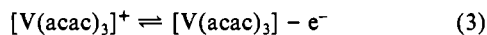
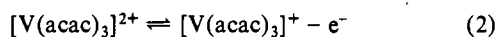


chloromethane solution reveals an oxidation at +0.90 V (NHE) ( $\Delta E_p$  90 mV,  $i_p^f/i_p^r = 1.01$ ) and a reduction at +0.58 V (NHE) ( $\Delta E_p$  80 mV,  $i_p^f/i_p^r = 1.01$ ) (Figure 4).  $[V(\text{acac})_3][\text{PF}_6]$  gave almost identical cyclic voltammograms. Dc voltammograms of  $[V(\text{bzac})_3]^+$  and  $[V(\text{acac})_3]^+$  each gave two waves with a current ratio of 1.01. These data suggest that in both steps the same number of electrons is involved. A blank run with the ligands in the same solution gave no peak in the potential range 0.0 to +1.5 V. The two couples are essentially reversible because the peak-current ratios were unity, and the  $\Delta E_p$  values were almost independent of scan rate below 500 mV s<sup>-1</sup>. The electrode reactions are concluded to be

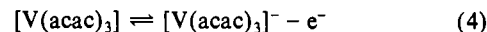


The system used was unable to detect the reduction of  $[V(\text{acac})_3]$  to the divalent state.

Boyd and co-workers, who studied  $[V(\text{acac})_3]$  in acetone, found a reversible oxidation at 0.94 V (Ag/AgCl, 0.1 M LiCl, acetone) and a reversible reduction at -1.33 V.<sup>34</sup> Applying a correction of +0.19 V to convert the potential to the NHE scale<sup>35</sup> yields potentials of +1.13 V (NHE) and -1.14 V (NHE), respectively, for presumably reactions 3 and 4. Earlier work in dimethyl

(34) Boyd, P. D. W.; Hope, J.; Martin, R. L. *J. Chem. Soc., Dalton Trans.* **1986**, 887.

(35) Lawrence, G. A., personal communication, 1987.



sulfoxide (H<sub>2</sub>O, 0.01%) obtained potentials of +0.73 and -1.35 V (NHE) for reactions 3 and 4, respectively.<sup>36,37</sup> Reaction 2 was not observed, with  $[VO(\text{acac})_2]$  and  $[V(\text{acac})_3]$  both giving on oxidation the same undisclosed vanadium(V) product.

From the above potential data it is seen that  $[V(\text{acac})_3]$  is very stable to reduction and oxidation. Although  $[V(\text{acac})_3]^+$  is easily reduced, it is stable to disproportionation. In contrast, for the catecholato complexes the +III state is not a stable state, being readily oxidized to the +IV state (in acetonitrile  $E_{1/2} = -0.84$ ;<sup>37</sup> in H<sub>2</sub>O  $E_{1/2} = -0.48$  V (NHE)<sup>38</sup>), but this oxidation state, although stable to disproportionation, is readily oxidized to the +V state (in acetonitrile  $E_{1/2} = -0.015$  V (NHE)<sup>37</sup>).<sup>5</sup>

**Acknowledgment.** Financial assistance from the Australian Research Grants Scheme (C.J.H.) is gratefully acknowledged.

**Supplementary Material Available:** Tables SI-SVIII, listing thermal parameters, hydrogen atom positional and thermal parameters, angles and distances associated with the ligands, and deviations from least-squares planes for  $[V(\text{acac})_3][\text{SbCl}_6]$  and  $[V(\text{bzac})_3][\text{SbCl}_6] \cdot \text{CH}_2\text{Cl}_2$  (8 pages); Tables SIX and SX, giving calculated and observed structure factors for the two compounds (48 pages). Ordering information is given on any current masthead page.

(36) Nawi, M. A.; Riechel, T. L. *Inorg. Chem.* **1981**, *20*, 1974.

(37) Measurements have been repeated here with ferrocene (0.400 V) as reference to give potentials relative to NHE.

(38) Potentials converted from SCE to NHE scale by addition of +0.24 V for aqueous solution.

Contribution from the Laboratory of Chemistry, Faculty of Education, Kanazawa University, Kanazawa 920, Japan, and the Department of Chemistry, Faculty of Science, Ochanomizu University, Tokyo 112, Japan

## Solid-Phase Thermal Square-Planar-to-Octahedral Isomeric Transformation of Nickel(II) Complexes Containing 1,2-Cyclohexanediamines

Yoshinori Ihara,\*<sup>1</sup> Yutaka Fukuda,<sup>2</sup> and Kozo Sone<sup>2</sup>

Received March 3, 1987

New examples of thermal square-planar (low-spin)-to-octahedral (high-spin) isomeric transformations were discovered and studied in the thermal reactions of bis(*dl*- or *meso*-1,2-cyclohexanediamine)nickel(II) complexes,  $[\text{Ni}(\text{dl- or } ms\text{-chxn})_2]\text{X}_2$  (X = Cl, Br, NO<sub>3</sub>), in the solid phase. These transformations proceeded endothermically and were accompanied by a reversible thermochromism from yellow to violet-blue. Obvious differences in the reactivity between the *dl*-chxn complexes and the *ms*-chxn ones were observed. They indicate that this type of reaction (and the stability of the square-planar species) is strongly dominated by the steric effect of the substituent groups in the coordinated diamines. The enthalpy changes for these endothermic transformations were found to be small (<8 kJ/mol). The activation energies for them were also estimated.

### Introduction

Nickel(II) complexes often show the peculiarity that their configuration can be readily converted into a different one by a change in their chemical and physical environments. This structural lability implies that the energy gap between different stereoisomers is small. Many instances of structural isomerism are known,<sup>3</sup> and in a few cases two isomers have been found together in one crystalline unit cell.<sup>4,5</sup>

Accordingly, nickel(II) complexes provide many examples of thermochromism in the solid phase, which is attributed to the change in coordination geometry.<sup>6-12</sup> In these complexes, small differences in the electronic properties and steric requirements of the ligand are reflected in the structures that they prefer when heated or cooled. However, a systematic knowledge is still lacking as to the factors that decide the preference of certain coordination geometries at different temperatures.

