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Concerning the Thermochromic Mechanism of Copper(II) and Nickel(II) Complexes of *N*,*N*-Diethylethylenediamine[1]

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The thermochromic mechanism of several Cu(II) and Ni(II) complexes of the type $M(dieten)_2X_2$, where dieten = *N*,*N*-diethylethylenediamine and X = inorganic anion, has not been clearly established. Pressure and thermal studies in the electronic and infrared region (mid-infrared and far-infrared) have been made. In the electronic region, the "d–d" transitions shift red with an increase in temperature for both Cu(II) and Ni(II) complexes. With pressure these transitions are toward the red with Cu(II) complexes and toward the blue with Ni(II) complexes. Mid-infrared data are indicative of axial interaction occurring with an increase in temperature and the lack of interaction with pressure increases. Although many factors are involved in determining these differences and anion and steric effects are important, the dominant factor appears to be the distortion of the tetragonal metal atom environment and axial interaction between the anions and the $M-N_4$ plane.

Some of the copper(II) and nickel(II) complexes of *N*,*N*-diethylethylenediamine (dieten) of the type $M(dieten)_2X_2$, where X is an anion, have demonstrated reversible thermochromic behavior.[3-8] Considerable physical studies have been made on these compounds. For example, temperature-dependent infrared, far-infrared, electronic spectra,[6] magnetic,[6] ESR,[7] and calorimetric measurements have been reported.[8-10] The visible absorption bands for the copper complexes demonstrate an abrupt red shift with a temperature increase. In the nickel complexes a similar red shift is observed, and except for the compounds containing BF_4^- or ClO_4^-, the shift increases regularly with a temperature rise. The two modes of behavior have been designated by Paoletti and co-workers as discontinuous and continuous thermochromism.[8] From these studies Lever has concluded that the mechanism for the thermochromism displayed by these complexes was associated with the distortion of the tetragonal metal atom environment and the axial interaction between the anions and the $M-N_4$ plane.[6]. It seems more than likely that there are other factors which could have a major role in delineating the mechanism. One such factor could be steric effects in complexes of substituted ethylenediamine containing bulky alkyl groups. By combining both pressure and thermal measurements and studying any changes observed in the electronic and infrared spectra, the relative importance of such factors may be better defined. This paper reports on the results of such studies and presents a suggested interpretation which supports Lever's conclusion.

Experimental Section

Materials. The preparation of the complexes has been previously reported.[8] Since some of the complexes were deliquescent, only desiccated material was used in the physical studies.

Spectral Measurements. For the region between 4000 and 650 cm^{-1} a Beckman IR-12 and the diamond anvil cell (DAC) were used.[11] For the region <650 cm^{-1}, measurements were made with a Perkin-Elmer Model 301 and a DAC.[12] In both instruments a 6X beam condenser was necessary.[11-12] Electronic spectra were recorded in a Cary 14 spectrophotometer interfaced with a special beam condenser.[13] Both ambient and nonambient spectra were obtained. For spectra recorded at elevated temperatures, a chromel–alumel thermocouple (with an ice junction as reference) was used to measure temperatures.

Results and Discussion

A. Electronic Region. Table I compares temperature, pressure, and environmental effects on the electronic transitions of $Cu(dieten)_2X_2$ complexes. Table II lists the comparison of temperature and pressure effects on the electronic transitions of $Ni(dieten)_2X_2$. It may be observed that with increasing temperature a red shift (toward lower energy) in the visible absorption occurs for both series of complexes, and thermochromism occurs with a conversion to a weakly tetragonally distorted octahedra. Thus a red shift may be viewed as the tendency of the complex to go toward an octahedral environment (increased axial interaction of the anions with the MN_4 plane) and a tendency toward thermochromism.

When the complexes are subjected to high external pressures, a strong anion dependency is noted. In the copper complexes small red shifts occur for the nitrate, perchlorate, and BF_4^- anions, but no color changes occurs. For the nickel complexes a strong anion effect is also observed, and the shift in the "d–d" transition appears to progress toward the blue region. However, as the anion becomes progressively softer (polarizable) the amount of blue shift becomes smaller, and for the complex containing the iodide anion a red shift occurs.

