Pergamon

PII: S0277-5387(97)00015-6

Polyhedron Vol. 16, No. 16, pp. 2871–2875, 1997

0277-5387/97 $17.00+0.00

Barium 1,4-dihydrotetrazine-3,6-dicarboxylate trihydrate complex: synthesis, crystal structure and thermolysis

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(Received 1 April 1996; accepted 12 December 1996)

Abstract—Single crystals of DHT·$2H_2O$ (**1a**; DHT = 1,4-dihydrotetrazine-3,6-dicarboxylic acid) and BaDHT·$3H_2O$ (**1b**) have been prepared and studied. Their structures have been determined. In **1a**, the structure consists of boat-shaped DHT molecules with typical C—N and C=N bond lengths defining the central ring. In **1b**, the barium atoms are surrounded by five water molecules and two O and one N atoms from two ligands; thus, the structure is an infinite chain of Ba(DHT) linked through hydration water molecules. The dehydration proceeds in well separated steps, yielding, respectively, BaDHT·H_2O, then anhydrous BaDHT which finally decomposes to $BaCO_3$. © 1997 Elsevier Science Ltd

Keywords: metalloorganic precursors; crystal structures; barium complexes; dihydrotetrazine derivatives; 1,4-dihydrotetrazine-3,6-dicarboxylates; metalloorganic thermolysis.

New synthesis methods using metalloorganic precursors have been recently developed to obtain mixed oxides at low temperatures [1]. Unlike the traditional ceramic method which does not always yield single-phase products of the required stoichiometry, the metalloorganic method allows a mixing of the different metal species on the molecular scale. In addition, this method reduces the particle size of the resulting oxide powder and might improve its physical properties.

The aminocarboxylates have been long known and studied as binding agents. The 1,4-dihydrotetrazine-3,6-dicarboxylic acid (hereafter DHT) may also be considered as an adequate ligand to complex various metal cations in order to obtain precursors of mixed metal oxides. As the DHT molecule is not commercially available, it is not widely used as a ligand and, to our knowledge, its crystal structure has not been determined yet.

The starting ligand, DHT·$2H_2O$ (**1a**) and one of its complexes, BaDHT·$3H_2O$ (**1b**), have been obtained as yellow crystals and their structures are reported in the present work. In addition, the thermal decomposition of the barium complex has been investigated by TGA and high-temperature X-ray diffraction, in order to understand its potential use as a precursor for Ba-based mixed oxides.

EXPERIMENTAL

Synthesis and characterization methods

The synthesis of the DHT was carried out as described in the literature [2].

DHT·$2H_2O$ crystals were obtained from evaporation of an aqueous solution of DHT.

An aqueous solution of $Ba(NO_3)_2$ (0.5×10^{-3} mol dm^{-3}, Merck) was added very slowly to a solution of DHT (0.5×10^{-3} mol dm^{-3}) at room temperature (DHT was previously dissolved in water around 80°C). After a few days, yellow crystals were filtered from this solution. The products obtained were examined by X-ray powder diffraction with a Guinier-de Wolff camera using monochromated Cu-K_α radiation.

An investigation of the crystallographic modifications associated with the thermal evolution of the barium complex was carried out on a high-tem-

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perature X-ray diffraction Guinier–Lenné camera (heating rate 13° h^{-1}; Cu-K_α radiation).

TGA were performed on a Dupont 951 model thermal analyser in static air with a heating rate of 60° h^{-1}. As a result, the determination of their hydration water content was (**1a**) DHT$\cdot$2H_2O and (**1b**) BaDHT$\cdot$3H_2O, respectively.

The experimental densities of the liquids in which **1a** and **1b** crystals were floating were determined with an Anton Paar density analyser 02C. They are 1.78 and 2.61, respectively. The density of anhydrous BaDHT was determined with a Micromeritics 1330 helium pycnometer (1 cm^3 sample capacity).

The IR spectra were obtained using a Perkin–Elmer 683 spectrophotometer.

X-ray structural solution and refinement

Single crystals of **1a** and **1b** were mounted on a Philips PW1100 diffractometer and data collected with graphite monochromated Mo-K_α radiation ($\lambda = 0.7107$ Å).

Unit-cell dimensions were determined using least-square refinement of 25 values of 2θ in the range 5–20°. Crystal data are listed in Table 1. Both data sets were corrected for Lorentz and polarization effects. Scattering factors were taken from the International Tables of X-ray Crystallography [3]. The crystal structures were solved, respectively: **1a** using a local modification of SFLS-5 [4]. For **1b**, the barium atom was located through the Patterson method and successive Fourier maps revealed the other atoms. All positional and thermal parameters were refined with SHELX-76 [5]. The hydrogen atoms were identified but not included in the refinement process.

