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The Crystal Structure of L-Asparaginato-D-aspartatocobalt(III) Monohydrate

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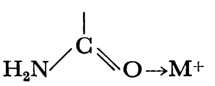
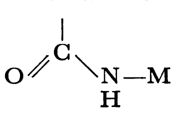
The crystal structure of L-asparaginato-D-aspartatocobalt(III) monohydrate, $[Co(H_2NCOCH_2CHNH_2COO)(OCOCH_2CHNH_2COO)]\cdot H_2O$, has been determined by an X-ray diffraction method and refined by a block-diagonal least-squares method to give $R=0.033$ for 1517 non-zero reflections. The crystals are orthorhombic with the space group $P2_12_12_1$, $a=11.790(2)$, $b=17.059(2)$, $c=5.830(2)$ Å, and $Z=4$. The complex molecule has a slightly distorted octahedral coordination with *fac*(*N*) geometry. The amide group of L-asparaginate ion is coordinated through the nitrogen atom, and an enolic system of $Co\leftarrow NH{=}C(OH){-}CH_2{-}$ is formed. The complex molecules are held together through hydrogen bonds which form two-dimensional networks parallel to the (010) plane. The networks are piled up through hydrogen bonds by water molecules to complete three-dimensional networks.

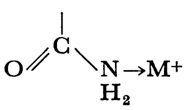
There are generally two coordination modes for an acid amide group: O-coordination(I)[1–5] and N-coordination (II),[6] the latter being accompanied by deprotonation of the amide group. Recently Takenaka and Shibata has suggested on the basis of infrared and visible spectra that the cobalt complex containing both L-asparaginate (L-2-aminosuccinamate, abbreviated as L-aspNH_2^-) ion and D-aspartate (D-2-aminosuccinate, D-asp^{2-}) ion, [Co(L-aspNH_2)(D-asp)]$\cdot H_2O$, has a *fac*(*N*) structure.[7] This means that the primary amide group of L-aspNH_2^- is coordinated through the nitrogen atom without deprotonation, and the coordinating mode is neither I nor II. A third mode, like III, seems probable, although no example of this mode has been found to date. In order to investigate the coordination mode of this cobalt(III) complex, an X-ray single-crystal analysis has been undertaken.



I



II



III

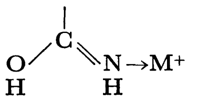
Experimental

The crystals prepared and supplied by Professor Muraji Shibata of Kanazawa University are reddish-violet prisms. A crystal with dimensions of 0.2×0.15×0.15 mm was selected, and the diffracted intensities were measured on a Philips PW 1100 four-circle diffractometer with Mo $K\alpha$ radiation monochromated by a graphite plate. The θ-2θ scan technique was used at a scan rate of 0.0668°/s in θ with a scan width of $(1.0+0.3\tan\theta)°$. The intensities of three reference reflections monitored every 2 h remained constant during data collection. A total of 2012 independent reflections was measured up to $2\theta=60°$, and 1517 of them with $|F|>3\sigma$ were used for the structure analysis. No corrections were made for absorption and extinction effects. Cell dimensions were obtained from the least-squares method based on 19 2θ values.

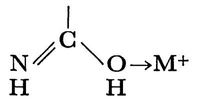
Crystal data: $Co(H_2NCOCH_2CHNH_2COO)(OCOCH_2CHNH_2COO)\cdot H_2O$. *F. W.*=339.15. Orthorhombic, $a=11.790(2)$, $b=17.059(2)$, and $c=5.830(2)$ Å. $U=1173(1)$ Å^3. $\rho_x=1.921$ g·cm^{-3}, $Z=4$. Space group $P2_12_12_1$. $\mu=3.9$ cm^{-1} (Mo $K\alpha$, $\lambda=0.7107$ Å).