Among several kinds of solid-phase isomeric transformations already studied, the transformations between a square-planar

structure and an octahedral one seem to be of special interest and importance, particularly in relation to the problem of spin

- (1) Kanazawa University.
- (2) Ochanomizu University.
- (3) Lifschitz, I.; Bos, J. G.; Dijkema, K. M. *Z. Anorg. Allg. Chem.* **1939**, *242*, 97.
- (4) Rayner, J. H.; Powell, H. M. *J. Chem. Soc.* **1958**, 3412.
- (5) Nakano, T.; Miyoshi, T.; Iwamoto, T.; Sasaki, Y. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 1297.
- (6) Bloomquist, D. R.; Willett, R. D. *Coord. Chem. Rev.* **1982**, *47*, 125. In this review, the authors classified the thermochromic changes of Ni(II) complexes into the following five kinds of isomeric transformations according to their origins: dimer to monomer,<sup>7</sup> square planar to distorted square planar,<sup>8</sup> tetragonally distorted octahedral to distorted tetrahedral,<sup>9</sup> octahedral to tetrahedral,<sup>10</sup> and square planar to tetrahedral.<sup>11,12</sup>
- (7) Laskowski, E. J.; Felthouse, T. R.; Hendrickson, D. N.; Long, G. J. *Inorg. Chem.* **1976**, *15*, 2908.
- (8) Fabbrizzi, L.; Micheloni, M.; Paoletti, P. *Inorg. Chem.* **1974**, *13*, 3019.
- (9) Goedken, V. L.; Vallarino, L. M.; Quagliano, J. V. *Inorg. Chem.* **1971**, *10*, 2682.
- (10) Ferraro, J. R.; Sherren, A. T. *Inorg. Chem.* **1978**, *17*, 2498.
- (11) Sacconi, L.; Paoletti, P.; Cini, R. *J. Am. Chem. Soc.* **1958**, *80*, 3583.
- (12) Clark, H. C.; O'Brien, R. J. *Can. J. Chem.* **1961**, *39*, 1030.

\* To whom correspondence should be addressed.

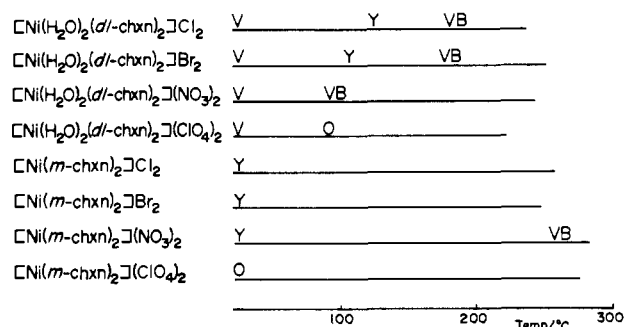
equilibrium in solution.<sup>13-17</sup> Proper examples of this kind are, however, quite rare. In most of the octahedral-to-square-planar transformations, a part of the ligands (e.g., H<sub>2</sub>O) is lost on heating (cf. the type b and type c reactions discussed later) so that the change is not isomeric. The reverse reaction, i.e., square-planar-to-octahedral isomeric transformation, was recognized first by Tsuchiya et al. in the anation of benzimidazole<sup>18</sup> and 2-aminobenzimidazole<sup>19</sup> complexes, but these changes also accompanied the liberation of ethanol or water of crystallization and were not reversible. No such isomerism was found among Ni(II) complexes with similar imine derivatives.

Recently, we found new examples of this last type of transformation in the (butanediamine)nickel(II) complexes,<sup>20</sup> where the reverse changes were also observed on cooling. It has become apparent, thereafter, that the C-substituted ethylenediamines are a group of ligands that is very suitable to study this type of transformation.<sup>21-23</sup> The ease and mode of structural changes observed in these complexes are strongly dependent on the nature and disposition of the substituent groups in the diamines; since these groups are somewhat apart from the donor nitrogen atoms, their inductive and steric influences are not so highly selective as in the case of the N-substituted ethylenediamine complexes<sup>24</sup> and make the structure-reactivity relations much more varied.

In continuation of these studies, the thermal reactions of (*dl*- and *meso*-1,2-cyclohexanediamine)nickel(II) complexes in the solid phase were investigated. The results obtained will be reported, and the square-planar-to-octahedral transformations will be compared with those of other C-substituted ethylenediamine complexes reported previously.

## Experimental Section

**Materials.** The ligands *dl*- and *meso*-1,2-cyclohexanediamine (*dl*- and *ms*-chxn) and their complexes [Ni(H<sub>2</sub>O)<sub>2</sub>(*dl*-chxn)<sub>2</sub>]X<sub>2</sub> and [Ni(*ms*-chxn)<sub>2</sub>]X<sub>2</sub> (X = Cl, Br, NO<sub>3</sub>, ClO<sub>4</sub>) were prepared by the known procedures<sup>25-27</sup> with a slight modification. The chemical formulas of the complexes were determined by elemental analyses and by spectral and magnetic measurements (SM Tables I and II<sup>28</sup>). It was confirmed that (1) all the *dl*-chxn complexes are violet and paramagnetic ( $\mu_{\text{eff}} \approx 3.2 \mu_{\text{B}}$ ) and show a series of d-d bands at ca.  $9.0 \times 10^3$  12.5 (sh)  $\times 10^3$  13.5  $\times 10^3$  18.0  $\times 10^3$  and 28.5  $\times 10^3$  cm<sup>-1</sup>, which indicates their trans-octahedral geometry,<sup>29-34</sup> and (2) all the *ms*-chxn complexes are yellow or



**Figure 1.** Results of visual observations on the thermochromic changes of the *dl*- and *ms*-chxn complexes: (V) violet; (VB) violet-blue; (Y) yellow; (O) orange. The colors are shown at the spots on the temperature scale (horizontal lines) where they begin to appear; the right-hand ends of the lines correspond to the decomposition points.

orange and diamagnetic and show a single d-d band at  $(22-23) \times 10^3$  cm<sup>-1</sup> corresponding to their square-planar geometry.

The thermal reaction products of these complexes were obtained by isothermal heating of the original complexes at the temperatures of their formation, which were inferred from the results of the thermal analyses, in an electric furnace under static air. They were studied immediately after preparation, or under a carefully dried atmosphere, to avoid the occurrence of backward reactions toward the original complexes (see later).

**Measurements.** The thermochromic changes of the complexes, which usually occur within a temperature range of several degrees, were observed by putting a small amount of finely powdered sample on the bulb of a spiral-form thermometer and heating it on a hot plate with a rate of ca. 5 °C/min.

Simultaneous TG (thermogravimetry)-DTA (differential thermal analysis) or DSC (differential scanning calorimetry) measurements were carried out with a Seiko SSC/580 TG/DTA-30 or a Seiko SSC/580 DSC-10 apparatus. The enthalpy changes of the square-planar-to-octahedral transformations were calculated on the basis of their DSC peaks. Kinetic analyses of them were performed by applying Ozawa's equation<sup>35-37</sup> to the data of DSC, by using a Seiko DS-50 data-analyzing system.

The electronic spectra in the solid phase were measured by the diffuse-reflectance method with a JASCO UVIDE-410 spectrophotometer equipped with a reflection attachment. For the spectra in the near-IR region, a Hitachi 340 spectrophotometer was used instead. IR spectra were recorded with a JASCO IR-A3 spectrophotometer in Nujol mulls.

The effective magnetic moments were evaluated from the susceptibilities measured by Faraday's method, by using a Shimadzu MB-100 torsion magnetometer at room temperature.

