September, 1978] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 51 (9), 2569—2573 (1978) 2569

Syntheses and Thermal Properties of Some Bivalent Transition Metal Complexes with 1,4-Diazabicyclo[2.2.2]octane

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(Received January 12, 1978)

New five-coordinate complexes $[MCl_3L(H^+L)]$, where M=Mn(II), Fe(II), Co(II), and Ni(II) and L=1,4-diazabicyclo[2.2.2]octane, were prepared in anhydrous ethanol. On being heated in the solid state, they begin to lose the non-charged ligand (L) in the order Co(147 °C)$\ll$Fe(184 °C)$<$Ni(190 °C)$<$Mn(196 °C) and are transformed into the tetrahedral complexes $[MCl_3(H^+L)]$. The thermal stability of the five-coordinate complexes depends markedly on the nature of M(II). The octahedral complex $[NiCl_4(H_2O)_2]H_2L\cdot H_2O$ obtained from an aqueous solution shows a series of complicated color and structural changes on heating according to stepwise decomposition: $[NiCl_4(H_2O)_2]H_2L\cdot H_2O$ (greenish yellow, octahedral)$\rightarrow$$[NiCl_4]H_2L$(light blue, tetrahedral)$\rightarrow$$[NiCl_3(H^+L)]$(cobalt blue, tetrahedral)$\rightarrow$$[NiCl_2L_{1/2}]$(reddish brown, probably square-pyramidal)$\rightarrow$$NiCl_2$(yellow, octahedral).

Ouagliano and co-workers reported that the protonated and methylated cations of the cagelike ditertiary amine 1,4-diazabicyclo[2.2.2]octane(dabco; denoted in this paper by L) react with some bivalent transition metal halides to form four- and/or five-coordinate complexes.[1-3] The trigonal-bipyramidal complexes $[MX_3(H^+L)_2]X$ formed with Mn(II), Fe(II), Ni(II), and Cu(II) (X=halide anions) are generally insoluble and stable only in the crystalline state in the absence of moisture. Thus to study their relative stability, we considered that thermogravimetry would be a favorable technique.

We prepared the five-coordinate complexes according to the reported method,[2] but somewhat different results were obtained, *i.e.*, the formula of the complexes was $[MCl_3L(H^+L)]$ and not $[MCl_3(H^+L)_2]Cl$, except in the case of Cu(II), a five-coordinate complex of the same type being obtained with Co(II). The complexes $[MCl_3L(H^+L)]$ were found to be transformed into the tetrahedral complexes $[MCl_3(H^+L)]$ by heating with evolution of L. We could thus compare the thermal stability of the five-coordinate complexes of Mn(II), Fe(II), Co(II), and Ni(II) from their initial weight-loss temperatures determined by thermogravimetric analyses.

The cobalt(II) and nickel(II) complexes with the cagelike ditertiary amine 1,3,5,7-tetraazatricyclo[3.3.1.$1^{3,7}$]decane (hmta), prepared from aqueous solutions, show striking color changes in the course of dehydration. With a proper combination of thermal analyses with visible and infrared spectroscopy, we have confirmed that these complexes can be formulated as $[M(H_2O)_6]X_2\cdot hmta\cdot nH_2O$ ($X=Cl^-$, Br^-, I^-), and the decrease in the number of coordinated water molecules brings about the coordination of halide ions first, and that of hmta only in the last stage of dehydration, with the decrease in coordination number from 6 to 4. This apparent reluctance of an amine, which usually shows a stronger coordination tendency than halide ions and water, is probably due to the bulkiness of hmta and its weak basicity($pK_b=8.87$). In continuation of this study on the color and structural changes of the complexes containing water, anions and a cagelike amine by heating,[4] we undertook preparation of such a complex with L from an aqueous solution. Owing to the strong basicity of L($pK_b=5.40$), hydroxide precipitates formed when cobalt and nickel salts were mixed with L in aqueous solutions. We therefore used the diprotonated species H_2LCl_2 and succeeded in the preparation of $[NiCl_4(H_2O)_2]H_2L\cdot H_2O$. As expected, the complex showed complicated color and structural changes involving dehydration and the elimination of HCl and L, which we could elucidate in some detail.

Experimental

Preparation of H_2LCl_2. A solution of 10 g of L in warm acetone was added with stirring to a warm solution prepared from 10 ml of concd HCl and 15 ml of 1,1-dimethoxypropane (dehydrating agent). The white crystals separated were recrystallized from anhydrous ethanol, and dried *in vacuo*. The analytical data are given in Table 1. Although the monoprotonated species HLCl has been reported,[1] only a diprotonated one was obtained in the present work, regardless of the L:HCl ratio.