The final R factors were $R = 0.037$ and $R_w = 0.040$ for **1a**, $R = 0.042$ and $R_w = 0.042$ for **1b**. The molecular drawings were made with a local version of ORTEP [6].

RESULTS AND DISCUSSION

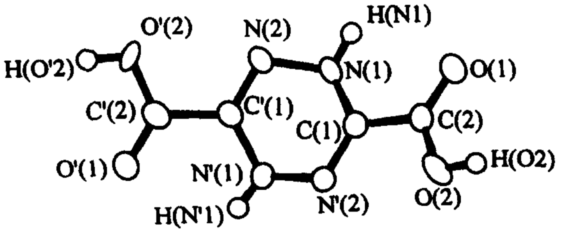
Description of the crystal structures

Crystal structure of DHT$\cdot$2H_2O (**1a**). The global structure of DHT$\cdot$2H_2O consists of DHT molecules organized in layers parallel to (010). This network is developed through hydrogen bonds from H_2O bridging molecules. A representation of the DHT molecule is given in Fig. 1.

If the central ring of the DHT molecule would be planar, the molecule would be antiaromatic since eight electrons belong to this ring. Actually, the molecule forms two planes (Fig. 2); at their intersections are located the 2 sp^3 hybridized nitrogen atoms. The four atoms C(1), N′(2), C′(1) and N(2) are all coplanar (Fig. 2, Table 2); they form the mean plane ($y - 0.63816 = 0$) of the DHT molecule, which is parallel to (010). The difference between the carbon–nitrogen single bond lengths [C(1)—N(1) and

Table 1. Crystallographic data for DHT$\cdot$2H_2O and BaDHT$\cdot$3H_2O

Compound	DHT$\cdot$2H_2O (**1a**)	BaDHT$\cdot$3H_2O (**1b**)
Formula	$C_4N_4O_6H_8$	$C_4N_4O_7H_8Ba$
Mol. wt	208.13	361.46
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$	$P2_1/a$
a (Å)	19.310(3)	13.28(2)
b (Å)	3.569(2)	7.152(6)
c (Å)	13.504(7)	10.54(2)
β (°)	120.4(2)	108.66(8)
V Å^3	802(3)	949(3)
Z	4	4
D_m (g cm^{-3})	1.78	2.61
D_o (G cm^{-3})	1.73	2.53
$F(000)$	432.0	695.96
Temperature (K)	298	298
θ range (°)	2–25	2–25
Scan type	$\omega/2\theta$	$\omega/2\theta$
No. of data collected	861	1926
No. of unique data	395	1563
hkl range	−20,20;0,5;0,14	−15,15;0,8;0,12
R_{merge}	0.011	0.020
Standard reflections	$(\bar{1}1\bar{1})$;$(\bar{2}0\bar{4})$;$(\bar{3}\bar{1}0)$	(112);$(0\bar{1}\bar{1})$;$(\bar{1}\bar{1}2)$
Observability criterion $n, I > n\sigma(I)$	2	2.5
No. of data in refinement	395	1466
No. of refined parameters	81	97
Final R	0.037	0.042
R_w	0.040	0.042



C'(1) is related to C(1) by symmetry.

Fig. 1. DHT molecule—(010) plane.

C'(1)—N'(1)] and double ones [C(1)=N'(2) and C'(1)=N(2)] (Table 2) also shows that the electrons are not delocalized on the whole ring. The relative stability of **1a** in air can be explained by the opposite locations of two protons H(N1) and H(N'1) outside the ring, which cannot both react with one oxygen molecule from the air. Nevertheless, DHT can be easily turned into tetrazine by removing these two protons in order to obtain an aromatic ring.

Crystal structure of BaDHT·$3H_2O$ (**1b**). When it complexes the barium atom, the DHT molecule keeps the same conformation as in **1a**. Both protons of the carboxylic acids have disappeared in order to ensure the electrical neutrality of the system. Thus, the C—O bond lengths are much closer to each other than in molecule **1a**. All significant bond lengths are listed in Table 2. As a result of the complexation, the N—H and C—C bonds are stretched.

The shortest distance between two barium atoms is 4.44 Å. Each metal atom is surrounded by five water molecules and two DHT molecules, as shown in Fig. 3.

However, the crystal structure of BaDHT·$3H_2O$ is quite similar to the DHT·$2H_2O$ structure. It consists of DHT layers parallel to (010).