Determination and Refinement of the Structure

The coordinates of the cobalt atom were determined from the Patterson map; the successive Fourier synthesis phased by the cobalt atom gave an approximate skeletal structure shown in Fig. 1. In this figure, the four positions marked with * should be occupied by one nitrogen and three oxygen atoms, but, at this stage, it was impossible to distinguish these two kinds of atoms. Accordingly, the distinction between L-aspNH_2^- and D-asp^{2-} was impossible. The block-diagonal least-squares refinement was carried out in expectation of getting a clue for the discrimination between oxygen and nitrogen. When all the four atoms marked with * (Fig. 1) were assumed to be oxygen, the R-value was 0.062. On the other hand when they were assumed to be nitrogen, R was 0.066. In both assumptions the isotropic temperature factors did not allow the two kinds of atoms to be distinguished. Anisotropic temperature factors were, then, introduced for all the atoms on the assumption that these four atoms were all oxygen. The R-value decreased to 0.050. The difference Fourier synthesis was calculated and gave the positions of all the 14 hydrogen atoms. The amide group could be distinguished at this stage from the carboxyl group. The obtained structure revealed the existence of both N–H and O–H bonds at the amide group, namely, the structure of the amide group is not I, II, nor III, but could be IV or V.



IV



V

Several cycles of the refinements were carried out for these two modes IV and V, including the hydrogen atoms, the isotropic temperature factors of which were assumed to be 4.0 Å^2. Both modes, IV and V, gave the equivalent isotropic temperature factors (B_{eq})[8] 1.8—2.2 Å^2 for the coordinating atoms of the three carboxyl groups. The corresponding values for the non-coordinating oxygen atoms of these carboxyl groups were 2.8—3.2 Å^2. Similarly, those for the coordinating

TABLE 1. FINAL ATOMIC PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES
Values for hydrogen atoms are multiplied by 10^3 and those for the others by 10^4.
Thermal parameters are in the form: $\exp[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+hk\beta_{12}+hl\beta_{13}+kl\beta_{23})]$.

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co	246(1)	1565(1)	584(2)	28(1)	10(1)	84(2)	−1(1)	−8(2)	−5(2)
O(1c)	−867(3)	2377(2)	595(7)	31(3)	15(1)	154(9)	3(3)	8(10)	−13(7)
O(1)	−1138(3)	3584(2)	−741(8)	46(3)	21(2)	243(12)	19(3)	27(12)	7(8)
C(1)	−616(4)	2967(3)	−747(10)	29(3)	15(2)	151(13)	−0(3)	−33(13)	−18(9)
C(2)	463(4)	2846(3)	−2129(8)	33(4)	12(2)	115(12)	3(4)	−14(11)	11(7)
N(2)	663(4)	1990(3)	−2358(7)	39(3)	11(2)	111(10)	1(3)	9(10)	−4(6)
C(3)	1441(4)	3226(3)	−855(10)	31(3)	16(2)	182(15)	−5(4)	−10(12)	−11(8)
C(4)	1699(4)	2902(3)	1517(9)	30(3)	18(2)	149(13)	2(4)	29(12)	−19(8)
O(4)	2342(4)	3263(3)	2793(7)	55(3)	25(2)	195(12)	−32(4)	−39(11)	−20(7)
O(4c)	1276(3)	2237(2)	2146(7)	46(3)	15(2)	149(10)	−11(3)	−35(10)	2(6)
O(5c)	−302(3)	1199(2)	3497(6)	55(3)	15(1)	94(8)	−16(4)	18(10)	−14(5)
O(5)	−1047(4)	128(2)	5076(7)	103(4)	15(2)	134(11)	−24(4)	55(11)	0(6)
C(5)	−749(4)	508(3)	3412(8)	40(4)	16(2)	117(12)	−1(4)	15(12)	−22(8)
C(6)	−840(4)	170(3)	989(8)	40(4)	14(2)	104(13)	−5(4)	13(11)	−15(7)
N(6)	−834(3)	833(2)	−640(8)	28(3)	15(2)	114(10)	−2(3)	−1(11)	−13(8)
C(7)	163(5)	−368(3)	508(10)	46(3)	12(2)	170(12)	−1(4)	−25(16)	−11(9)
C(8)	1293(4)	32(3)	507(10)	42(3)	17(2)	103(11)	12(4)	9(14)	−9(9)
O(8)	2207(3)	−413(2)	456(9)	44(3)	19(2)	276(13)	15(3)	−22(13)	16(8)
N(8)	1401(3)	782(3)	515(8)	32(3)	16(2)	142(11)	1(3)	−27(12)	0(8)
O(H_2O)	1957(4)	−1949(2)	727(8)	68(3)	23(2)	167(11)	18(4)	74(13)	17(8)
H(C2)	36(7)	307(4)	−382(13)						
H(N2-a)	136(7)	191(5)	−278(14)						
H(N2-b)	22(7)	180(4)	−362(13)						
H(C3-a)	127(6)	379(4)	−61(15)						
H(C3-b)	202(7)	333(5)	−190(14)						
H(C6)	−153(6)	−15(4)	87(15)						
H(N6-a)	−151(6)	102(4)	−43(15)						
H(N6-b)	−69(7)	69(5)	−218(14)						
H(C7-a)	11(6)	−63(4)	−86(14)						
H(C7-b)	19(7)	−79(4)	159(13)						
H(O8)	205(6)	−94(4)	48(15)						
H(N8)	203(6)	97(4)	45(15)						
H(H_2O-a)	194(6)	−218(4)	−20(15)						
H(H_2O-b)	170(7)	−213(5)	201(14)						