Table I. Comparison of Temperature, Pressure, and Environmental Effects on the Electronic Transitions of $Cu(dieten)_2X_2$ Complexes

$Cu(dieten)_2X_2$	*T*, °C	Max absorption,[e] cm^{-1}	Δ(LT-HT),[f] cm^{-1}	Pressure (25 °C), kbars	Max absorption, cm^{-1}	Δ(48-0 kbars),[f] cm^{-1}	Max absorption (hydrated solid), cm^{-1}	Max absorption (aq soln), cm^{-1}
$X^- = NO_3^-$	25	21 460	−3860	0	21 622	−1000	16 667	17 094
	125	17 605		48	20 619			
	(149)[d]							
$X^- = ClO_4^-$	25	20 700	−1400	0	20 700	−700	20 833[a]	17 241
	78	19 305		48	20 000			
	(35)[d]							
$X^- = BF_4^-$	0	20 750	−1520	0	20 750	−550	20 000[b]	16 667[c]
	78	19 230		48	20 202			
	(15)[d]							

[a] Does not hydrate in solid state readily—remains red. [b] Only partially hydrates in solid state—turns purple; probably only a surface effect. [c] Shoulders at 16 064 and 18 018 cm^{-1}. [d] These numbers are the temperatures at which the first changes in the baseline of the maximum of the visible absorption occur as the temperature is raised.[8] [e] Taken from A. B. P. Lever, E. Mantovani, and J. C. Donini, *Inorg. Chem.*, **10**, 2425 (1971). [f] Rounded to the nearest 10 cm^{-1}. LT = low temperature; HT = high temperature.

Table II. Comparison of Temperature and Pressure Effects on the Electronic Transitions of $Ni(dieten)_2X_2$ Complexes

$Ni(dieten)_2X_2$	*T*, °C	Max absorption, cm^{-1}	Δ(LT-HT),[b] cm^{-1}	Pressure (25 °C), kbars	Max absorption, cm^{-1}	Δ(40-0 kbars),[b] cm^{-1}
$X^- = NO_3^-$	25	21 858	−450	0	21 858	+1000
	101[a]	21 415		40	22 857	
$X^- = BF_4^-$	25	21 505	−1310	0	21 505	+470
	94[c]	20 200		40	21 978	
$X^- = ClO_4^-$	25	21 622	−1000	0	21 622	+360
	110[c]	20 619		40	21 978	
$X^- = Br^-$	25	21 978	−730	0	21 978	+240
	140	21 250		40	22 222	
$X^- = I^-$	25	21 739	−990	0	21 739	−230
	130	20 750		40	21 505	

[a] Temperature much lower than thermochromic transition temperature (estimated at ~220 °C). [b] Rounded to nearest 10 cm^{-1}. [c] Represent temperature at which the first changes in the baseline of the maximum of the visible absorption occur as the temperature is raised.[8]

Examining the data one can see that the effect external high pressure has on the electronic spectra is different from the effect produced by a change in temperature. With an increase in temperature one obtains electronic spectra characteristic of six-coordinate Cu(II) and Ni(II) (blue or violet and red or red-orange, respectively); pressure effects result in electronic spectra in which four-coordinate Cu(II) and Ni(II) are maintained (red and yellow, respectively).

Differences are observed in the results of the effects of pressure on the electronic transitions for the nickel and copper complexes. The blue shifts for the nickel complexes, as compared to the red shifts for the copper complexes, are indicative of the lesser tendency for axial interaction and thermochromism to occur for the nickel complexes. These results are in agreement with those obtained by temperature studies, which show that higher temperatures (about 70 °C higher) are necessary to reach the transition temperatures for the occurrence of thermochromism in the nickel complexes.[8]

It should be noted that some of the copper complexes are deliquescent, and blue solids are obtained, as the axial positions are filled by water molecules. The hydration reaction is not to be confused with the thermal effect on the anhydrous complexes giving blue or violet compounds. The hydration reaction is a competing reaction and illustrates the necessity of operating in a dry atmosphere when working with these solids.

B. Mid-Infrared Region. Some mid-infrared results for some of these complexes have been reported by Lever et al.[6] We have reexamined this region for these complexes as a function of both temperature and pressure. Interpretation of the results obtained in the mid-infrared region (mid-ir) at ambient and varying conditions of temperature and pressure is difficult. This is due primarily to ligand absorption interference. For complexes involving the anions NO_3^-, ClO_4^-, and BF_4^-, strong ligand bands are seen precisely where anion vibrations occur. Additional problems involving the BF_4^- copper complex arise since the hydrated compound is blue at room temperature. One must take proper precautions to ensure that one is making measurements on the red, desiccated complex.

