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NMR Studies of Thermochromic Transitions in Copper(II) and Nickel(II) Complexes with *N*,*N*-Diethylethylenediamine

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The temperature dependence of the proton and ^{19}F NMR spectra of bis(*N*,*N*-diethylethylenediamine)copper(II) perchlorate, bis(*N*,*N*-diethylethylenediamine)copper(II) tetrafluoroborate, bis(*N*,*N*-diethylethylenediamine)nickel(II) perchlorate, and bis(*N*,*N*-diethylethylenediamine)nickel(II) tetrafluoroborate were studied. The second moments of the ^{1}H spectra show a sharp decrease at the temperature of the thermochromic phase transition. This decrease is due to the onset of dynamic motion in the ligand molecule. A model of the motion is described, and it is used with the crystallographic data to calculate the second moments for various amplitudes of the flipping motion. No narrowing of the ^{19}F NMR line was observed.

Introduction

Several copper(II) and nickel(II) salts of the form bis(*N*,*N*-diethylethylenediamine)MX$_2$ (where M is a metal and X is an anion, hereafter (dieten)$_2$MX$_2$) are thermochromic.[1-3] Depending on the anion selected, the thermochromism can be either continuous or discontinuous. The salt of an easily polarizable anion (e.g., Br$^-$ or I$^-$) shows a color change due to the gradual change of the visible absorption spectra with temperature. In addition, the spectra of salts of less easily polarizable anions (e.g., ClO_4^- and BF_4^-) also show a rapid change over a narrow range of temperature. A plot of the visible absorption spectra vs. temperature is discontinuous at the transition.[4] For these discontinuously thermochromic salts, differential scanning calorimetry (DSC) experiments show that the thermochromism is accompanied by an endothermic transition.[4] Endothermic transitions have not been observed for the continuously thermochromic salts.

The thermochromism of bis(*N*,*N*-diethylethylenediamine)copper(II) perchlorate was first reported in 1938 by P. Pfeiffer and H. Glaser.[1] They found that the salt changes from red to violet at approximately 44 °C. A. B. P. Lever et al.[2] reported that the electronic spectrum maximum shifts from 20750 to 19230 nm when the salt goes to the high-temperature phase. The DSC experiment gave ΔH for the transition of 2.13 ± 0.16 kcal/mol.

It was initially thought that the thermochromism was due to increased axial interactions of the anion.[2,4-6] However, in 1979 Grenthe et al.[7] reported the crystal structure of both phases of bis(*N*,*N*-diethylethylenediamine)copper(II) perchlorate. The absence of axial coordination in both phases of the crystal was shown. They concluded that the thermochromism, both continuous and discontinuous, was due to a decreased strength of the in-plane ligand field, a mechanism first proposed by W. E. Hatfield et al.[8] in 1963.

It is reasonable to assume that the structural characteristics of the ClO_4^- and BF_4^- salts of both N and Cu are the same. In the $CuClO_4$ salt, the Cu(II) atom is coordinated to two molecules of *N*,*N*-diethylethylenediamine through the N atoms, which gives the copper atom square-planar coordinate geometry. In the low-temperature phase the five-membered rings are in a symmetrical skew conformation with the carbon atoms 0.332 and 0.329 Å above and below the Cu–N$_4$ plane.[7,9] The closest Cu–O distance is 3.65 (1) Å. It is assumed that the steric hindrance of the ethyl groups substituted on the N atoms prevents the coordination of the perchlorate anion. In the high-temperature phase, a twofold axis of rotation perpendicular to the Cu–N$_4$ plane replaces the center of symmetry at the Cu atom. The five-membered rings about the Cu atom appear to become approximately planar; the distance that the C atoms are displaced from the plane reduces from 0.329 to 0.1 Å. The C–C bond length in the ring shrinks to 1.37 (2) Å from 1.507 (5) Å. This, with the increased size of the thermal ellipsoids, indicates static or dynamic disorder that would cause averaged atomic positions to be observed. The closest Cu–O distance increases from 3.65 (1) to 4.16 (2) Å. The increase is probably due to increased motion of the ethyl groups. The O atoms of the perchlorate also show increased motion as indicated by the increase in size of the O atom thermal ellipsoids and a general decrease in the Cl–O bond length.

