Structure of Bis(triethanolamine)bis(2,4,6-trinitrophenolato)barium(II)*

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Abstract. \[\text{[Ba(C}_6\text{H}_2\text{N}_3\text{O}_7\text{)}_2\text{(C}_6\text{H}_4\text{NO}_3\text{)}_2}\text{_2,}~M_f = 891.9,\]
moniclinic, \(C2/c, ~a = 21.704 (3), b = 8.0224 (6),\)
\(c = 22.650 (4) \AA, \beta = 122.30 (1) ^\circ, V = 3333.5 (9) \AA^3,\)
\(Z = 4, ~D_x = 1.777 \text{ g cm}^{-3}, \text{Mo } K\alpha, \lambda = 0.71069 \AA,\)
\(\mu = 11.83 \text{ cm}^{-1}, F(000) = 1800, ~T = 294 \text{ K, } R = 0.0338\]
for 2837 observed reflections. Ba lies on a
twofold axis and is coordinated to eight O and two N
atoms which form a bicapped distorted cube. The N
atom and three O atoms of triethanolamine (tea) and
one O of the p-nitro-group of the picrate (tnp) are
involved in the coordination. The tea ligand is dis-
ordered over two positions which are approximately
related by pseudo mirror planes through N and each of
the terminal C atoms, with occupancies of 0.637 (7)
and 0.363 (7). Hydrogen bonds from the three tea OH
groups to two neighbouring tnp ligands link the Ba
complexes in extensive sheets. Two hydrogen bonds are
bifurcated and the phenolate O accepts three hydrogen
bonds.

Introduction. Recently we reported the structure
analyses of two complexes of Ban: Ba(dnp)_2(phen)_2
(Kanters, Postma, Duisenberg, Venkatasubramanian &
Poonia, 1983) and Ba(tnp)_2(phen)_2 (Postma, Kanters,
Duisenberg, Venkatasubramanian & Poonia, 1983)
dnp = 2,4-dinitrophenolato, tnp = 2,4,6-trinitrophenol-
ato, phen = 1,10-phenanthroline). In order to study
the relative binding capacities of nitrophenolates
and triethanolamine we also determined the structure of
Ba(dnp)_2(tea)_2 (Kanters, Smeets, Venkatasubramanian
& Poonia, 1984). In the latter compound the N and O
atoms of both tea ligands are coordinated to Ba,
whereas only one o-nitro-group O atom of one of the
dnp ligands contributes to the coordination. The
powerful binding capacity of triethanolamine in the
presence of 2,4,6-trinitrophenolate is studied in the
structure analysis of the title compound.

Experimental. Crystals obtained from the Chemistry
Department, University of Indore, India. Rod-shaped,
orange-reddish crystal 0.6 × 0.3 × 0.2 mm. Enraf-
Nonius CAD-4 diffractometer. Cell constants from
least-squares fit of positions of 25 reflections with 0
range 11-2-18.6 ^\circ. \(\omega-2\theta\) scan, \(\omega = (0-60 +
0.35 \tan\theta)^c, \sigma(I)/I < 1%\) or a maximum scan time of
60 s, horizontal and vertical slit widths 3 and 4 mm
respectively, Zr-filtered Mo K\alpha radiation. One quad-
rant, h 0-26, k 0-9, l -27-23, \(\theta_{\text{max}} = 26 ^\circ. 3143\)
unique reflections, 2837 above \(2.5\sigma(I)\) level. Three standard
reflections, measured every hour of X-ray exposure,
showed an average fluctuation of 0.9%. Intensities
corrected for Lp effects, but not for absorption. Ba
position from Patterson synthesis, non-H atoms of tnp,
N and three terminal C atoms of tea from Fourier
maps. Six maxima appeared around N, the densities of
which fell into two groups with a ratio of about 2:1. The
same feature was observed near the terminal C atoms
where three pairs of close-lying maxima were found.
This pattern was interpreted as a disorder of tea over
two positions. Accordingly, the two groups of positions
of the disordered C and O atoms were refined with
occupancy factors \(p\) and \((1-p)\) [refined value, \(p = 0.637 (7)\)]. The two H atoms of tnp were located
from difference maps. The H atoms of tea were placed

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at calculated C($sp^3$) positions, those bonded to the disordered C atoms with corresponding occupancies, whereas the four H atoms attached to each ordered terminal C atom were pair-wise allocated occupancies corresponding to those of the disordered C atoms. The H atoms bonded to O atoms with the greater occupancy could be located from a difference map.