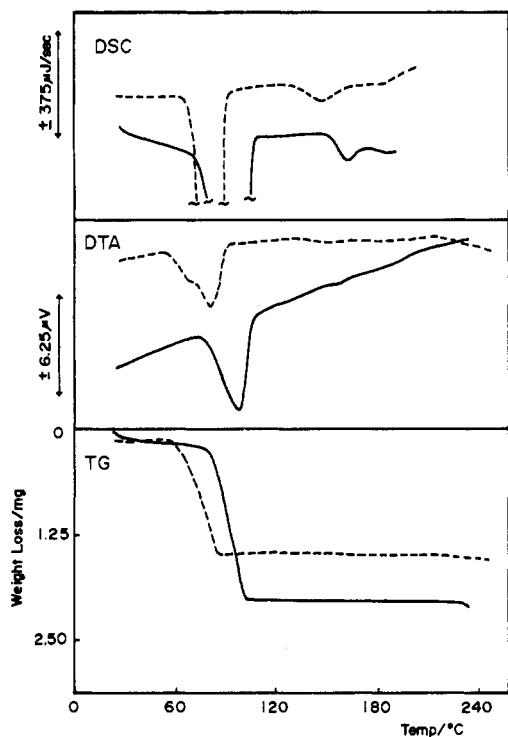
## Results and Discussion

**Thermochromism of the Complexes.** Figure 1 shows the results of visual observations on the solid-phase thermochromism of the complexes. If the desired transformation takes place, a drastic color change from yellow or orange (square planar) to blue or violet (octahedral) is expected to occur. The diaqua octahedral *dl*-chxn complexes lose their water molecules on heating and change their colors from violet to yellow (chloride and bromide), violet-blue (nitrate), or orange (perchlorate), at a relatively low temperature (ca. 100 °C or lower). Among the complexes, the changes observed in the chloride and bromide are especially noticeable, since they show a second color change from yellow to violet-blue upon continued heating, leading to a two-step thermochromism (violet → yellow → violet-blue). The second color changes (yellow → violet-blue) observed in them indicate that the desired transformation takes place there. These second changes are reversible under a nitrogen atmosphere; in open air, however, the anhydrous complexes absorb water molecules gradually and revert to the original violet diaqua complexes in several hours.

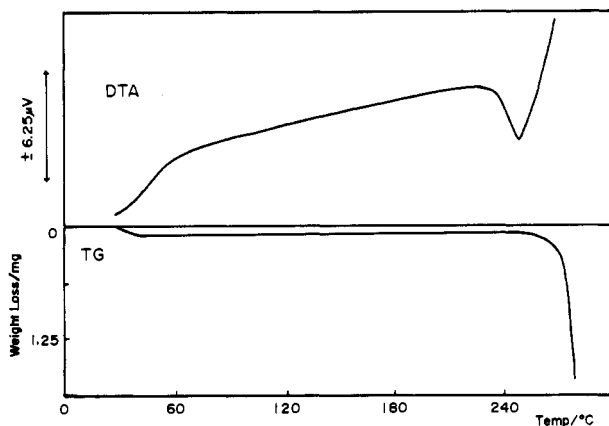
On the other hand, all the *ms*-chxn complexes are anhydrous, yellow, and diamagnetic at room temperature, among which only the nitrate exhibits an obvious color change to violet-blue upon

- (13) Melson, G. A.; Busch, D. H. *J. Am. Chem. Soc.* **1964**, *86*, 4830.
- (14) Vitiello, J. D.; Billo, E. J. *Inorg. Chem.* **1980**, *19*, 3477.
- (15) Fabbri, L.; Micheloni, M.; Paoletti, P. *J. Chem. Soc., Dalton Trans.* **1980**, 134.
- (16) Farkas, E.; Homoki, E.; Gergely, A. *J. Inorg. Nucl. Chem.* **1981**, *43*, 624.
- (17) Sone, K.; Fukuda, Y. *Ions and Molecules in Solution*; Elsevier: Amsterdam, 1982, pp 251-266.
- (18) Tsuchiya, R.; Kyuno, E.; Uehara, A.; Joba, S.; Ohba, S. *Chem. Lett.* **1976**, 911.
- (19) Ihara, Y.; Tsuchiya, R. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1614.
- (20) Ihara, Y.; Kamishima, T.; Tsuchiya, R. *Thermochim. Acta* **1983**, *67*, 23.
- (21) Ihara, Y.; Tsuchiya, R. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2829.
- (22) Ihara, Y. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 3248.
- (23) Ihara, Y.; Fukuda, Y.; Sone, K. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 2309.
- (24) Ihara, Y.; Izumi, E.; Uehara, A.; Tsuchiya, R.; Nakagawa, S.; Kyuno, E. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 1028.
- (25) Galsbøl, F.; Steenbøl, P.; Sørensen, B. S. *Acta Chem. Scand.* **1972**, *26*, 3605.
- (26) Treptow, R. S. *Inorg. Chem.* **1968**, *7*, 1229.
- (27) Saito, R.; Kidani, Y. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 159.
- (28) Supplementary material.
- (29) Rowley, D. A.; Drago, R. S. *Inorg. Chem.* **1968**, *7*, 795.
- (30) Cruse, D. A.; Gerboch, M. J. *Chem. Soc., Dalton Trans.* **1972**, 152.
- (31) Bertini, I.; Gatteschi, D.; Scozzafava, A. *Inorg. Chem.* **1976**, *15*, 203.
- (32) Martin, L. Y.; Sperati, C. R.; Busch, D. H. *J. Am. Chem. Soc.* **1977**, *99*, 2968.
- (33) Lever, A. B. P. *Coord. Chem. Rev.* **1968**, *3*, 119.
- (34) Ihara, Y.; Fukuda, Y.; Sone, K. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 1825.

- (35) Ozawa, T. *Bull. Chem. Soc. Jpn.* **1965**, *38*, 1881.
- (36) Ozawa, T. *J. Therm. Anal.* **1970**, *2*, 301.
- (37) Sakamoto, R.; Ozawa, T.; Kanashashi, M. *Thermochim. Acta* **1972**, *3*, 291.



**Figure 2.** TG-DTA and DSC patterns of  $[\text{Ni}(\text{H}_2\text{O})_2(\text{dl-chxn})_2]\text{X}_2$ , where  $\text{X} = \text{Cl}$  (—) and  $\text{Br}$  (---), under a constant flow of  $\text{N}_2$  at  $200 \text{ mL min}^{-1}$  (heating rate  $2 \text{ }^\circ\text{C min}^{-1}$  for all runs; sample weights  $20.3 \text{ mg}$  (TG-DTA) and  $10.0 \text{ mg}$  (DSC) for the chloride and  $19.3 \text{ mg}$  (TG-DTA) and  $10.3 \text{ mg}$  (DSC) for the bromide).



**Figure 3.** TG-DTA pattern of  $[\text{Ni}(\text{ms-chxn})_2](\text{NO}_3)_2$  under a constant flow of  $\text{N}_2$  at  $200 \text{ mL min}^{-1}$  (heating rate  $20 \text{ }^\circ\text{C min}^{-1}$ ; sample weight  $15.2 \text{ mg}$ ).