I. Grenthe et al.[7] also looked at the proton NMR resonance using the Fourier transform technique and found two overlapping peaks. One peak is much broader than the other. The peaks shift downfield 8 ppm at the transition and become 20–30% narrower. This is an indication of the averaging of local magnetic fields due to increased thermal motion.

It was concluded that the thermochromism was probably due to conformational changes in the copper–ligand ring. The onset of motion would affect the N atoms and cause a sudden decrease in the in-plane ligand field. Such a decrease in the in-plane ligand field strength is shown by the EPR data,[2,10] though earlier investigators thought the decrease signaled the increase of axial interactions of the anion.

Two possible conjectures can be imagined for the mechanism of the phase transition. In the first, the driving force for the transition is the thermal motion of the ligands, particularly of the diethyl groups. As the thermal amplitudes of vibrations increase, the lone pair on each nitrogen atom is less rigidly fixed in the optimal orientation for coordination, and the ligand field strength decreases. This accounts for the continuous thermochromism. At some temperature, a cooperative transition occurs to a new structure in which dynamic disorder of the ligand occurs. The role of the anion is rather passive in this model, merely providing a mechanism for damping the thermal vibration through hydrogen bonding to the NH$_2$ protons. This is in agreement with the fact that the transition temperature increases in the order $BF_4^- < ClO_4^- < NO_3^-$ and is not inconsistent with the fact that no transition is observed for X = Cl$^-$, Br$^-$, or I$^-$.

The second mechanism involves the active participation of the anion. Increasing temperature causes increasingly larger amounts of thermal motion in both the ligand and anion. For an anion that can undergo orientational reorientation (e.g.,

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Table I. NMR Second Moments

		^{1}H NMR			^{19}F NMR	
compd	T_{th}, °C	$\overline{\Delta H^2}$(static), G^2	$\overline{\Delta H^2}$(dynamic), G^2	R	$\overline{\Delta H^2}$(static), G^2	$\overline{\Delta H^2}$(dynamic), G^2
(dieten)$_2$Cu(ClO$_4$)$_2$	45	16	10	0.62		
(dieten)$_2$Cu(BF$_4$)$_2$	20	22	17.5	0.80	2.0	2.0
(dieten)$_2$Ni(ClO$_4$)$_2$	95	13	11	0.85		
(dieten)$_2$Ni(BF$_4$)$_2$	110	15	10	0.67	4.0	4.0

BF$_4^-$, ClO$_4^-$, NO$_3^-$), the onset of reorientation of the anion (via a cooperative mechanism) weakens the hydrogen bonding, allowing the ligand to become disordered. For simple anions (halogens), no reorientation is possible, and thus no phase transition occurs.

The purpose of this paper is to investigate more thoroughly the proton NMR spectra of (dieten)$_2$Cu(ClO$_4$)$_2$ along with (dieten)$_2$Cu(BF$_4$)$_2$, (dieten)$_2$Ni(ClO)4$_2$, and (dieten)$_2$Ni(BF$_4$)$_2$ (Table I). The ^{19}F NMR spectra of the BF$_4^-$ salts are also investigated. Changes in the second moment of an NMR resonance indicate changes in the amount of motion in a molecule. These data and the structural determination of I. Grenthe et al. will give insight into both the type and extent of motion causing the thermochromism.

Sample Preparation

The compounds studied were prepared by the method of Pfeiffer and Glaser.[1] The ligand was added to the metal salt in a water or an ethanol solution. The copper compounds were recrystallized from water. The nickel salts were recrystallized from absolute ethanol in a N$_2$ atmosphere. Samples were checked for purity by elemental analysis.

