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Color and Structural Changes of Bis(hexamethylenetetramine)cobalt(II) and nickel(II) Complexes in the Course of Thermal Dehydration in Solid State

Kenzo Nagase, Hiroko Yokobayashi, and Kozo Sone*
Colloge of General Education, Tohoku University, Kawauchi, Sendai 980
**Department of Chemistry, Faculty of Science, Ochanomizu University, Otsuka, Bunkyo-ku, Tokyo 112*

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The stoichiometry of thermal dehydration of $MX_2(hmta)_2 \cdot nH_2O$ (hmta=hexamethylenetetramine; X= Cl^-, Br^-, I^-, NO_3^-, NCS^-; n=4—10) was established by the TG-DTA methods. The nature of the structural changes caused by complete or partial dehydration was studied on the basis of the accompanying changes in the electronic and vibrational spectra. Anions and hmta in general get into the coordination sphere with a decrease in the number of the coordinated water, but the bulky and weakly basic amine often gets coordinated in the last stage.

It has been known for a long time that hexamethylenetetramine (hmta=1,3,5,7-tetraazatricyclo[3.3.1.1.^{3,7}]decane) forms a number of peculiar complexes with various metals, among which those of cobalt(II) and nickel(II) are of special interest because their colors change strikingly in the course of dehydration. For example, the color of $Co(hmta)_2Cl_2 \cdot 10H_2O$ turns from pink to blue, while the corresponding nickel(II) complex changes first from bluish green to yellow, and then from yellow to violet, when they are heated up to about 423 K.[1] More recently these phenomena were studied by Lodzinskaya *et al.*,[2] who showed that the octahedral cobalt(II) complexes obtained from aqueous solutions are transformed into tetrahedral complexes by heating or treatment with ethanol. Kovacs *et al.*[3] found by X-ray analysis that the crystals of $Mg(hmta)_2Cl_2 \cdot 10H_2O$ and $Ca(hmta)_2Br_2 \cdot 10H_2O$ belong to the triclinic system and these complexes are formulated as $[M(H_2O)_6]X_2 \cdot 2hmta \cdot 4H_2O$. Buhannic and Guerchais[4] successfully assigned the IR bands of the complexes $MX_2(hmta)$ and $MX_2(hmta)_2$ (M=Co(II), Zn(II); x=halide or pseudohalide ions) to various vibrational modes of hmta, indicating that the T_d symmetry of free hmta is lowered to C_{3v} in $MX_2(hmta)_2$ and C_{2v} in MX_2 (hmta). Allan *et al.*[5] obtained the complexes of Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) with different numbers of H_2O and hmta from ethanolic solutions, which they attempted to characterize on the basis of the electronic and vibrational spectra and magnetic moments.

Examining these previous works, the present authors came to the conclusion that a proper combination of thermal analyses with visible and infrared spectroscopy would lead to a better understanding on the nature of the dehydration process. The results of studies with some new information are presented in this paper.

Experimental

Materials. The complexes were crystallized at room temperature from aqueous solutions containing MX_2 and hmta in the molar ratio 1 : 2.5. Their compositions were checked by elemental analyses for C, H and N and weight-loss values in dehydration (Table 1).

Measurements. The infrared absorption spectra (400—4000 cm^{-1}) were measured with a Hitachi 215 spectrophotometer by the Nujol mull method. A Hitachi EPS-3T spectrophotometer equipped with a standard integrating sphere attachment was used for the measurements of the diffuse reflectance spectra (14000—30000 cm^{-1}). Deeply colored samples were diluted with finely powdered MgO. The X-ray diffraction charts were obtained with a Toshiba ADG-101 diffractometer using a manganese-filtered Fe$K\alpha$ radiation.

The TG-DTA curves were obtained with a Shinku Riko TGD-3000 differential thermal microbalance with a heating rate of 5K/min in static air. In each measurement, 15—20 mg of powdered sample in a platinum crucible was used.