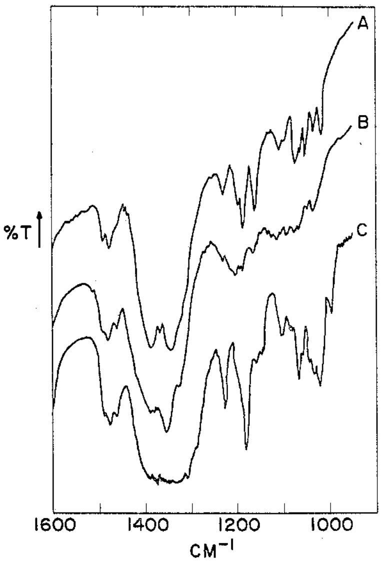

Figure 1. Spectra of $Cu(dieten)_2(NO_3)_2$ at ambient (A) and at 40-kbar pressure (B) and at 86 °C (C) in the 1600–1000-cm^{-1} region.

Figure 1 illustrates spectra of $Cu(dieten)_2(NO_3)_2$ obtained at ambient conditions, at 40-kbar pressure and 86 °C in the 1600–1000-cm^{-1} region. Comparing the spectra, it is observed that dramatic changes are not observed with temperature or pressure increases. It is noted that for the BF_4^- and ClO_4^- complexes, some infrared unallowed bands in T_d symmetry (e.g., ν_1 and ν_2) are already observed in the solid state at room temperature.

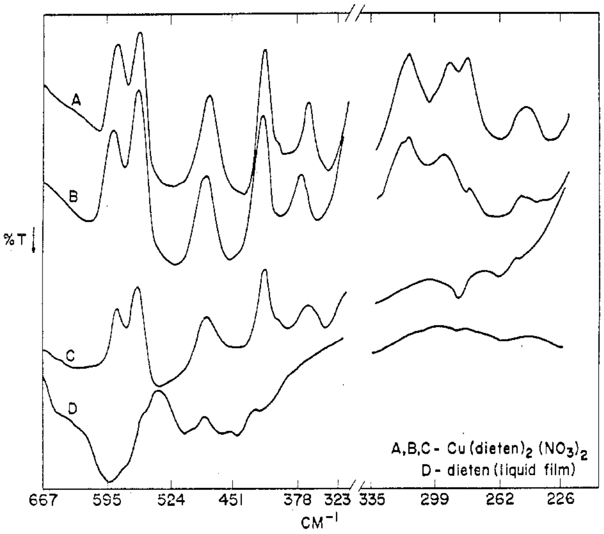

Figure 2. Far-infrared spectra of $Cu(dieten)_2(NO_3)_2$ in the 667-200-cm^{-1} region: A, spectrum at atmospheric pressure and temperature; B, spectrum at 48-kbar pressure; C, spectrum at 105 °C; D, spectrum of dieten liquid film.

Our mid-ir results for the Cu(II) and Ni(II) complexes are summarized as follows.

A. Spectra at Elevated Temperatures. (1) As one increases the temperature, the ν_3 vibration of the ClO_4^- complex shows an increased amount of splitting. The 937-cm^{-1} absorption (ν_1) appears to show an increase in intensity with temperature.

(2) The ~750-cm^{-1} absorption (ν_1) in the BF_4^- complex appears at ambient conditions and shows little or no change with a temperature increase. The neat ligand shows an absorption at ~730 cm^{-1}. Whether the ~750-cm^{-1} band is a vibration due to the BF_4^- entity or is a modified ligand absorption due to complexation is not certain.

(3) As one may observe from Figure 1, only minor changes are obtained in the ν_3 region of the NO_3^- complex. Some observations of others,[6] in the region of ~1750 cm^{-1}, have been interpreted in terms of coordinated nitrate.

These results are consistent with an increase in axial interaction occurring with the central atom and agree with the electronic data.

B. Spectra at High Pressures. Pressure effects are limited to small blue shifts of absorption and to the usual broadening of bands due to a pressure gradient in the DAC.[14,15]

It is apparent that little evidence is found from mid-ir experiments for axial interaction occurring in these complexes as they are subjected to pressure increases and this concurs with the electronic data taken at high pressure. However, the results in the mid-ir region, with an increase in temperature, provide some evidence for increased axial interaction of the anion with the central metal atom occurring.

C. Far-Infrared Region. The far-infrared (far-ir) or skeletal region appears to be more diagnostic for occurrence of axial interaction with the anions. Figure 2 demonstrates the changes occurring in this region when the $Cu(dieten)_2(NO_3)_2$ complex is heated to 105 °C. New absorptions occur at 304 and 272 cm^{-1}, which may possibly be associated with a copper–oxygen stretching vibration. These bands occur in the vicinity of absorptions assigned to copper–oxygen stretching vibrations in anhydrous $Cu(NO_3)_2$.[16] Minor changes also occur in the ~300-cm^{-1} region for the $Cu(dieten)_2(ClO_4)_2$ complex, a new band occurring at ~297 cm^{-1} as the temperature is increased.