NMR Instrumentation

The CW NMR instrumentation is the same as that described by D. R. Bloomquist.[13] With use of the temperature controller described, the dependence of the second moment on the temperature could be observed. The marginal oscillator was used to measure the proton resonance of each of the four salts studied and the ^{19}F resonances of (dieten)$_2$Ni(BF$_4$)$_2$ and (dieten)$_2$Cu(BF$_4$)$_2$. The frequency of the oscillator was set at 15.51 MHz for the proton NMR and 14.86 MHz for the ^{19}F NMR. Silicon oil was used in the temperature controller when collecting ^{19}F data, while perfluorotributylamine was used when proton data were collected. The samples were packed in 10-mm NMR sample tubes to a depth of 3 cm. For each spectrum, the second moment of the resonance line was calculated by

$$\overline{\Delta H^2} = \frac{\int_{-\infty}^{\infty} (H - H_0)^2 I(H)\, dH}{\int_{-\infty}^{\infty} I(H)\, dH} \qquad (1)$$

The correction for the modulation amplitude was estimated to be less than 0.1 G^2 and was ignored.

Experimental Results

The second moments of the proton NMR spectra for all four compounds show a discontinuous change at their respective thermochromic phase transitions. Results for (dieten)$_2$Cu(ClO$_4$)$_2$ are shown in Figure 1; the data for the other three salts are similar. The results are summarized in Table I, where second moments just above and below the phase transitions are tabulated, as well as the reduction ratio, $R = \overline{\Delta H^2}$(high T)/$\overline{\Delta H^2}$(low T). In addition, within each phase, there is a gradual narrowing of the resonances lines (and thus decrease of the second moment) as the temperature increases. This is indicative of a general increase in lattice and molecular vibrations.

Contrarily, the line widths and second moments of the ^{19}F NMR spectra are essentially independent of temperature. However, as seen in Table I, the second moments of the two compounds differ by a factor of 2. Qualitatively, the data argue that there is no change in the amount of orientational disorder of the anion at the phase transition.

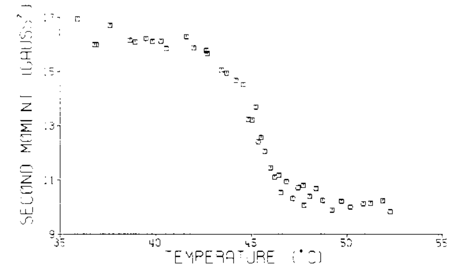

Figure 1. ^{1}H NMR second moment vs. temperature for (dieten)$_2$Cu(ClO$_4$)$_2$).

Application to Bis(*N*,*N*-diethylethylenediamine)copper(II) Perchlorate. In this section, we will seek to quantitatively explain the decrease in the proton second moment at the phase transition for (dieten)$_2$Cu(ClO$_4$)$_2$. As mentioned above, the ethylenediamine carbon atoms C(1) and C(2) (the numbering system of Figure 2 in Grenthe et al.[7] is used) are located above and below the Cu–N plane in a skew formation when the crystal is in the low-temperature phase. In accord with the structural data, we assume that the five-membered chelate rings under a rapid reorientation between the two possible skew conformations is the high-temperature phase.

The second moment for a rigid molecule in a powder sample is given by[11]

$$\overline{\Delta H^2}(\text{static}) = \tfrac{6}{5}I(I+1)g^2u_0^2N^{-1}\sum_{j<k} r_{jk}^{-6} \qquad (2)$$

Here g is the nuclear g factor, I is the nuclear spin, u_0 is the nuclear magneton, N is the number of nuclei at resonance for which binuclear interactions are summed, r_{jk} is the internuclear distance, and θ_{jk} is the angle between the applied field and the vector $\vec{r}_{jk}$. Calculations were carried out with the following constraints: (a) heavy-atom positions are given by the X-ray structure determination,[7] (b) H–H separations are assumed to be 1.79 Å for CH$_2$ groups and 1.64 Å for NH$_2$ groups, (c) the CH$_3$ group is assumed to be undergoing hindered threefold rotation,[12,13] and (d) only H–H distances less than 5 Å are included. This yields $\overline{\Delta H^2}$(static) = 23 G^2. The observed second moments (Table I) are generally considerably lower than this. This is due to the neglect of lattice vibration in the calculation. For a powder sample of a molecule undergoing reorientation between equivalent configurations, one calculates the powder average of the thermal average that is given by

$$\overline{\Delta H^2} = \tfrac{3}{2}I(I+1)N^{-1}g^2u_0^2 \sum_{j>k}^{N} \langle\langle((3\cos^2\theta_{jk} - 1)_{\text{thermal}})^2\rangle_{\text{powder}}\rangle r_{jk}^{-6} \qquad (3)$$

with the assumption that intranuclear distances are constant.