Results and Discussion

Structures before Heating. A cobalt complex and the corresponding nickel complex (*i.e.* that with the same

Table 1. Analyses of complexes

Complex	Found(%)				Calcd(%)			
	C	H	N	H_2O	C	H	N	H_2O
$CoCl_2(hmta)_2 \cdot 10H_2O$	24.36	7.46	18.93	30.7	24.42	7.52	18.99	30.5
$CoBr_2(hmta)_2 \cdot 9H_2O$	21.88	6.69	17.32	24.6	21.79	6.41	16.95	24.5
$CoI_2(hmta)_2 \cdot 8H_2O$	19.07	5.66	15.18	20.4	19.55	5.49	15.21	19.6
$Co(NO_3)_2(hmta)_2 \cdot 10H_2O$	22.21	7.05	21.95	27.3	22.40	6.90	21.78	28.0
$Co(NCS)_2(hmta)_2 \cdot 4H_2O$	31.99	6.35	26.68	14.1	31.88	6.12	26.57	13.7
$NiCl_2(hmta)_2 \cdot 10H_2O$	24.42	7.72	19.14	29.8	24.43	7.52	18.99	30.5
$NiBr_2(hmta)_2 \cdot 9H_2O$	21.39	6.61	16.87	24.6	21.79	6.41	16.96	24.5
$NiI_2(hmta)_2 \cdot 8H_2O$	19.49	5.73	15.38	19.7	19.56	5.50	15.33	19.7
$Ni(NO_3)_2(hmta)_2 \cdot 10H_2O$	22.17	6.96	21.85	27.3	22.41	6.90	21.79	28.0
$Ni(NCS)_2(hmta)_2 \cdot 4H_2O$	31.98	6.14	26.60	14.0	31.89	6.12	26.58	13.7

hmta=$C_6H_{12}N_4$

anion) have always the same composition (Table 1). Powder X-ray diffraction analyses indicate that, except for the cobalt iodide complex which was too poor in crystallinity to calculate the lattice constants, the crystals of all the complexes belong to the tetragonal system. As an example, the X-ray diffraction lines of the cobalt chloride complex and their assignments are given in Table 2. The lattice constants also indicate that the value of c/a is almost the same for each pair of a cobalt complex and a nickel complex with the same X (Table 3).

Table 2. X-Ray diffraction lines of $CoCl_2(hmta)_2 \cdot 10H_2O$ and their assignments

d/Å	I/I_0	hkl	$\sin^2\theta_{obsd}$	$\sin^2\theta_{calcd}$
8.97	100	001	0.0117	0.0119
7.78	5	101	0.0155	0.0158
6.96	30	111	0.0194	0.0197
5.84	10	201	0.0275	0.0275
5.49	40	220	0.0311	0.0311
4.49	10	301	0.0465	0.0469
4.09	40	112	0.0561	0.0554
3.45	30	222	0.0788	0.0787

Table 3. Lattice constants obtained from powder X-ray diffraction lines of $MX_2(hmta)_2 \cdot nH_2O$
Rad. Fe$K\alpha$, *Filter* Mn, *Syms.* Tetragonal

MX	a/Å	c/Å	c/a
CoCl	15.5	8.88	0.57
CoBr	16.4	9.19	0.56
$CoNO_3$	13.0	13.9	1.07
CoNCS	13.4	13.7	1.02
NiCl	15.6	8.84	0.57
NiBr	16.3	9.24	0.57
NiI	15.2	13.9	0.92
$NiNO_3$	12.9	13.9	1.08
NiNCS	12.5	13.8	1.11

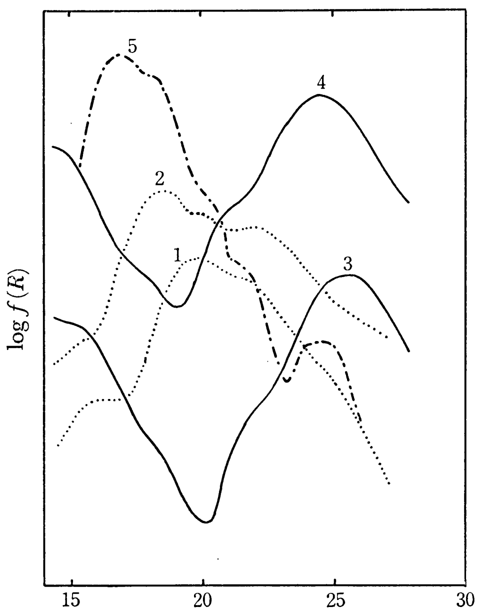

Fig. 1. Visible reflectance spectra of (1) $CoCl_2(hmta)_2 \cdot 10H_2O$, (2) $CoCl_2 \cdot 6H_2O$, (3) $NiCl_2(hmta)_2 \cdot 10H_2O$, (4) $NiCl_2 \cdot 6HO$ and (5) $CoCl_2(hmta)_2$.