The mid-ir and far-ir data together provide indications for increased axial interaction occurring with a temperature increase. On the other hand, no such evidence is provided by a pressure increase.

Table III. Shifts of the "d–d" Transition as a Function of X in $Ni(dieten)_2X_2$ Complexes (cm^{-1})

X^-	Δ^a	X^-	Δ^a
NO_3^-	1000	$^1/_2CdBr_4^{2-}$	100
BF_4^-	470	AgI_2^-	0
ClO_4^-	360	I^-	−230
Br^-	240		

^{a} $\Delta = \nu_{pressure(40\ kbars)} - \nu_{ambient}$, rounded to nearest 10 cm^{-1}.

D. Pressure Cycling Experiments. Several experiments were conducted making visual observations with a Leitz microscope. The complex $Cu(dieten)_2(ClO_4)_2$ was chosen since it had a reasonably low transition temperature of 35 °C, showed little hydration, and no evidence for decomposition. The $Cu(dieten)_2(NO_3)_2$ was not chosen since it has a high transition temperature (~149 °C) and demonstrates hysteresis when the temperature and pressure are lowered, as well as some possible decomposition. High external pressures, to 30 kbars, were applied to the perchlorate solid in a DAC followed by a rise in temperature to the transition temperature and beyond (~50 °C). No onset of a color change was observed. A release in pressure, while maintaining the temperature, produced the color change from red to violet. By cycling the pressure back and forth, while maintaining the temperature at the transition temperature, it was possible to cycle the color as well.

E. Polarizabilities of Anions. From Tables I and II and the discussion in section A, it can be observed that a strong anion effect on the d–d transitions exists as high external pressures are applied to the solid complexes. The relationship to the polarizabilities of the anion is more appropriately demonstrated by the complexes of dieten with Ni(II). Normally the effect of pressure on the d–d electronic transition is to shift it toward a higher energy level.[17,18] As may be observed from Table III, as one progresses from a hard acid (anion) to a soft one, there is a progressive decrease in the high-energy shifts (blue) with pressure; for the iodide a red shift occurs. The more polarizable or more easily deformable anions tend to show a very small blue shift with pressure or one that is a red shift. Since the color change results from the approach of the anions to the cations at the axial positions, the more polarizable anions should be able to more easily accomplish this with pressure. Nevertheless, even with the iodide complex the six-coordinate state is never obtained by pressure application, and no change in color occurs.

The relationships between hard and soft acids or bases, in the sense that Ahrland, Chatt, and Davies[19] and Pearson[20] have defined them, have previously been established by thermodynamic studies and nucleophilic reactivities made in solution.[21] The present study illustrates a technique which is accomplished in the solid state.

F. Mechanism of Thermochromic Behavior. In discussing the nature of the mechanism of the thermochromic effect observed for these complexes, a number of factors which may play a role are given as follows.

(1 and 2) Solid Packing Forces and Compressibilities and Hydrogen Bonding. The importance of the solid packing forces and compressibilities in cooling the crystal or subjecting it to high external pressures cannot be overemphasized. These factors would differ from crystal to crystal and therefore would be difficult to assess. Possible hydrogen bonding of the amino hydrogens to the more polar anions would be of some consequence to any axial interactions occurring with MN_4 plane. Again these forces would be difficult to estimate.

3. Phase Changes. Under the conditions of pressure used for this work, no solid phase changes were observed. We may safely conclude that this factor is not involved for these complexes as an increase in pressure occurs. With an increase in temperature, however, some x-ray evidence, as well as thermodynamic data,[8,9] indicates the possibility for phase changes occurring.[4]

4. Changes in Ligand Coordination (Bidentate → Monodentate). A change in coordination number of the ligand appears unlikely. The spectroscopic data indicate that the original four-coordinate spectrum is preserved with pressure, and only blue shifts of the absorptions are observed. In the case of an elevation of temperature the coordination number goes from 4 to 6 with the accompanying change in optical spectrum. For this to occur with monodentate ligands the anions would have to be bidentate, and no experimental evidence exists for this from spectroscopic studies. It does not appear likely that the chelate ring opens and that the ligand becomes monodentate for either the high-temperature or high-pressure measurements.