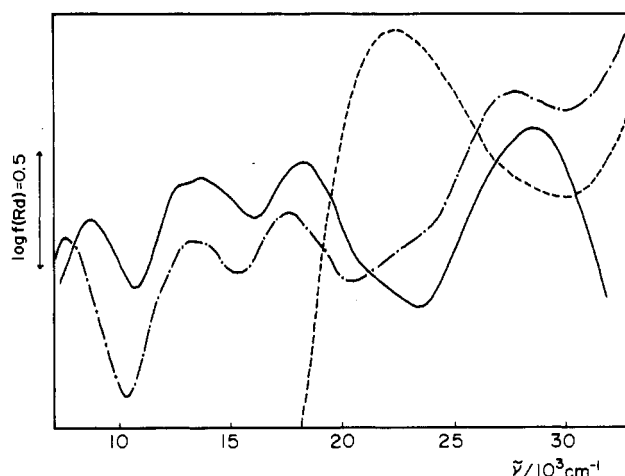
heating. The reverse change proceeds on cooling, but so slowly that it takes some days to return completely to the original yellow complex. The other complexes scarcely show any color changes until they decompose.

**Thermal Analyses.** The results of simultaneous TG-DTA for the chloride and bromide complexes with *dl*-chxn are shown in Figure 2. The abrupt weight losses observed in the TG curves and the corresponding endothermic DTA peaks are due to the liberation of 2 mol of coordinated water, which is responsible for the first-step color change (violet  $\rightarrow$  yellow). Figure 2 also contains the results of high-sensitivity DSC because the DTA peaks corresponding to the second color change (yellow  $\rightarrow$  violet-blue) could not be detected clearly under ordinary conditions. A small endothermic peak appears at  $161$  and  $147 \text{ }^\circ\text{C}$  in the DSC curves of the chloride and bromide, respectively, where their TG curves remain flat. These peaks are attributable to the color change in question. The features of TG-DTA curves of the remaining *dl*-chxn complexes are quite similar to those of the complexes in Figure 2, except that the second endothermic peak does not appear.

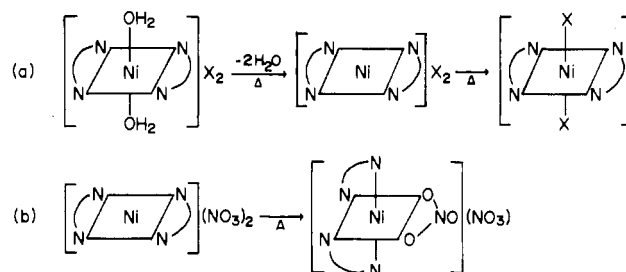
**Table I.** Results of Thermal Analyses of *dl*- and *ms*-chxn Complexes<sup>a</sup>

complex	dehydration		second color change	
	temp/ $^\circ\text{C}$	wt loss/% <sup>b</sup>	temp/ $^\circ\text{C}$	pattern <sup>c</sup>
$[\text{Ni}(\text{H}_2\text{O})_2(\text{dl-chxn})_2]\text{Cl}_2$	76–105	9.61 (9.15)	152–173	endotherm <sup>d</sup>
$[\text{Ni}(\text{H}_2\text{O})_2(\text{dl-chxn})_2]\text{Br}_2$	56–85	7.25 (7.46)	128–166	endotherm <sup>d</sup>
$[\text{Ni}(\text{H}_2\text{O})_2(\text{dl-chxn})_2](\text{NO}_3)_2$	45–73	8.03 (8.06)		
$[\text{Ni}(\text{H}_2\text{O})_2(\text{dl-chxn})_2](\text{ClO}_4)_2$	58–73	6.47 (6.90)		
$[\text{Ni}(\text{ms-chxn})_2](\text{NO}_3)_2$			231–260	endotherm <sup>e</sup>

<sup>a</sup>TG-DTA conditions are as follows: heating rate,  $2 \text{ }^\circ\text{C min}^{-1}$ ; gas flow,  $\text{N}_2$  at  $200 \text{ mL min}^{-1}$ ; sample weight, about  $20 \text{ mg}$  (see Figures 2 and 3). <sup>b</sup>Calculated values are in parentheses. <sup>c</sup>Enthalpy changes are indicated in Table III. <sup>d</sup>This was obtained by high-sensitivity DSC measurement (see Figure 2). <sup>e</sup>This was obtained by using a heating rate of  $20 \text{ }^\circ\text{C/min}$  (see Figure 3).



**Figure 4.** Electronic spectrum of  $[\text{Ni}(\text{H}_2\text{O})_2(\text{dl-chxn})_2]\text{Br}_2$  before heating (—) and those of the yellow and violet-blue products obtained after heating at  $100 \text{ }^\circ\text{C}$  (---) and at  $150 \text{ }^\circ\text{C}$  (-·-), respectively.



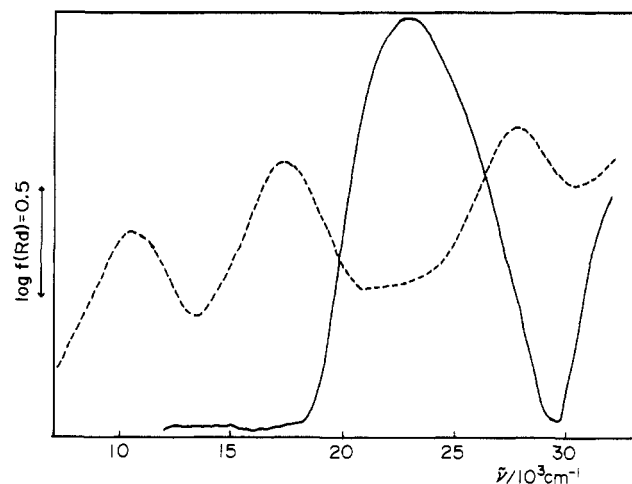
**Figure 5.** Thermal reaction schemes of (a) *trans*- $[\text{Ni}(\text{H}_2\text{O})_2(\text{dl-chxn})_2]\text{X}_2$  ( $\text{X} = \text{Cl}, \text{Br}$ ) and (b)  $[\text{Ni}(\text{ms-chxn})_2](\text{NO}_3)_2$ .

Figure 3 displays the TG-DTA results of the nitrate complex with *ms*-chxn. The color of this complex changes to violet-blue after the endothermic peak at  $250 \text{ }^\circ\text{C}$ . This peak is perceptible when the heating rate is sufficiently high (e.g.  $20 \text{ }^\circ\text{C/min}$ ) and is observed near the decomposition temperature of the complex, where a large exothermic peak appears. Table I summarizes the results of TG-DTA and DSC related to the color changes in the complexes.

