CRYSTAL STRUCTURE OF THE MOLECULAR COMPLEX OF PYRIDINE AND BIS(p-HYDROXYBENZOATO)TRIS(PYRIDINE)CADMIUM (II)

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An x-ray structural study of the triclinic crystals of $[Cd(p\text{-}HOC_6H_4COO)_2(C_5H_5N)_3]C_5H_5N$ has been carried out (diffractometer, Mo radiation, 3127 reflections, heavy-atom method, full-matrix refinement by the method of least squares in the anisotropic-H-isotropic approximation, R = 0.073). The cadmium atom is joined by coordinate bonds to three pyridine molecules and two molecules of para-hydroxybenzoic acid (PHBA); one of the PHBA molecules is coordinated to the central atom to give a chelate structure, and the second uses only one oxygen atom for this bond. The second oxygen atom of the carboxyl group of this acid molecule forms an intermolecular hydrogen bond with the hydroxyl oxygen atom of another PHBA molecule. This H-interaction leads to the formation of a dimer. In the compound studied, the noncoordinated pyridine molecule also forms an H-bond with a coordinated PHBA molecule. An interesting feature of the structure is the simultaneous existence of pyridine in two forms: as an included molecule and in the coordinated state.

The present work deals with the complex-forming properties of p-hydroxybenzoic acid [1]. There is almost no published information [2-5] on the structural behavior of this ligand. In this connection, it is of interest to compare the coordinating properties of p-aminobenzoic and p-hydroxybenzoic acids. The former often uses all three of its donor centers for bonding to a metal [6-9], whereas our preliminary studies [1] showed that this cannot be said of hydroxybenzoic acid.

The present work was undertaken to study these questions.

EXPERIMENTAL

The crystals studied were obtained by dissolving cadmium p-hydroxybenzoate (II) in pyridine.

The transparent crystals of the complex are triclinic: a = 9.902(8), b = 10.051(9), c = 17.56(3) Å, α = 98.58(9), β = 100.08(10), γ = 103.38(8)°, V = 1640.8 Å^3, Z = 2[$CdL_2 \cdot 4Py$], LH = p-HOC_6H_4COOH, space group $P\bar{1}$, d_{calc} = 1.418 g/cm^3.

The intensities of 3300 reflections were measured on a Syntex $P2_1$ four-circle automatic diffractometer ($\theta/2\theta$ scanning, θ_{max} = 25°). The structure calculations were carried out using 3127 reflections, for which the values of F^2 were greater than $3\sigma(F^2)$. No allowance was made for absorption. All the calculations were carried out using the programs Rentgen-75 on a BÉSM-6 computer [10].

The question of the choice of the two alternative groups P1 or $P\bar{1}$ was solved in favor of the latter on the basis of the statistics of the distribution of the E-amplitudes. The position of the cadmium atom was determined from the Patterson three-dimensional map. Two subsequent F-syntheses made it possible to locate all the atoms of the compound other than hydrogen (R = 0.19). Three cycles of the refinement in the block-diagonal approximation, followed by another two stages in the full-matrix version, gave R = 0.112. Three cycles of the anisotropic refinement by the method of least squares (R = 0.087) made it possible to use the difference Fourier synthesis, which located all the hydrogen atoms except the two belonging to the hydroxyl groups of the PHBA ligands. The subsequent refinement of all the atoms of the structure, except the H atoms, which were assigned identical thermal factors equal to 8, gave the value R = 0.073. Attempts to determine the positions of the above-mentioned two H atoms were unsuccessful, however.

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TABLE 1. Coordinates of the Atoms ($\times 10^4$)