The outlook of the visible reflectance spectra, the $\tilde{\nu}_{max}$ values of which are summarized in Table 4, show the existence of essentially octahedral coordination structures in all the complexes. The infrared spectra indicate that in all the complexes except the nickel thiocyanate complex, hmta molecules are not coordinated to the metals, since their symmetry was found to be T_d according to the criterion proposed by Buhannic and Guerchais.[4,6]

As examples, the visible reflectance spectra of $CoCl_2(hmta)_2 \cdot 10H_2O$, $NiCl_2(hmta)_2 \cdot 10H_2O$ and the anhydrous cobalt chloride complex are given in Fig. 1, together with those of $CoCl_2 \cdot 6H_2O$ and $NiCl_2 \cdot 6H_2O$

Table 4. Color and structural changes of $MX_2(hmta)_2 \cdot nH_2O$ caused by thermal dehydration

MX	Dehydration range/K	Loss of H_2O	Color[a] ($\tilde{\nu}_{max}/10^3$ cm^{-1})	C.N.	Sym. of hmta[c]
CoCl	324—402	10	*pink*(19.7)→blue(15.7)	6→4[b]	$T_d \rightarrow C_{3v}$
CoBr	327—377	9	*pink*(19.6)→blue(15.2)	6→4	$T_d \rightarrow C_{3v}$
CoI	326—384	8	*pink*(19.5)→green(15.2)	6→4	$T_d \rightarrow C_{3v}$
$CoNO_3$	322—373 374—389 397—417	6 2 2	*pink*(19.6)→*pink*(19.0) →violet(17.4) →violet(17.4)	6→6 →6 →6	$T_d \rightarrow T_d$ $\rightarrow T_d$ $\rightarrow C_{3v}$
CoNCS	356—400	4	*orange*(19.8)→bluish violet(16.1)	6→4	$T_d \rightarrow C_{3v}$
NiCl	330—381 395—427	8 2	*bluish green*(25.4)→*yellow*(22.8) →violet(16.4, 18.8)	6→6 →4	$T_d \rightarrow T_d$ $\rightarrow C_{3v}$
NiBr	341—397	9	*bluish green*(25.3)→blue(15.5)	6→4	$T_d \rightarrow C_{3v}$
NiI	334—401	8	*bluish green*(25.3)→green(15.3)	6→4	$T_d \rightarrow C_{3v}$
$NiNO_3$	320—373 373—405 405—433	6 2.5 1.5	*bluish green*(25.3)→*yellowish green*(25.3) →*yellowish green*(25.1) →*green*(24.7)	6→6 →6 →6	$T_d \rightarrow T_d$ $\rightarrow T_d$ $\rightarrow T(C_{3v})$
NiNCS	334—387 387—438	1.5 2.5	*blue*(25.1)→*green*(25.4) →yellowish green(26.3)	6→6 →6	$(T_d + C_{3v}) \rightarrow C_{3v}$ $\rightarrow (C_{3v} + C_{2v})$

a) Italics indicate pale color. b) Tetracoordinated species are all tetrahedral. c) Notations in parentheses are uncertain.

