The Crystal Structure of Ethylenediaminebis[2-(aminomethyl)pyridine]-cobalt(III) Hexacyanocobaltate(III) Dihydrate

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The crystal structure of ethylenediaminebis[2-(aminomethyl)pyridine]cobalt(III) hexacyanocobaltate(III) dihydrate, $[Co(H_2NCH_2CH_2NH_2)(C_5H_4NCH_2NH_2)_2][Co(CN)_6]\cdot 2H_2O$, has been determined by the X-ray diffraction method and subsequently refined by a block-diagonal least-squares method to give $R=0.050$ for 5238 non-zero reflections. The crystals are triclinic with a space group $P\bar{1}$; $a=9.034(2)$, $b=17.267(2)$, $c=8.395(2)$ Å, $\alpha=87.1(3)$, $\beta=96.2(3)$, $\gamma=104.6(3)°$, and $Z=2$. The crystal is ionic, comprising the $[Co(H_2NCH_2CH_2NH_2)(C_5H_4NCH_2NH_2)_2]^{3+}$ cation and the $[Co(CN)_6]^{3-}$ anion. The complex cation is a slightly distorted octahedron with three five-membered chelate rings in a *lel* conformation. The two pyridine nitrogen atoms occupy *trans* positions. Thus, the cation has an approximate twofold axis of rotation. The anion is also a distorted octahedron, with the coordination of CN^- through the carbon atom. The cobalt atoms of the anions occupy the special positions. Two cations in the unit cell are connected by these anions through hydrogen bonds to form a three-dimensional network typical of an ionic crystal.

The cobalt(III) complexes of bidentate 2-(aminomethyl)pyridine (2-picolylamine, abbreviated as pic) have been reported from the synthetic and spectroscopic points of view.[1-5] In a previous investigation,[4] a mixed-ligand complex, the ethylenediaminebis[2-(aminomethyl)pyridine]cobalt(III) cation, $[Co(en)(pic)_2]^{3+}$, was prepared and separated into all three possible geometrical isomers by means of a chromatographic method. The structures were assumed from the elution order and the PMR spectra. In the present investigation, a crystal-structure analysis has been carried out to confirm the previous assumption. One of the isomers has been selected in which two pyridine groups may occupy *trans* positions of the octahedron, and its hexacyanocobaltate(III) salt has been used.

Experimental

The complex was prepared and separated by the previously reported method.[4] Orange prismatic crystals were obtained by a diffusion method using aqueous solutions of the complex chloride and $K_3[Co(CN)_6]$. A crystal of $0.2\times0.2\times0.2$ mm was selected, and the X-ray diffraction intensities were measured on a Philips PW 1100 four-circle automatic single-crystal 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 $(0.90+0.30\tan\theta)°$. The intensities of three reference reflections monitored every 2 h remained constant during the data collection. Of 5326 observed independent reflections measured up to $\theta=30°$, 5238 with $|F_o|>3\sigma$ were used for the structure analysis. No corrections were made for absorption and extinction effects ($\mu r=0.14$). The cell dimensions were obtained from the least-squares method, based on 14 2θ values. The crystal data are listed in Table 1.

Determination and Refinement of the Structure

The coordinates of the three cobalt atoms were determined from the Patterson map; successive Fourier synthesis gave the approximate skeletal structure. The block-diagonal least-squares refinement was carried out based on 5238 non-zero reflections with the weight of 1.0 for $|F_o|>3.5$ and that of 0.5 for the others. The atomic scattering factors were taken from the International Tables for X-Ray Crystallography.[6]

At the beginning stage of refinement, both atoms of each cyano group were assumed to be carbon. After several cycles of refinement with isotropic temperature factors, the R-value was 0.088. Anisotropic temperature factors were, then, introduced for all the non-hydrogen atoms. At this stage, if the coordination atom of each cyano group was assumed to be nitrogen, the R-value was 0.073. On the other hand, if it was carbon, the R-value was lowered to 0.058. It was thus concluded that the cyano groups coordinate through the carbon atoms.

The positional parameters of all the hydrogen atoms except for those of the water molecules were calculated using sp^2 and sp^3 models. They were refined with the isotropic temperature factors fixed at 4.0 Å^2. The final R-value was 0.050.