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Table II. Second Moment Calculations for $(\text{dieten})_2\text{Cu}(\text{ClO}_4)_2$

atoms	θ'', deg	r_{jk}, Å	$\overline{\Delta H^2}$(static),[a] G^2	R_{jk}[a] $\phi = 25.7$	R_{jk}[a] $\phi_0 = 43$	$\overline{\Delta H^2}$,[b] G^2 $\phi_0 = 25.7$	$\overline{\Delta H^2}$,[b] G^2 $\phi_0 = 43$
H(1)-H(2)	86.9	1.64	2.30	0.843	0.624	1.94	1.43
H(1)-H(4)	96.6	2.09	0.537	0.845	0.627	0.45	0.34
H(9)-H(3)	62.7	2.44	0.21	0.875	0.692	0.19	0.15
H(2)-H(3)	124.5	2.11	0.507	0.891	0.730	0.45	0.37
H(2)-H(4)	97.3	2.50	0.183	0.845	0.628	0.15	0.11
H(3)-H(4)	125.5	1.79	1.36	0.673	0.335	0.44	0.22
H(3)-H(5)	86.7	2.27	0.327	0.543	0.250	0.18	0.08
H(3)-H(6)	69.6	2.29	0.310	0.586	0.361	0.18	0.08
H(4)-H(5)	105.1	2.27	0.327	0.566	0.253	0.19	0.08
H(4)-H(6)	88.4	2.86	0.820	0.542	0.25	0.04	0.02
H(5)-H(6)	125.3	1.79	1.36	0.671	0.334	0.44	0.22
H(5)-H(13)	77.1	2.46	0.202	0.854	0.646	0.17	0.13
H(5)-H(7)	120.0	2.81	0.091	0.883	0.711	0.08	0.06
H(5)-H(8)	109.7	3.34	0.032	0.863	0.666	0.03	0.02
H(5)-H(12)	101.2	3.44	0.027	0.852	0.642	0.02	0.02
H(6)-H(8)	92.7	3.98	0.011	0.847	0.631	0.01	0.01
H(6)-H(7)	97.4	3.66	0.019	0.849	0.635	0.02	0.01
H(6)-H(13)	57.7	2.77	0.099	0.888	0.723	0.09	0.07
H(6)-H(12)	85.6	3.48	0.025	0.847	0.632	0.02	0.02
H(7)-H(8)	79.4	1.79	1.360	0.851	0.641	1.16	0.87
H(7)-H(12)	77.0	3.29	0.035	0.854	0.646	0.03	0.02
H(7)-H(13)	56.5	3.53	0.023	0.891	0.730	0.02	0.02
H(7)-Me(1)	9.7	2.36	0.777	0.995	0.987	0.77	0.77
H(8)-M(12)	77.6	2.13	0.479	0.853	0.645	0.41	0.31
H(8)-Me(1)	25.7	2.27	0.982	0.970	0.921	0.95	0.90
H(8)-H(13)	54.4	2.83	0.087	0.896	0.742	0.08	0.06
Me(1)	163.8	1.86	1.020	0.987	0.967	1.01	0.99
H(12)-H(13)	42.4	1.79	1.360	0.928	0.816	1.26	1.11
H(12)-Me(2)	111.7	2.40	0.703	0.854	0.646	0.60	0.45
H(13)-Me(2)	113.7	2.55	0.488	0.917	0.791	0.488	0.39
Me(2)	111.7	1.86	1.020	0.866	0.673	0.88	0.69
total						12.7	10.0

[a] Static molecule with rotating methyl groups. [b] For twofold flipping.