which were found, by X-ray analyses,[7] to be formulated as $[MCl_2(H_2O)_4]\cdot 2H_2O$. In general, the visible reflectance spectra of $CoX_2(hmta)_2\cdot nH_2O$ ($X=Cl^-$, Br^-, I^-, NO_3^-; $n=8$—10) are similar to each other, *i.e.*, they are essentially independent of the nature of X^-. The same can be said of the spectra of $NiX_2(hmta)_2\cdot nH_2O$. The spectra of $MCl_2(hmta)_2\cdot 10H_2O$ differ somewhat from those of $MCl_2\cdot 6H_2O$ (Fig. 1). In the case of the nickel compounds the difference seems to be rather small, but the $\tilde{\nu}_{max}$ value of the hmta complex is somewhat higher. These facts suggest that X^- in these hmta complexes are not coordinated to the metals. This is supported by the fact that, in the case of the nitrate complexs, the infrared spectra indicate the presence of ionic NO_3^-. Moreover, the $\tilde{\nu}_{max}$ values of these complexes (Table 4) are very close to those of the $[M(H_2O)_6]^{2+}$ ions (Co: 19600 cm^{-1}, Ni: 25300 cm^{-1}) observed in the absorption spectra of cobalt(II) and nickel(II) salts in aqueous solutions. These complexes are thus all hexaaqua complexes, and can be described as $[M(H_2O)_6]\cdot 2hmta\cdot(n-6)H_2O$.

$Co(NCS)_2(hmta)_2\cdot 4H_2O$ is characterized by the fact that it gives ν(O–H) at 3150 cm^{-1} which is considerably lower than that of an ordinary crystalline water (3400—3500 cm^{-1}), and that it begins to lose its water molecules at a temperature 20—30 K higher than the corresponding temperatures of the other complexes (Table 4). For this complex, the formulation as $[Co(NCS)_2(H_2O)_4]\cdot 2hmta$ seems to be the most probable.

On the other hand, $Ni(NCS)_2(hmta)_2\cdot 4H_2O$ seems to contain two sets of waters since it gives ν(O–H) bands, which can probably be attributed to both crystalline and coordinated water (3450 cm^{-1} and 3150 cm^{-1}), and loses about 1.5 water molecules at low temperature as in the case of the halides. The infrared bands of hmta in this complex seems to consist of two sets which correspond to two types of hmta having T_d and C_{3v} symmetries, respectively. The complex gives a single δ(NCS) at 482 cm^{-1}, indicating the presence of M–NCS bonds as in the case of the cobalt thiocyanate complex (Fig. 6).

Color and Structural Changes Caused by Thermal Dehydration. The TG and DTA curves of the complexes investigated are shown in Fig. 2. The curves of the cobalt complexes (except for the thiocyanate complex) have been published by Rodzinskaya *et al.*,[2] but their data differ somewhat from ours.

Except for the nickel chloride and bromide complexes, the complexes with halide ions give a smooth TG-DTA curve, although they contain both crystalline and coordinated water, all of which are lost in succession. If we compare the reflectance spectra of anhydrous products with the absorption spectra of typical cobalt and nickel complexes,[8] and their infrared spectra with the data of Buhannic and Guerchais,[4] we come to the conclusion that dehydration is accompanied with the changes octahedral→tetrahedral for the coordination structure and $T_d \rightarrow C_{3v}$ for the symmetry of hmta (Table 4), and that the metals are surrounded tetrahedrally by two X and two hmta in the final anhydrous products (*cf.* curve 5, Fig. 1, which shows characteristic features of a tetrahedral cobalt(II) complex[8]).

The nickel chloride and bromide complexes are dehydrated in two steps, although no distinct plateau could be observed on the TG curve in the case of the bromide complex. The nickel chloride complex gives a stable intermediate with the composition of $NiCl_2(hmta)_2\cdot 2H_2O$ in the first step, during which the T_d symmetry of hmta and the octahedral structure were retained. The visible spectrum of this dihydrate ($\tilde{\nu}_{max}$: 22800 cm^{-1}) is now very close to that of $NiCl_2\cdot 2H_2O$ ($\tilde{\nu}_{max}$: 22800 cm^{-1}), which is obtained by heating $NiCl_2\cdot 6H_2O$ at 383 K in the air (Fig. 3). Since the nickel in $NiCl_2\cdot 2H_2O$ was found by X-ray analysis[9] to be surrounded octahedrally by two water molecules