The IR spectrum of **1a** shows bands at 3300vs, 3120m, 2620m, 1720vs, 1630s, 1420s, 1320s, 1200s, 1110s, 980vs, 900s, 780vs, 710vs, 570s. The IR spectrum of **1b** shows bands at 3500m, 3330s, 1640vs, 1400vs, 1220m. The broad bands of ν(OH) between 3200 and 2200 cm^{-1} in the **1a** spectrum are not present in **1b**, thus proving that the protons have disappeared from the carboxylic acids. In the **1a** spectrum, there is

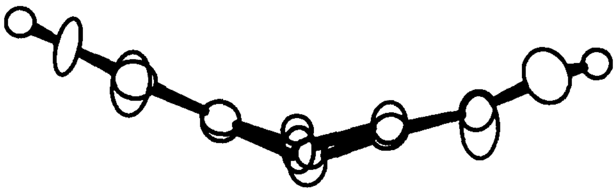
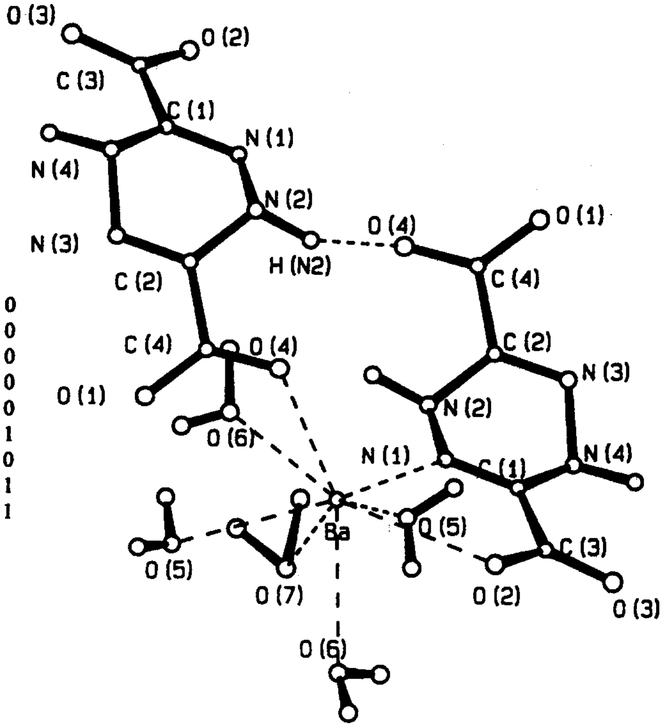


Fig. 2. DHT molecule in the perpendicular plane to (010).

Table 2. Selected bond distances (Å), bond angels (°) and deviations from the C(1)—N'(2)—C'(1)—N(2) mean plane (Å)

1a			
N(1)—N(2)	1.416	C(2)—O(1)	1.203
N(1)—C(1)	1.388	C(2)—O(2)	1.286
N(2)—C'(1)	1.275	O(2)—H(O2)	0.868
C(1)—C(2)	1.497	N(1)—H(N1)	0.852
N(2)—N(1)—C(1)	112.87°	N'(2)—C(1)—N(1)	122.22°
C(1)—N(1)—H(N1)	113.70°	N(1)—C(1)—C(2)	117.23°
N(2)—N(1)—H(N1)	111.88°	N'(2)—C(1)—C(2)	120.56°
1b			
C(3)—O(2)	1.265	C(2)—N(3)	1.273
C(4)—O(1)	1.262	C(1)—N(1)	1.276
C(4)—O(4)	1.240	N(1)—N(2)	1.440
C(3)—O(3)	1.235	N(3)—N(4)	1.431
C(2)—C(4)	1.525	C(2)—N(2)	1.386
C(1)—C(3)	1.514	C(1)—N(4)	1.388
N(4)—H(N4)	1.055	N(2)—H(N2)	1.088
Deviations from the mean plane $y-0.63816 = 0$			
N(2)	−0.019	N(1)	0.444
C(1)	0.019	N'(1)	0.444
N'(2)	−0.019	C(2)	−0.397
C'(1)	0.019	C'(2)	−0.397

Ba	1	0	0	0
N(1)	1	0	0	0
O(2)	1	0	0	0
O(4)	2	0	1	0
O(5)	1	0	0	0
O(5)	3	0	0	1
O(6)	1	0	1	0
O(6)	3	0	0	1
*O(7)	3	0	-1	1



*** O(7) atom generated by symmetry card number 3 and translated by 0a-1b+1c.**

symmetry cards :			
1	x	y	z
2	-x	-y	-z
3	1/2-x	1/2+y	-z
4	1/2+x	1/2-y	z

Fig. 3. Environment of the Ba atom.