Atom	x	y	z	Atom	x	y	z
Cd	2778(1)	2158(1)	3298(1)	C(27)	5217(16)	6604(12)	2460(8)
O(1)	1798(7)	1494(6)	4315(6)	C(28)	5698(16)	5421(14)	2325(9)
O(2)	2502(7)	3781(6)	4452(4)	C(29)	5033(12)	4270(11)	2594(7)
O(3)	−583(8)	3195(7)	7330(4)	C(30)	1749(10)	2445(10)	−1109(6)
O(4)	1866(7)	−627(6)	2505(4)	C(31)	1296(12)	1064(12)	−1031(6)
O(5)	3277(8)	1099(6)	2163(4)	C(32)	1626(14)	746(12)	−301(8)
O(6)	3715(7)	−3810(6)	−423(4)	C(33)	2311(14)	1743(12)	313(7)
N(1)	4885(8)	1805(7)	3979(4)	C(34)	2783(12)	3102(11)	206(6)
N(2)	486(8)	2278(7)	2642(4)	H(3)*	99	91	553
N(3)	3982(8)	4251(7)	2964(4)	H(4)	−22	109	657
N(4)	2481(9)	3455(8)	− 491(4)	H(6)	29	502	662
C(1)	1942(9)	2715(8)	4693(5)	H(7)	158	491	554
C(2)	1365(8)	2859(8)	5423(4)	H(10)	481	34	125
C(3)	911(9)	1708(8)	5758(5)	H(11)	514	−124	39
C(4)	305(9)	1825(9)	6404(5)	H(13)	154	−432	31
C(5)	75(9)	3069(9)	6715(5)	H(14)	98	−297	133
C(6)	528(11)	4247(9)	6390(5)	H(15)	425	−21	352
C(7)	1171(11)	4150(9)	5765(5)	H(16)	635	−72	424
C(8)	2645(10)	−179(8)	2075(5)	H(17)	795	103	515
C(9)	2897(9)	−1158(8)	1407(5)	H(18)	717	306	526
C(10)	4035(10)	−730(8)	1043(5)	H(19)	584	360	447
C(11)	4317(11)	−1612(10)	449(6)	H(20)	104	301	180
C(12)	3421(10)	−2969(9)	185(5)	H(21)	−101	335	106
C(13)	2271(10)	−3414(9)	524(5)	H(22)	−299	240	164
C(14)	2011(10)	−2523(9)	1122(5)	H(23)	−260	152	285
C(15)	5064(11)	510(11)	3885(6)	H(24)	−20	163	339
C(16)	6170(14)	175(12)	4340(8)	H(25)	269	521	324
C(17)	7140(12)	1176(13)	4908(7)	H(26)	410	762	309
C(18)	7004(11)	2524(12)	5003(6)	H(27)	566	741	248
C(19)	5851(11)	2789(10)	4542(6)	H(28)	661	510	209
C(20)	345(11)	2836(11)	1999(6)	H(29)	521	339	262
C(21)	−946(13)	2936(12)	1606(6)	H(30)	155	296	−151
C(22)	−2165(12)	2438(12)	1884(7)	H(31)	98	58	−136
C(23)	−2037(11)	1864(12)	2534(7)	H(32)	134	−9	−19
C(24)	−682(11)	1824(9)	2899(6)	H(33)	246	146	86
C(25)	3569(12)	5404(10)	3097(7)	H(34)	351	401	70
C(26)	4166(15)	6606(10)	2845(8)				

* The values of the coordinates of the H atoms should be multiplied by 10^3.

Table 1 gives the coordinates of the basis atoms.*

DESCRIPTION OF THE STRUCTURE AND DISCUSSION

The crystal structure of the complex is given in Fig. 1, the bond lengths in Table 2, and the values of the valence angles in Fig. 2. The cadmium atom is in a highly distorted octahedral environment. Its coordination environment includes two oxygen atoms O(1) and O(2) of the carboxyl group of the PHBA molecule with the chelate structure [Cd–O 2.289(7) and 2.502(7) Å], the O(5) oxygen atom of the other PHBA molecule [Cd–O 2.304(7) Å], which acts as a bridge (the O(4) oxygen atom, which is situated at a distance of 2.80 Å from the Cd atom, does not form a coordinate bond with it). The other coordination positions are occupied by the nitrogen atoms of three pyridine molecules [Cd–N 2.346(8), 2.397(8), and 2.376(8) Å]. The valence angles around the Cd atom are given in Table 3.

* The values of the thermal parameters can be obtained from the authors.