General Preparation of $[MCl_3L(H^+L)]$(M=Mn(II), Fe(II), Co(II), and Ni(II)). A hot solution of anhydrous metal chloride (0.001 mol) in anhydrous ethanol was added with stirring to a hot solution of L(0.005 mol) and H_2LCl_2(0.005 mol) in the same solvent. In the case of Co(II), slight excess of L was necessary in order to avoid formation of the tetrahedral complex. The resulting solutions were allowed to stand at 60—70 °C for several hours under anhydrous conditions. The crystals formed were filtered in a stream of dry nitrogen, and dried *in vacuo* (Table 1). The iron complex is partially decomposed by air oxidation, turning yellowish, so that its data differ somethat from theoretical values. We tried to prepare the same complexes of Zn(II) and Cu(II), but the reactions of $CuCl_2$ and $ZnCl_2$ with a large excess of the ligands yielded only $[ZnCl_3(H^+L)]$ and $[CuCl_3(H^+L)_2]Cl$, respectively, which have already been prepared by Quagliano *et al.*[1,2]

Preparation of $[NiCl_4(H_2O)_2]H_2L\cdot H_2O$. An aqueous solution of H_2LCl_2(0.003 mol) with a few drops of concd, HCl was added to an aqueous solution of $NiCl_2\cdot 6H_2O$(0.001 mol). The resulting solution was allowed to stand in the open air at roon temperature until greenish yellow crystals appeared, which were filtered and dried in the open air (Table 1).

Measurements. The electronic spectra of the samples be-

TABLE 1. ELEMENTAL ANALYSES OF THE COMPLEXES OBTAINED IN THE PRESENT WORK

Compound	Color	Found (%)			Calcd (%)		
		C	H	N	C	H	N
H_2LCl_2	white	38.81	7.81	15.32	38.92	7.75	15.14
$[MnCl_3L(H^+L)]$	white	36.95	6.67	14.80	37.27	6.52	14.49
$[FeCl_3L(H^+L)]$	white	35.81	6.40	14.06	37.19	6.51	14.46
$[CoCl_3L(H^+L)]$	cobalt blue	36.55	6.58	14.49	36.89	6.45	14.34
$[NiCl_3L(H^+L)]$	deep pink	36.57	6.65	14.61	36.91	6.45	14.35
$[CuCl_3(H^+L)_2]Cl$	yellow	32.73	6.25	12.79	33.38	6.07	12.98
$[NiCl_4(H_2O)_2]H_2L\cdot H_2O$	greenish yellow	19.32	5.81	7.75	19.54	5.47	7.60

fore and after heating were obtained by the diffuse reflection method with a Hitachi EPS-3T spectrophotometer equipped with a standard integrating sphere attachment. All the measurements were carried out at room temperature using MgO as a reference material. Thermogravimetry(TG) and differential thermal analysis(DTA) were performed simultaneously with a Shinku Riko TGD-3000 differential thermal micro balance in a nitrogen atmosphere with a heating rate of 5 °C/min, 15—20 mg of sample being used for each measurement. The infrared absorption spectra(4000—250 cm^{-1}) were measured with a Hitachi 215 spectrophotometer by the Nujol mull method. X-Ray diffraction charts were obtained with a Toshiba ADG-101 diffractometer using manganese-filtered Fe $K\alpha$ radiation.

Results and Discussion

Spectral and Thermal Properties of the Five-Coordinate Complexes. The reflectance spectra of the colored five-coordinate complexes are shown in Fig. 1. The blue $[CoCl_3L(H^+L)]$ showed three absoptions at 15300, 16700, and 18300 cm^{-1} in the region 10000—30000 cm^{-1}. High spin trigonal-bipyramidal cobalt(II) complexes show at least four well-separated absorption bands in the region 5000—25000 cm^{-1}. Bertini *et al.*[5] showed that $[CoBr(Me_6tren)]Br$ gives well-separated absorptions at 5700, 12300, 16100, and 19600 cm^{-1} in its diffuse reflectance spectrum. They also presented the spectra of the tetrahedrally distorted trigonal-bipyramidal cobalt(II) complexes with similar ligands, and discussed spectral changes in going from an octahedral to a tetrahedral structure. A comparison with their results indicates that the outlook of the spectrum of $[CoCl_3L(H^+L)]$ is understandable if we assume that Co(II) is in a nearly undistorted trigonal-bipyramidal environment.