TABLE 2. DETERMINATION OF THE ABSOLUTE CONFIGURATION

h	k	l	$F_c(hkl)$	Obsd	$F_c(h\bar{k}l)$	h	k	l	$F_c(hkl)$	Obsd	$F_c(h\bar{k}l)$
1	1	1	70	<	74	1	1	2	30	<	46
1	3	1	16	<	26	1	8	2	31	<	38
1	6	1	43	<	52	1	6	2	30	>	26
1	7	1	21	>	11	1	9	2	45	>	39
2	4	1	53	>	45	1	12	2	32	>	23
2	6	1	50	>	45	2	3	2	45	<	60
2	8	1	34	>	28	2	4	2	46	>	35
2	11	1	42	<	45	3	1	2	38	>	25
3	1	1	35	>	22	3	4	2	82	>	77
3	2	1	66	<	74	3	9	2	24	>	22
3	7	1	73	>	66	4	12	2	25	>	14
3	6	1	28	>	23	5	1	2	23	<	29
4	2	1	21	<	26	5	2	2	30	>	23
4	3	1	21	<	28	5	6	2	36	>	31
4	5	1	63	>	59						
5	1	1	60	>	51						
6	5	1	39	>	36						
7	1	1	22	>	14						
7	2	1	40	>	32						

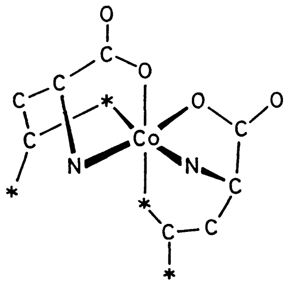


Fig. 1. Possible skeletal structure obtained from the Fourier synthesis.

and non-coordinating atoms of the amide group were 1.9 and 2.9 Å^2, respectively, for mode IV. But mode V gave reversed results: 3.1 and 1.9 Å^2, respectively. Usually, the thermal motions of binding atoms are smaller than those of terminal ones. Hence the structure of the amide group might be IV rather than V. Furthermore the *R*-value was 0.037 for IV while it was 0.042 for V. From a significance test,[9] the former might be prefered; this is in accordance with the suggestion of the spectroscopic investigation.[7]

The absolute configuration of the complex was obtained by comparing the absolute configurations of the two coordinating ligand ions with those of the respective free ligand molecules.

The anomalous scattering factor of the cobalt atom for Mo $K\alpha$ radiation was introduced into the refinement. The final *R*-value was 0.033 for the 1517 observed reflections. The final atomic parametes in a right-handed system of xyz-axes are listed in Table 1. The observed and calculated structure amplitudes are deposited with the Chemical Society of Japan (Document No. 7816).

To confirm the absolute configuration, equi-inclination Weissenberg photographs of the first and the second layers around the c axis were taken with Cu $K\alpha$ radiation. Differences between the intensities of 33 reflections and those of their counter-reflections were compared with the calculated intensity relations, as listed in Table 2.

The refinement of the structure and the drawing of thermal ellipsoids were carried out with the HBLS-IV[10] and ORTEP[11] programs, respectively. Other calculations were carried out with programs written by the author. The atomic scattering factors were taken from International Tables for X-Ray Crystallography.[12] The weights of reflections used in the refinements were 1.0 for $|F_o| \geqq 11.8$ and 0.5 for the others. A FACOM 230-75 computer at the Computation Center of Nagoya University and a FACOM 230-35 computer at the Data Processing Center of Kanazawa University were used.