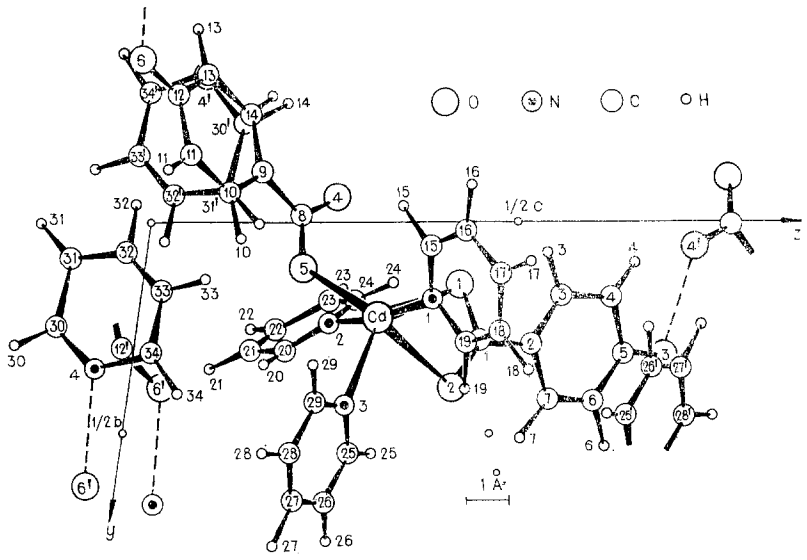

Fig. 1. Crystal structure of the complex (view along [100]).

TABLE 2. Bond Lengths d, Å

Bond	d	Bond	d	Bond	d
Cd—O(1)	2,289(7)	N(1)—C(15)	1,344(13)	O(3)—H(O3)	—
Cd—O(2)	2,502(7)	N(2)—C(19)	1,345(10)	O(6)—H(O6)	—
Cd—O(5)	2,304(7)	C(15)—C(16)	1,377(17)	C(3)—H(3)*	0,87
Cd—N(1)	2,346(8)	C(16)—C(17)	1,359(14)	C(4)—H(4)	0,91
Cd—N(2)	2,397(8)	C(17)—C(18)	1,381(18)	C(6)—H(6)	0,92
Cd—N(3)	2,376(8)	C(18)—C(19)	1,383(15)	C(7)—H(7)	0,95
O(1)—C(1)	1,269(9)	Average	1,365	C(10)—H(10)	1,13
O(2)—C(1)	1,256(10)	N(2)—C(20)	1,334(13)	C(11)—H(11)	0,85
C(1)—C(2)	1,494(12)	N(2)—C(24)	1,323(13)	C(13)—H(13)	1,00
C(2)—C(3)	1,393(12)	C(20)—C(21)	1,376(16)	C(14)—H(14)	1,16
C(3)—C(4)	1,376(13)	C(21)—C(22)	1,395(17)	C(15)—H(15)	0,99
C(4)—C(5)	1,373(13)	C(22)—C(23)	1,354(18)	C(16)—H(16)	1,00
C(5)—C(6)	1,405(13)	C(23)—C(24)	1,394(14)	C(17)—H(17)	0,89
C(6)—C(7)	1,364(14)	Average	1,359	C(18)—H(18)	0,62
C(7)—C(2)	1,416(12)	N(3)—C(25)	1,318(13)	C(19)—H(19)	0,85
Average	1,388	N(3)—C(29)	1,318(15)	C(20)—H(20)	0,82
O(3)—C(5)	1,361(4)	C(25)—C(26)	1,388(16)	C(21)—H(21)	1,09
O(4)—C(8)	1,230(11)	C(26)—C(27)	1,337(22)	C(22)—H(22)	0,85
O(5)—C(8)	1,265(9)	C(27)—C(28)	1,384(21)	C(23)—H(23)	0,90
O(6)—C(12)	1,376(11)	C(28)—C(29)	1,384(18)	C(24)—H(24)	0,98
C(8)—C(9)	1,510(12)	Average	1,355	C(25)—H(25)	0,93
C(9)—C(10)	1,405(13)	N(4)—C(30)	1,338(10)	C(26)—H(26)	1,07
C(10)—C(11)	1,376(14)	N(4)—C(34)	1,328(13)	C(27)—H(27)	0,82
C(11)—C(12)	1,404(11)	C(30)—C(31)	1,392(15)	C(28)—H(28)	1,15
C(12)—C(13)	1,390(14)	C(31)—C(32)	1,370(19)	C(29)—H(29)	0,94
C(13)—C(14)	1,376(13)	C(32)—C(33)	1,317(14)	C(30)—H(30)	0,97
C(14)—C(9)	1,410(10)	C(33)—C(34)	1,390(16)	C(31)—H(31)	0,66
Average	1,395	Average	1,356	C(32)—H(32)	0,89
				C(33)—H(33)	1,04
				C(34)—H(34)	1,16

*Standard deviations of the C—H bond lengths ~0.1 Å.