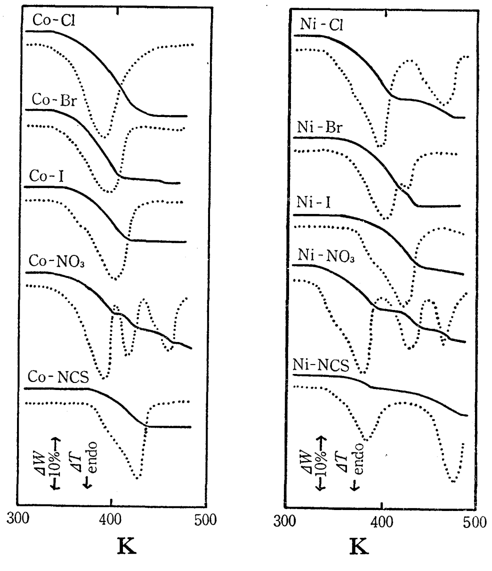

Fig. 2. TG(solid line), DTA(dotted line) curves of $MX_2(hmta)_2\cdot nH_2O$ in air.

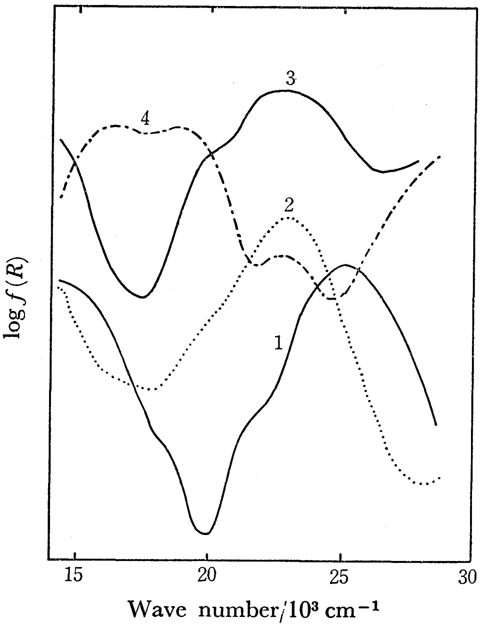

Fig. 3. Visible reflectance spectra of (1) $NiCl_2(hmta)_2\cdot 10H_2O$, (2) $NiCl_2(hmta)_2\cdot 2H_2O$, (3) $NiCl_2\cdot 2H_2O$ and (4) $NiCl_2(hmta)_2$.

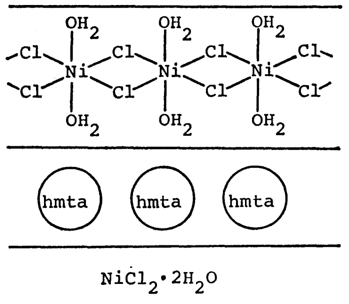

Fig. 4. Postulated structure of $NiCl_2(hmta)_2 \cdot 2H_2O$, in which hmta molecules are captured between chains of the composition of $NiCl_2 \cdot 2H_2O$.

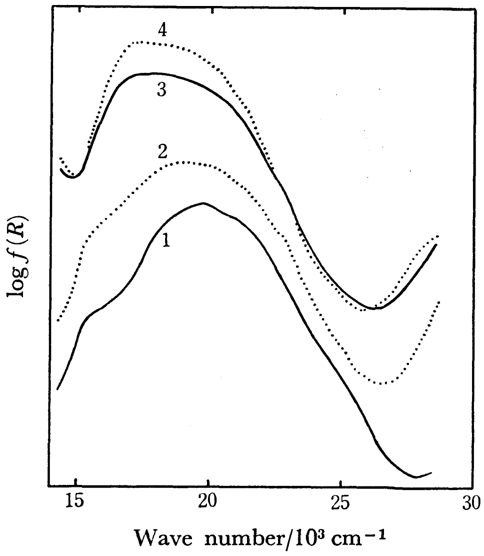

Fig. 5. Visible reflectance spectra of (1) $Co(NO_3)_2(hmta)_2 \cdot 10H_2O$, (2) $Co(NO_3)_2(hmta)_2 \cdot 4H_2O$, (3) $Co(NO_3)_2(hmta)_2 \cdot 2H_2O$ and (4) $Co(NO_3)_2(hmta)_2$.