Description of the Structure and Discussion

A projection of the structure along the c axis is shown in Fig. 2. The molecular structure and the

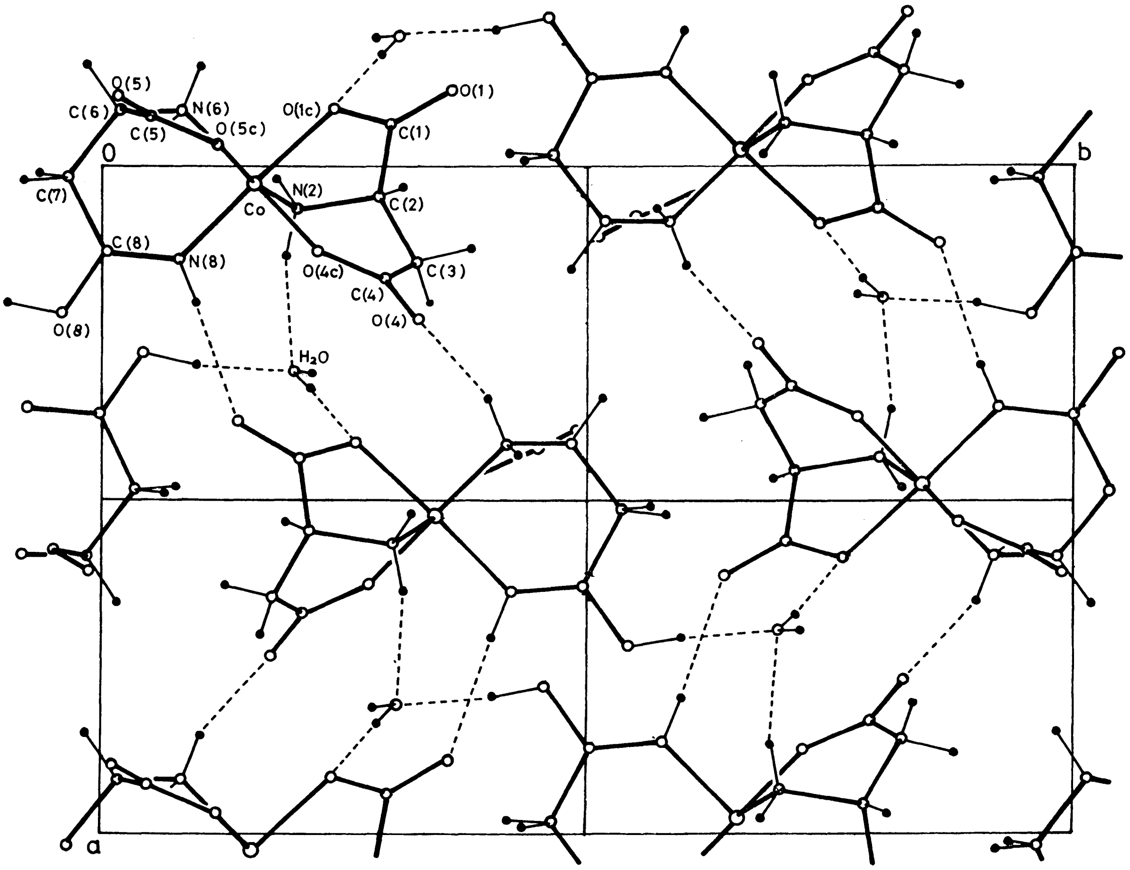


Fig. 2. Projection of the structure along the c axis.