The fourth pyridine molecule is not coordinated, but forms an adduct with the complex obtained.

The O(4) oxygen atom, which is not coordinated to the metal atom, forms a H-bond with the oxygen atoms O(3) of the hydroxyl group of the acidic ligand. The corresponding distance is 2.68 Å.

Two molecules with the composition $Cd(p\text{-}HOC_6H_4COO)_2 \cdot 3C_5H_5N$, related by a center of symmetry (see Fig. 1), are joined by the two hydrogen bonds O(3)—H . . . O(4') and O(3')—H . . . O(4) to form a dimer. The hydroxyl oxygen atom of the other acid molecule is joined by a hydrogen bond to the pyridine molecule included

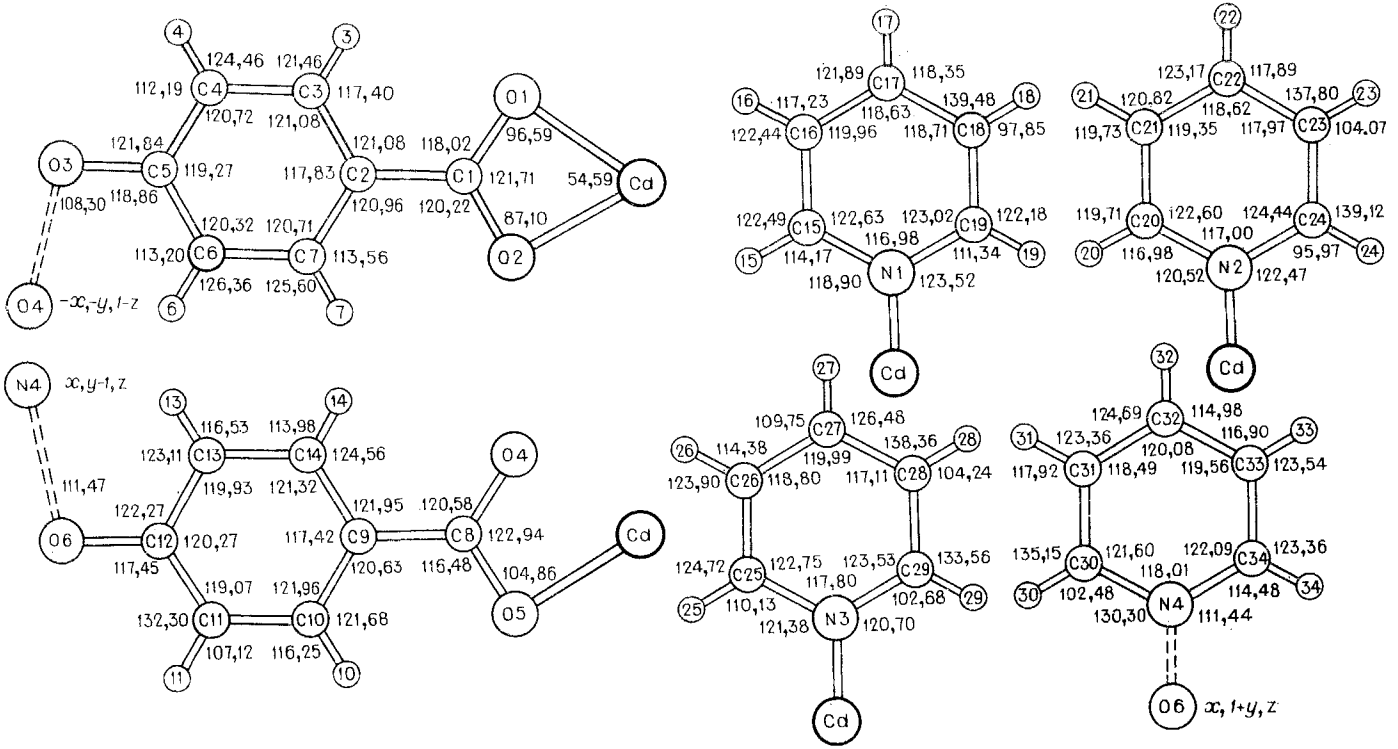

Fig. 2. Valence angles (the maximum error is 0.9° for the angles involving light atoms (not H), and 10° for the angles formed by light atoms including hydrogen atoms).

