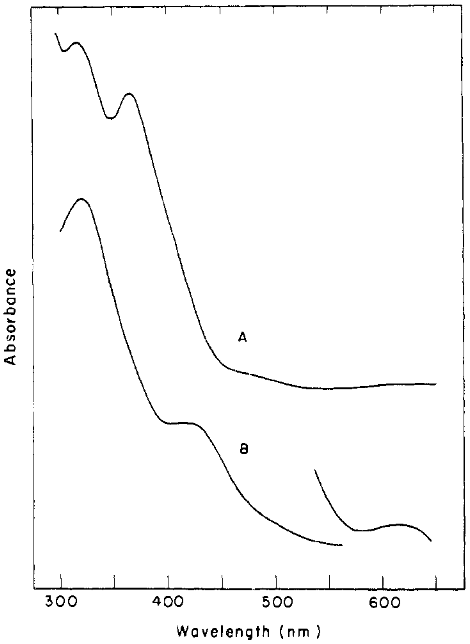

Figure 2. Visible spectra of (A) [Co((*c*-Hx)$_2$dtc)$_3$] and (B) [Co((*c*-Hx)$_2$dtc)$_3$]BF$_4$ in methylene chloride solution.

Mn(IV) complexes.[9] Thus, [Mn(R$_2$dtc)$_3$] BF$_4$ complexes are high spin from the magnetic data given in Table II.

Magnetic moments expected for octahedral Co(IV), a d^5 ion, are ~2.1 BM for low-spin or 5.89 BM for high-spin complexes.[18] The measured intermediate magnetic moment of 3.5 BM for [Co((*c*-Hx)$_2$dtc)$_3$]BF$_4$ suggests a mixed low-spin-high-spin equilibrium state at room temperature, similar to the mixed spin states of the isoelectronic [Fe(R$_2$dtc)$_3$] complexes.[19]

Acknowledgment. We wish to thank the National Science Foundation University Science Development Program (Grant No. GU-3184) for support of this research.

Registry No. [Mn(Et$_2$dtc)$_3$]BF$_4$·$^1/_3$Et$_2$O, 52699-13-5; [Mn(Et$_2$-dtc)$_3$]BF$_4$, 52699-12-4; [Mn((*i*-Pr)$_2$dtc)$_3$]BF$_4$, 52699-15-7; [Co(Et$_2$-dtc)$_3$]BF$_4$, 52637-78-2; [Co((*c*-Hx)$_2$dtc)$_3$]BF$_4$, 52637-82-8; [Mn(Et$_2$-dtc)$_3$], 15740-71-3; [Mn((*i*-Pr)$_2$dtc)$_3$], 25753-58-6; [Co(Et$_2$dtc)$_3$], 13963-60-5; [Co((*c*-Hx)$_2$dtc)$_3$], 52637-81-7; BF$_3$, 7637-07-2.

[18] B. N. Figgis and J. Lewis, *Progr. Inorg. Chem.*, **6**, 178 (1964).

[19] R. L. Martin and A. H. White, *Transition Metal Chem.*, **4**, 113 (1968).

Contribution from the Laboratorio CNR and
Istituto di Chimica Generale ed Inorganica,
Universita di Firenze, 50132 Florence, Italy

Continuous and Discontinuous Thermochromism of Copper(II) and Nickel(II) Complexes with *N,N*-Diethylethylenediamine[1]

L. Fabbrizzi, M. Micheloni, and P. Paoletti*

Received March 14, 1974 AIC401791

Some coordination compounds change color quite markedly with temperature. Such thermochromism is usually associated with temperature-dependent changes in the stereochemistry of the chromophore and depends on the nature of both the central metal ion and the ligand.