Table 3. Interatomic distances and angles within the complex molecule

Co-O(1c)	1.908(4) Å	Co-O(5c)	1.921(4) Å
Co-N(2)	1.926(4)	Co-N(6)	1.921(4)
Co-O(4c)	1.902(4)	Co-N(8)	1.907(5)
O(1c)-C(1)	1.310(6)	O(5c)-C(5)	1.292(6)
O(1)-C(1)	1.220(7)	O(5)-C(5)	1.219(7)
C(1)-C(2)	1.521(7)	C(5)-C(6)	1.529(7)
C(2)-N(2)	1.485(6)	C(6)-N(6)	1.476(6)
C(2)-C(3)	1.517(7)	C(6)-C(7)	1.524(7)
C(3)-C(4)	1.520(7)	C(7)-C(8)	1.497(7)
C(4)-O(4)	1.228(6)	C(8)-O(8)	1.319(7)
C(4)-O(4c)	1.293(6)	C(8)-N(8)	1.286(7)
O(1c)-Co-N(2)	84.5(2)°	O(5c)-Co-N(6)	83.9(2)°
O(1c)-Co-O(4c)	90.0(2)	O(5c)-Co-N(8)	91.8(2)
N(2)-Co-O(4c)	92.1(2)	N(6)-Co-N(8)	90.6(2)
Co-O(1c)-C(1)	113.7(4)	Co-O(5c)-C(5)	113.6(4)
Co-N(2)-C(2)	104.5(3)	Co-N(6)-C(6)	105.2(3)
Co-O(4c)-C(4)	129.8(4)	Co-N(8)-C(8)	128.7(4)
O(1c)-C(1)-O(1)	123.3(5)	O(5c)-C(5)-O(5)	125.0(5)
O(1)-C(1)-C(2)	122.8(5)	O(5)-C(5)-C(6)	120.9(5)
O(1c)-C(1)-C(2)	113.6(5)	O(5c)-C(5)-C(6)	114.1(5)
C(1)-C(2)-C(3)	108.6(4)	C(5)-C(6)-C(7)	110.0(4)
C(1)-C(2)-N(2)	108.3(4)	C(5)-C(6)-N(6)	107.8(4)
C(3)-C(2)-N(2)	110.1(4)	C(7)-C(6)-N(6)	109.9(4)
C(2)-C(3)-C(4)	116.2(5)	C(6)-C(7)-C(8)	114.5(5)
C(3)-C(4)-O(4)	119.4(5)	C(7)-C(8)-O(8)	117.7(5)
C(3)-C(4)-O(4c)	120.1(5)	C(7)-C(8)-N(8)	122.8(5)
O(4)-C(4)-O(4c)	120.5(5)	O(8)-C(8)-N(8)	119.4(5)
C(2)-H	1.06(8) Å	C(7)-Ha	0.92(8) Å
N(2)-Ha	0.87(8)	C(7)-Hb	0.95(8)
N(2)-Hb	0.96(8)	O(8)-H	0.93(9)
C(3)-Ha	0.99(9)	N(8)-H	0.81(9)
C(3)-Hb	0.93(8)	$O(H_2O)$-Ha	0.67(9)
C(6)-H	0.98(9)	$O(H_2O)$-Hb	0.86(8)
N(6)-Ha	0.87(9)		
N(6)-Hb	0.95(8)		

Table 4. Intermolecular contacts through hydrogen bonds

Key to symmetry operations

i	x	y	z
ii	x	y	$-1+z$
iii	$1/2+x$	$1/2-y$	$-z$
iv	$-1/2+x$	$1/2-y$	$1-z$
v	$1/2-x$	$-y$	$-1/2+z$

A··········	H——	——D a)	A-D	A-H
$O^{i}(4)$	Ha	$O^{i}(H_2O)$	2.937(6) Å	2.34(9) Å
$O^{ii}(H_2O)$	Ha	$N^{i}(2)$	3.021(6)	2.16(8)
$O^{ii}(5c)$	Hb	$N^{i}(2)$	2.992(6)	2.06(8)
$O^{ii}(5)$	Hb	$N^{i}(6)$	2.784(6)	1.91(8)
$O^{iii}(1)$	H	$N^{i}(8)$	3.098(6)	2.30(9)
$O^{i}(4)$	Ha	$N^{iii}(6)$	2.929(6)	2.28(9)
$O^{i}(1c)$	Hb	$O^{iv}(H_2O)$	2.752(6)	1.90(8)
$O^{v}(H_2O)$	H	$O^{i}(8)$	2.643(6)	1.72(9)

a) A, Hydrogen acceptor; D, Hydrogen donor.

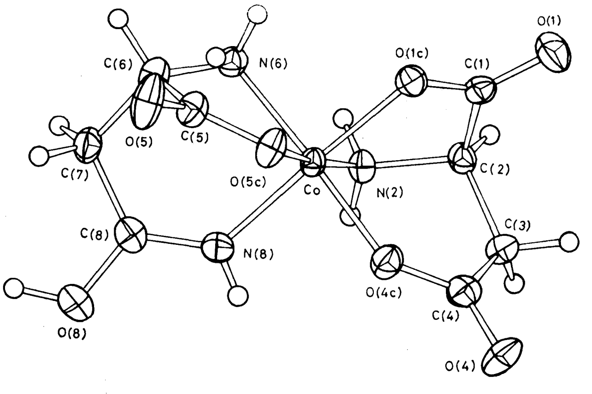


Fig. 3. The molecular structure and the absolute configuration with the anisotropic thermal ellipsoids of the atoms at 50% probability level.
Hydrogen atoms are drawn as spheres with a diameter of 0.1 Å.

absolute configuration are shown in Fig. 3, along with the thermal ellipsoids of the non-hydrogen atoms. The bond distances and angles are listed in Table 3 and the details of the hydrogen bonds in Table 4.