TABLE 3. Valence Angles ω around the Cd Atom, deg

Angle	ω	Angle	ω
O(1)CdO(2)	54,6(2)	O(2)CdN(3)	83,7(3)
O(1)CdO(5)	137,7(2)	O(5)CdN(1)	86,9(3)
O(1)CdN(1)	86,2(3)	O(5)CdN(2)	93,8(3)
O(1)CdN(2)	88,9(3)	O(5)CdN(3)	84,0(3)
O(1)CdN(3)	138,0(3)	N(1)CdN(2)	173,4(3)
O(2)CdO(5)	167,7(2)	N(1)CdN(3)	93,3(3)
O(2)CdN(1)	93,9(3)	N(2)CdN(3)	93,3(3)
O(2)CdN(2)	86,7(3)		

TABLE 4. Dihedral Angles between the Planes, deg

Plane	I	II	III	IV	V	VI	VII	VIII	IX	X
I		0		0		10,0		86,4		100,9
II			14,4		28,8		12,8		34,3	
III	14,3			14,0		21,7		72,1		97,5
IV		0			28,3		12,3		93,8	
V	28,7		35,7			19,2		95,0		76,1
VI		10,2		9,9			5,2		36,2	
VII	12,7		20,9		16,2			88,9		89,3
VIII		86,4		86,1		92,1			57,5	
IX	34,3		23,1		38,2		32,1			72,9
X		100,9		100,4		93,9		77,6		
XI	40,9	40,8	50,9	41,4	60,5	44,6	49,7	112,8	73,9	44,2

* Plane I CdO(1)O(2)C(1); II CdO(1)O(2); III C(2)C(3)C(4), C(5)C(6)C(7); IV O(1)O(2)C(1); V C(9)C(10)C(11)C(12)C(13)C(14); VI CdO(5)C(8); VII O(4)O(5)C(8)C(9); VIII N(2)C(20)C(21)C(22)C(23)C(24); IX N(3)C(25)C(26)C(27)C(28)C(29); X N(1)C(15)C(16)C(17)C(18)C(19); XI N(4)C(30)C(31)C(32)C(33)C(34).

in the lattice [O(3) . . . N(4) distance 2.71 Å]. This entire system of H-bonds leads to the formation of a molecular complex with the composition $2([Cd(p\text{-}HOC_6H_4COO)_2(C_5H_5N)_3]C_5H_5N)$.

It should be noted that this combination – the simultaneous coexistence, in a crystal structure, of two types of pyridine molecule in coordinated and noncoordinated states – is a fairly rare phenomenon, which has also been observed, for example, in bis(4-methylpyridine)phthalocyaninatocobalt [11].

The lengths of the coordinate bonds agree to within 3σ with the analogous distances in $Cd(NO_3)_2(Py)_3$ [12].

The aromatic fragments and the molecules present in the structure are planar (greatest deviation from the plane 0.02 Å). Table 4 gives the dihedral angles between the planes. The intermolecular contacts are equal to or greater than the sums of the van der Waals radii of the corresponding atoms. The volume corresponding to one chemical bond [13] is 10.3 $Å^3$.

LITERATURE CITED

1. G. N. Nadzhafov, Proceedings of the Conference of Young Scientists and Postgraduate Students of the Institutes of Inorganic and Physical Chemistry and Theoretical Problems of Chemical Technology of the Academy of Sciences of the Azerbaidzhan SSR, October, 1979 [in Russian], Elm, Baku (1979), p. 42.
2. K. Fukuama, K. Ohkura, S. Kashino, and M. Haisa, Bull. Chem. Soc. Jpn., 46, 804 (1973).
3. L. Manojlovic, Acta Crystallogr., B24, 326 (1968).
4. K. Fukuyama, S. Kashino, and M. Haisa, Acta Crystallogr., B29, 2713 (1973).
5. K. Harata, Bull. Chem. Soc. Jpn., 50, 1416 (1977).
6. I. R. Amiraslanov, Kh. S. Mamedov, E. M. Movsumov, et al., Zh. Strukt. Khim., 19, 1129 (1978).
7. I. R. Amiraslanov, Kh. S. Mamedov, E. M. Movsumov, et al., Zh. Strukt. Khim., 20, 498 (1979).