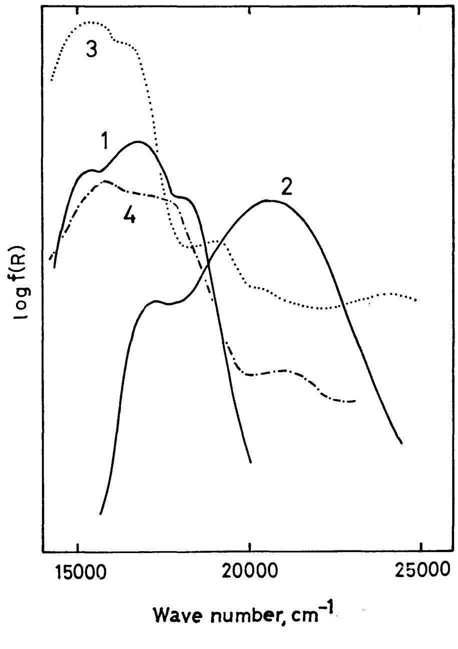

Fig. 1. Reflectance spectra of (1) $[CoCl_3L(H^+L)]$, (2) $[NiCl_3L(H^+L)]$, (3) $[CoCl_3(H^+L)]$, and (4) $[NiCl_3(H^+L)]$.

The deep pink $[NiCl_3L(H^+L)]$ shows two absorption bands at 17000 and 20600 cm^{-1}. This spectrum was quite similar to that of red $[NiCl_3(H_2O)(CH_3{}^+L)]$ which was found by X-ray analysis[6] to be in an almost undistorted trigonal-bipyramidal environment with three Cl atoms in the equatorial plane. Recently, similar structures were found for $[MCl_3(CH_3{}^+L)_2]ClO_4$ (M=Ni(II) and Cu(II)) by X-ray analyses.[7]

$[CoCl_3L(H^+L)]$ gives a very strong diffraction line at d=5.47 Å and some weak lines at 7.67, 4.22, 3.41, and 2.42 Å in its X-ray powder pattern. The corresponding Mn, Fe, and Ni complexes were found to be isomorphous with the cobalt complex. The infrared spectra of $[MCl_3L(H^+L)]$ were similar among the complexes of Mn, Fe, Co, and Ni. Thus, we conclude that the complexes of Mn and Fe have essentially the same trigonal-bipyramidal structure as that of Co and Ni. As an example, IR frequencies of the Co complex are given in Table 2, together with those of $[CuCl_3(H^+L)_2]Cl$ which shows a somewhat different spectrum.

The non-charged ligand L in $[MCl_3L(H^+L)]$ is expected to be released more easily than the protonated ligand H^+L on heating, a complex with a coordination number four being obtained. The TG-DTA curves of the complexes are shown in Fig. 2. A distinct break point is observed on each TG curve, the weight-loss values up to this point being 29.4(29.0), 21.3(28.9), 26.9(28.3), and 26.0(28.3)% for the Mn, Fe, Co, and Ni complexes respectively. The values in parentheses are the calculated ones for the evolution of L. The difference between the observed and calculated values for the Fe complex might be due to its partial decomposition owing to air oxidation before the TG measurement. The formation of the complex $[MCl_3(H^+L)]$ at this stage was also confirmed by IR and/or reflectance spectra of the products, together with their tetrahedral structure(*cf.* curves 3 and 4, Fig. 1).

Table 2. Comparison of IR frequencies (cm^{-1}) in the region 250—4000 cm^{-1} for [$CoCl_3L(H^+L)$] and [$CuCl_3(H^+L)_2$]Cl[a)]

[$CoCl_3L(H^+L)$]	[$CuCl_3(H^+L)_2$]Cl	Approximate description[b)]
	2600 m 2525 m 2450 m	ν(N-H$^+$)
1328 s	1327 s	ωCH_2
1293 mw	1282 w	τCH_2
	1248 mw	
1186 mw	1175 mw	
1058 vs	1052 vs	ν_{as}N-C-C
1031 m 998 m	1030 m 1000 m	ν_sN-C-C
915 w	920 w	$\nu_s NC_3$
847 s	850 s	$\nu_{as} NC_3$
808 sh 798 sh 783 s 756 w	802 sh 784 vs	ρCH_2
680 m	690 m	
	628 w	
	617 m	
421 m	423 m	$\delta_{as} NC_3$
282 s		ν(Co-Cl)

a) Relative intensities: vs = very strong, s = strong, m = medium, mw = medium weak, w = weak, sh = shoulder. b) Based on the assignments made for the ligand molecule.[13)]