The bidentate ligand *N,N*-diethylethylenediamine (dieten, $H_2NCH_2CH_2N(C_2H_5)_2$) forms the three copper complexes Cu(dieten)$_2$X$_2$ (X = BF$_4$, ClO$_4$, NO$_3$) which change color reversibly from red to violet at higher temperatures.[2-4] This behavior has been attributed to a thermally sensitive tetragonal distortion in the copper atom environment.[4] However, both a blue and a red from can be isolated at normal temperatures.[4] Other copper complexes (X = Br, I, AgI$_2$, PbI$_3$, $^1/_2$HgI$_4$, $^1/_2$CdBr$_4$) are not thermochromic.

The analogous nickel complexes Ni(dieten)$_2$X$_2$ change from orange-yellow to bright red at higher temperatures. With X = I, ClO$_4$, and BF$_4$ the change is reported to be reversible.[5] We have found similar behavior with the anions of X = NO$_3$, Br, AgI$_2$, PbI$_3$, $^1/_2$HgI$_4$, and $^1/_2$CdBr$_4$. The compounds are diamagnetic, showing that the anions are not strongly coordinated.

Increasing temperature provokes a red shift in the visible absorption band of the copper complexes: the frequency of this band is shown in Figure 1. There is a small temperature range for each compound within which the red shift increases sharply. The largest shift is observed in the nitrate where it also occurs at the highest temperature. Above this transition temperature the absorption band ceases to be temperature sensitive and the compounds behave in the same way as the other copper complexes.

The d–d absorption bands of the thermochromic nickel complexes also shift to lower frequencies with increasing temperature, as shown in Figure 2. With X = BF$_4$ and ClO$_4$ the spectral change is quite sharp, but with the other compounds the red shift increases regularly.

The infrared spectra of the six compounds M(dieten)$_2$X$_2$ (M = Cu, Ni; X = BF$_4$, ClO$_4$, NO$_3$) are reversibly temperature sensitive. In the spectrum of Cu(dieten)(NO$_3$)$_2$, a band at 1750 cm^{-1}, assignable as the combination $\nu_1 + \nu_4$ ($a_1' + e' = e'$) of the unbound nitrate ion,[4] decreases in intensity and disappears above 130°, only to reappear with pristine intensity upon cooling back to room temperature. Lever, *et al.*,[4] have examined the ir spectrum of the blue unstable form of Cu(dieten)(NO$_3$)$_2$ and found two bands in the combination region, at *ca.* 1748 and 1760 cm^{-1}, whose intensity is considerably reduced relative to the combination band in the stable low-temperature form. Lever, *et al.*, assigned these two bands to coordinated nitrate ion, where the degeneracy of the e′ mode is lifted on account of reduced symmetry. These bands are not observed at higher temperatures because they broaden as the temperature rises. The infrared spectra of the fluoroborates and perchlorates exhibit bands characteristic of coordinated anion (BF$_4^-$ 335 cm^{-1}, ClO$_4^-$ 460 cm^{-1})[6,7] even at room temperature.[4] We also find a shoulder forming at 750 cm^{-1} with rising temperature in the spectrum of Ni(dieten)$_2$(BF$_4$)$_2$ similar to the band observed by Lever in the copper analog.[4]

---

[1] Presented at the Annual Meeting on Calorimetry and Thermal Analysis (AFCAT), Rennes, France, 1974.

[2] P. Pfeiffer and H. Glaser, *J. Prakt. Chem.*, **151**, 134 (1938).

[3] W. E. Hatfield, T. S. Piper, and U. Klabunde, *Inorg. Chem.*, **2**, 629 (1963).

[4] A. B. P. Lever, E. Mantovani, and J. C. Donini, *Inorg. Chem.*, **10**, 2424 (1971).

[5] D. M. L. Goodgame and L. M. Venanzi, *J. Chem. Soc.*, 616 (1963).

[6] D. S. Brown, J. D. Lee , B. G. A. Melson, B. J. Hathaway, J. M. Procter, and A. A. G. Tomlinson, *Chem. Commun.*, 363 (1967).

[7] B. J. Hathaway and A. E. Underhill, *J. Chem. Soc.*, 3091 (1961).