8. I. R. Amiraslanov, Kh. S. Mamedov, E. M. Movsumov, et al., Dokl. Akad. Nauk Azerbaidzhan SSR, 35, (2), 23 (1979).
9. I. R. Amiraslanov, N. Kh. Dzhafarov, G. N. Nadzhafov, et al., Dokl. Akad. Nauk Azerbaidzhan SSR, 35, (2), 49 (1979).
10. V. I. Andrianov, Zh. Sh. Safina, and B. L. Tarnopol'skii, An Automatic System of Programs for Determining the Structure of Crystals, "Rentgen-75" [in Russian], OIKhF, Chernogolovka (1975).
11. F. Cariati, F. Morazzon, and M. Zocchi, Inorg. Chim. Acta, 14, L31 (1975).
12. A. F. Cameron, D. W. Taylor, and R. H. Nuttall, J. Chem. Soc. Dalton Trans., 15, 1608 (1972).
13. Kh. S. Mamedov and E. M. Movsumov, Azerbaidzhan. Khim., Zh., 2, 83 (1976).

CRYSTAL AND MOLECULAR STRUCTURE OF NEODYMIUM(III) p-AMINOBENZOATE

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An x-ray structural study of neodymium(III) p-aminobenzoate has been carried out (λMoK_α, automatic diffractometer, heavy-atom method, anisotropic refinement). The crystals are monoclinic: a = 9.882(5), b = 22.810(12), c = 9.851(8) Å, β = 100.02(5)°, V = 2186.59 Å^3, Z = 4, space group $P2_1/n$, R = 0.046. The crystal structure of $Nd(OOCC_6H_4NH_2)_3 \cdot H_2O$ consists of two-dimensional-periodic layers alternating along the b axis. The environment of the Nd atom in the chain is made up of four oxygen atoms of four carboxyl groups of a bidentate-bridging ligand and one carboxyl group of a bidentate-cyclic ligand, one water molecule, and the N atom of the amino-group of a ligand from a neighboring chain. The atom simultaneously joins neighboring chains to form an infinite layer. The average distances Nd–O and Nd–N are 2.45 and 2.74 Å. An attempt to determine the coordinates of the hydrogen atoms was unsuccessful.

INTRODUCTION

As shown in our previous papers [1, 2], the structures of $Dy(OOCC_6H_4NH_2)_3 \cdot 3H_2O$ and $Y(OOCC_6H_4OH)_3 \cdot 3H_2O$, in addition to the preservation of the general features characteristic of lanthanide carboxylates [3, 4], also show that the structure of the benzoate ligands has a significant influence not only on the mode of packing but also on such characteristic features as the coordination number, the degree of polymerization of the structural units,* etc. The study of the structure of complexes of these ligands and ligands with similar geometry with different lanthanides will obviously help to explain the general characteristic stereochemical features of the complexes of carboxylates containing additional active atoms in the substituent.

The present paper describes an x-ray structural analysis of the next complex from this series, namely $Nd(OOCC_6H_4NH_2)_3 \cdot H_2O$.

EXPERIMENTAL

Crystals of neodymium(III) p-aminobenzoate were obtained by the reaction of aqueous solutions of sodium p-aminobenzoate and $NdCl_3 \cdot 6H_2O$. The parameters of the monoclinic cell were determined on a Syntex $P2_1$ automatic diffractometer: a = 9.882(5), b = 22.810(12), c = 9.851(8) Å, β = 100.02(5)°, V = 2186.59 Å^3, Z = 4, space group $P2_1/n$, R = 0.046.

The determination and refinement of the structure were carried out using 2210 independent reflections with $I > 1.96\sigma$, measured on the same diffractometer (λMoK_α, graphite monochromator). All the calculations were carried out on a Nova-1200 minicomputer using the XTL Syntex programs.

* For the qualitative characterization of the complexity of the structural units, such as dimer, tetramer, chain, etc., we were forced to use the term "degree of polymerization."

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