5. Changes in Orientation of Alkyl Groups in Ligand. The case of dieten may be considered in more detail. Changes in orientation of the alkyl groups with changes in temperature and pressure and their effects on the axial interaction are important and may play a major role for complexes of a ligand where the alkyl groups are bulky. Evidence that changes in orientation of alkyl groups in substituted ethylenediamine complexes are possible comes from ultraviolet data.[22] It would be possible to have two orientations of the ethyl groups: one which sterically insulates the axial positions and one in which the axial positions are exposed. It is also possible to freeze the configuration which insulates the axial positions with application of high external pressures to the solids. Recent high-pressure results on complexes of *C*,*C*-dimethylethylenediamine (*C*,*C*-diMeen) and *N*,*N*-dimethylethylenediamine (*N*,*N*-diMeen)[23] indicate that pressure effects are similar to those found for dieten. For (*C*,*C*-diMeen) and (*N*,*N*-diMeen), the alkyl groups are always in a position which ensures exposure of the axial positions. This similarity with dieten would seem to provide evidence that steric factors from different orientations of the alkyl groups could play a dominant role only when the alkyl groups are very bulky (greater than ethyl).

6. Nature of Anions. The thermochromic effect is also seen to be related to the nature of the anion. For copper(II) complexes of dieten, the more polarizable anions (e.g., Br^-, I^-, and AgI_2^-) do no induce thermochromism.[8] With nickel(II) both hard and soft anions allow the thermochromism to appear in *N*,*N*-dimethylethylenediamine. Here the behavior is continuous. For dieten, soft and hard anions allow the thermochromism which is continuous for all anions with the exception of ClO_4^- and BF_4^- anions.

The crystal field stabilization energy (CFSE) due to the anions would also effect axial interaction.[24]

7. Complexing Ability of the Central Atom. The complexing ability of the central atom is important as well. This is illustrated by differences between the transition temperatures (70 °C higher for nickel) and thermodynamic data (the energy of the endothermic transition, ΔH, is higher for copper) for nickel vs. copper.[8]

8. Basicity of the Ligand (CFSE). The basicity and the CFSE of the ligands play a role in that the strengths of the MN bonds are determined in part by the basic nature of the ligand. This in turn determines the degree of expansion or contraction and the extent of the subsequent axial interaction that will take place.

9. Steric Effects. Steric factors play an important role. It has been observed that thermochromism depends on the size of the alkyl groups of the N,N-substituted ethylenediamine ligand. For the copper complexes, if the alkyl groups are *N*,*N*-di-*n*-butyl or *N*,*N*-diisopropyl, no thermochromism occurs and the complexes remain in the four-coordinate state.[5,8] Most of the dieten complexes are thermochromic, although some exceptions are noted, as previously mentioned. Most of the dieten complexes with nickel are thermochromic. Nickel complexes of the *C*,*C*-dimethylethylenediamine (*C*,*C*-diMeen) are thermochromic. The copper complex of *C*,*C*-diMeen with NO_3^- is thermochromic as well; those of ClO_4^-, BF_4^-, and the deformable ions AgI_2^- and PbI_3^- are not.[23]

It should be indicated that steric effects may result from the size of the anion as well.

10. Compression or Expansion along the MN_4 Plane. The most plausible explanation of the results obtained in this paper is provided by the mechanism described by Lever.[6] As temperature is increased, the metal–nitrogen bond distances are expanded. Axial interaction increases causing a change in coordination number from 4 to 6, accompanied by a color change (thermochromic effect). As the temperature is lowered, the reverse effect occurs as the metal–nitrogen distances are contracted.

The effects of pressure are observed to be the same for complexes of dieten, *N*,*N*-diMeen, and *C*,*C*-diMeen, where steric effects are expected to be different. This would tend to indicate that the Lever mechanism is the most dominant factor with the application of high external pressures, as it is with an elevation of temperature, but with differing results. Whereas thermochromism occurs with a rise in temperature, no color change occurs with an increase in pressure. With high external pressures the planar distances are more drastically contracted than they are at ambient temperatures. This minimizes the axial interaction as observed in the electronic and infrared experiments, causing no color change. This mechanism also explains the pressure cycling results.

It is felt that in combining pressure and temperature techniques, a confirmation of Lever's mechanism for the thermochromic effect for these complexes has been provided.

Registry No. $Cu(dieten)_2(NO_3)_2$, 52646-63-6; $Cu(dieten)_2(ClO_4)_2$, 52646-62-5; $Cu(dieten)_2(BF_4)_2$, 52646-61-4; $Ni(dieten)_2(NO_3)_2$, 52613-63-5; $Ni(dieten)_2(BF_4)_2$, 52613-62-4; $Ni(dieten)_2(ClO_4)_2$, 42534-35-0; $Ni(dieten)_2Br_2$, 42490-19-7; $Ni(dieten)_2I_2$, 42490-16-4; $Ni(dieten)_2(CdBr_4)$, 59888-76-5; $Ni(dieten)_2(AgI_2)_2$, 59888-77-6.

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