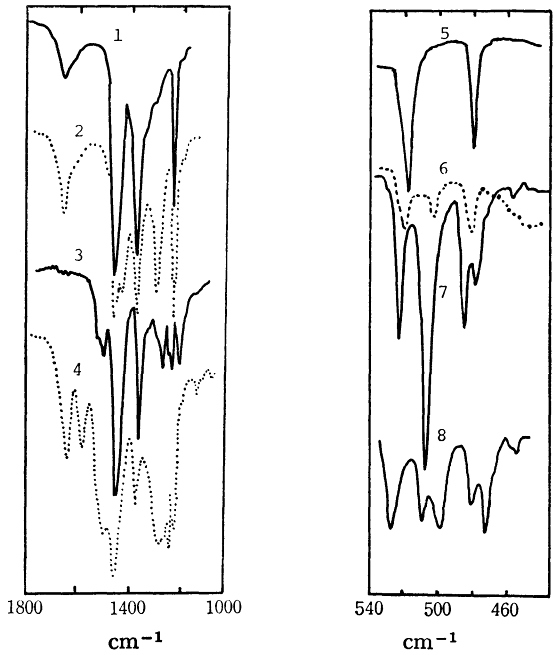

Fig. 6. Infrared spectra of (1) $Co(NO_3)_2(hmta)_2 \cdot 10H_2O$, (2) $Co(NO_3)_2(hmta)_2 \cdot 4H_2O$, (3) $Co(NO_3)_2(hmta)_2$, (4) $Ni(NO_3)_2(hmta)_2$, (5) $Co(NCS)_2(hmta)_2 \cdot 4H_2O$, (6) $Ni(NCS)_2(hmta)_2 \cdot 2.5H_2O$, (7) $Co(NCS)_2(hmta)_2$ and (8) $Ni(NCS)_2(hmta)_2$.

and four bridging chlorine atoms in a distorted square plane, the dihydrate complex also seems to be composed of similar units (or chains) of $NiCl_2 \cdot 2H_2O$ and of hmta captured between them, probably by hydrogen bondings (Fig. 4).

From the reflectance and infrared spectra, the structure of $NiCl_2(hmta)_2$ and $NiBr_2(hmta)_2$ formed in the next stage was found to be identical with that of the other anhydrous halide complexes. The results of the nickel chloride complex indicate that Cl^- enters into the coordination sphere more easily than hmta.

$Co(NO_3)_2(hmta)_2 \cdot 10H_2O$ loses its water molecules in three steps. The visible reflectance spectra of the cobalt nitrate complexes in each dehydration step are shown in Fig. 5, together with that of the decahydrate. In the first step ($-6H_2O$), the octahedral structure and T_d symmetry of hmta are retained, and the tetrahydrate formed gives strong infrared bands at 1300 and 1440 cm^{-1} (curve 2, Fig. 6), which can be ascribed to the two NO stretching bands of unidentate NO_3^- ligands.[10] The tetrahydrate can thus be described as $[Co(NO_3)_2(H_2O)_4] \cdot 2hmta$.

The dihydrate formed in the second step ($-2H_2O$) shows an electronic spectrum which is intermediate between the spectrum of a typically octahedral complex and that of a typically tetrahedral one. In this step, the $\tilde{\nu}_{max}$ value decreases and $\log f(R)$ increases, but the changes are not so large as those observed in typical octahedral→tetrahedral changes; no definite characteristic splitting of the "*tetrahedral band*" could be observed. This suggests that the dihydrate, and the anhydrous complex which shows a similar electronic spectrum, are deformed octahedral complexes and not simple tetrahedral ones.

On the other hand, the infrared spectra of these two complexes show strong bands at 1290 and 1505 cm^{-1}, which can be ascribed to the NO stretching bands of bidentate NO_3^- ligands.[10] It was also found that the anhydrous complex shows very weak bands at *ca.* 1710 and 1760 cm^{-1}, their positions indicating the presence of bidentate NO_3^-.[11] The symmetry of hmta in the dihydrate is T_d, and that in the anhydrous complex C_{3v}.