The final atomic parameters are listed in Table 2. The observed and calculated structure amplitudes are deposited with the Chemical Society of Japan (Document No. 7933).

The refinement of the structure and the drawing of the thermal ellipsoids were carried out with HBLS-IV[7] and ORTEP[8] programs respectively. The other calculations were carried out with programs written by one of the present authors (M. S.). A FACOM 230-75 computer at the Computation Center of Nagoya University and a FACOM M-160 computer at the

Table 1. The crystal data

$[Co(H_2NCH_2CH_2NH_2)(C_5H_4NCH_2NH_2)_2][Co(CN)_6]\cdot 2H_2O$

F. W. = 586.39.

Triclinic, $P\bar{1}$.

$a=9.034(2)$, $b=17.267(2)$, $c=8.395(2)$ Å,

$\alpha=87.1(3)$, $\beta=96.2(3)$, $\gamma=104.6(3)°$.

$V=1258$ Å^3.

$D_x=1.547$ g cm^{-3}, $Z=2$.

$\mu=14.2$ cm^{-1} (Mo $K\alpha$ radiation, $\lambda=0.7107$ Å).

Table 2a. Final atomic parameters with their estimated standard deviations in parentheses
Thermal parameters are in the form: $\exp -(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+hk\beta_{12}+hl\beta_{13}+kl\beta_{23})$.
Values are multiplied by 10^4.