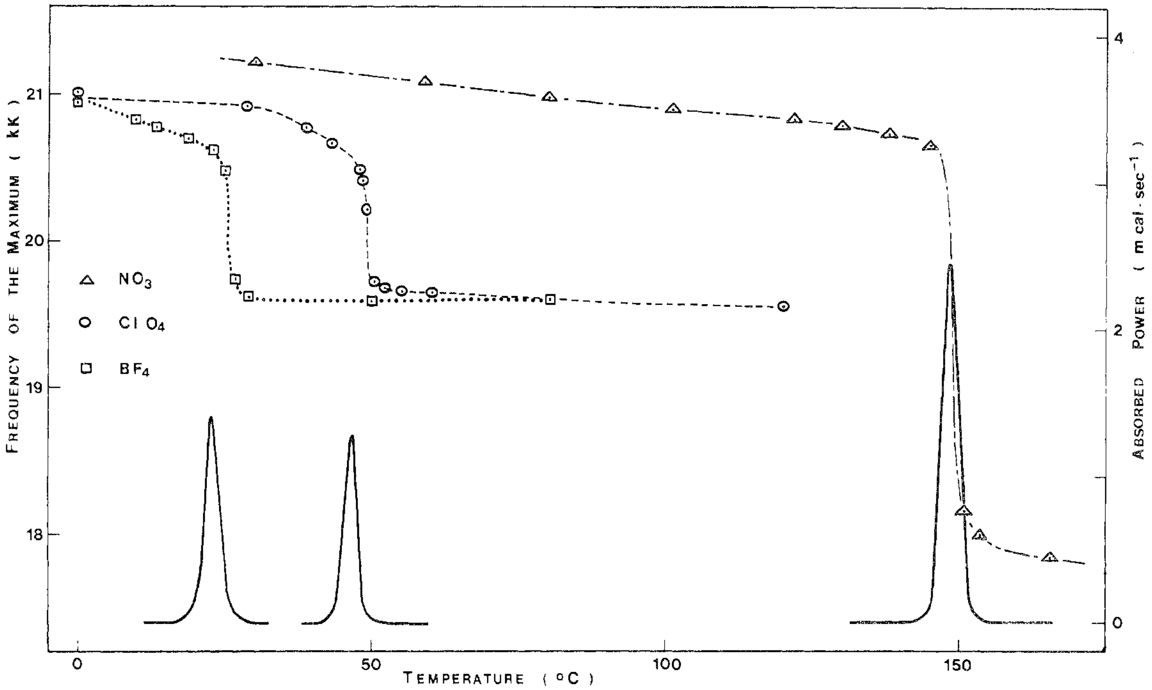

Figure 1. Thermal behavior of thermochromic copper(II) complexes of the general formula $Cu(dieten)_2X_2$.