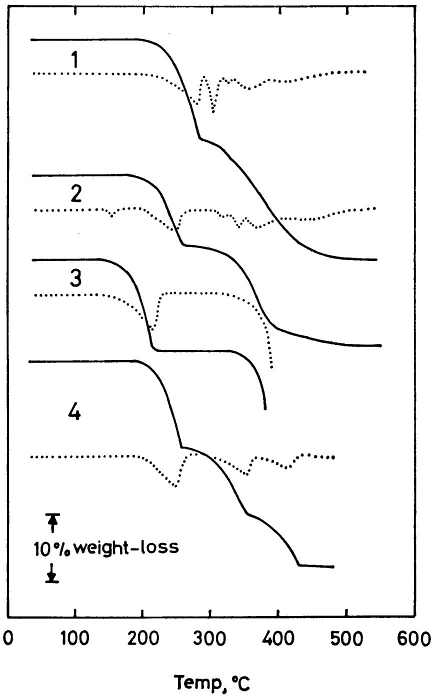

Fig. 2. TG(solid line) and DTA(dotted line) curves of [$MCl_3L(H^+L)$]. (1) Mn(II), (2) Fe(II), (3) Co(II), and (4) Ni(II).

From the spectral and thermal measurements, we can imagine the most probable structure of [$MCl_3L(H^+L)$] to be as shown in Fig. 3. The unusual trigonal-bipyramidal coordination seems to be brought about chiefly by the steric requirements of the bulky and rigid cagelike ligands. The orientation of the ligands which favor the formation of the –N–H--N– hydrogen bonding might greatly contribute to the stabilization of the complex including both L and H$^+$L.[8)]

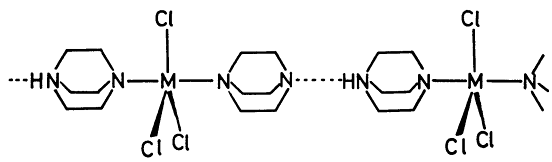

Fig. 3. Postulated structure of [$MCl_3L(H^+L)$].

It seems to be of interest to examine the effect of the nature of metal ion on the trigonal-bipyramidal coordination. The initial weight-loss temperatures(t_i) on the TG curves can be considered as a measure of the relative stability of the complexes if the elimination reactions of L from them proceed with the same mechanism for all the complexes. The TG and DTA curves in the first step are similar among the four complexes of Mn to Ni (Fig. 2), supporting the assumption. The t_i values are summarized in Table 3, together with those of the tetrahedral complexes formed, which were observed on further heating. The order of corresponding DTA peak temperatures(t_m) was the same as that of t_i. We can conclude that the thermal stability of the trigonal-bipyramidal coordination depends strongly on the nature of the metal, increasing in the order Co$\ll$Fe$<$Ni$<$Mn. In general, the trigonal-bipyramidal coordination seems to be favored with increase in the ionic radius of metal, except for the Ni complex which has the largest crystal field stabilization energy in the high-spin trigonal-bipyramidal environment.[9)]

It is also of interest to compare the order of t_i of the trigonal-bipyramidal complexes with that of the tetrahedral complexes. As seen in Table 3, the stability of the latter complexes also depends on the nature of the metal. The TG and DTA curves in the second step are not similar in the complexes studied, no plateau being observed in the case of Mn between the two steps on its TG curve. In spite of this, however, we can safely say that the Co complex shows the largest thermal stability. This may also be the driving force for the thermal decomposition of [$CoCl_3L(H^+L)$], which leads to its especially low thermal stability.