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co(1)	0	0	0	62 (2)	17 (1)	61 (2)	12 (1)	7 (2)	1 (1)
Co(2)	1/2	1/2	0	81 (2)	16 (1)	81 (2)	24 (1)	5 (2)	−2 (1)
Co(3)	3388 (1)	2346 (1)	5015 (1)	62 (1)	16 (1)	66 (1)	16 (1)	6 (2)	−1 (1)
N(1)	1993 (5)	2806 (3)	3579 (5)	65 (5)	17 (2)	104 (7)	14 (5)	9 (9)	9 (5)
C(2)	1827 (6)	2781 (4)	1952 (7)	80 (7)	27 (2)	101 (8)	21 (6)	13 (12)	23 (7)
C(3)	832 (7)	3149 (4)	1045 (7)	100 (8)	35 (3)	115 (9)	27 (7)	−33 (13)	23 (8)
C(4)	−32 (7)	3554 (4)	1796 (9)	99 (8)	39 (3)	201 (13)	67 (8)	−2 (16)	39 (10)
C(5)	110 (7)	3570 (4)	3449 (8)	87 (7)	31 (3)	174 (11)	48 (7)	45 (14)	12 (8)
C(6)	1112 (6)	3183 (3)	4309 (7)	73 (7)	24 (2)	137 (9)	29 (6)	38 (12)	12 (7)
C(7)	1369 (7)	3170 (4)	6117 (7)	119 (8)	34 (3)	116 (9)	61 (7)	70 (14)	−19 (8)
N(8)	2110 (5)	2515 (3)	6634 (6)	85 (6)	23 (2)	107 (7)	20 (5)	44 (10)	5 (6)
N(11)	4527 (5)	1771 (3)	6555 (5)	74 (5)	20 (2)	85 (6)	24 (5)	15 (9)	11 (5)
C(12)	5703 (6)	2097 (4)	7672 (7)	99 (7)	28 (2)	95 (8)	40 (7)	−4 (12)	−10 (7)
C(13)	6414 (7)	1628 (4)	8694 (7)	103 (8)	38 (3)	98 (8)	55 (7)	−30 (13)	−5 (8)
C(14)	5934 (7)	804 (4)	8603 (8)	117 (9)	40 (3)	134 (10)	73 (8)	29 (14)	42 (8)
C(15)	4753 (7)	469 (4)	7466 (8)	102 (8)	26 (2)	143 (10)	41 (7)	52 (14)	30 (7)
C(16)	4065 (6)	964 (3)	6465 (5)	82 (7)	21 (2)	92 (8)	20 (6)	41 (11)	5 (6)
C(17)	2830 (7)	643 (3)	5164 (8)	127 (9)	18 (2)	150 (10)	30 (6)	−38 (15)	−6 (7)
N(18)	2082 (5)	1276 (3)	4520 (5)	85 (6)	20 (2)	86 (6)	14 (5)	−15 (10)	−10 (5)
N(21)	4753 (5)	3422 (3)	5400 (5)	90 (6)	19 (2)	94 (7)	22 (5)	14 (10)	−2 (5)
C(22)	6206 (6)	3513 (4)	4623 (7)	72 (7)	24 (2)	114 (9)	−0 (6)	19 (12)	5 (7)
C(23)	5751 (6)	3090 (4)	3074 (6)	85 (7)	29 (2)	85 (8)	15 (6)	33 (11)	1 (7)
N(24)	4799 (5)	2271 (3)	3436 (5)	73 (6)	21 (2)	91 (6)	24 (5)	3 (9)	−2 (5)
C(101)	1962 (6)	691 (3)	537 (6)	85 (7)	20 (2)	76 (7)	22 (6)	26 (11)	−4 (6)
N(101)	3124 (6)	1120 (3)	948 (6)	96 (7)	32 (2)	137 (9)	1 (6)	30 (12)	−39 (7)
C(102)	−275 (6)	629 (3)	−1850 (6)	69 (6)	22 (2)	98 (8)	16 (5)	19 (11)	6 (6)
N(102)	−403 (6)	999 (3)	−3025 (6)	105 (7)	33 (2)	97 (7)	12 (6)	6 (11)	28 (6)
C(103)	−800 (6)	652 (3)	1267 (6)	69 (6)	21 (2)	81 (7)	11 (5)	−4 (10)	−4 (6)
N(103)	−1231 (6)	1047 (3)	2074 (6)	123 (8)	34 (2)	134 (9)	45 (7)	43 (13)	−31 (7)
C(201)	4535 (6)	3905 (3)	−470 (6)	104 (7)	22 (2)	78 (7)	36 (6)	9 (11)	3 (6)
N(201)	4222 (6)	3245 (3)	−804 (6)	147 (8)	24 (2)	98 (7)	33 (6)	25 (12)	−12 (6)
C(202)	4189 (6)	4790 (3)	2021 (7)	92 (7)	17 (2)	112 (8)	20 (6)	16 (12)	12 (6)
N(202)	3740 (6)	4691 (3)	3265 (6)	140 (8)	29 (2)	129 (9)	27 (7)	48 (13)	9 (7)
C(203)	3023 (7)	5011 (4)	−1021 (7)	106 (8)	24 (2)	124 (9)	44 (7)	9 (13)	−4 (7)
N(203)	1837 (7)	4988 (4)	−1673 (8)	121 (8)	44 (3)	203 (11)	64 (8)	−54 (15)	−18 (9)
O(1w)[a]	7335 (6)	1556 (4)	4533 (6)	194 (9)	75 (3)	129 (8)	177 (9)	62 (13)	16 (8)
O(2w)[a]	−1350 (7)	4085 (4)	−2260 (9)	205 (11)	65 (4)	410 (18)	76 (10)	−211 (22)	−177 (12)

a) Oxygen atoms of water molecules.

Table 2b. Positional parameters of the hydrogen atoms ($\times 10^3$)

	x	y	z		x	y	z
H(C2)	250 (9)	252 (5)	139 (8)	H(C17-a)	214 (9)	17 (5)	557 (8)
H(C3)	76 (9)	311 (5)	−18 (8)	H(C17-b)	334 (9)	47 (5)	429 (8)
H(C4)	−68 (9)	382 (5)	114 (8)	H(N18-a)	117 (9)	121 (5)	502 (8)
H(C5)	−47 (9)	388 (5)	407 (8)	H(N18-b)	192 (9)	125 (5)	344 (8)
H(C7-a)	37 (9)	312 (5)	663 (8)	H(N21-a)	427 (9)	382 (5)	493 (8)
H(C7-b)	211 (9)	374 (5)	651 (8)	H(N21-b)	494 (9)	353 (5)	656 (8)
H(N8-a)	143 (9)	208 (5)	680 (8)	H(C22-a)	690 (9)	328 (5)	537 (8)
H(N8-b)	279 (9)	264 (5)	771 (8)	H(C22-b)	674 (9)	409 (5)	455 (8)
H(C12)	601 (9)	271 (5)	778 (8)	H(C23-a)	661 (9)	302 (5)	249 (8)
H(C13)	721 (9)	193 (5)	959 (8)	H(C23-b)	507 (9)	332 (5)	227 (8)
H(C14)	636 (9)	45 (5)	937 (8)	H(N24-a)	542 (9)	197 (5)	388 (8)
H(C15)	431 (9)	−14 (5)	738 (8)	H(N24-b)	427 (9)	201 (5)	246 (8)