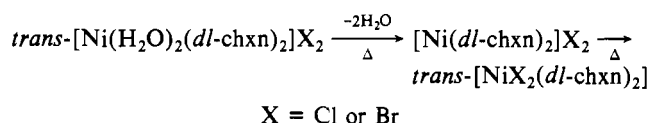
**Electronic Spectra.** The changes in the electronic spectra corresponding to the respective color changes of the bromide complex with *dl*-chxn are shown in Figure 4. The violet-blue product has a spectral pattern identical with that of the original *trans*-octahedral species except for a slight shift of the bands, which indicates a partial exchange of the ligands, while that of the yellow product is characteristic of a square-planar structure. It was also found that the former is paramagnetic ( $3.17 \mu_B$ ) and the latter

**Table II.** Data on Solid Reflectance Spectra and Magnetic Moments of *dl*- and *ms*-chxn Complexes Obtained upon Heating

complex	color	abs max, $\bar{\nu}/10^3 \text{ cm}^{-1}$					$\mu_{\text{eff}}/\mu_{\text{B}}$
$[\text{Ni}(\text{dl-chxn})_2]\text{Cl}_2$	yellow			22.4			diamag
$[\text{NiCl}_2(\text{dl-chxn})_2]$	violet-blue	8.3	13.2 sh	14.3	17.9	27.8	3.25
$[\text{Ni}(\text{dl-chxn})_2]\text{Br}_2$	yellow			22.4			diamag
$[\text{NiBr}_2(\text{dl-chxn})_2]$	violet-blue	7.6	13.2	14.0 sh	17.5	27.8	3.17
$[\text{Ni}(\text{NO}_3)_2(\text{dl-chxn})_2]$	violet-blue	8.8	13.5 sh	14.1	18.5	29.1 sh	3.18
$[\text{Ni}(\text{dl-chxn})_2](\text{ClO}_4)_2$	orange			22.8			diamag
$[\text{Ni}(\text{NO}_3)(\text{ms-chxn})_2](\text{NO}_3)$	violet-blue	10.6		17.4		27.8	3.19

**Figure 6.** Electronic spectra of  $[\text{Ni}(\text{ms-chxn})_2](\text{NO}_3)_2$  before heating (—) and after heating at 250 °C (---).

is diamagnetic. The chloride also shows similar changes in the electronic spectrum and magnetic moment in the course of heating (Table II). The thermal reactions of these two halides can thus be represented by the following equation, which is also shown in Figure 5a with structural formulas:



The mode of the splitting of the d-d band in the near-IR region, which results in the appearance of two bands (one in the red region and one in the near-IR region), proves that all the octahedral complexes in the equation are *trans*.<sup>29-34</sup> The second step of these thermal reactions was, therefore, confirmed to be the square-planar-to-octahedral isomeric transformation.

On the other hand, in the case of the nitrate complex with *dl*-chxn, the spectral pattern and magnetic moment remain nearly unchanged after dehydration (Table II), showing that the *trans*-octahedral configuration is retained during the thermal reaction. The perchlorate complex with the same diamine undergoes only deaquation to form an orange diamagnetic complex upon heating, because of the bulkiness and poor coordination ability of  $\text{ClO}_4^-$  (Table II). It is thus clear that the reactions of deaquation-anation (diaqua octahedral  $\rightarrow$  dianiono octahedral) and deaquation (diaqua octahedral  $\rightarrow$  square planar) take place in these two complexes, respectively.

The electronic spectrum of  $[\text{Ni}(\text{ms-chxn})_2](\text{NO}_3)_2$  is given in Figure 6, together with that obtained by heating it at the temperature where the endothermic reaction has been completed. The mother complex has one relatively strong absorption band at  $22.9 \times 10^3 \text{ cm}^{-1}$  due to a square-planar structure, while the violet-blue product gives a spectral pattern characteristic of octahedral Ni(II) complexes. The configuration of this product is *cis*, because its d-d band in the near-IR region scarcely shows any splitting.<sup>38,39</sup>

**Table III.** Activation Energies ( $\Delta E$ ), Enthalpy Changes ( $\Delta H$ ), and Temperatures ( $T$ )<sup>a</sup> of  $\text{SP} \rightarrow \text{O}_h$  Isomeric Transformations

complex	$\Delta E/\text{kJ mol}^{-1}$	$\Delta H/\text{kJ mol}^{-1}$	$T/^\circ\text{C}$
$[\text{Ni}(\text{dl-chxn})_2]\text{Cl}_2$	778 ( $\pm 102$ )	1.81	160
$[\text{Ni}(\text{dl-chxn})_2]\text{Br}_2$	466 ( $\pm 60$ )	7.87	148
$[\text{Ni}(\text{ms-chxn})_2](\text{NO}_3)_2$			230 <sup>b</sup>

<sup>a</sup>  $T$  is defined as the peak temperature of the DSC curve for the transformation. These values were taken from DSC data under the same conditions (sample weight about 10 mg, heating rate  $2^\circ\text{C min}^{-1}$ , flow rate of  $\text{N}_2$  200 mL  $\text{min}^{-1}$ ). <sup>b</sup> This was obtained from the DTA peak by using a heating rate of  $20^\circ\text{C min}^{-1}$ .

The change of magnetic moments before and after heating, diamagnetic to 3.19  $\mu_{\text{B}}$ , is compatible with the spectral data.

**IR Spectra.** The coordination mode of  $\text{NO}_3^-$  in the violet-blue product from  $[\text{Ni}(\text{ms-chxn})_2](\text{NO}_3)_2$  was studied by its IR spectrum, by making use of the criteria devised by Lever et al.<sup>40</sup> The key region is  $1700\text{--}1800 \text{ cm}^{-1}$  where a weak combination band of  $\text{NO}_3^-$  ion in a metallic complex appears. A peak assignable to the free  $\text{NO}_3^-$  ions was observed at  $1757 \text{ cm}^{-1}$  in the mother complex. On the other hand, the violet-blue product (nitrate complex) gave three peaks at 1727, 1757, and  $1767 \text{ cm}^{-1}$ . Of them, the peak at  $1757 \text{ cm}^{-1}$  shows that a part of the  $\text{NO}_3^-$  ions remains uncoordinated. The large separation ( $40 \text{ cm}^{-1}$ ) between the other two peaks indicates that the coordinated  $\text{NO}_3^-$  ions are acting as bidentate ligands.<sup>34,40,41</sup> Therefore, this product can be formulated as *cis*- $[\text{Ni}(\text{NO}_3)(\text{ms-chxn})_2](\text{NO}_3)$ , containing both free and bidentate nitrate ions. Accordingly, this thermal reaction can be expressed as in Figure 5b. In this transformation, it is interesting that the octahedral complex obtained by heating has a *cis* geometry, because the formation of a *cis* complex is a peculiar case in the stereochemistry of bis(diamine)nickel(II) complexes.<sup>38,42,43</sup> In addition, this is the first example of an octahedral (*ms*-chxn)<sub>2</sub>Ni<sup>II</sup> complex. It should be noted that such a new type of complex was obtained only by a thermal reaction in the solid phase, because its ligand strongly tends to form diamagnetic square-planar Ni(II) complexes, as in the case of *meso*-2,3-butanediamine.<sup>20,44</sup>

In contrast to the case for this complex, the violet-blue product from  $[\text{Ni}(\text{H}_2\text{O})_2(\text{dl-chxn})_2](\text{NO}_3)_2$  showed two peaks at 1752 and  $1768 \text{ cm}^{-1}$  in the same region. Their small separation ( $16 \text{ cm}^{-1}$ ) indicates that the  $\text{NO}_3^-$  ions in this complex are acting as unidentate ligands<sup>40</sup> and supports the view given above, i.e., that it should be formulated as a *trans*-dianiono octahedral complex, *trans*- $[\text{Ni}(\text{NO}_3)_2(\text{dl-chxn})_2]$ .