The asparaginate ion, L-aspNH_2^-, acts as a terdentate ligand coordinating through carboxyl oxygen,

Table 5. The C–O and C–N bond distances of the amide groups of some amide complexes

Complex	C–O	C–N	Corrdinating atom	Ref.
$[Ni(H_2O)_2(piaH)_2]Cl_2$[a)]	1.24 Å	1.31 Å	O	5
$[Ni(pia)_2]\cdot 2H_2O$[a)]	1.24	1.27	Deprotonated N	6
$[Cu(pyaH)_2](ClO_4)_2$[b)]	1.26	1.30	O	1
$[Cu\{HN(CH_2CONH_2)_2\}_2](ClO_4)_2$	1.265	1.31	O	2
$[Ni\{HN(CH_2CONH_2)_2\}_2](ClO_4)_2$	1.25	1.32	O	3
$[Cu(\text{L-aspNH}_2)_2]_n$	1.22	1.37	O	4
$[Co(\text{D-asp})(\text{L-aspNH}_2)]\cdot H_2O$	1.32	1.29	Protonated N	Present work

a) piaH: pyridine-2-carboxamide. pia: deprotonated piaH. b) pya: pyrazine-2-carboxamide.

amino nitrogen, and amide nitrogen atoms. The amide group forms an enolic system on coordination. The aspartate ion, D-asp^{2-}, acts also as a terdentate ligand coordinating through two carboxyl oxygen atoms and one amino nitrogen atom. The cobalt atom is surrounded by these coordinating atoms in the *facial* $[Co(N)_3(O)_3]$ geometry. This structural feature agrees with the suggestion by Takenaka and Shibata.[7)]

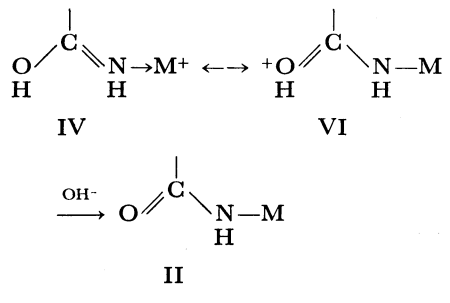
The coordination bond lengths are 1.902—1.926 Å, which agree with those of $[Co(\text{L-asp})_2]^-$ within the estimated standard deviations.[17)] The coordination bond angles around the cobalt atom are about 84° in the five-membered chelate rings, whereas they are 90—92° in the six- and seven-membered chelate rings. Hence the octahedron around the cobalt atom is slightly distorted.

The C–O and C–N bond lengths of L-aspNH$_2^-$ are listed in Table 5 along with those of other amide complexes. The C–N bond is longer than the C–O bond in the other complexes. But the present complex gives a reversed result, *i.e.* the C–N bond is slightly shorter (0.03 Å) than the C–O bond. This must be due to the difference between the enolic (the present complex) and keto (others) forms

Some other facts which support the N-coordination of the amide group are as follows:

1. Spectroscopic evidence supports the N-coordination.[7)]

2. The complex is easily deprotonated in an alkaline solution.[7)] This is explained by the following reaction:



3. Several examples which have structure IV have been reported for the secondary amide groups based on the spectroscopic evidence.[13–15)] Furthermore, one example of structure IV has been reported for a primary amide on the basis of NMR.[16)]

4. No example of structure V has so far been found.

The complex molecules are connected with one another through hydrogen bonds $N^{i}(2)\cdots O^{ii}(5c)$, $N^{i}(6)\cdots O^{ii}(5)$, and $N^{i}(2)\cdots O^{ii}(H_2O)$, forming infinite chains along the c axis. These chains are connected with the adjacent ones through hydrogen bonds $N^{i}(8)\cdots O^{iii}(1)$, $O^{i}(1c)\cdots O^{iv}(H_2O)$, and $O^{i}(4)\cdots N^{iii}(6)$. Thus, two-dimensional networks are formed parallel to the (010) plane. Among these networks no contact shorter than 3.3 Å is observed, except for a hydrogen bond $O^{i}(8)\cdots O^{v}(H_2O)$. The networks are piled up through this hydrogen bond to complete three-dimensional networks.

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