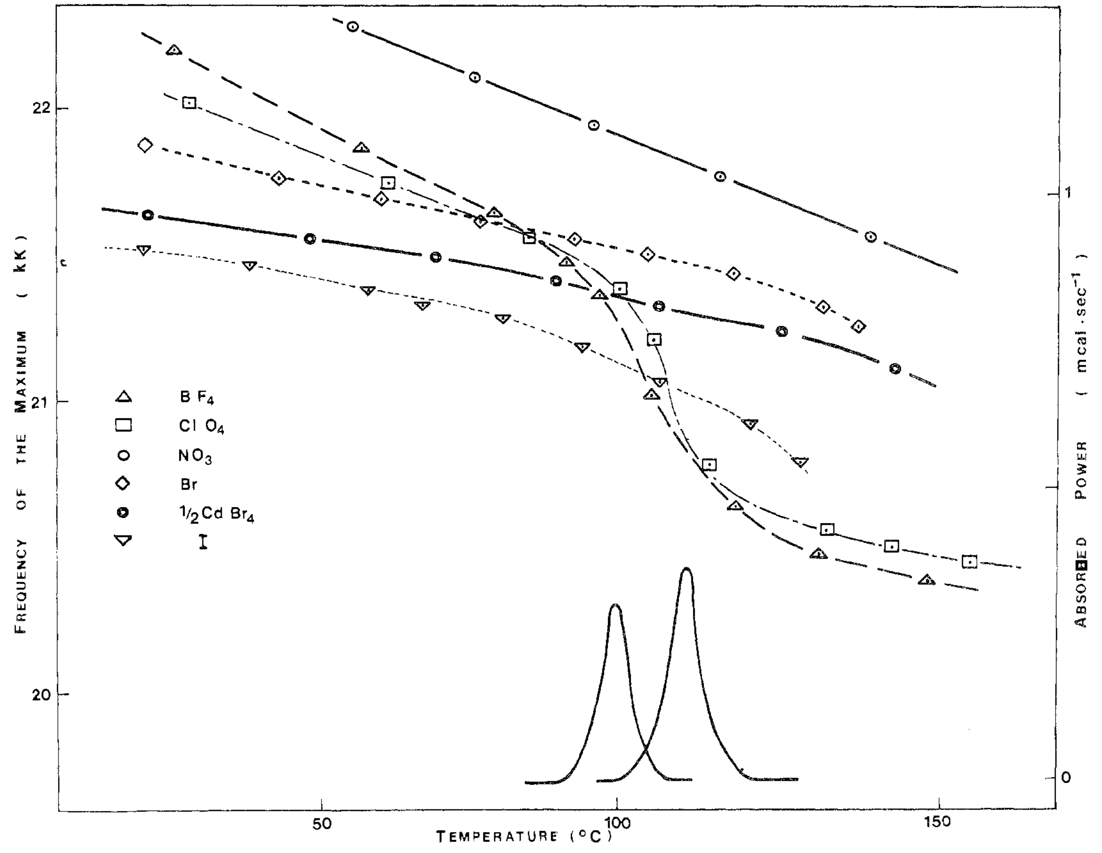

Figure 2. Thermal behavior of thermochromic nickel(II) complexes of the general formula $Ni(dieten)_2X_2$.

The totally symmetric Cl-O stretching band of the perchlorate ion (933 cm^{-1}) is ir forbidden in the free anion but appears with increasing intensity in the spectrum of $Cu(dieten)_2(ClO_4)_2$ as the temperature rises.[4] We find similar behavior in the nickel analog.

Differential scanning calorimetry (dsc) has been used to determine the heat change involved in the transition between high- and low-temperature forms; see Table I. In the temperature range between −100° and the melting decomposition temperature (*ca.* 200°) those compounds which show a sharp spectral transformation also show an endothermic transition; see Figures 1 and 2. The compounds which show gradual spectral changes do not exhibit an endothermic change. The transition temperature measured by dsc is

Table I. Threshold Temperature (T_i) and the Enthalpy Changes Associated with the Endothermic Transitions for Copper(II) and Nickel(II) Complexes with *N,N*-Diethylethylenediamine (L)

Complex	T_i,[a] °C	ΔH,[b] kcal $\mathrm{mol^{-1}}$
$\mathrm{CuL_2(BF_4)_2}$	15	2.40 ± 0.16
$\mathrm{CuL_2(ClO_4)_2}$	35	2.13 ± 0.16
$\mathrm{CuL_2(NO_3)_2}$	149	4.18 ± 0.20
$\mathrm{NiL_2(BF_4)_2}$	94	1.37 ± 0.06
$\mathrm{NiL_2(ClO_4)_2}$	110	1.59 ± 0.06

[a] T_i refers to the temperature at which the pen deflects from the base line; reported values refer to measurements carried out at the temperature scan rate of 1°/min. [b] The reported heat changes are the mean of at least six measurements carried out in the sensitivity range of 4 mcal (full scale deflection)$^{-1}$ sec^{-1}.

identical with that measured spectroscopically (Figures 1 and 2). The endotherm is exactly mirrored by the exotherm obtained by reverse dsc, *i.e.*, upon cooling, and the measured heat changes agree within experimental error (±4%). The transition can be repeated indefinitely by successive heating and cooling cycles, as long as the decomposition temperature is not attained. Thermogravimetric analysis shows that there is no weight change upon heating.