For a twofold reorientation, the vector $\vec{r}_{jk}$ (with spherical coordinates θ'' and ϕ'') flips between orientations θ_a'' and θ_b'', with $j_b'' - j_a'' = 2\phi$.

$$\overline{\Delta H^2}(\text{dynamic}) = \tfrac{6}{5}I(I+1)g^2u_0^2\sum_{j<k}^{N}R_{jk}r_{jk}^{-6} \qquad (4)$$

$$R_{jk} = [3(\sin^2\theta''\cos 2\phi_0 + \cos^2\theta'')^2]/4 \qquad (5)$$

The second moment calculations (Table II) were made only for the interactions having an internuclear vector of constant length. This includes interactions between H atoms bound to the same atom, which are the major contributors to the second moment. For atoms C(1) and C(2), the approximation is made that the C–H vectors do not move about the C(1)–C(2) bond axis when considering H atoms of different carbons. These approximations are made in order to be able to calculate the second moment with some ease. Determining second moments for interactions of varying lengths becomes quite complex; therefore, these approximations allow a qualitative determination of the second moments due to various amplitudes of flipping.

In the motion postulated for the twofold disorder of the five-membered chelate rings, the C(1)–C(2) bond rotates 51.9°, therefore $\phi_0 = 25.9°$. The corresponding rotation of the N atoms is calculated by using the law of cosines. The details of the second moment calculations for the $\vec{r}_{jk}$ vectors considered are tabulated in Table II, yielding $\overline{\Delta H^2}$(dynamic) of 12.7 G^2, which corresponds to a reduction factor, R, of 0.55. Comparison with the experimental data indicates that the molecule is undergoing more motion than assumed in the calculation. Though the approximation of neglecting the torsional motion prevents the calculation of the second moment of the flipping molecule from being exact, it should give a good estimate of the magnitude of the flip that must take place to cause the drop in the second moment that has been observed. On the basis of this, it is estimated that the flipping of $(\text{dieten})_2(\text{ClO}_4)_2$ is on the order of $\phi_0 = 43°$. Since the salts are isomorphous, this model will be used to estimate the motion of the other salts studied.

It is obvious that a potential barrier must be overcome before the flipping can take place. This barrier opposes the movement of atoms C(1) and C(2) through the Cu–N plane. The energy of the molecule must be high enough to overcome this barrier before any flipping can take place. Steric factors, adding to the rigidity of the molecule, would increase the potential barrier. J. D. Curet et al. reports that hydrogen bonding between the primary amine and the oxygen atoms of the perchlorate molecule is present. The N–H···O distance of 3.07 Å is close to the average separation of 3.04 Å found for hydrogen bonds of O atoms to amines. Any such interaction would tend to resist rotation of the primary amine, and that resistance would increase the overall potential barrier of the transition.

Proton Second Moments in Other Salts. The transition of $(\text{dieten})_2\text{Cu}(\text{BF}_4)_2$ is similar to the transition of $(\text{dieten})_2\text{Cu}(\text{ClO}_4)_2$. The change in the second moment of the proton resonance at the transition is slightly less than that for the ClO_4^- salt (5 G^2 vs. 6 G^2). Other than the temperature at which the transition takes place, the major difference between the two salts is the magnitude of the second moments just before and after the transitions. The magnitude of the second moments shows that the $(\text{dieten})_2\text{Cu}(\text{BF}_4)_2$ molecule is undergoing less motion both before and after the transition than $(\text{dieten})_2\text{Cu}(\text{ClO})4_2$. As the temperature is increased above the transition, the second moment continues to decrease. However, even at 50 °C, the second moment for the BF_4^- salt is 3 G^2 higher than that for the ClO_4^- salt, indicating that the latter is undergoing considerably more thermal motion.

$(\text{dieten})_2\text{Ni}(\text{ClO}_4)_2$ has the highest transition temperature of the four compounds investigated. At the transition, the second moment drops by 1.5 G^2 to 11 G^2. This decrease is much less than the 5–6-G^2 decreases observed for the other salts. The magnitude of the second moment indicates there is slightly less motion just above the transition than found for the $Cu(ClO_4)_2$ salt at the same point. The moment of 11 G^2 above the transition is in good agreement with the moment calculated for a flip of $\phi_0 = 37°$.

At room temperature the salt has a second moment of 17.3 G^2, which drops slowly to 12.7 G^2 just before the transition. Such a low value shows that the amplitude of the molecular vibrations are high though C atoms of the ethylenediamine are not yet flipping across the Cu–N plane. The onset of the flipping comes at the transition temperature, affecting the Cu–N interactions that cause the thermochromism to take place.