All these data lead to the formulation of the dihydrate as $[Co(NO_3)_2(H_2O)_2] \cdot 2hmta$, and that of the anhydrous complex as $[Co(NO_3)_2(hmta)_2]$.

The nickel nitrate complex $Ni(NO_3)_2(hmta)_2 \cdot 10H_2O$ also loses its water molecules in three steps. The visible reflectance spectra indicate that the octahedral structure is retained through all the steps. The ionic NO_3^- of the original complex is transformed into unidentate NO_3^- in the first step, further change into bidentate NO_3^- occurring in the final step (curve 4, Fig. 6). The T_d symmetry of hmta was retained until the second step and changed to C_{3v} in the final step. The nickel in the anhydrous complex thus seems to be surrounded octahedrally by two bidentate

TABLE 5. SUGGESTED STRUCTURE CHANGES
(L=hmta, X^-=anion)

CoCl, CoBr, CoI, NiBr, NiI:
$[M(H_2O)_6]X_2\cdot(2—4)H_2O\cdot 2L \rightarrow [ML_2X_2]$
$CoNO_3$:
$[M(H_2O)_6]X_2\cdot 4H_2O\cdot 2L \rightarrow [M(H_2O)_4X_2]\cdot 2L \rightarrow$
$[M(H_2O)_2X_2{}^*]\cdot 2L \rightarrow [MX_2{}^*L_2]$
CoNCS:
$[M(H_2O)_4X_2]\cdot 2L \rightarrow [MX_2L_2]$
NiCl:
$[M(H_2O)_6]X_2\cdot 4H_2O\cdot 2L \rightarrow$ (Fig. 4) $\rightarrow [MX_2L_2]$
$NiNO_3$:
$[M(H_2O)_6]X_2\cdot 4H_2O\cdot 2L \rightarrow [M(H_2O)_4X_2]\cdot 2L$
$\rightarrow$ (1.5 hydrate) $\rightarrow [MX_2{}^*L_2]$

* Bidentate.

NO_3^- and two unidentate hmta.

$Co(NCS)_2(hmta)_2\cdot 4H_2O$ loses four water molecules in one step to form the tetrahedral anhydrous complex. The infrared spectrum of the anhydrous complex indicates the presence of the unidentate hmta, and its ν(CN) and δ(NCS) are split into two by dehydration (Fig. 6). The anhydrous complex might thus be described as $[Co(NCS)_2(hmta)_2]$.

On the other hand, $Ni(NCS)_2(hmta)_2\cdot 4H_2O$ loses its water molecules in two steps, the octahedral structure being kept through the dehydration steps. In the first step, the symmetry of hmta changes clearly to C_{3v}, a single band of δ(NCS) being observed at 480 cm^{-1} (Fig. 6). In the next step, the C_{3v} symmetry of hmta changes to C_{3v} or $C_{2v}+C_{3v}$ and δ(NCS) is split into two as in the case of the cobalt thiocyanate complex, although ν(CN) does not change. The nickel thiocyanate complexes formed at each of these dehydration steps can not be formulated at present because of incomplete data.

The color and structural changes caused by thermal dehydration of all the complexes investigated are summarized in Tables 4 and 5. We see that the decrease in the number of coordinated water molecules brings about the coordination of anions and hmta. However, in many cases the coordination of anions takes place first, and that of hmta only in the last stage of dehydration. This apparent reluctance of an amine, which usually shows a stronger coordination tendency than anions and water, toward coordination is probably due to the bulkiness of hmta and its weak basicity ($pK_b=8.87$). This might be the reason why hmta forms no amine complex and gives no hydroxide precipitate in aqueous solution, when a cobalt or nickel salt is mixed with hmta in it, precipitating only a "*complex*" which contains uncoordinated hmta molecules between hydrated cations and anions (or aqua-anion complexes such as $[M(H_2O)_4X_2]$). The only possible exception to this rule found in this study is the thiocyanate complex of nickel, but its actual structure is not known. Heating, however, drives out the water from the coordination sphere of each cation, enabling the reluctant amine to be coordinated, but this change can only occur after all the more avid anions have got their seats in the coordination sphere.

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