et al.¹² with respect to the classification of the various absorption bands as either d–d or CT bands. The assignment is indeed a bit problematic since the observed absorptivities lie in between those typically found for d–d and CT bands.

MO Calculations. The MO calculations were carried out in order to find a possible explanation for the surprising experimental fact that, in contrast to other planar four-coordinate Cu(II) and Ni(II) complexes such as bis(*N*-alkylsalicyladiminato) complexes, Cu(amben) and Ni(amben) do not tend to increase their coordination number by addition of nucleophiles.

The calculated charge distributions are presented in Table 4. Although the individual charges of the atoms forming the chromophore vary considerably with the method used, some qualitative agreement is evident. It is consistently found that there is an excess of d electrons on the metal; i.e., there are more than eight d electrons on the nickel in Ni(amben) and more than nine d electrons on the copper in Cu(amben). This result is in line with the experimental finding that, due to the low Lewis acidity of the metal center, the addition of nucleophiles is not observed. The hydrogen-carrying nitrogen atoms N_H have an excess of negative charge, whereas the hydrogen

(36) Margerum, D. W.; Cayley, G. R.; Weatherburn, D. C.; Pagenkopf, G. K. In *Coordination Chemistry*; Martell, A. E., Ed.; ACS Monograph 174; American Chemical Society: Washington, DC, 1978; Vol. 2, pp 165–174.

(37) It is practice to assume that the ratio e_σ/e_π is almost identical for Cu(II) and Ni(II) complexes having similar bonding conditions.³⁸ In the present case however this is not correct since the π -bonding interaction in the Cu(II) complex is increased significantly. This follows from a marked separation of the Δ_1 transition from the rest of the absorption bands of Cu(amben).

(38) Lever, A. B. P. *Inorganic Electronic Spectroscopy*, 2nd ed.; Elsevier: Amsterdam, 1984.

(39) Hitchman, M. A.; Bremner, J. B. *Inorg. Chim. Acta* **1978**, 27, L61.

atoms bound to nitrogen (H_N) are positively charged to a considerable extent.

Conclusions

In solutions of square planar Cu(amben) and nickel salts NiX_2 in DMF, nickel replaces the copper irreversibly to form Ni(amben), which seems to contradict the order of thermodynamic stability following from the Irving–Williams series. Interestingly, the rate of the nickel for copper substitution is strongly dependent on the nature of the anion X. The slow substitution with X = perchlorate on the time scale of days is contrasted by a remarkably fast substitution with X = chloride on the time scale of minutes. It follows from the kinetic analysis of the system Cu(amben)/Ni(DMF) $_6^{2+}$ /Cl $^-$ that (i) the overall process consists of a nickel- and chloride-dependent first step, followed by two nickel- and chloride-independent consecutive steps, and (ii) the first step can be described as a second-order reaction between Cu(amben) and a dichloro species “NiCl $_2$ ”. The species “NiCl $_2$ ” is suggested to be (distorted) tetrahedral Ni(DMF) $_2$ -Cl $_2$, which reacts with the N $_2$ donor ligand Cu(amben) to form the binuclear complex Cu(amben)·NiCl $_2$ as an intermediate. This intermediate rearranges in two first-order steps to form Ni(amben).

A plausible explanation for the (at first glance) unexpected nickel for copper substitution comes from the fact that, even in polar solvents such as DMF, Cu(amben) and Ni(amben) are planar, only four-coordinate species. The consideration of ligand field stabilization effects predicts that planar, four-coordinate Cu(amben) (3d 9) should be less stable than planar, four-coordinate Ni(amben) (3d 8). The catalytic role of the anions X in NiX $_2$ is remarkable in the sense that their kinetic efficiency seems to be linked with their ability to favor the formation of nickel species with reduced coordination number, such as four-coordinate Ni(DMF) $_2$ X $_2$.

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Supporting Information Available: Text describing theoretical methods used for the analysis of the electron spectra and MO calculations and Figures S1–S4, showing visible spectra (7 pages). Ordering information is given on any current masthead page.

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