^{19}F Resonances. In addition to the proton NMR, ^{19}F NMR resonances were measured. For $(dieten)_2Cu(BF)_2$, the second moment is 1.9 G^2 and shows no change at the transition. Using eq 4 and 5 and an F–F separation of 2.31 Å, theoretical calculations show that a BF_4^- anion undergoing threefold rotation would have a second moment of 1.9 G^2. It is also possible that the motion is not the simple one described above but a combination of various motions. No addition dynamic disorder of the BF_4^- counterion occurs at the phase transition.

The increased transition temperature for the ClO_4^- salt indicates that the potential barrier of the flipping motion is higher. Since powder patterns indicate that the two crystals are isomorphous, the shifted transition temperature is probably an anion effect. Hydrogen bonding is present in the ClO_4^- salt and thus is expected to increase the potential barrier of the flipping motion. It is therefore likely that any N–H···F hydrogen bonds would be weaker in the BF_4^- salt. Weaker bonds or the absence of them would decrease the potential barrier and allow the onset of the twofold flip at lower temperature.

The second moment of the ^{19}F resonances for the Ni salt is not as easy to interpret as for the Cu analogue. The second moment is higher than the second moment for a BF_4^- molecule undergoing threefold rotation (1.9 G^2) and lower than both a static molecule (6.2 G_2) or a molecule undergoing twofold reorientation (4.8 G^2). The motion is most probably some combination of reorientations though the total amount of motion is less than that observed for $(dieten)_2Cu(BF_4)_2$. The second moment shows a drop of about 0.5 G^2 at the transition. The decrease is probably due to the onset of the twofold flip of the ligand that affects the contribution of F–H interactions to the second moment.

Summary and Conclusion

The thermochromism exhibited by these salts coincides with a sharp drop of the second moment. This sudden increase in the molecule's motion occurs when the potential barrier of the flipping motion is overcome. From the data of the $(dieten)_2Cu(ClO_4)_2$ crystal structure, a model was made to approximate the second moment due to various amplitudes of the flipping motion. The second moments of $(dieten)_2Cu(ClO_4)_2$, $(dieten)_2Ni(BF_4)_2$, and $(dieten)_2Ni(ClO_4)_2$ immediately after the transition fit a flipping twofold rotation with ϕ_0 ranging from 37 to 48°. Only $(dieten)_2Cu(BF_4)_2$ does not fit this trend. The second moment directly after the transition is about 7 G^2 higher than the other salts. Much less motion is present for this salt than is observed for the others in the region directly after the transition.

The effect that the anion has in determining the temperature at which the transition occurs shows its ability to change the potential barrier. Crystallographic data indicate that hydrogen bonds exist in the $Cu(ClO_4)_2$ salt. Such bonds would be expected to hinder the rotation of the primary amine that takes place when the flip occurs. The lower potential barrier for the BF_4^- salt transitions would be the result of weaker hydrogen bonds.

It should be noted that the values of ϕ_0 for the various transitions are only approximate. The model for the second moment calculation is not sensitive to the angle ϕ_0. Changing ϕ_0 from 38 to 47° only shifts the second moment by 1 G^2. This insensitivity coupled with the approximations used when the second moment is calculated prevents an accurate determination from being made. No other types of motion other than those associated with the flipping motion were considered in the model. Any form of additional motion would cause additional reductions of the second moment and would have significant effects on the angle ϕ_0, giving results that are not as large. This is not a problem that is inherent to the method but a limitation due to the approximations made in applying it to a molecule undergoing complex motion.

The absence of a significant change in the ^{19}F NMR line width indicates no major change in the BF_4^- counterion motion at the phase transition. This would appear to rule out the model in which the counterion thermal motion triggers the phase transition.

Registry No. $(dieten)_2Cu(ClO_4)_2$, 52646-62-5; $(dieten)_2Cu(BF_4)_2$, 52646-61-4; $(dieten)_2Ni(ClO_4)_2$, 42534-35-0; $(dieten)_2Ni(BF_4)_2$, 52613-62-4.