The non-H atoms were refined anisotropically, the H atoms of tnp isotropically; all other H atoms were kept fixed at their calculated positions with a constant U of 0.05 Å$^2$. Because of the large number of parameters (308) the refinement was split into two blocks: one for Ba and tnp, the other for tea. At convergence $R = 0.0338$, $wR = 0.0355$ with $w = [\sigma^2(F_o) + 0.00182F_o^2]^{-1}$, $S = 3.12$, $(\Delta/\sigma)_{max} = 0.24$, $(\Delta/\sigma)_{av} = 0.042$. The final difference map showed intensities of $\pm 0.8$ e Å$^{-3}$ at about 1 Å from Ba, with other features below 0.4 e Å$^{-3}$. Scattering factors for non-H atoms from Cromer & Mann (1968), for H from Stewart, Davidson & Simpson (1965); anomalous-dispersion coefficients from Cromer & Liberman (1970). Calculations were performed with EUCLID (structure determination and refinement) and the EUCLID package (Spek, 1982) (geometry and illustrations) on the CDC Cyber-175 of the University of Utrecht.

**Discussion.** Final atomic coordinates and equivalent isotropic thermal parameters are given in Table 1,* derived distances and angles in Table 2. The complex with the atom numbering scheme is shown in Fig. 1.

In the complex Ba is coordinated to two tnp and two (disordered) tea ligands. Each tnp ligand is only coordinated by one O atom of the p-nitro group and the phenolic O of dnp is also not involved in the coordination, whereas in nitrophenolate complexes with 1,10-phenanthroline as a ligand, Ba(tnp)$_2$(phen)$_2$ (Postma, Kanters, Duisenberg, Venkatasubramanian & Poonia, 1983) and Ba(dnp)$_2$(phen)$_3$ (Kanters, Postma, Duisenberg, Venkatasubramanian & Poonia, 1983) the distance Ba-O(phenolate) is the shortest contact, which illustrates the great coordination capacity of tea. This loss of coordination energy is compensated for by the extensive participation of phenolic O in hydrogen bonding (Table 3).

The cluster of Ba with its surrounding tnp and tea ligands is built in such a way that the two tea’s with their eight coordinating atoms effectively screen Ba from the tnp fragments which approach the cluster from one side. The distances between Ba and the O atoms of tea with the greater occupancy range from 2.728 (5) to 2.809 (5) Å and the Ba–N(4) distance is 2.728 (5) Å to 2.809 (5) Å.

**Table 1.** Fractional atomic coordinates and equivalent isotropic thermal parameters, with e.s.d.’s in parentheses

\[
U_{eq} = \frac{1}{3} \sum_{ij} u_{ij} a_i a_j
\]