Both nickel and copper complexes are basically square planar with the tertiary nitrogen atoms in mutually trans positions. The anions may approach the cation along the fourfold axis, as shown by structure determinations on analogous complexes.[8,9] The energy of the d-d transition reflects, to a first approximation, changes in the equatorial environment. Increasing temperature shifts the band ($^1A_{2g} \leftarrow {}^1A_{1g}$ for $\mathrm{Ni(dieten)_2}^{2+}$, D_{4h} symmetry[10]) to lower energy, suggesting a weakening of the M-N bond. Along with this weakening there is increasing axial perturbation. This is clearly shown in the ir spectra where bands due to "coordinated" anion appear at high temperature.

The progressive decrease in the distance between the anion and cation is accompanied by a progressive increase in the nonbonding interaction between the anion and the ethyl groups of the tertiary nitrogen atoms. With the easily deformable anions $\mathrm{Br^-}$, $\mathrm{CdBr_4}^{2-}$, $\mathrm{I^-}$, $\mathrm{AgI_2}^-$, $\mathrm{PbI_3}^-$, and $\mathrm{HgI_4}^{2-}$ this process can occur continuously. With the less easily deformable anions $\mathrm{BF_4}^-$, $\mathrm{ClO_4}^-$, and $\mathrm{NO_3}^-$ the process is discontinuous because there is an energy barrier of a steric nature which must be exceeded by the change in bonding energy resultant upon anion coordination. This energy change is reflected in the dsc measurements. The transition temperatures of the nickel complexes are some 70° higher than for the corresponding copper complexes. The predicted transition temperature for $\mathrm{Ni(dieten)_2(NO_3)_2}$ is therefore *ca.* 220°, that is, higher than the decomposition temperature. This explains why $\mathrm{Ni(dieten)_2(NO_3)_2}$ shows no sharp transition temperature even though the anion is not easily deformable.

The energy of the endothermic transition, ΔH, correlated well with the spectral energy change as measured by the red shift $\Delta\nu$. For example both ΔH and $\Delta\nu$ are higher for copper than for nickel. If the $\Delta\nu$ value is corrected into energy units, it is seen to be 50 ± 5% of the ΔH value in the copper complexes. Clearly factors additional to the change in ligand field energy are included in the measured ΔH change. One such factor would be a phase change associated with the spectral change, and in fact X-ray measurements show that the two forms of $\mathrm{Cu(dieten)_2(ClO_4)_2}$ are not isomorphous.[11]

Experimental Section

Materials. *N,N*-Diethylethylenediamine, Fluka purum, was distilled under reduced pressure and the middle fraction was used in the preparation of complexes. Copper(II) complexes, red isomers, were obtained as described.[2,4] Furthermore reaction of equimolecular amounts of $\mathrm{Cu(NO_3)_2 \cdot 6H_2O}$ and ligand in ethanolic solution at 60° gives the less stable blue form of $\mathrm{Cu(dieten)_2(NO_3)_2}$. The blue isomer slowly converts into the red species. The transformation was nearly complete in 2 months.

Some of the nickel(II) complexes were previously reported.[5] In general they were obtained by reaction of stoichiometric amounts of the amine and the appropriate nickel(II) salt in butanol at room temperature, followed by recrystallization from the same solvent. Anhydridization of the solvent and of the reactants is required in order to prevent hydrolysis. In the case of complexes with $\mathrm{X^-}$ = $\mathrm{AgI_2}^-$, $\mathrm{PbI_3}^-$, $^1/_2$ $\mathrm{HgI_4}^{2-}$, and $^1/_2$ $\mathrm{CdBr_4}^{2-}$, an ethanol solution of the halo complex was obtained dissolving the metal halide in a large excess (1:5, 1:10) of the sodium halide (*e.g.*, AgI + NaI). The complex was obtained by mixing the latter solution with an ethanolic solution of nickel(II) chloride and diamine. All of the complexes were analyzed for C, H, and N. In the case of soluble compounds, copper and nickel contents were determined electrolytically. The analysis gave satisfactory results.