Thermal Decompositions of the Complex [$NiCl_4(H_2O)_2$]$H_2L\cdot H_2O$. The reflectance spectrum of the greenish yellow [$NiCl_4(H_2O)_2$]$H_2L\cdot H_2O$ shows a pattern

Table 3. Comparison of initial weight-loss temperatures (t_i)

[$MCl_3L(H^+L)$] → [$MCl_3(H^+L)$]+L		[$MCl_3(H^+L)$] → Decomposition	
M	t_i/°C	M	t_i/°C
Mn	196	Mn	<281
Fe	184	Fe	266
Co	147	Co	300
Ni	190	Ni	263

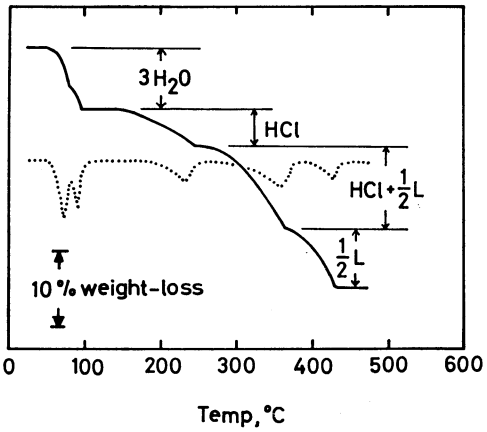

Fig. 4. TG(solid line) and DTA(dotted line) curves of $[NiCl_4(H_2O)]H_2L\cdot H_2O$.

characteristic of an octahedral coordination, and its ν_{max} (23000 cm^{-1}) lies between that of $NiCl_2\cdot 2H_2O$ (22800 cm^{-1}) and $NiCl_2\cdot 4H_2O$(23400 cm^{-1}), but is closer to the former, which is in fact a $NiCl_4O_2$-type complex with bridging Cl atoms. The IR spectrum indicates that L in this complex is not coordinated to the metal but is held in the crystal lattice as a counter cation(H_2L^{2+}). The formulation of this complex is based on these spectral data. Similar Ni(II) complexes with protonated *N*-methyl-dabco[1] and protonated piperazine[10] have been described.

The TG and DTA curves of $[NiCl_4(H_2O_2)_2]H_2L\cdot H_2O$ show that this complex decomposes in five steps up to 500 °C as shown in Fig. 4. In the first step, it loses $2H_2O$ and becomes yellow; in the second step, it loses the rest of water turning light blue. In the third step, HCl is evolved, and a cobalt blue substance of the composition $NiCl_3(H^+L)$ remains. In the fourth step, a reddish brown substance is obtained. Both TG and elemental analyses indicate that its composition is close to $NiCl_2L_{1/2}$. In the last step, yellow anhydrous $NiCl_2$ is obtained.

There were some difficulties in isolating these intermediate substances in pure form and/or in large quantities, except for the light blue one, since (i) there were no well-developed plateaus on the TG curve except for the second stage, (ii) the sample formed in the fourth step melted when it was kept in a crucible forming a thick layer, and (iii) the products formed in the last two stages contained a small amount of free carbon when the sample was heated in an inert gas atmosphere. We found that the melting can be avoided when the sample is heated very slowly in the form of a thin layer. No free carbon is formed when the sample is heated in the air, probably owing to the reaction $C+O_2\rightarrow CO_2$, although $NiCl_2$ formed at the last stage is transformed gradually into NiO in the air. We could thus obtain only a mixture of $NiCl_2$ and NiO at the last stage.

We obtained each of the intermediates in an almost pure form by heating the complex at the desired temperatures in the air, and measured their reflectance and infrared spectra. The reflectance spectra of the light blue and reddish brown substances are shown in Fig. 5, together with that of the original complex.

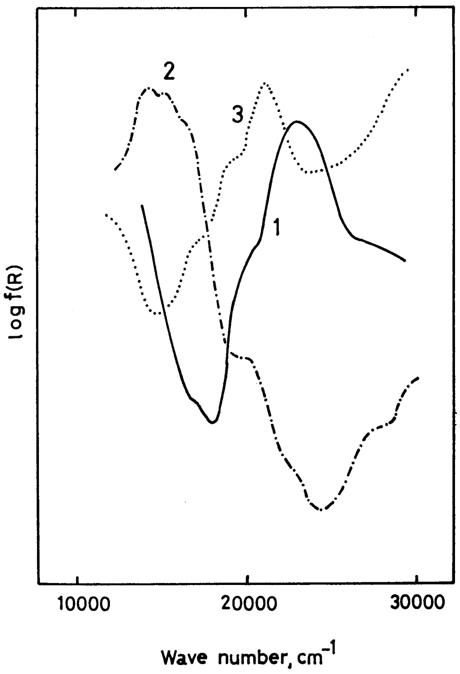

Fig. 5. Reflectance spectra of (1) $[NiCl_4(H_2O)_2]H_2L\cdot H_2O$, (2) $[NiCl_4]H_2L$, and (3) $[NiCl_2L_{1/2}]$.