<table>
<thead>
<tr>
<th>Ba</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>$U_{eq}(\AA^2)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(1)</td>
<td>0.4847 (2)</td>
<td>0.8144 (4)</td>
<td>-0.0698 (1)</td>
<td>0.079 (1)</td>
</tr>
<tr>
<td>O(2)</td>
<td>0.3660 (2)</td>
<td>0.0118 (5)</td>
<td>-0.1209 (2)</td>
<td>0.091 (1)</td>
</tr>
<tr>
<td>O(3)</td>
<td>0.2813 (2)</td>
<td>0.8633 (6)</td>
<td>-0.1295 (2)</td>
<td>0.125 (2)</td>
</tr>
<tr>
<td>O(4)</td>
<td>0.3329 (2)</td>
<td>0.6154 (4)</td>
<td>0.0870 (2)</td>
<td>0.092 (1)</td>
</tr>
<tr>
<td>O(5)</td>
<td>0.5642 (2)</td>
<td>0.6531 (4)</td>
<td>0.1672 (2)</td>
<td>0.093 (1)</td>
</tr>
<tr>
<td>O(6)</td>
<td>0.6259 (1)</td>
<td>0.5607 (5)</td>
<td>0.1141 (2)</td>
<td>0.093 (1)</td>
</tr>
<tr>
<td>O(7)</td>
<td>0.6140 (2)</td>
<td>0.6908 (5)</td>
<td>0.0265 (2)</td>
<td>0.097 (1)</td>
</tr>
<tr>
<td>N(1)</td>
<td>0.3447 (2)</td>
<td>0.8994 (5)</td>
<td>-0.1004 (2)</td>
<td>0.063 (1)</td>
</tr>
<tr>
<td>N(2)</td>
<td>0.3981 (2)</td>
<td>0.6077 (4)</td>
<td>0.1090 (2)</td>
<td>0.068 (1)</td>
</tr>
<tr>
<td>N(3)</td>
<td>0.5897 (1)</td>
<td>0.6474 (4)</td>
<td>0.0612 (2)</td>
<td>0.059 (1)</td>
</tr>
<tr>
<td>N(4)</td>
<td>0.4847 (2)</td>
<td>0.7778 (5)</td>
<td>0.0261 (2)</td>
<td>0.054 (1)</td>
</tr>
<tr>
<td>N(5)</td>
<td>0.3971 (2)</td>
<td>0.8805 (4)</td>
<td>0.0381 (2)</td>
<td>0.052 (1)</td>
</tr>
<tr>
<td>N(6)</td>
<td>0.3733 (2)</td>
<td>0.7513 (4)</td>
<td>0.0031 (2)</td>
<td>0.053 (1)</td>
</tr>
<tr>
<td>N(7)</td>
<td>0.4223 (2)</td>
<td>0.6687 (4)</td>
<td>0.0641 (2)</td>
<td>0.053 (1)</td>
</tr>
<tr>
<td>C(5)</td>
<td>0.4932 (2)</td>
<td>0.6388 (5)</td>
<td>0.0839 (2)</td>
<td>0.052 (1)</td>
</tr>
<tr>
<td>C(6)</td>
<td>0.5122 (2)</td>
<td>0.6906 (4)</td>
<td>0.0392 (2)</td>
<td>0.051 (1)</td>
</tr>
</tbody>
</table>

* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and least-squares-planes’ data have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42326 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH 1 2HU, England.
Table 2. Interatomic distances (Å), bond angles (°) and selected torsion angles (°)

<table>
<thead>
<tr>
<th>Bond Pairs</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba-O(10)</td>
<td>2.728 (5)</td>
</tr>
<tr>
<td>Ba-O(8)</td>
<td>2.711 (5)</td>
</tr>
<tr>
<td>Ba-O(9)</td>
<td>2.808 (5)</td>
</tr>
<tr>
<td>Ba-N(4)</td>
<td>3.030 (2)</td>
</tr>
<tr>
<td>Ba-O(5)</td>
<td>3.142 (2)</td>
</tr>
<tr>
<td>Ba-O(8')</td>
<td>1.496 (6)</td>
</tr>
<tr>
<td>Ba-O(9')</td>
<td>1.496 (6)</td>
</tr>
<tr>
<td>Ba-O(9)</td>
<td>1.502 (6)</td>
</tr>
<tr>
<td>Ba-O(10)</td>
<td>1.502 (6)</td>
</tr>
<tr>
<td>Ba-O(11)</td>
<td>1.494 (2)</td>
</tr>
</tbody>
</table>

Interatomic distances

Table 3. Hydrogen-bonding geometry (D: donor; A: acceptor)