Calorimetric Measurements. Calorimetric measurements were carried out with a differential scanning calorimeter, Perkin-Elmer DSC-1B. The instrument was connected to a pen recorder (Speedomax W, Leeds and Northrup) and the heat was measured from the area traced by the pen. The instrument was calibrated in the sensitivity range of 4 mcal (full scale deflection)$^{-1}$ sec^{-1}, at the temperature scan speed chosen, from the heat of fusion of several substances: indium, furnished by Perkin-Elmer, $\Delta H_\mathrm{f} = 0.781\ 1$ kcal mol^{-1};[12] tin, Schuchardt 99.999%, $\Delta H_\mathrm{f} = 1.720$ kcal mol^{-1};[12] zinc, Schuchardt, 99.999%, $\Delta H_\mathrm{f} = 1.595$ kcal mol^{-1};[13] sodium nitrate, Erba ACS, $\Delta H_\mathrm{f} = 3.76$ kcal mol^{-1}.[12] The instrument constant separately obtained was reproducible within the 4% and the mean value was used. Calorimetric measurements both on standard samples and on thermochromic compounds were carried out at different temperature scan rate (from 1 to 8°/min) but the heat measured was the same to within the experimental error (4%). Dry nitrogen flowed through the system at a rate at 30 ml/min. Samples (4-8 mg) were weighed on a Cahn gram electrobalance.

Spectral Measurements. Visible reflectance spectra (filter paper technique) were recorded on a Beckman DK-2A spectrophotometer at various temperatures. The temperature of the sample was determined with a thermocouple. Infrared spectra were recorded on a Perkin-Elmer Model 457 grating spectrophotometer employing mulls in Nujol supported on CsI plates. In recording spectra at higher temperatures the accessory furnished by Perkin-Elmer Bodenseewerk was used. The temperature scale (50-200°) was calibrated from the fusion of chosen organic samples.

Registry No. $\mathrm{Cu(dieten)_2(BF_4)_2}$, 52646-61-4; $\mathrm{Cu(dieten)_2(ClO_4)_2}$, 52646-62-5; $\mathrm{Cu(dieten)_2(NO_3)_2}$, 52646-63-6; $\mathrm{Ni(dieten)_2(BF_4)_2}$, 52613-62-4; $\mathrm{Ni(dieten)_2(ClO_4)_2}$, 42534-35-0; $\mathrm{Ni(dieten)_2(NO_3)_2}$, 52613-63-5.

(8) A. McPherson, M. G. Rossmann, D. W. Margerum, and M. R. James, *J. Coord. Chem.*, 1, 39 (1971).
(9) S. C. Nyburg and J. S. Wood, *Inorg. Chem.*, 3, 468 (1964).
(10) C. J. Ballhausen and A. D. Liehr, *J. Amer. Chem. Soc.*, 81, 588 (1959).
(11) C. E. Pfluger and J. W. Eihausen, private communication cited in ref 3.
(12) "Handbook of Chemistry and Physics," 50th ed, The Chemical Rubber Co., Cleveland, Ohio.
(13) *Nat. Bur. Stand. (U. S.), Circ.*, No. 500 (1952).

Contribution from the Department of Chemistry,
University of Cincinnati, Cincinnati, Ohio 45221

Spectroscopic Studies of Dialkyltellurium Tetraiodides

Kenneth V. Smith and John S. Thayer*

Received April 22, 1974 AIC40263G

The first dialkyltellurium tetraiodide, $\mathrm{(CH_3)_2TeI_4}$, was reported in 1921 by Vernon.[1] Subsequent workers have pre-