**Enthalpy Changes and Activation Energies of Square-Planar-to-Octahedral Transformations.** The values of enthalpy change and activation energy ( $\Delta H$  and  $\Delta E$ ) of the transformation were evaluated. The enthalpy changes were recorded directly in millijoules per second with our DSC instrument. The activation energies were estimated by Ozawa's method, which seems to be most suitable for studying these transformations. The results are given in Table III, together with the transformation temperatures.

(38) Birdy, R.; Goodgame, D. M. L.; McConway, J. C.; Rogers, D. J. *Chem. Soc., Dalton Trans.* 1977, 1730.

(39) Lever, A. B. P.; Walker, I. M.; McCarthy, P. J. *Can. J. Chem.* 1982, 58, 823.

(40) Lever, A. B. P.; Mantovani, E.; Ramaswamy, B. S. *Can. J. Chem.* 1971, 49, 1957.

(41) Fukuda, Y.; Morishita, R.; Sone, K. *Bull. Chem. Soc. Jpn.* 1976, 49, 1017.

(42) Farago, M. E.; James, J. M.; Trew, V. C. G. *J. Chem. Soc. A* 1967, 820.

(43) Goldberg, M. J.; Marsh, R. E. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* 1979, B35, 960.

(44) Pettit, L. D.; Swash, J. M. L. *J. Chem. Soc., Dalton Trans.* 1977, 697.

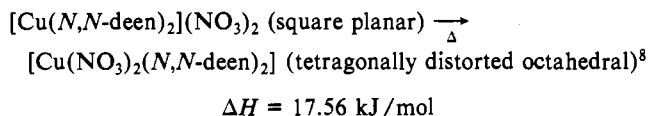
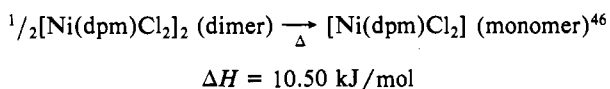
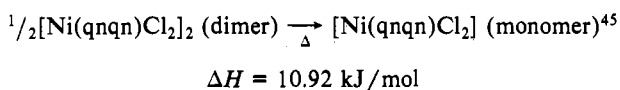
**Table IV.** Classification of Thermal Reactions of [Ni(diamine)<sub>2</sub>]X<sub>2</sub> or [Ni(H<sub>2</sub>O)<sub>2</sub>(diamine)<sub>2</sub>]X<sub>2</sub> Complexes Containing C-Substituted Ethylenediamines<sup>a-e</sup>.

diamine	X = Cl	X = Br	X = NO <sub>3</sub>	X = ClO <sub>4</sub>	ref
<i>dl</i> -bn	$O_h \rightarrow \underline{SP} \rightarrow O_h'$ (176)	$O_h \rightarrow \underline{SP} \rightarrow O_h'$ (183)	$O_h \rightarrow SP$	$O_h \rightarrow SP$	20
<i>dl</i> -chxn	$O_h \rightarrow \underline{SP} \rightarrow O_h'$ (160)	$O_h \rightarrow \underline{SP} \rightarrow O_h'$ (148)	$O_h \rightarrow O_h'$	$O_h \rightarrow SP$	this work
<i>dl</i> -stien	$O_h \rightarrow \underline{SP} \rightarrow O_h'$ (165)	$O_h \rightarrow \underline{SP} \rightarrow O_h'$ (175)	$O_h \rightarrow \underline{SP} \rightarrow O_h'$ (170)	SP	21
<i>ms</i> -bn	SP	SP	$\underline{SP} \rightarrow O_h'^*$ (188)	SP	20
<i>ms</i> -chxn	SP	SP	$\underline{SP} \rightarrow O_h'^*$ (230)	SP	this work
<i>ms</i> -stien	SP	SP	SP	SP	21

<sup>a</sup> For the definitions of  $O_h$ ,  $O_h'$ , and SP, see text. "SP" with no arrow means "prepared as an SP complex from solution and shows no thermal reaction until decomposition". <sup>b</sup> The  $SP \rightarrow O_h'$  transformations are indicated by underlines. <sup>c</sup> Most of the  $O_h$  and  $O_h'$  complexes are trans; cis-octahedral complexes are marked with asterisks. <sup>d</sup> The  $SP \rightarrow O_h'$  transformation temperatures are shown in parentheses (°C). They were defined as the peak temperatures of the DTA or DSC curves for the transformations. The DTA or DSC measurements were carried out under the same conditions (sampling weight 10–20 mg; heating rate 2 °C min<sup>-1</sup>; flow rate of N<sub>2</sub> 200 mL min<sup>-1</sup>). <sup>e</sup> The abbreviations are as follows: *dl*- or *ms*-bn, *dl*- or *meso*-2,3-butanediamine; *dl*- or *ms*-stien, *dl*- or *meso*-1,2-diphenyl-1,2-ethanediamine.

In the case of the nitrate complex with *ms*-chxn, it was impossible to obtain the  $\Delta H$  and  $\Delta E$  values with the same accuracy, because this transformation began to take place near the decomposition point so that the desired peak was overlapped by the exothermic decomposition peak (see Figure 3).

The  $\Delta H$  values in Table III show that the energy gap between the square-planar and octahedral structures in these systems is less than 10 kJ/mol. The enthalpy changes in the thermal isomeric transformations of Ni(II) or Cu(II) complexes were reported in a few cases as follows:



In these equations qnqn is *trans*-2-(2-quinolylmethylene)-3-quinuclidinone, dpm is bis(3,5-dimethylpyrazolyl)methane, and *N,N*-deen is *N,N*-diethylethylenediamine. The  $\Delta H$  values in Table III are smaller than these values. The fact that  $\Delta H$  is so small means that its two main components, i.e., the exothermic contribution arising from the formation of Ni–X bonds and the endothermic one reflecting the weakening of four Ni–N bonds in going from the low-spin to the high-spin state, and other factors like the changes in lattice energy, steric repulsion, etc. are effectively canceled among themselves.

The values of  $\Delta E$  are much larger than the energy of a coordinate bond and are even larger than that (100–200 kJ/mol) of the cis–trans isomerization of [(Co or Cr)X<sub>2</sub>(diamine)<sub>2</sub>]X.<sup>47</sup>

**Effects of C-Substituents in the Diamine and Anions upon the Transformation.** Table IV summarizes the patterns of the thermal reactions, including those of other C-substituted ethylenediamine complexes previously reported by us.<sup>20,21</sup> They can be classified into the following four types: (a) single-step deaquation–anation ( $O_h \rightarrow O_h'$ ); (b) simple deaquation ( $O_h \rightarrow SP$ ); (c) two-step deaquation–anation ( $O_h \rightarrow SP \rightarrow O_h'$ ); (d) simple anation ( $SP \rightarrow O_h'$ ). Here,  $O_h$ ,  $O_h'$ , and SP represent octahedral diaqua, octahedral aniono, and square-planar species, respectively.