Table 3. Bond distances (l/Å) and angles (φ/°)

Co(3)-N(1)	1.938(4)	Co(3)-N(11)	1.953(4)
Co(3)-N(8)	1.953(4)	Co(3)-N(18)	1.961(4)
N(1)-C(2)	1.360(7)	N(11)-C(12)	1.364(7)
N(1)-C(6)	1.356(7)	N(11)-C(16)	1.354(6)
C(2)-C(3)	1.372(8)	C(12)-C(13)	1.371(8)
C(3)-C(4)	1.386(9)	C(13)-C(14)	1.381(9)
C(4)-C(5)	1.381(9)	C(14)-C(15)	1.381(9)
C(5)-C(6)	1.380(9)	C(15)-C(16)	1.380(8)
C(6)-C(7)	1.510(8)	C(16)-C(17)	1.493(8)
C(7)-N(8)	1.480(7)	C(17)-N(18)	1.476(7)
Co(3)-N(21)	1.974(4)	Co(3)-N(24)	1.966(4)
N(21)-C(22)	1.498(7)	N(24)-C(23)	1.494(7)
C(22)-C(23)	1.490(8)		
Co(1)-C(101)	1.892(5)	Co(2)-C(201)	1.882(5)
Co(1)-C(102)	1.881(5)	Co(2)-C(202)	1.903(5)
Co(1)-C(103)	1.902(5)	Co(2)-C(203)	1.900(6)
C(101)-N(101)	1.150(7)	C(201)-N(201)	1.144(7)
C(102)-N(102)	1.158(7)	C(202)-N(202)	1.150(7)
C(103)-N(103)	1.147(7)	C(203)-N(203)	1.141(8)
C(2)-H	1.01(8)	C(12)-H	1.04(8)
C(3)-H	1.03(8)	C(13)-H	1.04(8)
C(4)-H	0.95(8)	C(14)-H	0.98(8)
C(5)-H	1.03(8)	C(15)-H	1.03(8)
C(7)-Ha	1.02(8)	C(17)-Ha	0.96(8)
C(7)-Hb	1.09(8)	C(17)-Hb	1.01(8)
N(8)-Ha	0.86(8)	N(18)-Ha	0.94(8)
N(8)-Hb	1.04(8)	N(18)-Hb	0.90(8)
N(21)-Ha	0.95(8)	N(24)-Ha	0.90(8)
N(21)-Hb	0.99(8)	N(24)-Hb	0.97(8)
C(22)-Ha	0.98(8)	N(23)-Ha	1.00(8)
C(22)-Hb	0.99(8)	C(23)-Hb	0.99(8)
N(1)-Co(3)-N(8)	83.2(2)	N(1)-Co(3)-N(11)	171.7(2)
N(11)-Co(3)-N(18)	84.4(2)	N(8)-Co(3)-N(24)	174.8(2)
N(21)-Co(3)-N(24)	84.8(2)	N(18)-Co(3)-N(21)	176.8(2)
Co(3)-N(1)-C(2)	126.3(4)	Co(3)-N(11)-C(12)	127.0(4)
Co(3)-N(1)-C(6)	115.1(4)	Co(3)-N(11)-C(16)	114.4(4)
C(2)-N(1)-C(6)	118.6(5)	C(12)-N(11)-C(16)	118.5(5)
N(1)-C(2)-C(3)	121.6(5)	N(11)-C(12)-C(13)	121.6(6)
C(2)-C(3)-C(4)	119.6(6)	C(12)-C(13)-C(14)	119.7(6)
C(3)-C(4)-C(5)	119.2(7)	C(13)-C(14)-C(15)	119.1(6)
C(4)-C(5)-C(6)	119.0(6)	C(14)-C(15)-C(16)	119.3(6)
N(1)-C(6)-C(5)	122.0(6)	N(11)-C(16)-C(15)	121.8(5)
N(1)-C(6)-C(7)	114.6(5)	N(11)-C(16)-C(17)	116.0(5)
C(5)-C(6)-C(7)	123.4(6)	C(15)-C(16)-C(17)	122.1(5)
C(6)-C(7)-N(8)	108.3(5)	C(16)-C(17)-N(18)	110.3(5)
Co(3)-N(8)-C(7)	110.4(4)	Co(3)-N(18)-C(17)	111.4(4)
Co(3)-N(21)-C(22)	110.1(4)	Co(3)-N(24)-C(23)	109.1(4)
N(21)-C(22)-C(23)	106.2(5)	N(24)-C(23)-C(22)	107.3(5)
C(101)-Co(1)-C(102)	90.3(3)	C(201)-Co(2)-C(202)	92.8(3)
C(102)-Co(1)-C(103)	91.6(3)	C(202)-Co(2)-C(203)	90.6(3)
C(101)-Co(1)-C(103)	87.2(3)	C(201)-Co(2)-C(203)	87.3(3)
Co(1)-C(101)-N(101)	175.9(5)	Co(2)-C(201)-N(201)	177.6(5)
Co(1)-C(102)-N(102)	176.8(5)	Co(2)-C(202)-N(202)	177.3(5)
Co(1)-C(103)-N(103)	177.3(5)	Co(2)-C(203)-N(203)	176.9(6)