The yellow substance of the composition $NiCl_4\cdot H_2L\cdot H_2O$ shows the peak maximum at 22300 cm^{-1}, the frequency of which is still lower than that of the original complex. Thus the nickel atom in it seems to be surrounded by five or more chlorine atoms. The spectrum of the light blue substance of composition $NiCl_4\cdot H_2L$ is very similar to that of $[NiCl_4]^{2-}$ in the literature[11] and therefore it should be formulated as $[NiCl_4]H_2L$. The spectrum of the cobalt blue substance of composition $NiCl_3(H^+L)$ is just the same as that of tetrahedral $[NiCl_3(H^+L)]$.

The reddish brown substance of composition $NiCl_2L_{1/2}$ shows three absorption bands at 17000, 19200, and 21000 cm^{-1}. The spectrum is somewhat similar to that of trigonal-bipyramidal $[NiCl_3L(H^+L)]$ except for a shoulder at 19200 cm^{-1} (*cf.* curve 2, Fig. 1). However, since the difference between the electronic spectrum of a trigonal-bipyramidal complex and that of a square-pyramidal one is not very large[12] in the region 15000—30000 cm^{-1}, this can not be taken as proof for its geometry. On the other hand, the infrared spectral pattern of $NiCl_2L_{1/2}$ in the region 650—1400 cm^{-1} was essentially similar to that of free L

TABLE 4. COMPARISON OF IR FREQUENCIES (cm^{-1}) IN THE REGION 700—1400 cm^{-1} FOR $[NiCl_2L_{1/2}]$ AND L

$[NiCl_2L_{1/2}]$	L[a]	Assignment
1321 m	1350 w	ωCH_2
1055 s	1057 vs	ν_{as}N-C-C
1013 m	986 m	ν_sN-C-C
928 m	897 m	$\nu_s NC_3$
844 m	830 m	$\nu_{as} NC_3$
812 s	755 m	ρCH_2

a) Values taken from Ref. 13.

molecule although there are considerable differences in the frequency values(Table 4). This indicates that the bands of L in the complex can be best assigned in terms of its D_{3h} symmetry.[13] This suggests that the complex consists of polymeric chains in which the nickels are surrounded by four bridging chlorines in a plane, and one bridging L perpendicular to the plane, forming a square-pyramidal coordination structure as shown in Fig. 6.

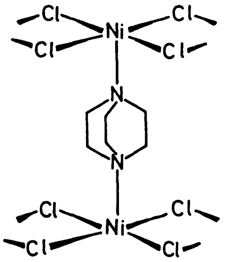

Fig. 6. Postulated structure of $[NiCl_2L_{1/2}]$.

The decomposition processes of $[NiCl_4(H_2O)_2]H_2L\cdot H_2O$ can be summarized as follows: $[NiCl_4(H_2O)_2]H_2L\cdot H_2O$(greensih yellow, octahedral) $\xrightarrow{-2H_2O}$ $NiCl_4H_2L\cdot H_2O$(yellow, octahedral) $\xrightarrow{-H_2O}$ $[NiCl_4]H_2L$(light blue, tetrahedral) $\xrightarrow{-HCl}$ $[NiCl_3(H^+L)]$ (cobalt blue, tetrahedral) $\xrightarrow{-(HCl+1/2L)}$ $[NiCl_2L_{1/2}]$(reddish brown, probably square-pyramidal) $\xrightarrow{-1/2L}$ $NiCl_2$(yellow, octahedral).

Comparing the results of the present study on the dabco complexes with those of our previous study on hmta complexes,[4] we find some differences between the two amines. (i) When hmta reacts with a heavy metal halide(MX_2) in aqueous solution, a complex containing $[M(H_2O)_6]^{2+}$ and uncoordinated hmta precipitates easily, whereas dabco precipitates only $M(OH)_2$ from aqueous solution (only when H_2L^{2+} is used instead of L, the complex $[NiCl_4(H_2O)_2]H_2L\cdot H_2O$ could be obtained). (ii) The complexes containing coordinated hmta, which are formed only at the last stage of dehydration of the complexes with $[M(H_2O)_6]^{2+}$, are mostly tetrahedral, but those of coordinated dabco obtained from ethanolic solutions are trigonal-bipyramidal. (iii) Heating of the anhydrous hmta complexes leads to decomposition, but heating of the anhydrous dabco complexes leads to the elimination of L and formation of new complexes with different geometries. These remarkable differences between the two amines are probably related to their difference in size, basicity, and the number and disposition of N atoms.

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