Table IV shows the higher reactivity of the complexes with *dl*-form diamines toward the  $SP \rightarrow O_h'$  transformation than that of *meso*-form diamines. Furthermore, the transformation observed in each of these two groups of complexes possesses the following characteristics.

**Complexes with Meso-Form Diamines (Type i Complexes).** The transformation was confirmed only in the nitrate complexes. These complexes are obtained as square-planar species at room temperature, and they are converted into the  $O_h'$  species at temperatures that are notably higher than those for the type ii complexes described below (Table IV). The thermochromism accompanying the  $SP \rightarrow O_h'$  change is remarkably reversible. Interestingly, all the aniono complexes obtained upon heating were found to be cis-monoaniono species.

**Complexes with *dl*-Form Diamines (Type ii Complexes).** The transformation was observed mainly in the complex halides. The complexes favor octahedral structures in both the original species and the final products. Here, the square-planar species appear temporarily in the course of the thermal deaquation–anation, which occurs in two steps (deaquation and then anation), so that the transformation temperature is lower than that of type i complexes. In these cases, the aniono complexes formed as the final products were all trans-dianiono species. When they were let stand to cool down, they were readily converted into the yellow SP complexes under a dry atmosphere and into the violet diaqua complexes in open air.

The difference of the reactivities of these two types is apparently due to the steric effect of the substituted groups in the diamines. As stated above, the SP species of the type ii complexes easily undergo anation, producing aniono complexes and restoring octahedral configuration. An important reason for this easy anation can be found in the structure of the planar complex [Ni(diamine)<sub>2</sub>]<sup>2+</sup>. It is clear that there is enough space above and below the chelate plane in these complexes to permit the approach and bonding of counterions, since the substituent group(s) in each diamine can occupy the equatorial position(s) on the chelate plane.<sup>48,49</sup> On the other hand, in the type i complexes, at least one of the substituents in each diamine is forced to occupy the axial position.<sup>50,51</sup> Such a conformation generates a large steric hindrance, preventing the approach of other ligands and stabilizing the square-planar structure.

In the case of the nitrate and perchlorate complexes, their thermal reactions are affected also by the nature of the counteranion. As shown by the thermal reactions of the nitrate complexes with *ms*-chxn and *ms*-bn, a nitrate ion can interact with Ni(II) ion more strongly than a halide ion, acting as a bidentate ligand; in such cases, the rearrangement of coordinated diamines is caused by heating, decreasing the steric hindrance. In the perchlorates, the SP structure is predominant in the process of the thermal reactions because of the bulkiness and poor coordination ability of the ClO<sub>4</sub><sup>-</sup> ion.

**Acknowledgment.** We are sincerely grateful to Professor Sigeo Kida of Kyushu University, for his useful advice and discussions. This work was partially supported by Grants-in-Aid for Scientific Research (No. 59430009 and 61740343) from the Ministry of Education, Science, and Culture.

(45) Long, G. J.; Bertrand, G. L.; Noel, D.; Wu, S. H.; Mayhan, K. G. *J. Chem. Soc., Dalton Trans.* **1975**, 762.

(46) Trofimenko, S. *J. Am. Chem. Soc.* **1970**, *92*, 5118.

(47) Mitra, S.; Yoshikuni, T.; Uehara, A.; Tsuchiya, R. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 2569.

(48) Fitzgerald, R. J.; Drago, R. S. *Inorg. Chem.* **1969**, *8*, 2254.

(49) Evilia, R. F.; Young, D. C.; Reilly, C. N. *Inorg. Chem.* **1971**, *10*, 433.

(50) Zink, J. I.; Drago, R. S. *J. Am. Chem. Soc.* **1970**, *92*, 5339.

(51) Nyburg, S. C.; Wood, J. S. *Inorg. Chem.* **1964**, *3*, 468.

**Registry No.** [Ni(H<sub>2</sub>O)<sub>2</sub>(*dl*-chxn)<sub>2</sub>]Cl<sub>2</sub>, 53748-64-4; [Ni(H<sub>2</sub>O)<sub>2</sub>(*dl*-chxn)<sub>2</sub>]Br<sub>2</sub>, 65859-01-0; [Ni(H<sub>2</sub>O)<sub>2</sub>(*dl*-chxn)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub>, 53748-66-6; [Ni(H<sub>2</sub>O)<sub>2</sub>(*dl*-chxn)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>, 65835-90-7; [NiCl<sub>2</sub>(*dl*-chxn)<sub>2</sub>], 110454-60-9; [NiBr<sub>2</sub>(*dl*-chxn)<sub>2</sub>], 110417-89-5; [Ni(NO<sub>3</sub>)<sub>2</sub>(*dl*-chxn)<sub>2</sub>], 110392-11-5; [Ni(*dl*-chxn)<sub>2</sub>]Cl<sub>2</sub>, 53748-60-0; [Ni(*dl*-chxn)<sub>2</sub>]Br<sub>2</sub>, 53748-61-1; [Ni(*dl*-chxn)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>, 53748-63-3; [Ni(NO<sub>3</sub>)(*ms*-chxn)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub>, 110392-13-7; [Ni(*ms*-chxn)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub>, 110454-56-3; [Ni(*ms*-chxn)<sub>2</sub>]Cl<sub>2</sub>,

110454-57-4; [Ni(*ms*-chxn)<sub>2</sub>]Br<sub>2</sub>, 110454-58-5; [Ni(*ms*-chxn)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>, 110454-59-6.

**Supplementary Material Available:** Listings of analytical data (SM Table I) and electronic spectral data and magnetic moments of the prepared complexes (SM Table II) (2 pages). Ordering information is given on any current masthead page.

Contribution from the Departments of Chemistry, Washington State University, Pullman, Washington 99164-4630, and Leiden University, 2300 RA Leiden, The Netherlands

## Crystal Structures and Magnetic Behavior of Pyridinium Bis(oxalato)cuprate(II)-Oxalic Acid and Bis(2-methylimidazole)copper(II) Oxalate

U. Geiser,<sup>1a</sup> B. L. Ramakrishna,<sup>1a</sup> R. D. Willett,\*<sup>1a</sup> F. B. Hulsbergen,<sup>1b</sup> and J. Reedijk<sup>1b</sup>