Data Processing Center of Kanazawa University were used.

Description of the Structure and Discussion

The crystal is ionic, comprising $[Co(en)(pic)_2]^{3+}$ and $[Co(CN)_6]^{3-}$ ions and water molecules. The arrangement of the ions in the crystal is shown in Fig. 1. The unit cell has two formula units, which are related to each other by an inversion center. The cobalt atoms of the cations occupy the general positions, while those of the anions occupy the special positions, (0, 0, 0) and (1/2, 1/2, 0), of the triclinic cell.

The structure of the cation is shown in Fig. 2, together with the anisotropic thermal ellipsoids of the non-hydrogen atoms. Each of the 2-(aminomethyl)pyridine molecules acts as a bidentate ligand through the amino nitrogen and pyridine nitrogen atoms. The two pyridine nitrogen atoms are located at *trans* positions, while the two amino nitrogen atoms are at *cis* positions of the octahedron. The remaining two coordination positions are occupied by the ethylenediamine nitrogen atoms. Thus, the cation has an approximate twofold axis of rotation through the cobalt atom and bisecting the C–C bond of ethylenediamine. This structural feature agrees with the assumption by the previous investigation.[4,5]

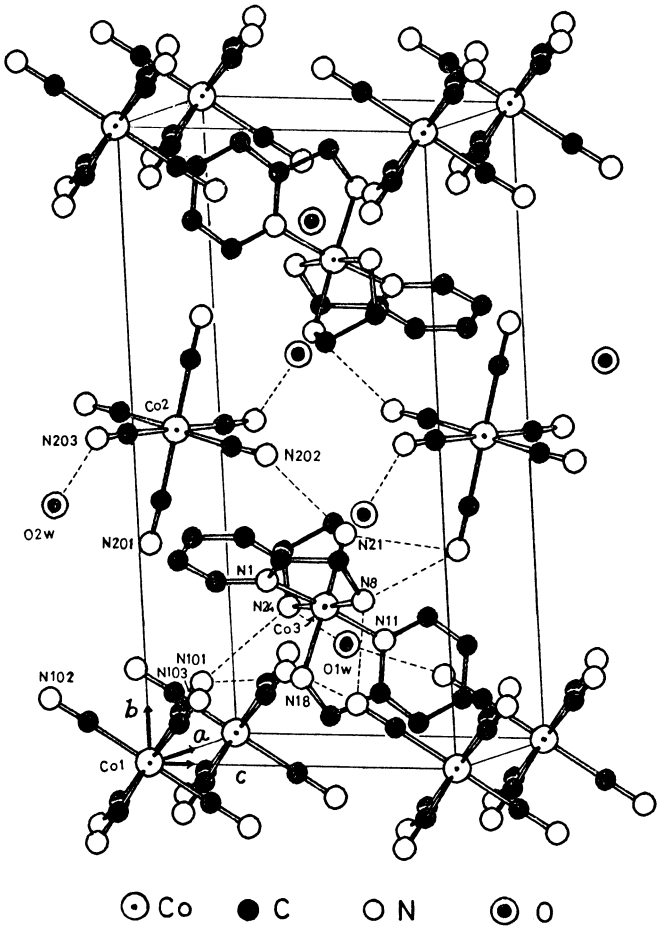

Fig. 1. Atomic arrangement in the crystal. Dashed lines exhibit hydrogen bonds.