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>O8-H10-11</td>
<td>1.00 (1)</td>
<td>1.76 (1)</td>
<td>2.71 (1)</td>
<td>141 (1)</td>
</tr>
<tr>
<td>O8-H10-11</td>
<td>1.00 (1)</td>
<td>2.19 (1)</td>
<td>3.03 (1)</td>
<td>131 (1)</td>
</tr>
<tr>
<td>O9-H10-11</td>
<td>0.90 (1)</td>
<td>2.29 (1)</td>
<td>3.10 (1)</td>
<td>151 (1)</td>
</tr>
<tr>
<td>O9-H10-11</td>
<td>0.90 (1)</td>
<td>2.46 (1)</td>
<td>3.15 (1)</td>
<td>135 (1)</td>
</tr>
<tr>
<td>O10-H11-11</td>
<td>0.87 (1)</td>
<td>2.00 (1)</td>
<td>2.86 (1)</td>
<td>174 (1)</td>
</tr>
</tbody>
</table>

Symmetry code: (*1) 1 - x, y, z.
This deviation is probably due to disorder, as in the other tea complexes the conformations are all close to gauche. As is usual in picrates the phenyl ring is moderately planar \( \sigma_{av} = 0.024 (9) \), with the immediate ring substituents showing appreciable deviations from the best plane, the average distance of the three N atoms being 0-05 (1) \( \text{Å} \) and of phenolic O(1) 0-143 (8) \( \text{Å} \). The three C—NO\(_2\) fragments are planar and the nitro groups display various degrees of twisting, moderate for one of the ortho groups [3·1 (2)°] and the p-nitro group [10·1 (2)°] but large for the other ortho group [33·6 (3)°], which corresponds to the twisting in Ba(tnP)\(_2\)(phen)\(_2\) where these twist angles are 0·4 (2), 14·9 (2) and 38·9 (2)° for tnp1 and 5·9 (2), 14·9 (2) and 38·9 (2)° for tnp2. The bond-length and bond-angle variation of the phenyl ring of tnp is similar to that observed in other picrates and mono- and di-o-nitrophenolates (Bush & Truter, 1971; Hughes, 1973, 1975; Hough, 1976; Postma, Kanters, Duijzenberg, Venkatasubramanian & Poonia, 1983) in that both C—C bonds at the phenolic site are long [av. 1·446 (4) \( \text{Å} \)] and the four remaining bonds are short [av. 1·375 (7) \( \text{Å} \)], the bond angle at the phenolic site is small [111·8 (4)°], and the angles subtended at the ortho C atoms are enlarged to 123·9 (4) and 125·0 (4)°, whereas the remaining angles approach normal values (Table 2). The dimensions of tnp are consistent with significant contributions of resonance forms with an essentially normal C=O bond (Ferguson, Ruhl, Wieckowski, Lloyd & McNab, 1984).

The OH groups of tea are involved in intermolecular hydrogen bonds, two of which are bifurcated, and they donate to acceptors O(1), O(2) and O(7) of the tnp fragments (Fig. 4). Only the hydrogen bonds relating to tea with occupancy 0·637 are given in Table 3, though the O atoms of tea with the smaller occupancy are within 3·40 \( \text{Å} \) of potential O acceptors. The phenolic O(1) accepts three hydrogen bonds and as in Ba(dnp)\(_2\)- (tea)\(_2\), where O(1) is also excluded from the Ba coordination, this acceptor therefore contributes effectively to the interaction energy. The hydrogen bonds connect each tea molecule to two tnp's belonging to two different Ba coordination spheres which are related by translations of \( \frac{1}{2}(b + c) \) and \( \frac{1}{2}(b - c) \) respectively. As these hydrogen bonds are all directed towards the phenolic site of the tnp's, whose p-nitro groups are coordinated to Ba, a strongly hydrogen-bonded sheet of Ba polyhedra is formed parallel to \( bc \). The structure is built up by stacking of these infinite sheets along \( a \).

**References**