Received April 1, 1987

The crystal structure and magnetic properties of two oxalato complexes of copper(II) are reported. Pyridinium bis(oxalato)cuprate(II)-oxalic acid (triclinic, *P* $\bar{1}$ ,  $a = 8.980$  (6) Å,  $b = 14.159$  (7) Å,  $c = 3.697$  (3) Å,  $\alpha = 92.47$  (7)°,  $\beta = 101.17$  (7)°,  $\gamma = 97.69$  (4)°,  $R = 0.039$ ) contains stacks of Cu(ox)<sub>2</sub><sup>2-</sup> anions with long semicoordinate bonds between copper(II) ions in one anion to a coordinated oxygen atom in each adjacent anion in the stack. Magnetic susceptibility data reveal weak antiferromagnetic coupling ( $\theta = -3.6$  K from Curie-Weiss law behavior). Analysis of the EPR spectrum sets a lower limit of  $|J| \sim 10^{-2}$  cm<sup>-1</sup> for the intrachain coupling. Bis(2-methylimidazole)(oxalato)copper(II) (orthorhombic, *Pbc*2<sub>1</sub>,  $a = 8.235$  (2) Å,  $b = 19.565$  (5) Å,  $c = 7.994$  (2) Å,  $R = 0.049$ ) contains a distorted square pyramidally coordinated copper(II) ion. The equatorial plane contains two nitrogen atoms (one each from an imidazole ligand) and two oxygen atoms from a chelated oxalato ligand. The apical site is occupied by an uncoordinated oxygen atom from an oxalato group on an adjacent complex. This forms a chain structure parallel to the *c* axis. The magnetic susceptibility data indicate weak ferromagnetic coupling for this compound with  $J/k = 0.45$  (4) K. Analysis of the EPR line width data yields an estimate of  $|J| \sim 0.1$  cm<sup>-1</sup>.

### Introduction

Magnetostructural correlations (i.e., the change of magnetic interaction with slight variations in the bridging geometry) have been demonstrated in copper(II) and chromium(III) compounds with ligands bridging through one atom between the metal centers.<sup>2</sup> It has been known for a long time that magnetic exchange can take place through more complex bridging networks, the most famous compound probably being the classical dimer (H<sub>2</sub>O)Cu(CH<sub>3</sub>CO<sub>2</sub>)<sub>4</sub>Cu(H<sub>2</sub>O).<sup>3</sup> More recently, the polyatomic anions azide, N<sub>3</sub><sup>-</sup>, and oxalate, C<sub>2</sub>O<sub>4</sub><sup>2-</sup>, have been shown to form magnetically coupled dimers and chains with copper(II).<sup>4,5</sup>

Kahn<sup>5</sup> demonstrated that the strongest antiferromagnetic interaction occurs when the bridging oxalate ion is coplanar with the copper  $d_{x^2-y^2}$  magnetic orbitals, assuming an essentially tetragonal ligand field geometry (see Figure 1a). On the other hand, very little exchange is observed when one oxalate oxygen atom coordinates to an apical site (Figure 1b). Asymmetric bridging with one copper of each of these types leads to intermediate coupling.

The role of oxalate as a bridging ligand is not confined to dimeric systems. The strongly antiferromagnetically coupled compound CuC<sub>2</sub>O<sub>4</sub>· $\frac{1}{3}$ H<sub>2</sub>O is believed to consist of ribbons with the bridge framework as shown in Figure 1a.<sup>6</sup> Several salts of the bis(oxalato)cuprate(II) anion have been investigated in a search of strong magnetic interaction, preferably of low-dimen-

sional nature. Benzylammonium copper oxalate forms layers of Cu(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub><sup>2-</sup> ions connected by long (2.6 Å) bonds between an outer oxygen atom and an adjacent copper ion at the axial position. The magnetic interaction for such a bridging arrangement is very small,  $J/k = -0.2$  K.<sup>7</sup> Propylenediammonium copper oxalate forms stacks of bis(oxalato)cuprate(II) anions (vide infra). The coupling is very weak, and obscured in the noise of the susceptibility data.<sup>7</sup> Other bis(oxalato)cuprate(II) salts with known crystal structures include the sodium,<sup>8</sup> ammonium, potassium,<sup>9</sup> and 1,3-diammonium-2-propanol salts.<sup>10</sup> The first three of these all show weak antiferromagnetic coupling.<sup>7,8,11</sup> The aim of this paper is to present two new linear-chain copper oxalate compounds, pyridinium bis(oxalato)cuprate(II)-oxalic acid (PCOX) and bis(2-methylimidazole)(oxalato)copper(II) (MICO) with their synthesis, crystal structures, magnetic susceptibilities, and electron paramagnetic resonance spectra. The planar nature of the counterions and ligands were expected to induce different crystal packing and, hopefully, as a consequence, different magnetic properties.

### Experimental Section

**Synthesis.** Copper(II) oxalate hydrate was prepared by reacting green copper(II) carbonate (CuCO<sub>3</sub>·Cu(OH)<sub>2</sub>) with a slight excess of oxalic acid hydrate in warm aqueous suspension. After the mixture was stirred for 2 h, gas evolution ceased and the suspended solid was light blue. Filtering proved to be very difficult. Instead, the suspension was allowed to stand, and most of the supernatant could be drawn off after several hours. Meanwhile, a stoichiometric amount of pyridine was carefully neutralized with oxalic acid in water. This solution was added to the copper(II) oxalate slurry, which in turn became darker blue. Pyridine

- (1) (a) Washington State University. (b) Leiden University.
- (2) Hatfield, W. E. In *Magneto-Structural Correlations in Exchange Coupled Systems*; Willett, R. D., Gatteschi, D., Kahn, O., Eds.; NATO ASI Series, Series C 140u; Reidel: Dordrecht, The Netherlands, 1985; p 555. Hodgson, D. J. *Ibid.*; p 497.
- (3) Bleaney, B.; Bowers, K. D. *Proc. R. Soc. London, A* **1952**, *214*, 451.
- (4) Hendrickson, D. In *Magneto-Structural Correlations in Exchange Coupled Systems*; NATO ASI Series, Series C 140u; Reidel: Dordrecht, The Netherlands, 1985; p 523.
- (5) Girerd, J. J.; Kahn, O.; Verdager, M. *Inorg. Chem.* **1980**, *19*, 274. Julve, M.; Verdager, M.; Kahn, O.; Gleizes, A.; Philoche-Levisalles, M. *Inorg. Chem.* **1983**, *22*, 368. Julve, M.; Verdager, M.; Charlot, M.-F.; Kahn, O.; Claude, R. *Inorg. Chem. Acta* **1984**, *82*, 5.
- (6) Michalowicz, A.; Girerd, J. J.; Goulon, J. *Inorg. Chem.* **1979**, *18*, 3004.

- (7) Bloomquist, D. R.; Hansen, J. J.; Landee, C. P.; Willett, R. D.; Buder, R. *Inorg. Chem.* **1981**, *20*, 3308. Mennenga, G.; Bartolome, J.; deJongh, L. J.; Willett, R. D. *Chem. Phys. Lett.* **1984**, *105*, 351.
- (8) Gleizes, A.; Maury, F.; Galy, J. *Inorg. Chem.* **1980**, *19*, 2074.
- (9) Viswamitra, M. A. *J. Chem. Phys.* **1962**, *37*, 1408. Viswamitra, M. A. *Z. Kristallogr., Kristallgeom., Kristallphys., Kristallchem.* **1962**, *117*, 437.
- (10) Kivekäs, R.; Pajunen, A. *Cryst. Struct. Comm.* **1977**, *6*, 477.
- (11) Jeter, D. Y.; Hatfield, W. E. *Inorg. Chim. Acta* **1972**, *6*, 523.