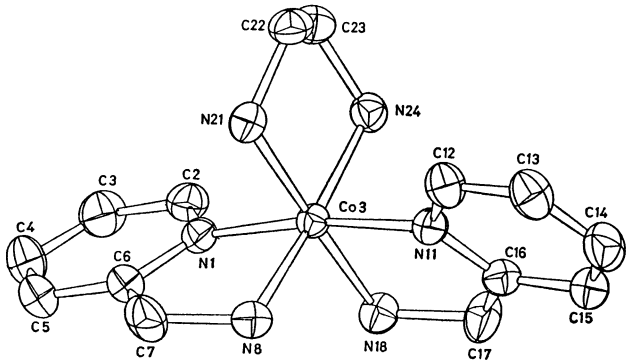

Fig. 2. The structure of the cation with the anisotropic thermal ellipsoids of the non-hydrogen atoms at the 50% probability level.

Table 4. Hydrogen bonds

D – H ··· A[a]			D-A (*l*/Å)	H-A (*l*/Å)
N(18)	Hb	N(101)[b]	3.282	2.50
N(21)	Ha	N(202)	3.020	2.11
N(24)	Hb	N(101)	2.969	2.04
N(24)	Ha	O(1w)	2.913	2.04
O(2w)	H	N(203)	2.910	—
O(1w)	H	N(103)^{i}	2.836	—
N(8)	Ha	N(102)^{ii}	3.025	2.17
N(8)	Hb	N(201)^{ii}	2.833	1.85
N(18)	Ha	N(102)^{ii}	3.143	2.24
N(21)	Hb	N(201)^{ii}	3.262	2.37
O(1w)	H	N(102)^{iii}	3.033	—
O(2w)	H	N(202)^{iv}	3.402	—

a) D, Hydrogen donor; A, Hydrogen acceptor.
b) Key to symmetry operation:

No mark	x	y	z
i	$1+x$	y	z
ii	x	y	$1+z$
iii	$1+x$	y	$1+z$
iv	$-x$	$1-y$	$-z$

Three five-membered chelate rings exhibit the *lel* conformation. The value of the dihedral angle between the N(21)C(22)C(23) and C(22)C(23)N(24) planes is 51.2°. On the other hand, those between the C(6)C(7)N(8) and N(1)C(6)C(7) planes and between the C(16)C(17)N(18) and N(11)C(16)C(17) planes give smaller values of 19.6° and 15.3° respectively. These values indicate that 2-(aminomethyl)pyridine nearly forms a plane in contrast to the usual *gauche* conformation of ethylenediamine.

The bond distances and angles are listed in Table 3. The coordination bond distances of the cation show an average value of 1.96 Å; the coordination bond angles in the chelate rings are smaller than 90° (average, 84°). These results are similar to those for $[Co(en)_3]^{3+}$.[9] All the three coordination bond angles in *trans* positions of the octahedron deviate from 180°. Especially the N(1)–Co–N(11) angle is considerably small (171.7°). Thus, the octahedron of the cation is distorted.

The octahedral coordination in the anion is also

slightly distorted. The Co–C and C–N bond distances are normal,[9] with the mean values of 1.89 and 1.15 Å respectively. The average value of the Co–C–N angles is 177°.

The complex cations and anions are connected to one another through hydrogen bonds between amino and cyano nitrogen atoms, in addition through electrostatic interactions. The water molecules are also hydrogen-bonded with these ions. These hydrogen bonds are summarized in Table 4 and are also shown in Fig. 1. No contacts shorter than 3.5 Å are observed between any cations or between any anions. Thus, a three-dimensional network typical of the ionic crystal is completed by these intermolecular interactions.

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