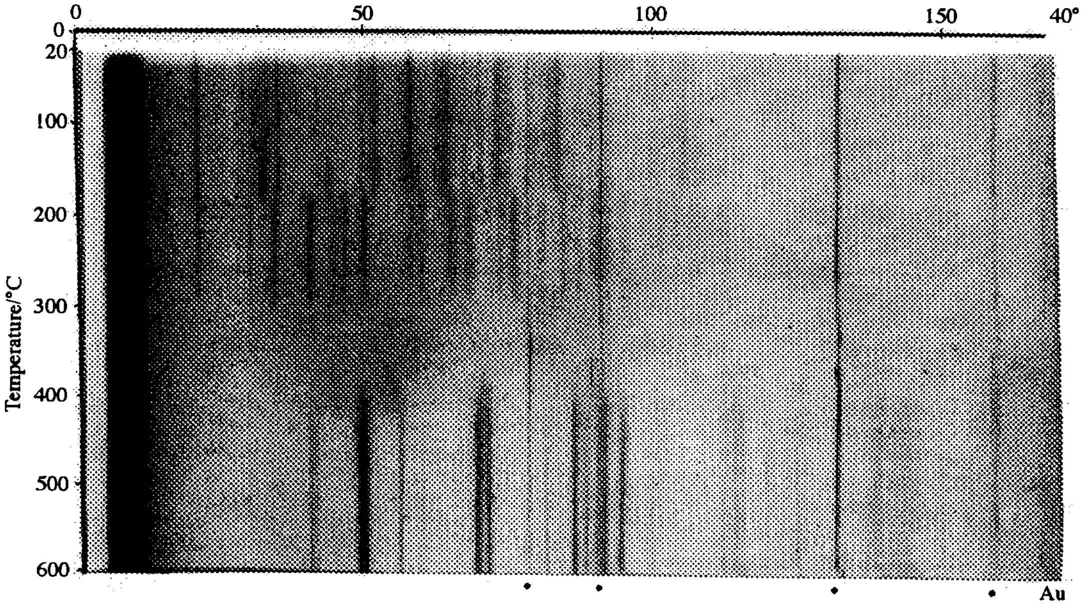


Fig. 4. High-temperature X-ray diffraction of BaDHT · $3H_2O$.

Table 3. X-ray pattern of anhydrous BaDHT

h	k	i	d_{obs}	d_{calc}	I/I_0
0	0	2	8.803	8.835	69
1	0	0	6.088	6.110	31
0	1	2	5.375	5.387	94
1	1	0	4.545	4.544	100
1	1	−2	4.121	4.119	35
1	1	2	3.962	3.967	49
1	0	−4	3.689	3.691	99
0	2	2	3.171	3.172	22
2	0	0	3.057	3.055	44
2	0	2	2.832	2.833	44
1	2	2	2.789	2.790	19
2	1	−2	2.704	2.702	36
0	2	4	2.692	2.693	10
2	1	−3	2.574	2.576	15
1	2	−4	2.504	2.500	36
1	2	4	2.430	2.431	29
2	0	−6	2.190	2.190	15
2	1	5	2.132	2.130	12

a strong ν(CO) band characteristic of the carboxylic acid at 1720 cm^{-1}. In **1b,** it has shifted to 1640 cm^{-1} for the —COO^- anion. Moreover, the characteristic C—O band of the acid function at 1320 cm^{-1} is absent in the **1b** spectrum.

Thermal decomposition of 1b

The TG and high-temperature X-ray diffraction analysis (Fig. 4) show that at 100°C, the barium complex has lost two water molecules, thus leading to BaDHT·H_2O; at 200°C it is further dehydrated to anhydrous BaDHT. Then at 400°C the complex is fully decomposed and barium carbonate is formed, and identified as the final residue. The dehydrated BaDHT complex has been characterized from the thermodiffraction data at 232°C, using the TREOR [7,8] indexing program (Table 3). The diffraction angles were evaluated and corrected from the diffraction lines of the sample holder gold grid used as an internal standard. The unit-cell parameters, refined from a least-square method, are: $a = 6.122(4)$, $b = 6.796(6)$, $c = 17.71(2)$ Å, $\beta = 93.58(5)^\circ$; the unit-cell volume is 734.2(8) $Å^3$. The measured density, 2.7921(8) g cm^{-3} is in good agreement with $Z = 4$ ($d_{cal} = 2.775$ g cm^{-3}).

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